

# JOURNEES DE LA DIFFUSION NEUTRONIQUE

# JDN 2019

MULTIDISCIPLINARY  
SCIENCE WITH  
NEUTRONS

## ORGANIZERS :

Anne-Caroline Genix,  
Julian Oberdisse  
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## DEADLINES :

June 1, 2019 >> Abstract  
submission (oral or posters)  
July 15, 2019 >> Registration

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Domaine Le Hameau de  
l'Etoile, Saint-Martin-de-  
Londres

# SEPTEMBER 16-19



## General information

The French Neutron Society (SFN) organises, with the neutron facilities Institut Laue-Langevin and Laboratoire Léon Brillouin, the Neutron Scattering Meeting 2019 (JDN2019), in Saint-Martin-de-Londres (Hérault, France), from September 16th to 19th, 2019.

This multidisciplinary workshop (traditionnally entitled "Rencontres Rossat-Mignod") will be dedicated to new results, obtained using neutron scattering techniques, in various scientific domains representative of the whole neutron users community.

This year, we are glad to welcome more than 80 participants at the Conference, to attend more than 40 talks. Two sessions regrouping *Condensed Matter & Magnetism* on the one side, and *Soft Matter, Biology and Environment* on the other side, have been organized.

The SFN and the organizers are grateful to the participants and the sponsors of the conference.

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# Program

## Monday September 16<sup>th</sup>

- 18:00      *Shuttle departure, from Montpellier Saint-Roch Station*
- 19:00-20:00      *Welcome drink*
- 20:00      *Dinner*

## Tuesday September 17<sup>th</sup>

- 08:15-08:30      *Opening*
- 08:30-09:15      Plenary session: **Arantxa ARBE**, *CSIC-UPV/EHU*      7  
Investigating Systems Based on Single-Chain Nano-Particles by Neutron Scattering (and Others)
- 09:15-09:45      Keynote: **Annie BRULET**, *LLB, CEA-CNRS*      8  
Stimuli responsive polymersomes: Small Angle Neutron Scattering studies
- Keynote: **Mechthild ENDERLE**, *ILL*      9  
Examples of quantum ground states and excitations
- 09:45-10:05      **Fabien DUTERTRE**, *IMP, Univ Jean Monnet*      10  
Structure and Persistence of High Generation Dendronized Polymers
- Dalila BOUNOUA**, *LLB, CEA-CNRS*      11  
Orbital Currents in the Quasi-1D Spin Ladders Compound  $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$
- 10:05-10:35      *Coffee break*
- 10:35-11:20      Plenary session: **Markus BRADEN**, *Physics Institute, Univ Köln*      12  
Pourquoi va-t-on regretter Orphée? 39 years of ground-breaking results
- 11:20-11:50      Keynote: **Urs GASSER**, *PSI*      13  
Spontaneous deswelling of microgels controlled by counterion clouds
- Keynote: **Jean-Noël CHOTARD**, *LRCS, Univ Picardie Jules Verne*      14  
Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations
- 11:50-12:10      **Marian CORS**, *Univ Bielefeld*      15  
Structure determination of core-shell microgels for the use as nano-actuators
- Iurii KIBALIN**, *LLB, CEA-CNRS*      16  
Rietveld method for polarized neutron powder diffraction
- 12:10-12:30      **Neutrons & Food: Camille LOUPIAC**, *AgroSup Dijon*      17  
Neutron: a unique probe to understand food structure under processes
- 12:30-14:00      *Lunch*

14:00-14:20	<b>Nathalie MALIKOVA</b> , PHENIX, CNRS-Sorbonne Univ Flocculation of clay colloids: combining scattering and imaging techniques	18
	<b>Morgane LEMAIRE</b> , PhLAM, Univ Lille-CNRS Influence of the alkaline feldspar-surrogates on the kinetic formation and the selectivity of pure CO <sub>2</sub> and CO <sub>2</sub> -N <sub>2</sub> mixed gas hydrates	19
14:20-14:40	<b>Simeon MINIC</b> , LLB, CEA-CNRS Unfolding of food proteins by high pressure	20
	<b>Cyrielle METAIS</b> , ILL Investigation of the impact of silica media on gas hydrates selectivity	21
14:40-15:00	<b>François BOUE</b> , LLB, CEA-CNRS How Necklace Pearls Evolve in Hydrophobic Polyelectrolyte Chains under Good Solvent addition: using the SANS-Zero Average Contrast method to study the Conformation	22
	<b>Geoffrey MONET</b> , LPS, CNRS-Univ Paris-Saclay Specific water structure in a geo-inspired nanotube and interrelated dynamics	23
15:00-16:00	<i>Free time</i>	
16:00-16:30	<i>Coffee break</i>	
16:30-17:45	Instrumentation session	
16:30-16:45	<b>Frédéric OTT</b> , LLB, CEA-CNRS First neutrons on IPHI – Neutrons @ Saclay	24
16:45-17:00	<b>Stéphane ROLS</b> , ILL PANTHER: the new thermal time of flight spectrometer at the ILL.	25
17:00-17:15	<b>Patrick JUDEINSTEIN</b> , LLB/LPS, CEA-CNRS-Univ Paris-Saclay Measuring SANS and NMR simultaneously: a new tool for transient physics	26
17:15-17:30	<b>Viviana CRISTIGLIO</b> , ILL D16 diffractometer: more neutrons, more space, more fun	27
17:30-17:45	<b>Patrick BARONI</b> , LLB, CEA-CNRS Using Light to see Neutrons: a new 2D detector with high resolution	28
17:45-19:30	News from the Neutron Centers ILL, LLB, ESS, PSI, ENSA, 2FDN	
20:00	<i>Dinner</i>	
21:00-22:30	40 Years Of Science With Neutrons From Orphée Christiane Alba-Simionesco, Michel RAWISO, François BOUE, Frédéric OTT	

## Wednesday September 18th

08:30-09:15	<u>Plenary session:</u> <b>Stéphane PAILHES</b> , <i>ILM, Univ Lyon 1</i> Phonon dynamics in energy materials	29
09:15-09:45	<u>Keynote:</u> <b>Leonardo CHIAPPISI</b> , <i>ILL</i> The Journey of a Correlation Peak through the Small-angle Scattering, Spin-Echo, and Reflectometry domains	30
	<u>Keynote:</u> <b>Philippe BOURGES</b> , <i>LLB, CEA-CNRS</i> Magnetism in spin-orbit coupled iridates	31
09:45-10:05	<b>Zijun LU</b> , <i>ICSM, Univ Montpellier-CEA-CNRS-ENSCM</i> Structural effect of phase modifier n-octanol on solvent extraction mechanism revealed by SANS	32
	<b>Arno HIESS</b> , <i>ESS</i> Low energy excitations in intermetallic superconductors - revisiting previous results to prepare for first science at ESS	33
10:05-10:35	<i>Coffee break</i>	
10:35-11:20	<u>Plenary session:</u> <b>Giovanna FRAGNETO</b> , <i>ILL</i> Planar lipid bilayers as model biological membranes for structural neutrons studies	34
11:20-11:40	<b>Julie WOLANIN</b> , <i>LIPhy, Univ Grenoble Alpes-CNRS</i> Study of the adsorption conditions of surfactants on surfaces mimicking rock reservoirs (EOR application) by the combination of QCM-D and neutron reflectivity experiments	35
	<b>Diane REBISCOUL</b> , <i>ICSM, Univ Montpellier-CEA-CNRS-ENSCM</i> Dynamical and Structural Properties of Water in Silica Nanoconfinement – Impact of Surface Curvature, Ion Nature and Electrolyte Concentration	36
11:40-12:00	<b>Yazhao LIU</b> , <i>ICS, Univ Strasbourg-CNRS</i> Photosensitive Polymer - surfactant complexes	37
	<b>Jean-Louis BANTIGNIES</b> , <i>L2C, CNRS-Univ Montpellier</i> Confinement of dyes inside carbon nanotubes: correlation between vibrational, structural and electronic properties	38
12:00-13:30	<i>Lunch</i>	
SFN PhD Award		
13:30-13:40	<b>José TEIXEIRA</b> , <i>LLB, CEA-CNRS</i> President of the PhD award committee	
13:40-14:30	<u>PhD awardee:</u> <b>Raphael DOS SANTOS MORAIS</b> , <i>LIBio, Univ Lorraine</i> Dystrophin-membrane interaction: 3D structure of dystrophin fragments in the presence of phospholipids	39

14:30-14:50	<b>Marion GRZELKA</b> , LLB/LPS, CEA-CNRS-Univ Paris-Saclay Direct probing of slip mechanisms for solid / polymer solutions interfaces	40
	<b>Shelby TURNER</b> , ILL Mechanisms of Thermal Transport in Zirconia	41
14:50-15:10	<b>Michel RAWISO</b> , ICS, CNRS-Univ Strasbourg Structure of aqueous solutions of interpolyelectrolyte complexes: A SAXS and SANS study	42
	<b>Mickaël BEAUDHUIN</b> , ICGM, Univ Montpellier-CNRS-ENSCM Effect of the dimensionality on the lattice dynamics and anharmonicity of the thermoelectric silicide CrSi <sub>2</sub>	43
15:10-15:30	<b>Romain VIENNOIS</b> , ICGM, Univ Montpellier-CNRS-ENSCM Lattice dynamics and anharmonicity of thermoelectric BiCuSeO	44
15:30-16:30	<u>Posters</u>	50
16:30-17:00	<i>Coffee break</i>	
17:00-17:20	<b>Aïcha JANI</b> , IPR, CNRS-Univ Rennes 1 Toluene/butanol binary solvents confined in periodic organosilicates	46
	<b>Victor BALEDENT</b> , LPS, CNRS-Univ Paris-Saclay New insights in RMn <sub>2</sub> O <sub>5</sub> multiferroics: rare earth and pressure influence	47
17:20-17:40	<b>Oriana OSTA</b> , LLB, CEA-CNRS Water confined in amphiphilic nanopores	48
	<b>Elodie TAILLEUR</b> , LLB, CEA-CNRS Structure-properties investigations in a new family of multiferroic compounds	49
17:40-19:00	AG SFN	
19:00	<i>Pre-dinner drinks</i>	
20:00	<i>Gala dinner</i>	

## Thursday September 19th

09:00	<i>Shuttle departure, to Montpellier Saint-Roch Station</i>
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# Abstracts

# Investigating Systems Based on Single-Chain Nano-Particles by Neutron Scattering (and Others)

Arantxa ARBE<sup>1</sup>

<sup>1</sup>*Centro de Física de Materiales (CFM) (CSIC-UPV/EHU), San Sebastián, Spain*

Single-Chain Nano-Particles (SCNPs) obtained by intra-molecular cross-linking of linear macromolecules (precursors) are emerging soft nano-objects showing unique and remarkable physicochemical and rheological properties as a result of their locally collapsed structure and ultrasmall size. Sensing capabilities, controlled drug delivery and catalytic applications of SCNPs have been demonstrated in dilute conditions. The impact of internal cross-linking on the structural and dynamical properties of systems containing these nano-objects is the key question to answer in this context. During the last years we have applied neutron scattering techniques combined with other experimental methods and supported by coarse grained molecular dynamics simulations to contribute to this field (see, e. g., [1-9]). Our studies include dilute and crowded solutions of SCNPs, all-polymer nano-composites and melts of SCNPs. Here we show the microscopic insight provided by our investigations on these intriguing systems.

- [1] D. Bhowmik, J. A. Pomposo, F. Juranyi, V. García-Sakai, M. Zamponi, Y. Su, A. Arbe and J. Colmenero, *Macromolecules* **47**, 304 (2014).
- [2] D. Bhowmik, J. A. Pomposo, F. Juranyi, V. García-Sakai, M. Zamponi, A. Arbe and J. Colmenero, *Macromolecules* **47**, 3005 (2014).
- [3] A. J. Moreno, F. Lo Verso, A. Arbe, J. A. Pomposo and J. Colmenero, *J. Phys. Chem. Letters* **7**, 838 (2016).
- [4] A. Arbe, J. A. Pomposo, I. Asenjo Sanz, D. Bhowmik, O. Ivanova and J. Colmenero, *Macromolecules* **49**, 2354 (2016).
- [5] A. Arbe, J. A. Pomposo, A. J. Moreno, F. LoVerso, M. González-Burgos, I. Asenjo-Sanz, A. Iturrospe, A. Radulescu, O. Ivanova, and J. Colmenero, *Polymer* **105**, 532 (2016).
- [6] M. González-Burgos, A. Arbe, A. J. Moreno, J. A. Pomposo, A. Radulescu, J. Colmenero, *Macromolecules* **51**, 1573 (2018).
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- [9] A. Arbe, J. Rubio-Cervilla, A. Alegría, A. J. Moreno, J. A. Pomposo, B. Robles-Hernández, P. Malo de Molina, P. Fouquet, F Juranyi, and J. Colmenero, *Macromolecules* (asap).

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## Stimuli responsive polymersomes: Small Angle Neutron Scattering studies

A. Brûlet<sup>1</sup>

<sup>1</sup> *Laboratoire Léon Brillouin UMR12 CEA CNRS, C.E.A. Saclay, 91191 Gif sur Yvette Cedex*

Amphiphilic copolymers self-assemble in water solution into stable and robust polymersomes (vesicles), which combined to a chemical design flexibility make them excellent candidates as drug or imaging agent carriers. The introduction of actuator in polymersomes and the engineering of their targeted cell adhesion are critical issues for the applications of disease imaging and therapy.

Numerous works are focusing on the development of stimuli-responsive and functionalized (smart) polymersomes. They generally respond to physical or chemical stimuli by bursting, change of membrane permeability (thickness and hydrophobicity), or by important structural modifications of the membrane or of the polymersome shape. Stimuli can be temperature or pH changes, magnetic field application, light irradiation (UV-VIS), osmotic shocks... Small Angle Neutron Scattering (SANS) is perfectly suited to the determinations of vesicles sizes and of the thickness and membrane structure of polymersomes. In the presentation, several examples will be given.

We first focused on polymersomes with photo-responsive liquid crystalline polymers as hydrophilic block. External stimuli such as heating and/or magnetic field application or UV irradiation have been applied to induce modifications of polymersomes membrane at the molecular level [1, 2].

Another study related to the purpose of theranostics is the incorporation of inorganic particles (magnetic nanoparticles or quantum dots) in polymersomes. As example, in hyperthermia, drug delivery can be finely tuned by the right amount of magnetic nanoparticles inserted in the polymersomes membrane. SANS can proved the shell structure of magnetic nanoparticles embedded in the polymeric membrane of polymersomes [3].

Hybrid vesicles resulting from the simultaneous self-assembly of amphiphilic copolymers (P) and phospholipids (L) integrate the bio-functionality of lipids and the enhanced stability and various coupling chemistries of polymers in a single hybrid vesicular structure. In such systems, composition (polymer/lipid ratio) and polymer architecture (graft copolymer vs. diblock or triblock) can be varied to obtain either homogeneous or nanostructured membranes. By varying the block length of the hydrophobic polymer, we can tune the thickness mismatch between lipid polymer membranes and play with the conformational constraints of the polymer chains at the L/P boundary. SANS is used to determine the homogeneous or the nanostructured character [4, 5] within the membranes of these hybrid vesicles.

[1] S. Hocine, A. Brûlet, L. Jia, J. Yang, A. Di Cicco, L. Bouteiller, M.H. Li, *Soft Matter*, 7 (6) (2011) 2613 – 2623.

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[4] Dao TPT., Brûlet A., Fernandes F., Er-Rafik M.; Ferji K.; Schweins R.; Chapel J.P., Schmutz F.M., Prieto M., Sandre O., *Langmuir* 33,7 (2017) 1705-1715.

[5] T. P. Tuyen Dao, F. Fernandes, M. Er-Rafik, R. Salva, M. Schmutz, A. Brûlet, M. Prieto, O. Sandre and J.-F. Le Meins, *ACS Macro Lett.* 4 (2015) 182–186.

## Examples of quantum ground states and excitations

Mechthild Enderle<sup>1</sup>

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Many crystalline materials with interacting magnetic moments perform a phase transition into magnetic long-range order with a periodic arrangement of vector-like ordered moments and excitations that are small oscillations around this order (spin waves). When the interacting momenta are spins  $1/2$  or  $1$ , and the interaction low-dimensional and/or frustrated in such a manner that fluctuations prevent long-range order partially or entirely, the material may find a more exotic way to reduce the entropy towards zero temperature, a collective quantum ground state. The ground state wave function depends on the local spin and the interactions (there are many different types), and unlike magnetic long-range order, the inner structure of the wave function is usually not accessible to neutron diffraction. The magnetic excitations of such collective quantum ground states are often 'topological', soliton-like, they are strong perturbations of the ground state and change it qualitatively. These excitations can be probed with neutron scattering, their spectrum, field dependence and/or polarisation can be very different from spin waves and therefore serve as fingerprint of the respective ground state. Neutron scattering on magnetic-field induced phases may likewise display characteristic traits of the 'hidden' collective quantum ground state. The talk presents examples of neutron diffraction on field-induced phases and inelastic neutron scattering on materials with dominant collective quantum behaviour.

# Structure and Persistence of High Generation Dendronized Polymers

F. Dutertre<sup>1</sup>, E. Vereroudakis<sup>2,3</sup>, K.-T. Bang<sup>4</sup>, B. Loppinet<sup>2</sup>, T.-L. Choi<sup>4</sup>, and G. Fytas<sup>2,5</sup>

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Well-defined dendronized polymers (denpols) formed by polymer with high-generation dendron side chains have been proposed as exemplar nano-objects. However, their structural complexity and steric hindrance makes their syntheses very challenging. Here, we report the characterization of a unique series of high generation denpols of poly(norbornene) (PNB) containing ester dendrons. Denpols with large degree of polymerization were synthesized by ring-opening metathesis polymerization (ROMP), up to the sixth generation (G6), the highest generation ever polymerized among dendronized polymers prepared by graft-through approach. Combination of size-exclusion chromatography (MALLS-GPC), light scattering (SLS/DLS) and neutron scattering (SANS) allowed a thorough structural study of these large denpols in dilute solution [1,2]. A semi-flexible cylinder model was successfully applied to represent both the static and dynamic experimental quantities yielding persistent length ( $l_p$ ), cross-section radius ( $R_{CS}$ ) and contour length ( $L$ ). The denpol persistency was found to increase with generation, with  $l_p$  reaching 27 nm (Kuhn length = 54 nm) for PNB-G6. Denpols with a different backbone, poly(endo-tricyclo[4.2.2.0]deca-3,9-diene) (PTD), exhibited larger persistency presumably due to the higher grafting density of the PTD denpols. High values of the aspect ratio  $l_p/R_{CS}$  attained for the high generation denpols could possibly lead to formation of liquid crystalline phase at larger concentration.

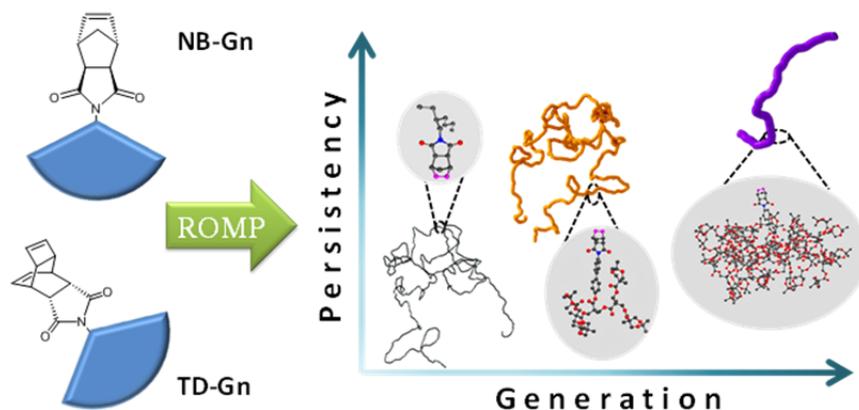


Illustration of macromonomer and denpol conformation vs dendron generation

[1] F. Dutertre, K.-T. Bang, B. Loppinet, I. Choi, T.-L. Choi, G. Fytas, Structure and Dynamics of Dendronized Polymer Solutions: Gaussian Coil or Macromolecular Rod? *Macromolecules* (2016), 49 (7), 2731-2740.

[2] F. Dutertre, K.-T. Bang, E. Vereroudakis, B. Loppinet, S. Yang, S.-Y. Kang, I. Choi, T.-L. Choi, G. Fytas, Conformation of Tunable Nano-cylinders: Up to Sixth Generation Dendronized Polymers via Graft-Through Approach, *Macromolecules* (2019), 52 (9), 3342-3350.

# Orbital Currents in the Quasi-1D Spin Ladders Compound $(\text{Sr,Ca})_{14}\text{Cu}_{24}\text{O}_{41}$

**D. Bounoua**<sup>1</sup>, L. Mangin-Thro<sup>2</sup>, J. Jaehong<sup>3</sup>, A. Wildes<sup>2</sup>, R. Saint-Martin<sup>4</sup>, L. Pinsard-Gaudart<sup>4</sup>, Y. Sidis<sup>1</sup> and P. Bourges<sup>1</sup>

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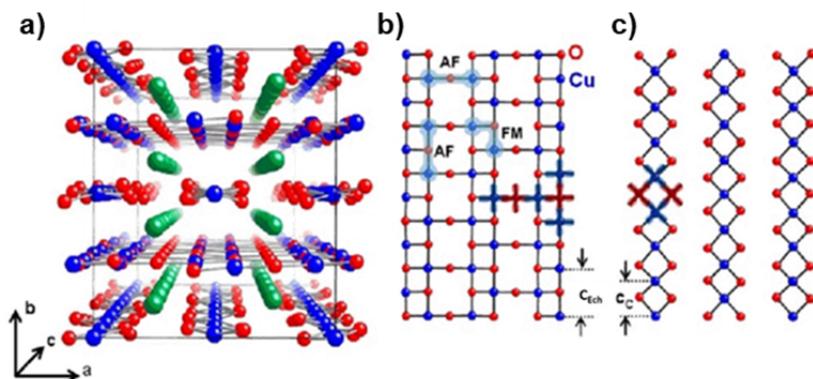
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The onset of an intra-unit cell magnetism (IUC), when entering the pseudogap state ( $T=T^*$ ) of High-Tc cuprates was shown to occur in four different families of layered cuprates, using polarized neutron diffraction (PND) [1]. This IUC magnetism breaks the time reversal symmetry but preserves the translational symmetry of the lattice giving rise to a  $q=0$  antiferromagnetic order, consistent with other reports on time reversal and inversion symmetry breaking at  $T^*$  (Fig.1) [2]. The  $T_{\text{mag}}$  corresponding to the IUC magnetism tightly follows the temperature vs hole dependence of the pseudogap state boundary with  $T_{\text{mag}}=T^*$ . Its magnetic structure factor measured by PND is consistent with the loop current model proposed by C.Varma [3], which predicts the existence of spontaneously circulating orbital currents within the  $\text{CuO}_2$  planes, with two-loops per Cu site turning clockwise and anti-clockwise and producing two out-of-plane antiparallel magnetic moments per site.

We probed the signature of such magnetism using PND in a quasi-1D SC cuprate family, the so-called “telephone number” series  $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41}$  (with  $x_{\text{Ca}}=5$  and 8), where the existence of such orbital magnetism was predicted by [4]. This compound has an incommensurate nuclear structure consisting of an alternating stack of  $\text{CuO}_2$  chains and  $\text{Cu}_2\text{O}_3$  two legs-ladders along the b-axis. The chains and the ladders interpenetrate incommensurably along the c-axis with an incommensurability ratio:  $\gamma = \frac{c_{\text{chains}}}{c_{\text{ladders}}} \sim 0.7$  (Fig.1).

The pure compound ( $x_{\text{Ca}}=0$ ) is intrinsically hole-doped, with holes localized within the  $\text{CuO}_2$  chains, giving an effective valence of  $\text{Cu}^{2.25+}$ . The Ca-doping produces a chemical pressure leading to a transfer of holes from the chains to the ladders subsystem giving rise to a rich electronic phase diagram. A superconducting transition also occurs for Ca doping, in the range:  $10 \leq x_{\text{Ca}} \leq 13.6$  [5]. Our PND measurements on  $x=5$  and 8 Ca-doped compounds reveal the systematic emergence of an unprecedentedly reported low temperature IUC-magnetism within the ladders subsystem. This IUC magnetism exhibits short [a,c] in-plane correlation lengths and no inter-plane correlations and satisfies the expected structure factor for spontaneously circulating loop currents patterns, as predicted by two different models [3,7]. Our measurements further show an increase of the correlations upon increasing the Ca-(or equivalently hole-) doping along with an enhancement of the onset temperature of this IUC magnetism. Results from PND will be presented and discussed.



**Figure 1.** Crystal structure of  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ . (a) Stack of  $\text{CuO}_2$  chains and  $\text{Cu}_2\text{O}_3$  ladders along the b-axis (Cu in blue and O in red), intercalated by Sr ions (green). (b) Two-leg  $\text{Cu}_2\text{O}_3$  ladders within the [a,c] plane. Neighboring ladders are shifted

[1] L. Mangin-Thro *et al.*, Nat. Comm. 6 (2015) 7705 (and references therein).

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[3] C.M. Varma, Phys.Rev.B 73 (2006) 15.

[4] P. Chudzinski *et al.*, Phys. Rev. B 76 (2007) 161101(R); Phys. Rev. B 78 (2008) 075124.

[5] T. Vuletić *et al.*, Phys. Rep. 428 (2006) 169.

[6] M. S. Scheurer *et al.*, Phys. Rev. B 98 (2018) 235126.

[7] D. M. Radheep *et al.*, arXiv:1303.0921 (2013)

## **Pourquoi va-t-on regretter Orphée? 39 years of ground-breaking results**

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Pourquoi va-t-on regretter Orphée? I will try answering this question by reviewing some of the main scientific highlights that were obtained at the Orphée reactor during the 39 years of its operation. In the broad area of hard condensed-matter physics, scientists could answer key-questions of topical problems with elastic or inelastic neutron scattering experiments at Orphée. Truly ground-breaking results, that had enormous impact, were obtained in: structural phase transitions and incommensurate phases, charge and spin-density wave ordering, high-temperature superconductivity in cuprates and unconventional superconductivity, spin-Peierls transition, giant magneto-resistance in doped manganites, and multiferroics and magnetoelectrics. The reasons for the impressive list of scientific success are not only the very good properties of the Orphée neutron source and its instrumentation but also its excellent integration in the surrounding scientific communities.

## Spontaneous deswelling of microgels controlled by counterion clouds

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Microgels based on poly(N-isopropylacrylamide) (pNIPAM) show a unique, spontaneous deswelling behavior at constant temperature below the deswelling transition of pNIPAM at 32C when brought above a critical concentration. We have shown that counterion clouds of pNIPAM microgels provide the mechanism for this spontaneous deswelling [A. Scotti et al., PNAS 113, 5576 (2016)]. Although pNIPAM is uncharged, charged groups are incorporated on the particle surface during synthesis. Counterions not bound by the surface charge set the osmotic pressure of the microgel suspension. At high concentration, the overlap of counterion clouds of neighboring particles causes an increase of the osmotic pressure in the space between the particles, while the pressure in the interior of the microgels does not increase. The resulting pressure difference deswells the microgels, if it exceeds their bulk modulus. Measurements of the microgel size at high concentrations using small-angle neutron scattering show that the volume fraction remains below random close packing up to effective volume fractions of about 1.0. We show that the essential aspects of the observed deswelling are captured with a Poisson-Boltzmann model of the microgels and without direct interaction of the microgels.

We find that crystallization in polydisperse suspensions is directly linked to this deswelling mechanism: crystallization only occurs when particle deswelling of the softest and largest microgels has reduced the polydispersity [A. Scotti et al., Phys. Rev. E. 96, 032609 (2017)].

# Operando Diffraction During Li Battery Operation using Neutron and Synchrotron X-Ray Radiations

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Performing *in situ* and *operando* measurements on electrode materials for Li-ion and Na-ion batteries is of importance for their understanding and improvement. Electrode materials need to be studied in their environment (*in situ*) and in real time while they function (*operando*), since they normally operate in non-equilibrium conditions. Real-time experiments upon charge/discharge of the electrodes (i.e. upon lithium or sodium extraction/insertion from/into the electrodes) unveil dynamics that are not accessible by other means and allow a more complete understanding of the electrodes' functioning. The use of different probes is an important requirement for the study of such reactions. The combined use of X-Ray Powder Diffraction (XRPD), Synchrotron radiation XRPD and Neutrons Powder Diffraction (NPD) allows observing any atomic element in any crystalline electrode. However, custom setups are required to carry out *operando* diffraction experiments on batteries.

We recently designed an electrochemical cell manufactured with a completely neutron-transparent (Ti,Zr) alloy [1]. Used with deuterated electrolytes, the cell is able to combine good electrochemical properties and the ability to collect ND patterns *operando*, with good statistics and no other Bragg peaks than those of the electrode material of interest. Importantly, this allows detailed structural determinations by Rietveld refinement during operation. The cell was validated using well-known battery materials such as LiFePO<sub>4</sub> and Li<sub>1.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> demonstrating real *operando* experiments conducted on the D20 high flux neutron powder diffractometer at ILL Grenoble, France.

## Acknowledgements

This research is performed in the frame of the French network RS2E (<http://www.energie-rs2e.com>) and of the European network ALISTORE-ERI (<http://www.alistore.eu>).

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## Structure determination of core-shell microgels for the use as nano-actuators

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Microgels are colloidal gels smaller than 10  $\mu\text{m}$  and can be used in a wide range of applications like drug delivery and smart surface coatings.<sup>[1]</sup> Microgels consisting of acrylamides like *N*-isopropylmethacrylamide (NIPMAM) or *N*-*n*-propylacrylamide (NNPAM) as network component, show a monomer-specific change in size with the temperature. For NIPMAM-NNPAM core-shell microgels this change in size is linear. These systems could be useful for nano-actuators.

We synthesized such core-shell and NIPMAM core-only microgels and studied their structure and swelling behavior with photon correlation spectroscopy and small-angle neutron scattering (SANS) in suspension. The use of a core-shell microgel with a hydrogenated core and a deuterated shell allowed us to investigate each compartment separately by contrast matching SANS. For the data analysis we used a recently developed Monte Carlo approach.<sup>[2]</sup> It is based on a multi-shell model and reveals the monomer density in the microgel particle. Figure 1 shows the monomer density profile of a NIPMAM microgel at different temperatures. The two sets of profiles show unambiguously that the core density in the microgel center is higher without shell (a) than with a contrast matched shell (b).<sup>[2,3]</sup> Hence, the shell leads to a more expanded core.

Furthermore, we coated a surface with these microgels and analyzed the surface structure and behavior of the microgel coating with Ellipsometry and AFM.

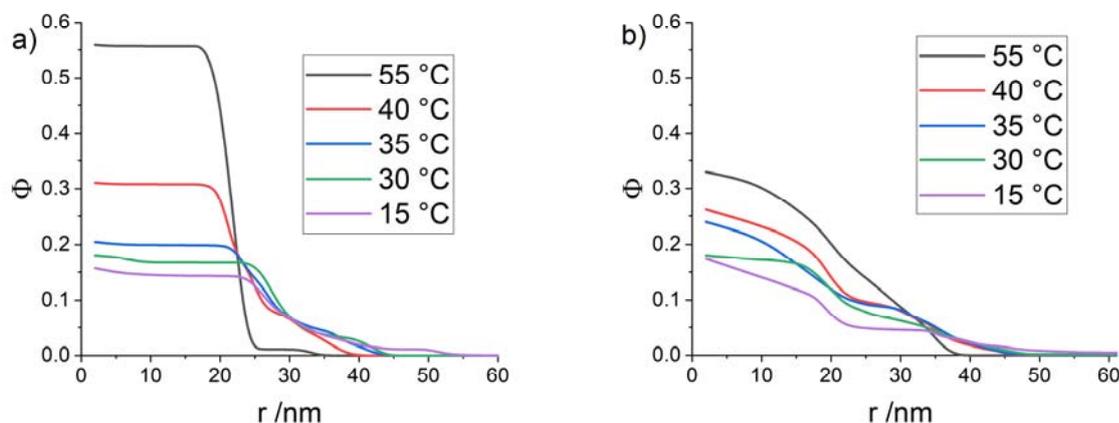


Figure 1: Density profile of a NIPMAM microgel (a) without shell (b) with an invisible shell.<sup>[2,3]</sup>

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## Rietveld method for polarized neutron powder diffraction

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Polarized neutron diffraction is a powerful tool to investigate interatomic or intermolecular magnetic interactions. It can be used to determine the atomic susceptibility tensor characterizing the magnetic response of individual atoms to an external magnetic field [1]. Recently it has been demonstrated that the information about local magnetic susceptibility can be obtained from polarized neutron diffraction on magnetized powder samples [2]. However, due to the absence of a general Rietveld type software adapted to the analysis of diffraction profiles of polycrystalline samples the polarized neutron diffraction is hardly applicable to a number of highly interesting materials like molecular magnets or nanoscale systems.

An implementation of 1D and 2D Rietveld method for the analysis of local magnetic susceptibility by polarized neutron powder diffraction (PNPD) is presented. The expression for the powder averaging in PNPd in field is given for the general scattering geometry. The results of 2D Rietveld analysis of diffraction spectra from soft ( $\text{Fe}_3\text{O}_4$ ) and high ( $\text{Ho}_2\text{Ti}_2\text{O}_7$ ) magnetic compound are in a perfect agreement with these previously reported in single crystal experiments [3, 4]. It is demonstrated that using the "magnetically textured" powder and the 2D Rietveld refinement allow to obtain the precision in the determination of the susceptibility parameters close to that obtained in the single crystal measurements. This should open route to PNPd for data from large area detectors commonly used at modern neutron sources.

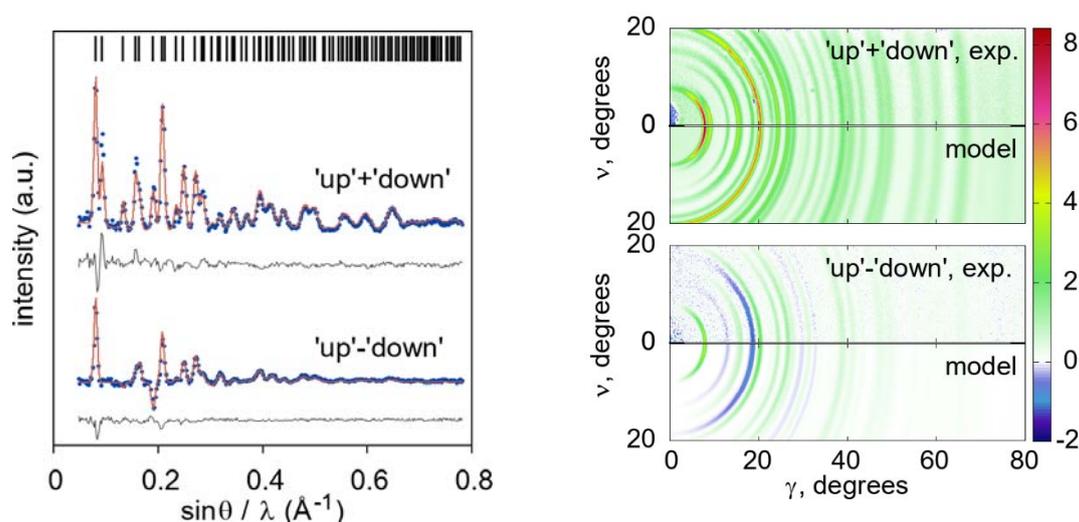


Fig. The measured and calculated flipping sum (top) and difference (bottom) diffraction spectra collected on  $\text{Ho}_2\text{Ti}_2\text{O}_7$  at diffractometer 5C1 (LLB),  $T=5\text{K}$ ,  $H=1\text{T}$  for 1D (left) and 2D (right) diffraction profiles.

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## Neutron: a unique probe to understand food structure under processes

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The food scientist is commonly confronted with the challenge of modifying the formulation of a food product. The objective may be to enhance the taste, texture or appearance of the food, to produce a product with a longer shelf-life or a healthier image, or to improve manufacturing efficiency by incorporating a cheaper ingredient or adopting a new processing technology. The speed with which these objectives can be accomplished depends on the level of fundamental understanding that exists on the key physico-chemical factors affecting products properties. In the case of foods proteins, it is especially important to understand how the interfacial and aggregation behaviour of the proteins are affected by processing conditions (heat, drying, freezing, shear forces), or by molecular interactions with other constituents (fat, hydrocolloids, aroma, water...). One of our goals is to improve insights into such factors by taking advantage of polymer science concepts and neutron scattering and imaging techniques. We tried these last years to increase the applications of neutron tools to food science, food proteins and food ingredients [1, 2].

We will illustrate the powerful of the neutron imaging and tomography techniques by studies made on milk, cereals and meat. Neutron images of food samples contain information on components dynamics, size and shape of the particles in solution, gels or powders and can be obtain under processes (T, HP, RH...). Neutron imaging and tomography offers unique capabilities for in situ measurements because neutrons can penetrate materials such as metals even several centimeters [2]. Their special sensitivity to organic materials, especially water, makes them an ideal tool for the non-destructive inspection of industrial components. We will present our most recent projects of application of neutron imaging to predict dynamic hydration of milk powders, cereals porosities as function of relative humidity and to observe meat during cooking. [3,4].

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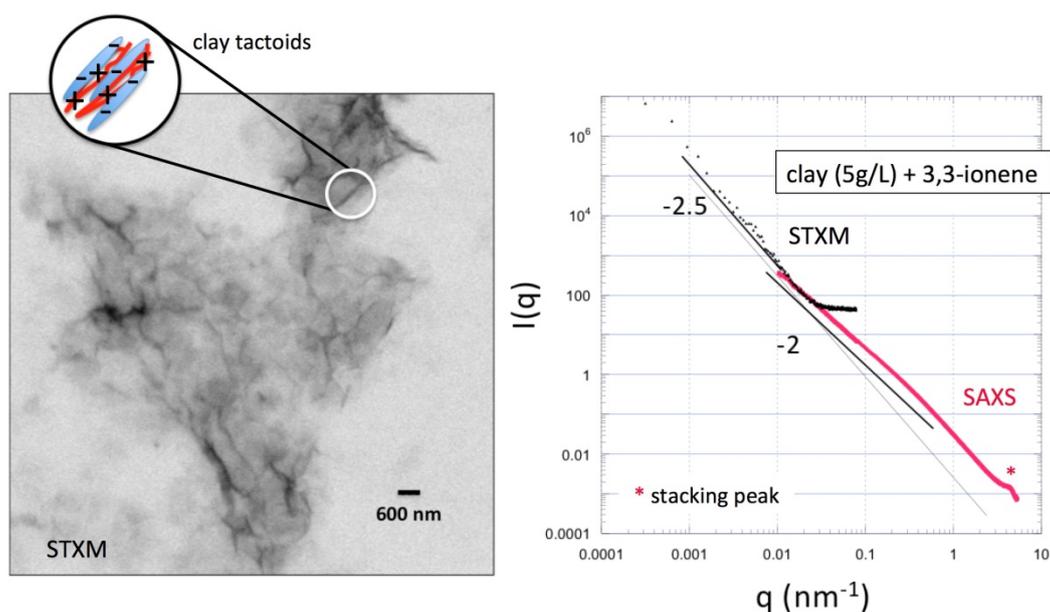
## Flocculation of clay colloids: combining scattering and imaging techniques

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Flocculation is a key process in numerous environmental and industrial technologies, such as purification of waste-water and civil engineering. We study flocculation of the plate-like clay colloids by ionenes, cationic polyelectrolytes with a regular charge density, which can be tuned to match/mismatch the clay charge density [1,2]. Combination of turbidity and zeta-potential measurements allowed us to identify the optimal flocculation conditions for ionene-clay mixtures. For all systems studied flocculation started consistently at ratios of positive and negative charge significantly below 1 (as low as 0.3), indicating highly ionene-deficient aggregates [4]. This early onset of flocculation in clay–ionene mixtures is reminiscent of the behaviour of multivalent salts and contrasts with that of monovalent salts, for which a large excess amount of ions is necessary to achieve flocculation [3].

We studied the structure of clay-ionene aggregates by a combination of small angle X-ray and neutron scattering (SAXS, SANS) and scanning transmission X-ray microscopy (STXM) (Fig. 1). The combined SAXS+STXM data gives us access to scattering curves spanning four decades in length scale, necessary for a multi-scale structure of the aggregates [5]. SANS measurements, under the contrast matching condition of the clay particles, gave us information on the conformation of the polyelectrolyte chains inside the aggregates formed. We see a clear evidence for the formation of clay tactoids within the otherwise loose aggregates, demonstrated by the presence of a stacking peak in the SAXS spectra [6]. The relative charge density of ionene chains and clay surfaces is a key parameter for the repeat distance within tactoids, but also tactoid abundance and possibly even the macroscopic aggregate density.



**Fig. 2: Structure of clay-ionene aggregates, STXM and SAXS.**

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# Influence of the alkaline feldspar-surrogates on the kinetic formation and the selectivity of pure CO<sub>2</sub> and CO<sub>2</sub>-N<sub>2</sub> mixed gas hydrates

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Gas hydrates are ice-like crystals composed of molecular gases encaged in a lattice of hydrogen-bonded water molecules<sup>1</sup>. They can be found in a variety of natural environment such as hydrate-bearing marine sediments or permafrost<sup>2</sup>. A lot of methods have been developed to extract hydrocarbons from hydrate-bearing marine sediments<sup>3,4</sup>. One of them is the methane recovery by carbon dioxide replacement in natural gas hydrates. This method is more efficient with CO<sub>2</sub>-N<sub>2</sub> gas mixture, instead of pure CO<sub>2</sub>, because of the preferential cage occupancy of the CO<sub>2</sub><sup>5,6</sup>. Petuya et al. (2018)<sup>6</sup> showed that, for this gas mixture, the N<sub>2</sub> would not impede the hydrate formation and CO<sub>2</sub> may trigger mixed hydrate formation. Because of the industrial relevance, special interest is given to the natural sediment influence on this mixed hydrate. Natural gas hydrates are found more easily in coarse sediments whose grains size exceeds 125 μm thanks to the greater permeability but with a low formation kinetic. When the grains are less than 125 μm, the mineralogical surface in contact with water and gas is increased thus promoting gas hydrate formation<sup>7</sup>.

Aluminosilicates (sodium, calcium and potassium feldspar) are minerals with Si-Al substitution and charged with alkali. This replacement allows them to have both larger reaction and hydrophobic surface, promoting CO<sub>2</sub>-hydrate dissociation<sup>8</sup>. In most of studies, only SiO<sub>2</sub> has been considered as a natural sediment analogue, leading to a lack of understanding on how the chemical surface properties of the mineral influence gas hydrate properties. In this way, different chemicals and particles sizes of feldspar surrogates have been synthesized, in order to understand the influence of the surrogate chemical composition.

Our recent study, using the high-resolution neutron two-axis powder diffractometer (D1B-ILL) showed that alkaline surrogates (sodium and calcium silicate) act like inhibitor of the induction time but allow to reach the diffusion plateau faster than a silica powder substrate. This inhibitory behaviour on the formation kinetics of CO<sub>2</sub>-hydrate may be attributed to reactions between the surrogate, the ice and the host gas. Indeed, the alkaline-silicate surrogate could interact with the carbon dioxide and the ice to form some hydroxide and carbonates, that act like an inhibitor of hydrate formation<sup>7,9</sup>.

Moreover, additional investigations using Raman microspectroscopy, shows that the selectivity, and therefore the preferential encapsulation of certain gas molecules, depends on the chemical composition of the surrogate. Indeed, the more the surrogate is charged with alkaline, the more the mixed hydrate is selective in N<sub>2</sub>. This selectivity is also influenced by the formation of carbonate, leading to competition between the two reactions. Thus, the chemical composition of the surrogates, in particular the alkali, plays a key role in the gas hydrates formation<sup>10</sup>.

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## Unfolding of food proteins by high pressure

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The understanding of protein folding, misfolding, and unfolding is a key question in structural biology. It is now very well known that applying high pressure (HP) results in the disruption of the protein native structure due to the decrease of the volume of the protein/solvent system upon denaturation [1]. Recent studies demonstrate that pressure unfolds proteins because of hydrophobic cavities that are present in the folded state and which are eliminated in the unfolded state [2]. Internal cavities are thus important structural features for proteins and sources of fluctuations between different conformational states, which can be stabilized by subsequent ligand binding. Food treatment by HP represents an interesting approach with numerous advantageous. Proteins are one of the major components in food and modifications of proteins by HP treatment can significantly change techno-functional properties of food. Bovine beta-lactoglobulin (BLG) is the major whey protein with wide applications in food industry. Taking into account the ability of BLG to bind various ligands, as well as its high propensity towards unfolding under HP [3], it represents a good model system to study the effects of ligand binding on pressure stability of proteins.

Small-angle neutron scattering (SANS) of protein solutions upon HP is a useful technique to provide direct information on the three-dimensional conformation of proteins in solution, their isothermal compressibility, but also more indirectly the protein-ligand interactions. The main challenge in studying the protein behaviour under HP by SANS is to design a resistant HP cell with the smallest scattering intensity and the highest transmission possible.

In the present study, we designed a new HP cell for SANS measurements on proteins in solution (at concentrations of a few g/L) with the pressure resistance up to 600 MPa using removable metallic alloys windows, which display both reasonable transmission and scattering [4]. For this purpose, the HP-SANS cell was tested using solutions of myoglobin (Mb), a protein with high resistance to HP. The obtained scattering profiles of Mb solution in HP and quartz cells superimpose well. Therefore, although the HP cell displays scattering *per se*, it is possible to recover the signal arising from the protein solution. This HP-SANS system has been recently used for studying the effects of the bioactive -antioxidant- ligand resveratrol on pressure stability of BLG. Our preliminary data have revealed that resveratrol binding could decrease protein radius of gyration ( $R_g$ ) at 100 MPa by about 5%, while free protein has negligible changes of  $R_g$  at this pressure. Higher pressures (280 MPa) induce increasing of  $R_g$  in both samples; however  $R_g$  of BLG-resveratrol complex is lower for 10% in comparison to free BLG. Therefore, our results suggest that the ligand binding to BLG hydrophobic cavities increases the protein compactness at HP conditions.

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## Investigation of the impact of silica media on gas hydrates selectivity

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Clathrate hydrates (also called gas hydrates) are nanoporous crystalline solids composed of hydrogen-bonded water molecules forming cages within which gaseous molecules are encapsulated. They are naturally present on Earth, on permafrost regions and on oceans floors, but also on other comets and planets of the Solar System. [1] This natural occurrence makes them relevant for many geophysical and astrophysical applications [2]. In natural media, they are formed in the presence of sediments. What influence do these sediments have on the physico-chemical properties and the formation of gas hydrates? Answering this question is of prime importance to fully understand the properties of these systems [3].

We have studied the properties of mixed gas hydrates, i.e., co-encapsulating two gaseous species formed from CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> gas mixtures. The substrate was an artificial environment, using silica beads (diameter ranging from 0.075 to 250 μm) as an idealized environment to substitute to the natural sediments. Several properties have been investigated: the molecular selectivity (i.e. which gaseous specie is preferentially trapped), the gas diffusion at the silica/hydrate interface, the formation kinetics of mixed clathrate hydrates and the structural stability of these systems. Both theoretical and experimental techniques have been used to study all these properties: *Raman spectroscopy, quasi-elastic neutron scattering, neutron diffraction or quantum mechanics DFT calculations.*

The theoretical results made it possible to study the structural and energy stability of two pure hydrates as a function of the amount of gas trapped inside. In addition, the experimental results obtained show that the sediment surrogates have an influence on the properties of gas hydrates, such as the improvement of the molecular selectivity within the mixed hydrate or the modification of the formation kinetics. Some of these results will be presented and discussed.

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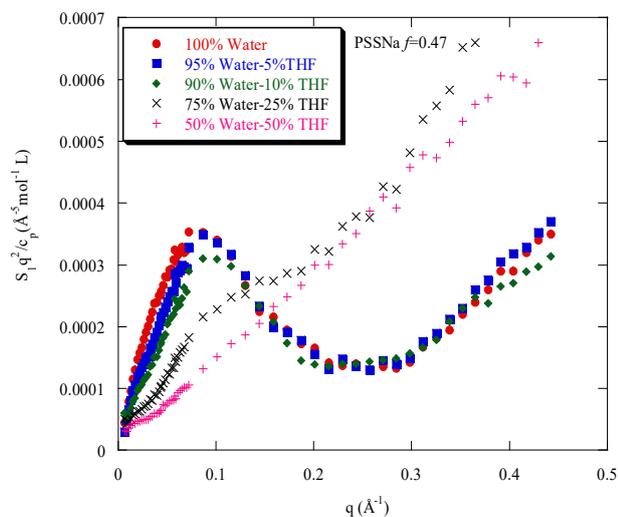
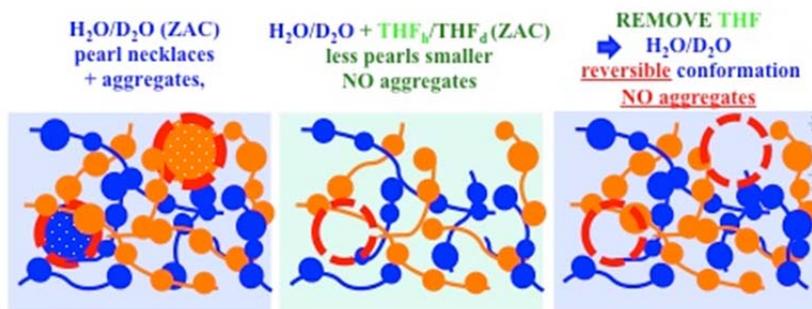
# How Necklace Pearls Evolve in Hydrophobic Polyelectrolyte Chains under Good Solvent addition: using the SANS-Zero Average Contrast method to study the Conformation

**Boué François**<sup>1</sup>, Brûlet Annie<sup>1</sup>, Ben Mahmoud Souha<sup>2</sup>, Essafi Wafa<sup>2</sup>

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The chain conformation in sulfonated polystyrene PSSNa of a degree of sulfonation  $0.34 \leq f \leq 1$ , i.e., of various hydrophobicity, is followed in mixtures of water and increasing content of tetrahydrofuran (THF), a good solvent of the hydrophobic polystyrene moieties (which improves the solvent quality of the mixture). This is achieved by measuring the chain form factor by small angle neutron scattering using the zero average contrast method (ZAC). Polymer concentrations 0.17 and 0.34 M correspond in our case to the semidilute regime or its limit with dilute regime depending on the chain conformation. The main result is the monitoring with added THF of the pearl necklace conformation. This heterogeneous structure, made of wormlike chain parts (strings) and pearls, was observed formerly in water: when  $f$  decreases, the string contribution decreases, and the pearls size, characterized by a maximum in Kratky  $q^2 S_1(q)$  representation, slightly increases. Here we see that in the presence of increasing content of added THF (i) the pearls contribution decreases, as expected, and (ii) their size does not change by more than 10% in most cases (30% at the most). Among different modeling, the most complete has been done following the pearl necklace models of Schweins, Huber et al. [1] and Lages, Huber et al. [2]; beyond the size and distribution of pearls, it addresses the radius of gyration, the correlation distance between spheres, weakly visible, and, importantly their number  $N$ . The values of  $R_g$ , as well as the modeling, suggest that while the sphere size varies a few,  $N$  decreases clearly with added good solvent. A link with the simulation of Liao et al. [3] can be found.



**Figure 1** (besides)

Single chain scattering times squared scattering vector,  $q^2 S_1(q)$  vs  $q$ : the bump, signalling the pearls, vanishes with increased THF concentration.

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- [3] Q. Liao; A. V. Dobrynin; M. Rubinstein, *Macromolecules* 2006, 39, 1.

## Specific water structure in a geo-inspired nanotube and interrelated dynamics

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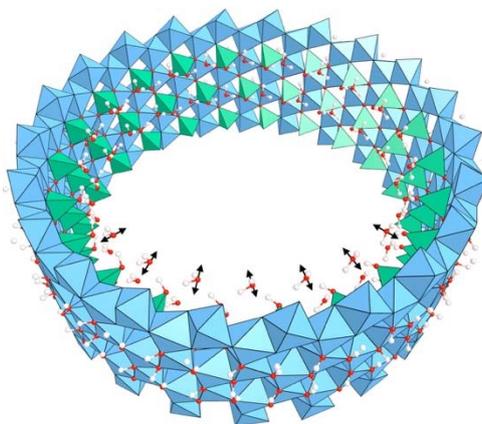
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Imogolite-like nanotubes are ideal platforms for studying the novel properties of molecules confined at the nanoscale. Compared to the well-known carbon nanotubes (CNT), the diameter of inorganic imogolite tube (INT) is well defined and can be adjusted at the angstrom level. Moreover, the molecular affinity of their inner cavity is tunable [1]. It should be underlined that such properties confer to these tubular structures a wide range of potential applications, from filtration to depollution of water.

Here, we show that alumino-germanate imogolite nanotubes are nanocontainers of interest in the growing field of nanofluidics. Nanotubes of nominal composition  $\text{SiAl}_2\text{O}_3(\text{OH})_4$  and  $\text{GeAl}_2\text{O}_3(\text{OH})_4$  (Si-INT and Ge-INT) are hydrophilic nanochannels. The structure and dynamics of water in Si-INT have been recently investigated [2, 3]. Surprisingly, the properties of water are modified when molecules are confined inside Ge-INT of slightly larger diameter [4]. Inelastic neutron scattering experiments coupled to ab-initio molecular dynamics simulations reveal a unique structure of the water layer adsorbed inside Ge-INT. It differs from that of water in Si-INT and, to the best of our knowledge, from that of any kind of two-dimensional water. We show that the dynamics of INT and water are interrelated, which has not been evidenced in Si-INT. A well-defined translation vibrational mode of water molecules with respect to the nanotube wall (illustrated with black arrows in the figure) is also observed. Finally, the evolution of mean square displacements of water molecules as a function of temperature is found to differ markedly in Ge-INT and in CNT [5], in which water slips without friction, which is attributed to the peculiar bonding of water molecules with germanol groups.



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## First neutrons on *IPHI – Neutrons @ Saclay*

***F. Ott***

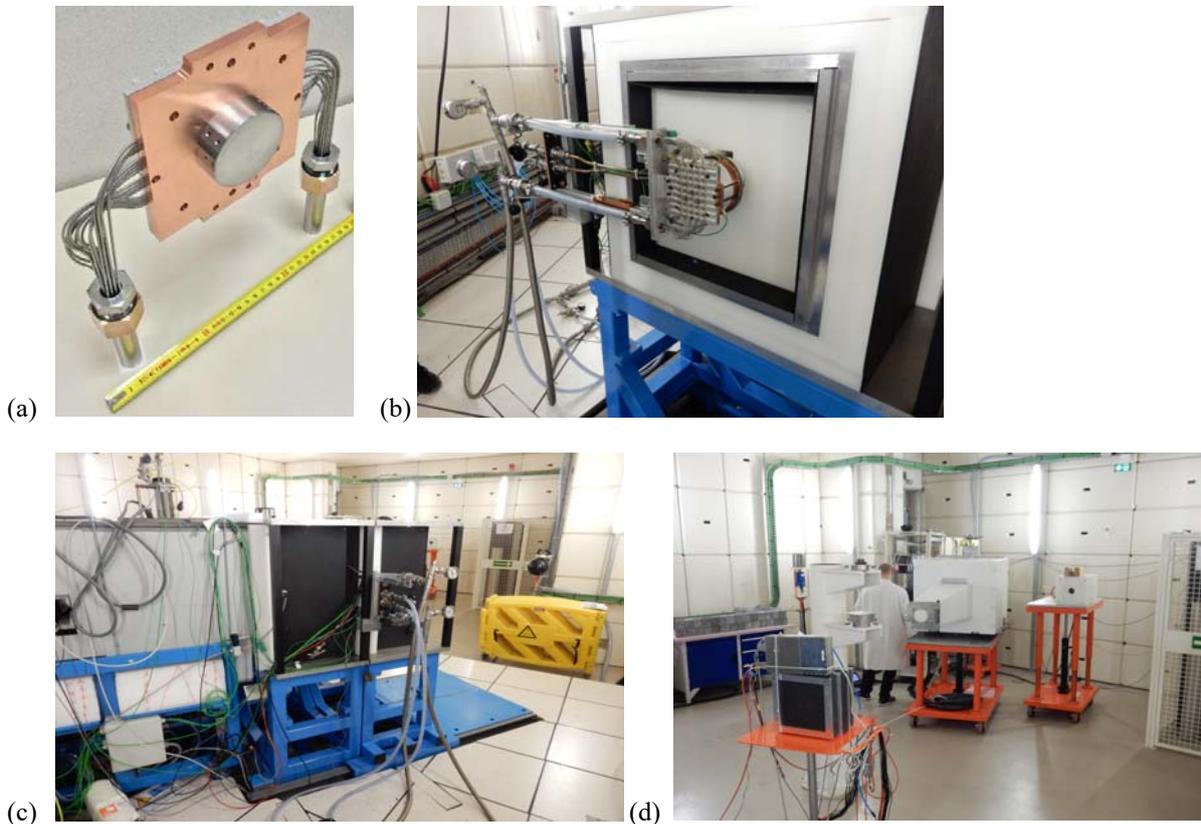
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The region Ile-de-France is currently supporting the construction of a small Compact Accelerator-based Neutron Source (CANS). The project is using the existing accelerator IPHI at Saclay. Design and construction of the source elements were achieved in winter 2019 including a target system, a shielding set-up and a “generic” scattering instrument DIoGENE. The target consists of solid beryllium which emits neutrons when it is split by incident protons. The moderator consists of polyethylene. The first version of the set-up is aimed at demonstrating that the target system is capable of handling a high power density ( $500\text{W}/\text{cm}^2$ ) as well as very high proton fluences.

In spring 2019, the source has been operating at power of up to 3kW for several hours. Further tests will be performed during summer time to demonstrate the durability of the target system ( $>100$  hours).

Assuming no dramatic failure we expect to produce neutron scattering data during this period.

These tests are aimed at qualifying the target system as well as demonstrate the performances of CANS for neutron scattering. The outcome of successful tests would be to upgrade the system to operate at a power on the order of tens of kW in 2020.



*(a) The Be target and its cooling system. (b) The target integrated in the (half) moderator assembly. (c) The accelerator tunnel and the TMR assembly. (d) Parts of the DIoGENE instrument.*

## **PANTHER: the new thermal time of flight spectrometer at the ILL.**

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PANTHER (Polarization ANalysis on a THERmal time-of-flight) is a multi-purpose direct geometry thermal neutron time-of-flight (TOF) spectrometer optimized for studies of magnetism, single crystals, and small samples. Its high neutron flux, medium resolution, large detector coverage, and wide span of incoming energies allows for fast mapping of magnetic and structural excitations over a large range of wave-vector and energy transfers. PANTHER will allow for the use of complex sample environment, including the 10 Tesla « IN5 » magnet. It will also be equipped with full longitudinal polarization analysis using a  $^3\text{He}$ -filter device (PASTIS-3). The instrument is under construction at the H12 beam tube and will replace IN4C.

Compared to IN4C, the main improvements are the use of position-sensitive detectors (PSD), a well-shielded flight chamber connected to a wide-diameter sample area with a common vacuum, fully double focusing monochromators, additional background choppers, and non-magnetic construction materials. This will lead to a gain in flux of about two, an increased solid area of a factor of three, and a reduced background by a factor of ten. The improved signal-to-noise ratio of 60 will be profitable for studies of magnetism, lattice dynamics, and vibrational spectroscopy in the incoming energy range 6-120 meV. The use of  $^3\text{He}$  PSD's will allow for single-crystal studies.

In this presentation we will review most of the critical aspects of this project, from the focusing principle to the description of the last generation of background choppers to be installed on PANTHER. We will also discuss PANTHER's timeline, from the present state to the first experiment in the user program.



## Measuring SANS and NMR simultaneously: a new tool for transient physics

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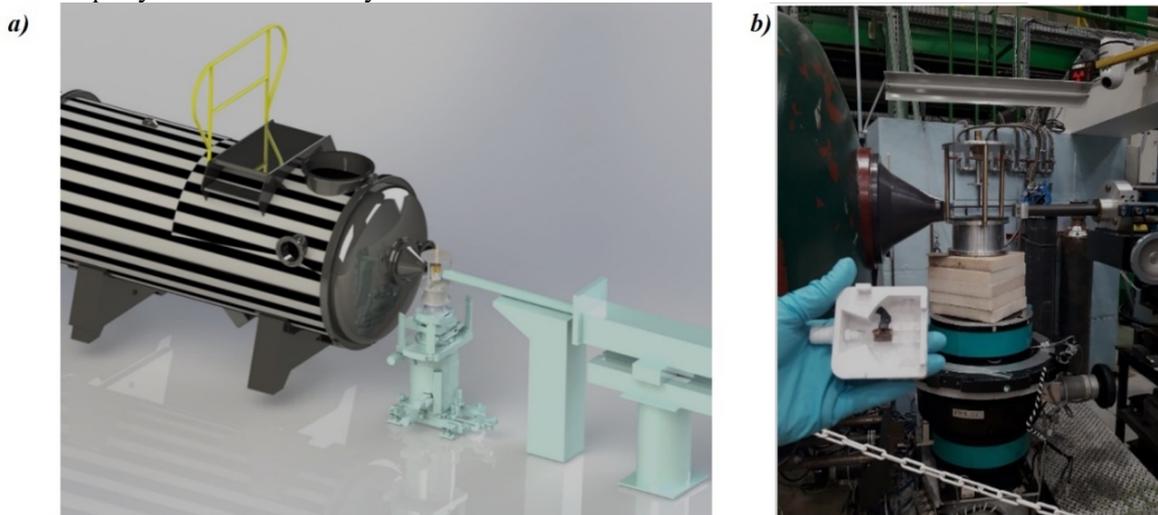
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Specific properties of soft condensed matter result from the control of subtle interactions which trigger macroscopic variations. In such (macro)molecular assemblies, tuning molecular interactions via external chemo/thermo/photo (...) stimuli is often the key point to control self-aggregation mechanisms and the visible properties (optical, viscosity, color ...). Analysis of such multi-scale transformations requires usually a multi-technique approach to probe both structural and dynamical changes. To this respect, Small Angle Neutron Scattering (SANS) is a central tool to probe nanometric structures while Nuclear Magnetic Resonance (NMR) is a versatile technique which can easily probe dynamical information such as local reorientation mechanisms (relaxation times) and self-diffusion coefficients of molecules.

In this talk, we report on an **original setup** which allows to measure simultaneously *in-situ* SANS and NMR using a low-field spectrometer<sup>[1]</sup>. We illustrate the capabilities of alliancing these experimental methods by following the critical temperature-induced phase separation of a concentrated Poly(Methacrylic Acid) (PMAA) solution at its Lower Critical Solution Temperature (LCST). The characteristic size related to the domain growth of the polymer-rich phase of the gel is monitored by the evolution of the SANS spectra, while the dynamics of the sol phase (H<sub>2</sub>O and polymer) is simultaneously characterized by NMR by measuring  $T_1$ ,  $T_2$  and the diffusion coefficient. A specific cell was carefully designed to optimize thermalization of the sample and in particular its equilibration time. The acquisition time needed to reach good signal-to-noise ratios, for both NMR and SANS, match: it is of the order of one hour. Altogether, we show that *in-situ* low-field NMR/SANS coupling the NMR is meaningful and is a promising experimental approach. Such multimodal approach is of major interest when a sample experiences transient physical states or evolves rapidly and/or irreversibly.



**Figure 1** : a) 3D model of the implementation of a low field NMR spectrometer on the LLB SANS instrument PAXY – the on-sided NMR magnet is seen in the middle of the drawing between the neutron guide (in turquoise blue) and the neutron detector box (zebra) (courtesy P. Lavie). b) Real picture of the central part and the NMR-Neutron probehead.

[1] R. de Oliveira-Silva, A. Bélimé, C. Le Coeur, A. Chennevière, A. Helary, F. Cousin, P. Judeinstein, D. Sakellariou, J.-M. Zanotti, *J. Neutron Research*, (2019) in print.

## **D16 diffractometer: more neutrons, more space, more fun**

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D16 is one of ILL's 2-axis cold neutron diffractometer. In terms of Q-space and Q-resolution, D16 nicely fills the gap between the small angle instruments and classical diffractometers.

Because of its special characteristics, D16 remains unequalled for the study of a wide range of systems in biology, physics and material science.

Its specifications have been optimized for the study of structures with relatively large periodicities of about 5 nm. These include large unit-cell lamellar organizations such as membranes or clays, two-dimensional membrane and surface lattice structures, colloidal and liquid structures, magnetic systems with large fluctuations giving rise to satellite reflections very close to Bragg peaks or small-angle scattering.

The instrument geometry offers a variable vertical focussing which allows working in reflectivity or diffraction mode. The scattering geometry obtained with large, vertically oriented samples, profits the most from the large vertical cross section of the beam at the sample position. A high resolution SANS setup is used routinely in experiments requiring the 1% wavelength bandwidth and the high angular resolution of the instrument.

In this presentation the new design, the major characteristics, performances and new directions of the instrument will be showed, as well as recent examples of research on D16.

In particular the ENDURANCE II detector project will be presented as well as examples where a major gain would be provided by a large banana detector (protein arrangement at nm scale, nanoporous materials, semi-crystalline polymers, time resolved and/or small sample experiments, as levitation, samples under mechanical stress).

## Using Light to see Neutrons: a new 2D detector with high resolution

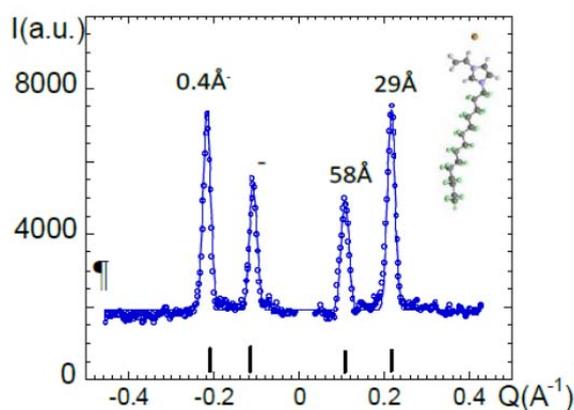
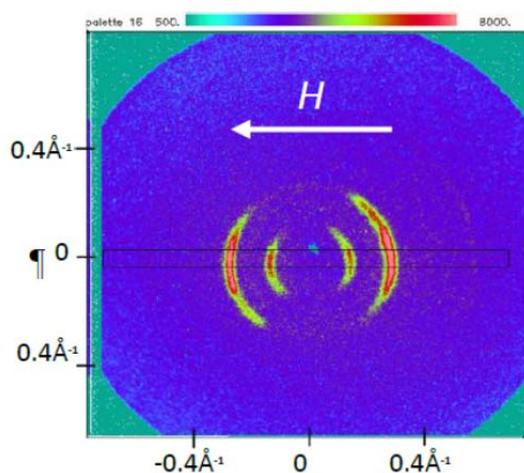
**P. Baroni**<sup>1</sup>, G. Exil<sup>1</sup> and L. Noirez<sup>1</sup>

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The evolution of light sensors enjoyed unprecedented growth since the last 20 years. This evolution is such that the camera of a smartphone can be used for Raman spectroscopy [1]. We will illustrate how the recent advances in light sensors revolutionize the observation tools in physics. Today this technology is sufficiently powerful to be exploited quantitatively in neutron spectrometry for the study of both elastic or inelastic scattering (time of flight). The two-dimensional High Resolution Neutron Detector, Barotron, is derived from this technology [2,3].

With a basis of 250 000 pixels, a resolution of 16 bits for each pixel, a very low detection limit ( $\ll 1 / \text{cm}^2 / \text{s}$ ), a high dynamic (16 bits) and an excellent spatial resolution ( $0.5 * 0.5 \text{ mm}^2$  or less), the Barotron performances compete the best current two-dimensional gas detectors. This new technology presents the huge advantage of being constantly upgraded by new sensors. This development opens a new generation of high-performance neutron detectors, versatile and adapted to new spallation sources for an ever more precise characterization of the properties of the samples.

We will give some examples of exploitation of the high resolution detector including imaging, diffraction or SANS.



Left figure: 2D-neutron pattern (without correction, smoothing or binning) recorded on Barotron detector enlightening the structure of a room temperature ionic liquid (RTIL). The azimuthal distribution of the intensity centered along the magnetic field direction reveals its ability to orient in a magnetic field together with its layer organization. With the courtesy of P. Judeinstein.

[1] A. Sences et al, ACS Photonics, 2014, 1, 17-26; D. Gallegos et al, Lab chip, 2013, 13,2124-2132, D. Pile Nature Photonics, 8 (2014) 168.

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## Phonon dynamics in energy materials

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Nowadays, the emerging field of phononics breathed new life into the study of the quasi-particle which is responsible for the transmission of sound and heat, the phonon. In fact, determining phonon's individual properties to understand microscopic origins of thermal transport is the basis of any knowledge-driven thermal engineering approach in a wide range of energy materials, including thermoelectrics or thermal management materials. Our understanding of thermal transport in dielectrics and semiconductors requires the knowledge of the phonon states in the phase space in momentum and in energy ( $q, E$ ) and as a function of temperature. Their experimental investigation, and more specifically, that of the anharmonicity which limits their lifetime and is responsible for the thermal resistance, is essential for the theoretical development. While phonon energies can be relatively easily measured by (X-rays, Neutrons) inelastic scattering techniques, this is not the case for its intrinsic energy width whose detection in crystals still remains beyond the current resolution limits of state-of-the-art spectrometers. However, it is fundamental to overcome such limitations for getting a microscopic understanding of thermal transport, as acoustic phonon lifetime is the only missing parameter for solving the Boltzmann transport equation. This has become urgent face to the recent progresses in *ab initio* computational methods which have allowed to achieve major breakthroughs on the understanding and prediction of the lattice thermal conductivity.

In this talk, I will present the neutrons and X-rays spectroscopy techniques currently used for measuring thermal phonon energies, specifically illustrating their technical limitations, which have prevented until now any measurement of phonons lifetime in most crystals. We will focus on the phonon dynamics in clathrates, a family of thermoelectric materials with complex crystal unit cell renowned for their puzzling low lattice thermal conductivity. Here, the first measurement of acoustic phonon lifetimes in a clathrate single crystal by means of the Neutron Resonance Spin Echo technique (NRSE) will be shown. Surprisingly, the materials is a very poor thermal conductor, acoustic phonons with long lifetimes, travelling over distances from a hundred to tens of nanometers have been observed. This finding challenges the common belief that low thermal conductivity implies short mean free paths.

# The Journey of a Correlation Peak through the Small-angle Scattering, Spin-Echo, and Reflectometry domains

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Elastic and inelastic neutron scattering techniques are fundamental tools to probe the molecular behaviour of at smallest length and time scales. In particular, static and dynamic properties of soft matter systems are extensively studied using small-angle neutron scattering, neutron spin-echo, and neutron reflectometry.

In this contribution, the typical features of the scattering experiments on multilayered system are presented. Focus will be put on the analysis of the small-angle scattering and spin-echo data measured on multilayer vesicle solutions, and on the interpretation of reflectometry curves from multilayer coatings. The multilayered systems are spontaneously formed in mixtures of the cationic polysaccharide chitosan and fatty acid derivates, and the multilayers are obtained upon spin-coating the corresponding multilayered vesicles solution.

Despite the fundamental difference between the three techniques, they all bear in common the presence of a correlation peak, clear signature of the periodic arrangement of thin layers making up the vesicles and the coating. This peak will be the common thread through our multiple scattering analysis.

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## Magnetism in spin-orbit coupled iridates

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All 5d iridium oxides are of huge interest due to the potential for new quantum states driven by strong spin-orbit coupling. The strontium iridate  $\text{Sr}_2\text{IrO}_4$  is particularly in the spotlight because of the novel  $J_{\text{eff}} = 1/2$  state consisting of a quantum superposition of the three  $t_{2g}$  orbitals with nearly equal population, which stabilizes an unconventional Mott insulating state. The similarity of its crystallographic, electronic and magnetic structures to the 3d layered perovskite  $\text{La}_2\text{CuO}_4$ , which evolves from a  $S=1/2$  AFM Mott insulator to a high  $T_c$  superconductor upon doping, makes the doped  $\text{Sr}_2\text{IrO}_4$  a promising candidate to discover new states of matter. We have been investigating the magnetic properties of  $\text{Sr}_2\text{IrO}_4$  and Rh doped compounds using polarized neutron diffraction.

On the one hand, we recently reported novel magnetic order in the antiferromagnetic iridates system  $\text{Sr}_2(\text{Ir,Rh})\text{O}_4$  [1] below a temperature different from  $T_N$  suggesting the existence of loop-current electronic states in different oxides. We observe additional magnetic scattering superposing to certain Bragg peak reflections. It suggests that time-reversal symmetry is broken in the hidden odd-parity order phase which has been recently established through broken spatial inversion and rotational symmetries using optical second-harmonic generation measurements in the  $\text{Sr}_2(\text{Ir,Rh})\text{O}_4$ . This is reminiscent of similar type of magnetic ordering reported in high temperature superconducting copper oxides which has been theoretically proposed to explain the pseudogap phase in cuprate superconductors. The orbital-induced loop currents produce magnetic moments that can be measured with neutron diffraction at a certain  $q$ -position depending on an arrangement of toroidal pseudo-vector anapoles.

On the other hand, we report an anisotropic and aspherical magnetization density distribution measured by polarized neutron diffraction in a magnetic field up to 5 T at 4 K, which strongly deviates from a local  $J_{\text{eff}} = 1/2$  picture. Once reconstructed by the maximum entropy method and multipole expansion model refinement, the magnetization density shows cross-shaped positive four lobes along the crystallographic tetragonal axes with a large spatial extent, showing that the  $xy$  orbital contribution is predominant. Theoretical considerations based on a momentum-dependent composition of the  $J_{\text{eff}} = 1/2$  orbital and an estimation of the different contributions to the magnetization density casts the applicability of an effective one-orbital  $J_{\text{eff}} = 1/2$  Hubbard model into doubt. The analogy with the  $S=1/2$  AFM Mott insulator might thus be weaker than commonly thought.

I wish to thank my co-authors listed in references [1] and [2].

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# Structural effect of phase modifier n-octanol on solvent extraction mechanism revealed by SANS

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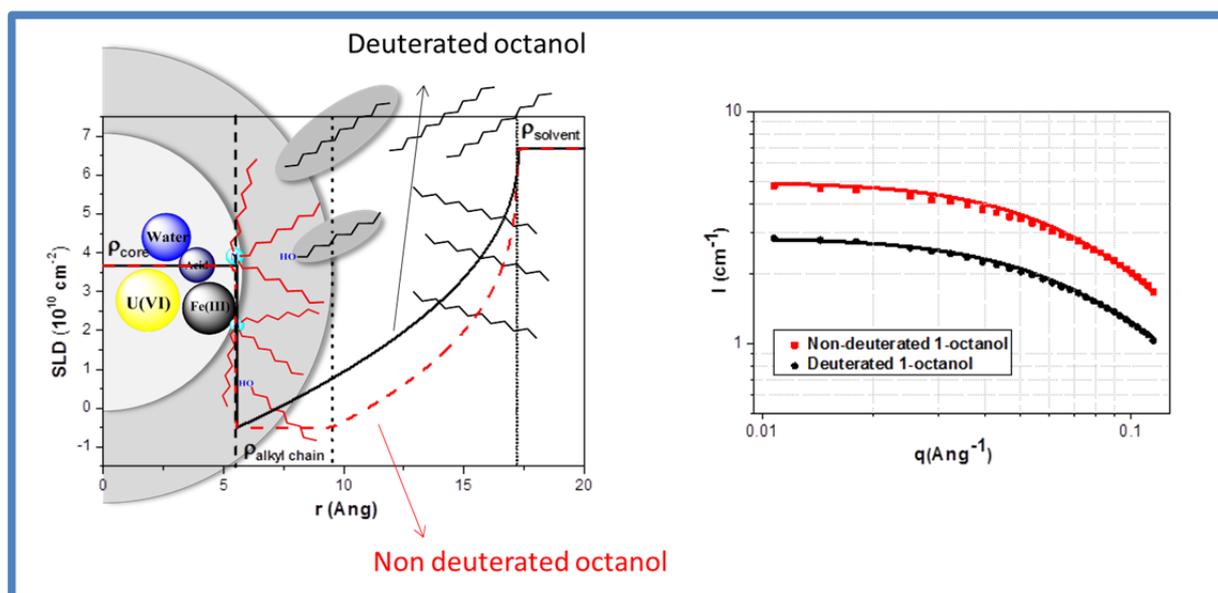
Solvent extraction processes are widely applied to extract selectively uranium from sulfuric media with ternary amines ligands such as Trioctylamine (TOA) and Aliquat 336. The AMEX process is for instance based on the use of tertiary amines as a selective extracting agent and of 1-octanol as a phase modifier, which as believed, can avoid the formation of a third phase by modifying the structural state of the aggregates. However, the effect of the phase modifiers on aggregation and extraction properties is not fully understood.

Small-angle neutron scattering (SANS) intensities are sensitive to the contrast between the deuterated parts (organic diluent and phase modifier) and non-deuterated parts of the organic phase which allows us to “locate” the 1-octanol and understand its role in forming aggregates and avoiding the third phase formation. To quantitatively estimate the function of octanol, a SANS Model with a spherical SLD form factor (intra-particle scattering) and a sticky hard sphere structure factor (inter-particle scattering) is employed to fit the SANS data.

As proposed in previous study, 1-octanol may play a role as a co-surfactant or a co-solvent [1]. With the help of SANS and interfacial tension measurements, we successfully obtained experimental evidence of the co-surfactant and co-solvent effects of octanol on the TOA aggregation. The supramolecular structure obtained from SANS showed that 1-octanol is present in the solvent and in the aggregates as well. By penetrating into the shells of aggregates, 1-octanol molecules act as a shielding barrier. Meanwhile, we observed an increase of critical aggregation concentration of TOA along with added 1-octanol quantities, indicating a co-solvent effect of 1-octanol. Besides, 1-octanol tends to stay in the organic diluent and form a hydrogen-bond network to separate the aggregates while the ligand/octanol molar ratio increases.

In conclusion, this study shows for the first time how a phase modifier contributes by two essential roles of co-solvent and co-surfactant to prevent the third phase formation.

At next stage, in order to optimize the extraction efficiencies of AMEX process and understand the mechanisms behind it, we would vary the alkyl chain length or the branching situation of the extractant molecules. Therefore, combining SANS and SAXS measurements can help us to characterize the aggregates, to confirm the Critical Aggregation Concentration measurement and to derive crucial information such as packing parameter of the aggregates.



**Figure 1.** Scattering length density profiles (left) and SANS spectra (right) of organic solutions containing 0.2 mol/L TOA and 3%vol non-deuterated 1-octanol or deuterated 1-octanol

[1] Abecassis, B., *et al*, Langmuir, 2003. 19(17): P. 6638-6644.

## **Low energy excitations in intermetallic superconductors - revisiting previous results to prepare for first science at ESS**

A. Hiess<sup>1</sup>

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Investigating magnetic and vibrational excitations by inelastic neutron scattering has enabled to shed light on the microscopic origin of the very diverse electronic properties observed, which not only continue to fascinate many scientists but have proven their relevance for many applications. Prominent examples are unconventional superconductors. Here neutron scattering reveals the relation of magnetism and superconductivity, which is most relevant for a theoretical description of the quantum system and to identify parameters to tune their electronic properties.

I shall revisit previous experimental findings focusing on intermetallic superconductors, illustrate the current challenges and identify future methodological needs. Important to prepare for first science at ESS in this scientific area, I shall provide an update on the relevant instruments within the initial suite and also discuss our strategy for laboratory infrastructure and sample environment specifically for low temperatures, high magnetic fields and high pressure as the parameters most relevant to tune the properties in these compounds.

Recognising the diverse needs of our first ESS users I shall provide a brief review of further provisions for both - user, sample & laboratory services as well as sample environment systems.

## **Planar lipid bilayers as model biological membranes for structural neutrons studies**

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Cells, the basic units of living organisms, are well delineated and separated from the external environment by membranes. Capable of both enclosing the cellular constituents and allowing exchanges with the outside world, these membranes are only a few nanometers thick. To study the dynamics and function of these amazing objects, physicists first seek to understand their structure. This involves experiments on model systems, simpler and better controlled than real membranes, and can profit from a probe that is able to access different scales of size and time: thermal neutrons.

Since the pioneering work in the seventies on cell membrane structure by neutron scattering, developments driven by constantly improving neutron instrumentation, coupled with development of measurement and analysis methods, have involved both the optimization of samples towards more biologically relevant model systems and include the use of more complex lipid mixtures up to natural extracts.

The lecture will review current developments in planar lipid bilayer studies carried out mostly at the Institut Laue-Langevin in Grenoble.

# Study of the adsorption conditions of surfactants on surfaces mimicking rock reservoirs (EOR application) by the combination of QCM-D and neutron reflectivity experiments

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Surfactant adsorption at the solid-liquid interface is an important phenomenon that occurs in many industrial processes. Surfactants may form adsorbed layers on solid surfaces and change the properties of the solid surface. In many applications (such as enhanced oil recovery), surfactant adsorption at the solid-liquid interface is considered as an unwanted effect.

Chemical flooding, which is one method used in Enhanced Oil Recovery (EOR), consists in injecting a surfactant formulation in order to mobilize oil trapped in the reservoir rock. Anionic surfactants such as sulfonate surfactants are generally used as they provide the best performances in terms of oil recovery. However, surfactants loss due to adsorption onto reservoir rock surface has a significant negative economic impact for EOR processes.

The aim of this study is to characterize the anionic surfactant layer adsorbed on silica at room temperature at three different pH values. As model surfactant, we used AOT (sodium bis(2-ethylhexyl)sulfosuccinate)) in brine 1.5wt% NaCl. Silica has been chosen to mimic the reservoir rock. AOT aggregates in brine solution have been characterized at different length scales by cryo-TEM and the combination of three scattering techniques (SAXS, MALS, DLS). Results show a polydisperse vesicle size distribution mainly composed of small vesicles (14 nm diameter). The characterization of the adsorbed layer has been done by means of a Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) and neutron reflectivity. QCM-D follows temporal variations of the resonant frequency ( $\Delta f$ ) of a quartz crystal and its dissipation ( $\Delta D$ , which represents the loss of energy caused by the adsorbed layer). QCM-D was used to obtain information on the dynamics of surfactant adsorption and on the structure of the adsorbed layer formed at the equilibrium state. Generally,  $\Delta f$  is linearly related to the adsorbed mass in the case of a rigid film ( $\Delta D \approx 0$ ). If  $\Delta D$  is not zero, it can inform about the softness of the adsorbed layer. Neutron reflectivity experiments allowed the determination of the thickness, structure and composition of the adsorbed layer (Figure 1).

In acidic conditions, after a structural rearrangement step evolving with time and rupture of vesicles initially adsorbed, the formation of a bilayer has been observed. At intermediate and basic pH, in spite of the electrostatic repulsion between the negatively charged surfactants and silica, results demonstrated the existence of an adsorbed layer composed of AOT vesicles more or less closely packed depending on the pH of the solution. Combining both techniques gave evidence of vesicle adsorption even during unfavorable conditions.

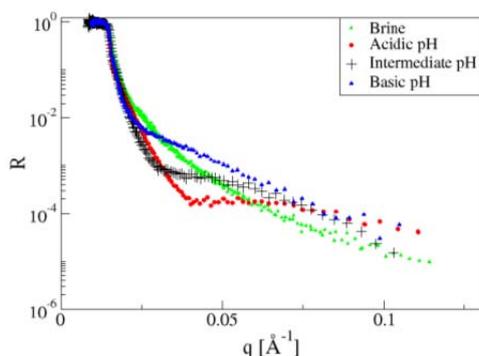


Figure 1: Reflectivity profiles obtained for the bare silicon wafer (in contact with brine) and AOT surfactant at the three pH investigated (acidic 1.5, intermediate 6.0 and basic 9.0) in D<sub>2</sub>O brine.

# Dynamical and Structural Properties of Water in Silica Nanoconfinement – Impact of Surface Curvature, Ion Nature and Electrolyte Concentration

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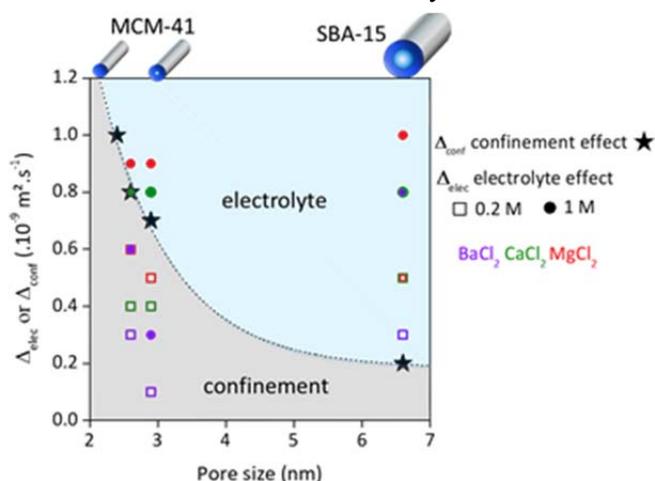
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Processes taking place at the solid/aqueous solution interface have a strong impact on the evolution of materials in the fields of construction, environment, geochemistry, membranes, catalysis, and nuclear wastes. Since many materials in these application fields are completely or partially nanoporous (cementitious materials, biominerals, clay, secondary minerals...) and filled with aqueous solutions, the processes and chemical reactions occurring in this nanoconfinement have a major impact on the materials evolution on a macroscopic scale. The study of such processes and chemical reactions occurring in nanometer-sized porosities in contact with aqueous solutions (ions sorption [1], electrolyte diffusion [2], phase precipitation [3–6], pore wall dissolution and recondensation of dissolved species [7,8]) is important since it differs from the ones occurring with dense materials. Since water takes part in most of these processes and chemical reactions, the understanding of water molecules behavior in such media is essential to be able to predict the behavior of nanoporous materials.

In this study, we characterized the structure and the dynamics at a picosecond scale of water molecules in aqueous solutions with cations having various kosmotropic properties ( $XCl_2$  with  $X = Ba^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$ ) confined in highly ordered mesoporous silica (SBA-15[9], MCM-41 and grafted MCM-41[10]) by Fourier Transform InfraRed spectroscopy and quasi-elastic neutron scattering. We pinpointed the critical pore size and the electrolyte concentration at which the influence of the ion nature becomes the main factor affecting the water properties. These results suggest that whatever the ions kosmotropic properties, for pore sizes  $\phi_p < 2.6$  nm and  $[XCl_2] \leq 1$  M, the water dynamics (translational diffusion coefficient  $D_t$ ) at ps timescale is mainly slowed down by the confinement and thus the surface concavity. For pore sizes of 6.6 nm, the water dynamics depends on the concentration and kosmotropic properties of the ion more than on the confinement. The water properties within the interfacial layer were also assessed and related to the surface ion excesses obtained by sorption isotherms. We showed that for pore sizes  $\phi_p \geq 2.6$  nm, the surface ion excess at the pore surface is the main driver affecting the structural properties of water molecules and their dynamics within the interfacial layer.

Figure 1: Evolutions of the factors  $\Delta_{conf}$  ( $\Delta_{conf} = D_{tH_2Obulk} - D_{tH_2Oconf}$ ) and  $\Delta_{elec}$  ( $\Delta_{elec} = D_{tH_2Oconf} - D_{tXCl_2conf}$ ) as a function of the pore size  $\phi_p$  for the electrolyte solutions at 0.2 M and 1 M. The predominant effect,



## Photosensitive Polymer - surfactant complexes

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Polyelectrolytes (PEs) are polymers with ionisable groups that dissociate in water [1]. This water-solubility is a remarkable property commonly used in industrial applications (modification of rheological properties: thickener, gel...). The presence of electrical charges opens up additional possibilities through the formation of electrostatic complexes with oppositely charged species (colloids, surfactants, PEs, proteins...) leading to new potential applications (flocculent, drug delivery, chemosensors, coatings...). The structure of these complexes results from a subtle balance between hydrophilic, hydrophobic and ionic interactions [2] but also depends on the intrinsic stiffness of the polymers and the shape of the oppositely charged species. The structural organisation is a fundamental point to control in order to improve applications. That concerns the average conformation and the dispersion state of polyions, but also, the organization of oppositely charged species. In this context, small angle neutron scattering (SANS) combined with isotopic substitution and contrast variation is the best technique since it allows to determine the partial structure functions of the different components and the form factor of the polyions in dilute or semidilute regimes.

In this work we are interested in “smart” polyelectrolytes complexes (PECs) made of PEs and oppositely charged photosensitive surfactants able to change their morphology upon application of an external light stimulus. The photoactive surfactant consists of a charged hydrophilic head group and a hydrophobic tail incorporating an azobenzene group (AZO, figure 1) [3].

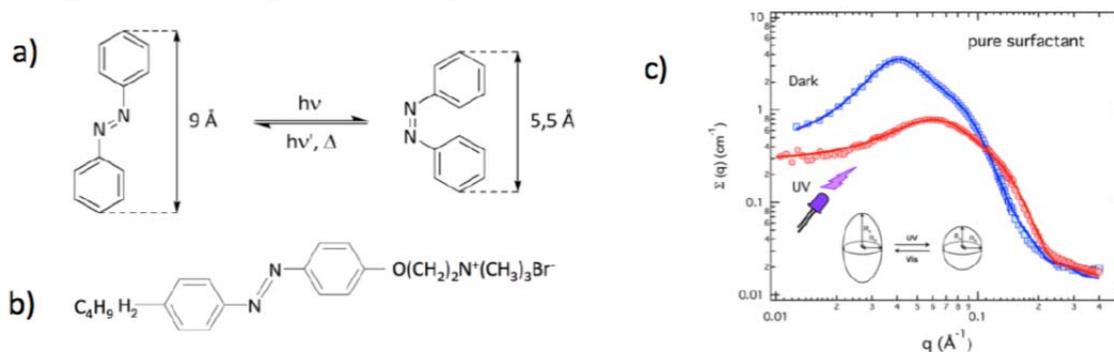


Figure 1. a) Azobenzene group (AZO): photoisomeric transition between trans (stable apolar) and cis (metastable polar) isomers. b) photosensitive surfactant (trans isomer). c) SANS measurements on azosurfactant in dark and under UV irradiation.

Under UV illumination ( $\lambda \approx 365\text{nm}$ ), AZO undergoes a reversible photoisomerization from a trans stable apolar state (dark state) to a cis metastable polar isomer. The variation of the dipole moment changes the hydrophobic/hydrophilic balance and induces a shift of the CMC of pure azo-surfactants (figure 1 b). In addition, modification of the molecular shape changes the packing parameter and finally, the organization of micellar aggregates [4,5] (LLB SANS measurements figure 1 c).

Physical properties (viscosity, gelation) of aqueous solutions containing PEs and photosensitive surfactants can be reversibly changed and controlled using UV illumination [6,7]. The goal of the present study is to determine the respective organisations of polyions and azo-surfactants in these photoswitchable complexes, in semidilute regime, with and without UV radiation. SANS experiments have been performed on PAXY at the LLB using a particular UV illumination setup.

In this presentation we will introduce first results on deuterated sulfonated polystyrene / azo-surfactants systems. Structural modifications induced by UV illumination will be discussed in the light of the partial structure functions.

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# Confinement of dyes inside carbon nanotubes: correlation between vibrational, structural and electronic properties

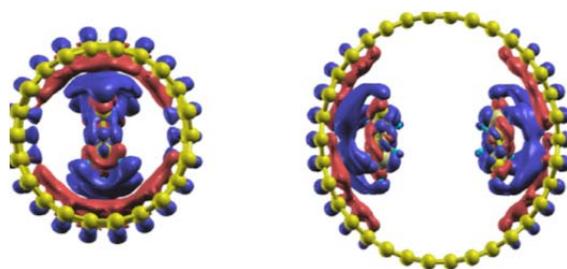
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Encapsulating molecules inside nanotubes (called hybrid nanotubes in the following) is a common strategy to add new functionalities to the nanocontainer. The one-dimensional nature of single-walled carbon nanotubes (SWCNT) internal channels is exploited here to induce a molecular order and specific interactions which are dependent of the size of the nano container (figure 1). We present here the study of the relation between structural, vibrational and electronic properties of hybrid nanotubes encapsulating dyes. Dimethyl-quarterthiophene (4TCH3) confined inside single-walled carbon nanotubes is studied by inelastic neutron scattering. The results reveal specific dynamics of the 4TCH3 modes characterized in particular by a large sensitivity in the low frequency domain of the methyl libration to the confinement. DFT based calculations consistently describe the observed phenomena and give insights on the structure of the hybrid nanotubes at low temperature where molecules preferentially interact with the nanotube wall.

We evidence also by means of Raman spectroscopy and transmission electron microscopy that the supramolecular organizations of the confined oligothiophenes depend on the nanocontainer size. Charge transfer between the dyes and the nanocontainer is shown<sup>1,3</sup>. A strong dependence on the infrared response of the hybrid nanotube due to confinement effect is finally investigated. The results are compared to experiments performed on nanotubes where dyes are  $\pi$ -stacked at the outer surface. Surprisingly, the confinement properties lead to an exaltation of the infrared absorption response in the carbon nanotubes from dye molecule interactions<sup>2</sup>. Thanks to the comparison between the experimental investigations and DFT calculations, we elucidate the origin of the large enhancement of this infrared absorption.



**Figure 1:** Electronic charge density as the function of size of the nano container controlling the molecular order

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# Dystrophin-membrane interaction: 3D structure of dystrophin fragments in the presence of phospholipids

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Dystrophin is a large peripheral membrane protein (~427 kDa) supporting the plasma membrane of muscle cells<sup>1</sup>. This protein plays a key-role against shear stress induced by the contraction/elongation process of muscles. Some gene mutations lead to a total deficit of dystrophin and are responsible of the serious and currently incurable Duchenne muscular dystrophy (DMD) which affects 1/5000 male births<sup>2</sup>. Exhaustive knowledge of dystrophin/membrane interactions is essential to contribute to the design of gene therapy strategies devoted to DMD. An example of gene therapy consists to design a minimal functional mini-dystrophin in order to restore a normal phenotype. Most part of the dystrophin (~75%) consists in a central domain, made of 24 spectrin-like repeats (R1 to R24), meaning that each repeat is structured in a triple  $\alpha$ -helix bundle. The accurate determination of the 3D organization of dystrophin central domain is not accessible by classical high-resolution methods and thus alternative approaches were employed to obtain structural information<sup>3</sup>. During this project, we focused on two fragments belonging to the central domain, R1-3 and R11-15, that are both known to interact with membrane lipids *in vitro*<sup>4</sup> and *in vivo*<sup>5</sup>. R1-3 appears to be an essential subdomain since it is found in potential therapeutic mini-dystrophins<sup>6</sup>, whereas R11-15 has the ability to bind membrane lipids and cytoskeletal actin at the same time<sup>7</sup>. We characterized protein/lipid interactions of R1-3 and R11-15 using zwitterionic or anionic phospholipid-based bicelles as a membrane mimic. Then, using small-angle neutron scattering (SANS) and the contrast variation method, we specifically probed the solution structure of R1-3 or R11-15 either free in solution or bound to zwitterionic as well as anionic contrast-matched bicelles<sup>8</sup>. Our results highlight that when bound to zwitterionic bicelles, no significant conformational modifications of the protein fragments are detected. On the other hand, when they are bound to anionic bicelles, SANS data demonstrate that structural modifications occur especially for R1-3<sup>9</sup>. The R1-3/anionic bicelle complex was further analyzed by classical coarse-grained molecular dynamic simulations (CG-MD) and interactive CG-MD. The *in silico* model obtained for R1-3 bound to membrane lipids are totally in adequacy with the experimental SANS data<sup>9</sup>. To complete our findings, we also investigated the behavior of R1-3 and R11-15 at the interface by using Langmuir lipid monolayers and supported lipid bilayers as a lipid environment. Thanks to neutron reflectometry, we can reasonably assume that both protein fragments interact with the polar head group without penetrating the hydrophobic tails of the phospholipids (Dos Santos Morais *et al.*, in preparation for submission in *Biomolecules*). Finally, we deciphered the molecular basis involved in the formation of the ternary complex formed by actin, R11-15 and bicelle (Mias-Lucquin and Dos Santos Morais *et al.*, under review in *J. Struc. Biol.*). Understanding accurately the molecular behavior of R1-3 and R11-15 during lipid and/or actin binding, may contribute to the design of rationalized efficient mini-dystrophins. We also expect that our approaches might be relevant to characterize other peripheral and even integral membrane proteins.

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## Direct probing of slip mechanisms for solid / polymer solutions interfaces

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Friction of polymers fluids has been actively studied for its importance in many fields such as enhanced oil recovery, biolubrication or machine lubrication. More precisely, a strong enough attractive interaction can lead to adsorption of polymer chains at interfaces. These adsorbed chains can entangle with free chains present in the vicinity of the interface when the flowing media is a polymer fluid. This surface/bulk chains coupling leads to a non-linear shear-rate dependent slippage. For low shear rates, the polymer chains of the bulk stretch the surface attached chains (either adsorbed or end grafted), but these surface chains relax rapidly enough so that the number of entanglements between surface and bulk chains remains constant. Therefore, the friction force between the fluid and the surface is high, leading to a small slippage. For higher shear rates, the bulk and surface chains can disentangle and the friction force decreases. A direct proof of this change in the conformation has been obtained thanks to neutron reflectivity in the particular case of chains that were end-grafted at the surface, in contact with a polymer melt [1].

In the specific case of ideal surfaces (*i.e.* no chain adsorption), de Gennes predicted that the friction coefficient  $k = \sigma/V_{\text{surface}}$  defined as the shear stress at the interface divided by the surface velocity, does not depend on the macromolecular structure of polymer chains and results from the local monomer friction coefficient. This leads to slip lengths  $b$  proportional to the melt viscosity. Hénot *et al.* have proved experimentally that the friction coefficient of melts does not depend of the length of the polymer chains confirming de Gennes assumption [2].

The slippage of semi-dilute polymer solutions could be more complex than the one of polymer melts. Thanks to a velocimetry technic based on fluorescence photobleaching, we have studied the slippage of polystyrene solutions ( $M_n = 10 \text{ Mg} \cdot \text{mol}^{-1}$ ) in diethyl phthalate (DEP) on a silicon wafer. We have investigated the dependence of the slip length  $b$  on the concentration  $\phi$  of the solutions in the Newtonian regime. These experiments showed that the slip length scales as  $b \propto \phi^3$ . This scaling is consistent with two possible local molecular mechanisms: either there is a depletion layer, inducing concentrations inhomogeneities close to the substrate; or polymer solutions are slipping with a mechanism similar to that of melts, with the pertinent scale being the screening length of hydrodynamic interactions,  $\xi$ . As our slippage experiment does not allow us to distinguish between these two mechanisms, neutron reflectivity is the only technique allowing to probe the presence or the absence of such a depletion layer.

Such neutron reflectivity experiments have been done on HERMES at LLB for solutions of PS-D  $M_n = 180 \text{ kg} \cdot \text{mol}^{-1}$  in hydrogenated diethyl phthalate (DEP-H) for two concentrations (3% and 6%) in front of a quartz substrate. We directly prove that in the vicinity of these interfaces, there is no depletion layer, but rather an adsorbed layer of PS-D. The concentration profile can be extracted from the reflectivity data : the concentration decays from the surface concentration to the bulk concentration over the range of the correlation length  $\xi$ . This profile is close to the one predicted by de Gennes for attractive surfaces [3]. Moreover, such an adsorbed layer explains the transition in slippage experimentally observed for polymer solutions. It is a proof that the same change in the conformation of the adsorbed chains can occur for slippage of polymer solutions as well as for melts.

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## Mechanisms of Thermal Transport in Zirconia

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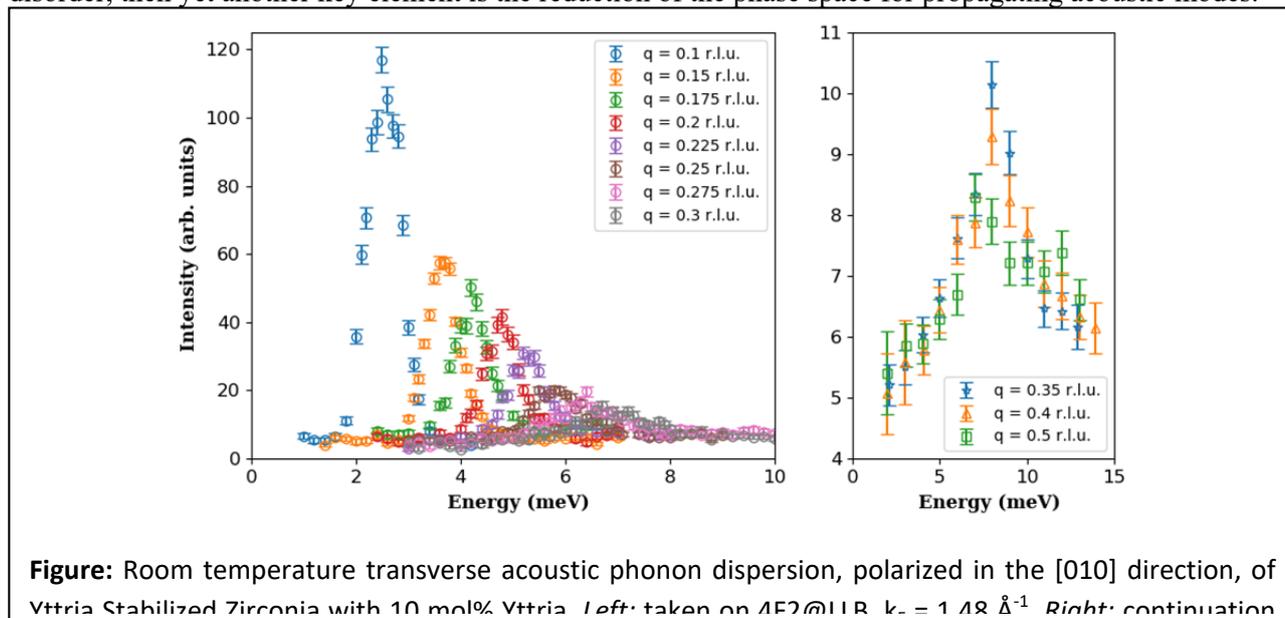
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Yttria Stabilized Zirconia (YSZ,  $(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$ ) is a ceramic well-known for its use as an electrochemical cell, a thermal barrier coating, and for many other applications designed for high temperature [1,2]. Monoclinic at room temperature (RT), Zirconia can also be tetragonal, then cubic, at higher temperatures (above 1478 K). These same structures can be stabilized by Yttria doping. Introducing Yttria causes first the tetragonal structure to be stabilized, then, for Yttria doping of more than 8 mol%, the cubic structure. This Yttria doping has the consequence of introducing oxygen vacancies, which leads to a large amount of disorder in the system. This is considered to be responsible for the different thermal properties of YSZ with respect to pure Zirconia, the latter having a thermal conductivity of 8.2 W/mK at RT, while YSZ with 10 mol% Yttria has a thermal conductivity of 2 W/mK. Moreover, YSZ is almost temperature independent, while pure Zirconia exhibits the typical anharmonic-induced decrease of thermal conductivity at high temperature [2].

When more than 10 mol% Yttria doping is applied, however, the thermal conductivity of YSZ begins to increase again at room temperature. This has been explained by a local rearrangement of the oxygen vacancies, which appear to order themselves, thus reducing the amount of scattering due to disorder.

Previous Inelastic Neutron Scattering (INS) experiments [3,4] have shown that while the phonon dispersions along high symmetry directions exhibit a rapid broadening with  $q$ , the acoustic phonons continue to disperse to high energies ( $\sim 20$  meV for the transverse acoustic (TA) mode). Strangely, no optical mode(s) could be observed. The strong broadening, however, which was observed for YSZ with 10 and 25 mol%, was considered to be the origin of the low thermal conductivity.

Here we present new high resolution INS measurements on a single crystal YSZ sample with 10 mol% Yttria content, which clearly show that **the TA mode disperses only until 9 meV before mixing with a continuum of low-energy optical branches** (See Figure). Our results significantly change the understanding of thermal transport in YSZ, indicating that, if lifetime is shortened due to the oxygen-vacancy-induced disorder, then yet another key element is the reduction of the phase space for propagating acoustic modes.



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# Structure of aqueous solutions of interpolyelectrolyte complexes: A SAXS and SANS study

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We investigate the structure of aqueous solutions of model polyelectrolyte complexes (PECs) by the use of the Small Angle X-ray and Neutron Scattering (SAXS and SANS) techniques. PEC solutions are prepared by mixing two initial aqueous solutions of polyelectrolytes of opposite charge. A polycation, poly(diallyl dimethyl ammonium) (PDADMA), of non-electrostatic persistence length  $l_p^0=3$  nm and two polyanions, poly(styrene sulfonate) (PSS) and hyaluronan (HA) of non-electrostatic persistence lengths  $l_p^0=1$  and 9 nm, respectively, are thus considered. The choice of these polyelectrolytes results from the aim of studying the role of the macroion intrinsic persistence length,  $l_p^0$ , on the PEC formation and structure.

SAXS and SANS results mainly show that the complexation between polycations and polyanions in the semidilute and concentrated regimes can be described as a gelation process. This analogy is reliable for both couples PSS-PDADMA as well as HA-PDADMA. It can be considered as universal. There is however a difference between both complexes, which is associated with the primary self-assembling process. PSS and PDADMA interact through monomer units forming punctual junctions randomly dispersed in semidilute or concentrated solutions, while HA and PDADMA interact through large sequences of macroions. Such a difference is obviously related to that in the polyanion intrinsic stiffness.

# Effect of the dimensionality on the lattice dynamics and anharmonicity of the thermoelectric silicide CrSi<sub>2</sub>

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The interest in renewable energies to sustain economic growth and environmental concerns has increased dramatically these last decades. Among renewable energies, thermoelectric materials, which allows to convert heat into electricity, without moving part, can participate to this effort. Their thermoelectric performances are characterized by their dimensionless figure of merit  $ZT = \alpha^2 \sigma T / \lambda$ , with  $\alpha$  the Seebeck coefficient,  $\sigma$  the electrical conductivity and  $\lambda$  the thermal conductivity. It is about 1 for the best conventional thermoelectric materials such as Bi<sub>2</sub>Te<sub>3</sub> or PbTe [1]. In this work we investigate thermoelectric silicides, which could be competitive with such alloys, and more particularly on CrSi<sub>2</sub>. Its power factor  $\alpha^2 \sigma$  is similar to the best thermoelectric materials but its thermal conductivity, about 15 W/m.K at room temperature, limits strongly its maximum figure of merit to  $\sim 0.25$  [1]. Different routes can be investigated to increase the phonon scattering and to decrease the lattice contribution of  $\lambda$ : by alloying in order to distort the unit-cell or by nanostructuring in order to create multiple interfaces [2]. In this work we will focus on the effect of nanostructuration on CrSi<sub>2</sub> and will present the effect of size reduction and strain on the lattice dynamics and on the thermal conductivity with the support of DFT calculations.

We report here the phonon dispersion curves of single crystalline CrSi<sub>2</sub> as well as the phonon density of states of bulk and nano-CrSi<sub>2</sub> [3,4]. We show that the experimental results for the bulk materials are in good agreement with DFT calculations. Alongside that, we also show a spectral weight transfer at low energy for nano-CrSi<sub>2</sub> which is related to a decrease of both the Debye temperature and the sound velocity and could be associated to both an increase of the interfaces and of the strains. These observations could be at the origin of the strong decrease of the thermal conductivity that we also observe on densified nanostructured CrSi<sub>2</sub> pellets [5,6].

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## Lattice dynamics and anharmonicity of thermoelectric BiCuSeO

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Study of thermoelectric materials is a growing field due to the emergency to find new energy sources without polluting emissions. During the 15 last years, new thermoelectric materials were found to be more efficient for high temperature thermoelectric generation following some simple guidelines leading to ideas such as the “phonon glass – electron crystal” concept proposed by Slack [1]. The efficiency of thermoelectric materials is represented by the dimensionless Figure of Merit  $ZT = S^2\sigma T/\kappa$ , with  $S$ =Seebeck coefficient,  $\sigma$ =electrical and  $\kappa$ =thermal conductivity. Hence, thermoelectric materials need to be poor thermal conductors. The best thermoelectric materials used in commercial applications have  $ZT$  of about 1.

Very recently, new classes of thermoelectric materials with very low thermal conductivity  $\lambda$  (less than 1 W/m.K at room temperature and above) and mainly composed of chalcogen and pnictogen atoms have been developed [2-4]. It was proposed that the increase of the anharmonicity due to the electron lone pair of the pnictogen atoms was the reason behind this low thermal conductivity. However, direct spectroscopic proof confirming this scenario is still lacking, hence the usefulness of inelastic neutron scattering studies of the lattice dynamics of such kind of materials. Among these materials, the Orsay’s group has discovered in 2010 that BiCuSeO has large  $ZT$  (0.5 for undoped samples and up to 1.4 for doped samples at 950K) because notably of its very low thermal conductivity [5]. Recent work has also confirmed the presence of electron lone pair of the 6s states of bismuth in this compound [6]. Other interesting points making appealing the study of this material are its very simple tetragonal crystal structure with 8 atoms/unit-cell and also its close crystallographic proximity with the 1111 Fe superconducting compounds.

In the present communication, we report for the first time inelastic neutron scattering (INS) experiments on powdered sample of BiCuSeO in function of the temperature using time-of-flight (TOF) spectrometers IN6 and IN4 at ILL. Our DFT calculations of the lattice dynamics can well explain the experimental results. We find a large broadening of the phonon density of states when the temperature increases, a fingerprint of the large anharmonicity of this system, especially at the higher energies. Another manifestation of these properties is the large thermal expansion found with neutron diffraction experiments. Our results are discussed via an analysis of the DFT calculations of the anharmonic properties of the lattice dynamics of BiCuSeO.

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## Toluene/Butanol binary solvents confined in periodic organosilicates

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The confinement of liquid mixtures in porous channels provides new insight into fluid ordering at the nanoscale. In this presentation, we address a phenomenon of microphase separation, which appears as a novel fascinating confinement effect for fully miscible binary liquids. This phenomenon was firstly investigated for tert-butanol-toluene mixtures confined in the straight and mono-dispersed cylindrical nanochannels of MCM-41 and SBA-15 mesoporous silicates ( $D = 3.6$  nm and  $8.3$  nm) [1,2].

The present study aims at extending this approach to different fluid-wall interactions. It shows that novel types of nanostructures can be generated using functionalized porous organosilicates with periodic alternating surface chemistry along the pore channel.

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<https://doi.org/10.1021/acs.jpcc.6b01446>

# New insights in $\text{RMn}_2\text{O}_5$ multiferroics: rare earth and pressure influence

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$\text{RMn}_2\text{O}_5$  materials (R being a rare earth) have long been presented as spin induced multiferroic family, where the electric polarization develops concomitantly with a magnetic transition at low temperature. What makes them particularly interesting lies in their singular properties: an electric polarization among the strongest reported so far ( $3600\mu\text{C}\cdot\text{cm}^{-2}$  in  $\text{GdMn}_2\text{O}_5$ ), a strong magneto-electric coupling (enabling a polarization flip under a magnetic field of 2T in  $\text{TbMn}_2\text{O}_5$ ), and a magnetism that indicates a different fundamental mechanism than the standard Dzyaloshinskii Moriya Interaction. Indeed, among the universal properties of this  $\text{RMn}_2\text{O}_5$  family is the quasi-colinear magnetic ordering in the (a,b) plane.

In this presentation, we will give an overview of universal properties of  $\text{RMn}_2\text{O}_5$  that single them out from most of multiferroics: two valences, strong polarization, remarkable magneto-electric coupling and rare earth influence. We will present recent results that shed light on the underlying mechanism responsible for magneto-electric coupling in all the members of the family. Using neutron diffraction, we investigated several members of the series to unravel the common mechanism to the whole family: the exchange striction model.

We will also present results on a systematic study of magnetic ordering under high pressure with 5 members of the family investigated. One of the striking conclusions of this study is the presence of a universal magnetic phase at high pressure despite different room pressure magnetic order it originates from. This common high pressure magnetic phase stabilization can be explained by the combination of both X-ray diffraction under pressure and ab-initio calculations of super-exchange couplings.

Based on the mechanism revealed by neutron diffraction and the new magnetic high pressure phase, we will conclude this presentation by reporting the first case of pressure induced multiferroicity.

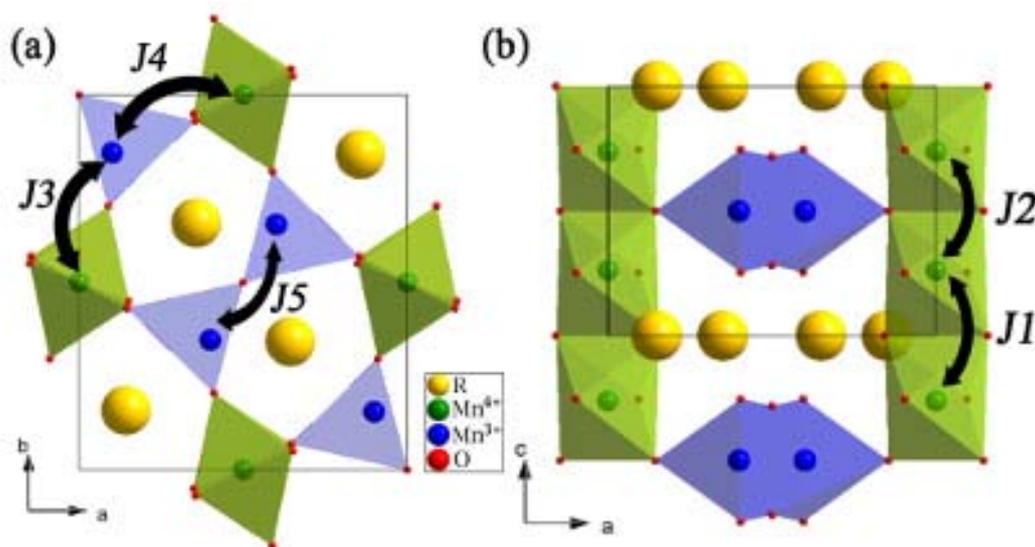


Fig. 1 Structure of the  $\text{RMn}_2\text{O}_5$  family and their 5 super-exchange interactions.

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## Water confined in amphiphilic nanopores

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Interfacial and confined water plays a vital role in all biological and geophysical systems. The properties of the universal solvent under such conditions are significantly different than in bulk. More precisely, confinement of water causes a shift on its melting temperature ( $\Delta T_m$ ), the magnitude of this shift depends on the dimensions of the cavity where it is confined, as described by the Gibbs-Thomson equation [1, 2]. It has also been found that  $\Delta T_m$  does not only vary with the pore size, but also with the surface chemistry. In fact, it has been reported that the melting point depletion is significantly larger for water confined in hydrophobic nanopores [3]. So far, experimental studies have been made for water confined in either completely hydrophilic or completely hydrophobic nanopores [4 – 6]. Here we present our studies on the effect of the surface chemistry on water's behaviour using materials with different levels of hydrophobicity. The materials used are periodic mesoporous organosilicas (PMOs) issued from a direct synthesis in which the organic groups are homogeneously distributed along the surface. Our most recent results of Differential Scanning Calorimetry (DSC) and Neutron Diffraction (ND) reveal that subtle changes in the surface chemistry of the nanoenvironment modulate the freezing and melting temperatures of water, as well as the stacking defects on the hexagonal structure of confined ice.

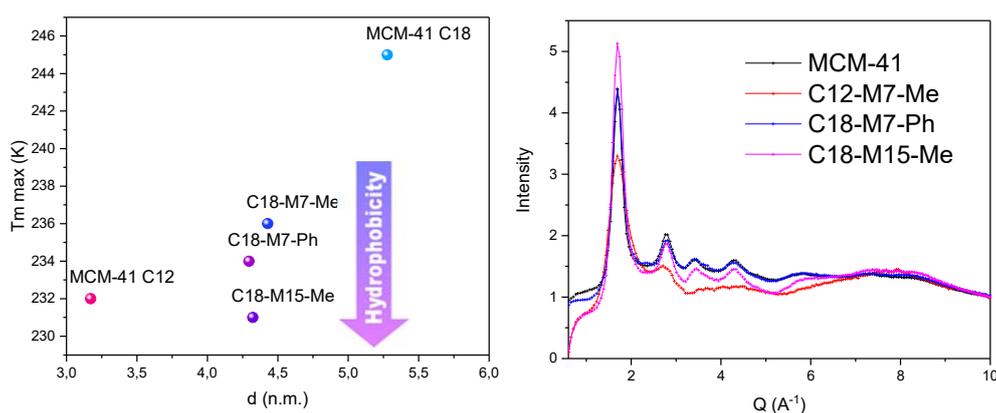


Figure 3: Melting temperature of water confined in amphiphilic PMOs of different hydrophobicity levels (left). Neutron Diffraction curves of confined ice (right).

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# Structure-properties investigations in a new family of multiferroic compounds

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Multiferroic materials are of particular interest due to their novel physical properties. They present a coupling between two ferroic orders such as ferroelectricity and (anti)ferromagnetism which is very appealing for applications in memory devices. In the scientific community, there is an important research effort towards novel materials with improved magnetoelectric coupling. In this context, the “429” family of compounds of formula  $A_4X_2O_9$  (where  $A = \text{Mn, Fe or Co}$  and  $X = \text{Nb or Ta}$ ) has been attracting a lot of attention. Indeed, varying the 3d orbitals filling and/or the size of the X cation leads to unusual and complex properties [1-5].  $\text{Fe}_4\text{Ta}_2\text{O}_9$  is probably one of the most intriguing members as it exhibits a series of low temperature magnetic transition (figure 1-b) with a rare combination of multiferroism and linear magnetoelectricity [1, 6].

The compounds reported in the literature crystallize in the  $P\bar{3}c1$  space group with honeycomb lattice (figure 1-a). Their magnetic structures are still unknown or strongly debated [7, 8], and effects of the substitution of A transition metal and/or X cation have not been investigated yet. The aim of this research project is to establish the relationships between crystal and magnetic structures, and physical properties, in this family of multiferroics, depending on the nature of A and X, in order to understand the microscopic origin of multiferroicity in these compounds.

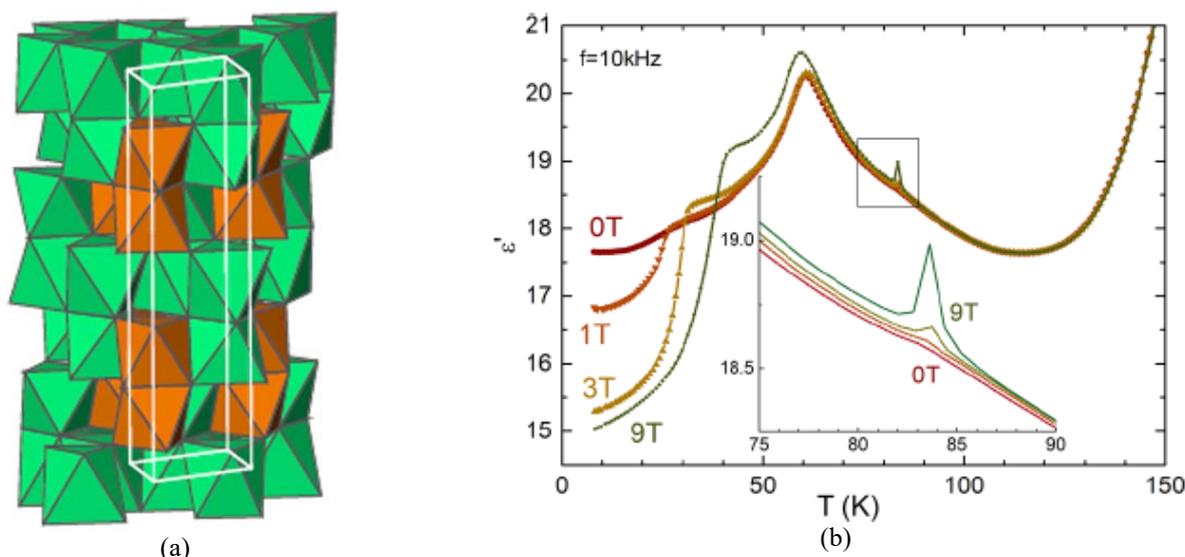


Figure 4 : (a)  $\text{Fe}_4\text{Ta}_2\text{O}_9$  structure where the  $\text{FeO}_6$  and  $\text{TaO}_6$  octahedra are in green and orange, respectively, (b)  $\text{Fe}_4\text{Ta}_2\text{O}_9$ , real part of the dielectric permittivity ( $\epsilon'$ ) collected at  $f=10\text{kHz}$  as a function of  $T$ . The  $\epsilon'(T)H$  curves have been registered for different external applied magnetic field  $H$  values indicated in the graph. Inset: enlargement of the 84K region showing the growth of the  $\epsilon'$  peak as  $H$  increases.

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# Posters

# Microheterogeneity in aqueous solutions by scattering and computer simulations

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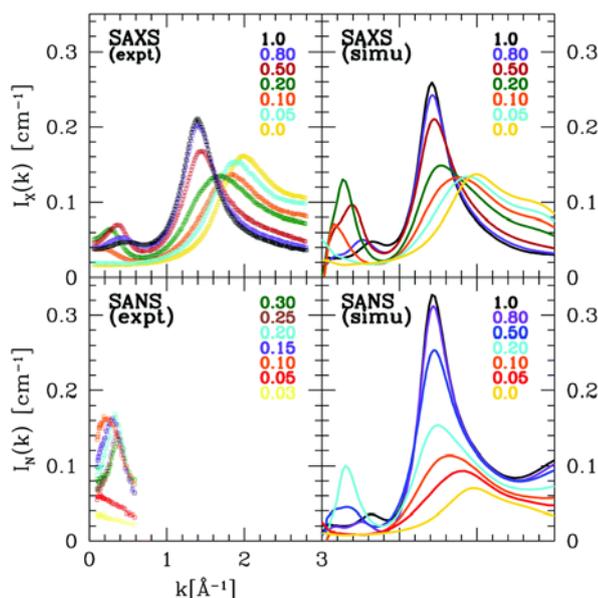
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Mixtures of various amines with water often display strong self-aggregation of the two types of molecules, which leads to strong deviations from ideality of their thermodynamic functions, and can be detected by scattering methods such as small-angle neutron and X-ray scattering. In this presentation we show our recent results on various types of amines: cyclic amines such as piperidines and pyrrolidines, and linear short alkyl chain amines such as propylamine. The structure of these mixtures is investigated through X-ray and neutron scattering experiments, and computer simulations.

In aqueous solutions of 1-propylamine, scattering and molecular dynamics simulation data show a prominent scattering pre-peak, which first appears at propylamine mole fraction  $x \geq 0.1$  around scattering vector  $k \approx 0.2 \text{ \AA}^{-1}$ , and evolves towards  $k \approx 0.8 \text{ \AA}^{-1}$  for neat propylamine (Figure) [1]. Similar feature appears in several other amines, too [2-4]. The existence of a scattering pre-peak in these mixtures is unexpected, as no such features appear in aqueous solutions of very similar molecules such as linear or branched alcohols, or pyridine and its methyl derivatives[5]. The detailed analysis of the various atom-atom structure factors and snapshots reveals pre-peaks in the atom-atom structure factors, positive for like species and negative for

cross species correlations, and their cancellation or not-cancellation results in peak in the measured structure factor. The way the amines bind with water produces a pre-peak through an imbalance of the positive and negative scattering contributions, unlike in short chain alcohols where these contributions compensate exactly. Hence molecular simulations demonstrate how chemical details influence the microscopic segregation in different types of molecular emulsions.



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## Solid-liquid extraction with hollow nanospheres to liquid-liquid extraction with porous liquids

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Nowadays, separation of chemical elements is an important stake for many applications. Although liquid-liquid extraction represents the most applied method at industrial scale, it involves many economic and environmental constraints related to the use of large quantities of solvents. There is therefore a growing interest for alternatives as solid-liquid separation and flotation processes which however, require re-designing the actual industrial installations and present limited performances, in terms of extraction capacity and selectivity.

This project proposes to evaluate a new approach allowing to maintain the existing separation installations, by replacing the organic phases of liquid-liquid extraction processes, with a porous liquid. Porous liquids were discovered in 2014 by the Oak Ridge Corporation. They are solid materials made up with hollow nanoparticles of silica, that present the particularity to become liquid when grafted with ionic functions. To date, these materials have only been tested for gas separation. Being at the exact junction between liquid-liquid and solid-liquid extraction processes, porous liquids would allow exploiting the advantages of the two processes.

The first part of the project, based on the article of Zhang and al.<sup>[1]</sup>, is to synthesized nanostructured hollow spheres in both solid and liquid state, and to understand the influence of the different step of synthesis on the morphology and permeability of the nanospheres. An important aspect of this project is therefore to characterize the morphology and the permeability of the hollow nanospheres when they are solid and liquid. For extraction application, it appears indeed essential to optimize the different steps of the synthesis to ensure accessibility of the inside volume of the cavities to hydrophilic solvents, solutes, and metallic cations. For this, the solid and liquid materials were characterized with TEM, BET, and SAXS.

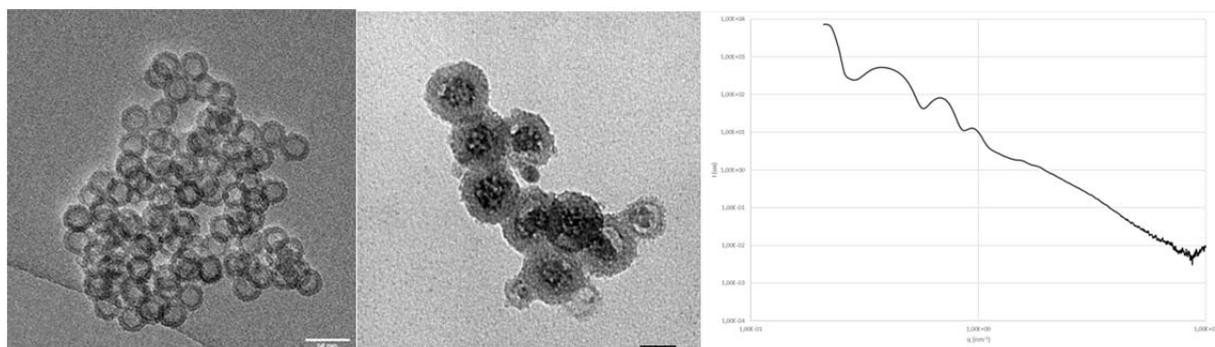


Figure 5 : TEM images of a) hollow silica nanospheres and b) silica nanospheres full of metallic cations and c) SAXS spectra

TEM images and SAXS spectra (Fig. 1) show very well defined and monodisperse hollow spheres with a radius of 17nm. For the solid spheres, gas adsorption indicates an opened porosity with a surface area of roughly 550m<sup>2</sup>/g. It was also observed that the solid spheres are permeable to water and solutes, as that they can induce the precipitation of metallic cations into the cavities.

When grafted with ionic shell the solid nanospheres become liquid. The challenge is herein to characterize the diffusion of water and solutes when this porous liquid is put in contact with an aqueous solution.

For this we plan to combine SAXS and SANS measurements to identify the contrast variation in presence of water and solutes (contrast matching D<sub>2</sub>O/H<sub>2</sub>O). NMR and QUENS measurements will also be performed to identify the diffusion and confinement of the various species.

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# Quantum Spin Liquid in triangular $S_{\text{eff}}=1/2$ rare-earth based antiferromagnets

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The rise of quantum materials observed in the past decades has been a source of great excitement for condensed matter scientists [1], with the flourishing of new concepts and electronic phases of matter. In quantum magnetism the Quantum Spin Liquid (QSL) state has attracted a lot of attention as it shows intriguing collective phenomena such as fractionalized excitations or emergent gauge fields [2]. The original scenario proposed by P. W. Anderson in 1973 was to use a frustrated triangular quantum antiferromagnet to stabilize a quantum spin liquid. However, since then numerical calculations have rather shown that  $S=1/2$  Heisenberg spins do order at  $T=0$ . Nevertheless, QSL candidates with triangular lattices have emerged recently, calling for more refined studies and/or investigations of new materials [3]. Apart from the organic triangular compounds [3], a new rare-earth based material,  $\text{YbMgGaO}_4$ , was recently shown to avoid any spin freezing down to  $T = 50\text{mK}$  and to display a continuum of excitations [4,5]. Despite a large total angular momentum  $J=7/2$ , Yb-based rare earth magnet offers the opportunity to study quantum effects thanks to the large spin orbit coupling that creates a fundamental doublet ground state, well isolated from the first excited doublet, akin to an effective spin  $S=1/2$  [6]. In  $\text{YbMgGaO}_4$ , a large site mixing between  $\text{Mg}^{2+}$  and  $\text{Ga}^{3+}$  within the interplane layers was reported and is likely to be important to explain the low energy magnetic excitations observed with inelastic neutron scattering.

Here, we report on our recent inelastic neutron scattering and muon spin relaxation measurements on a new  $S_{\text{eff}}=1/2$  triangular compound,  $\text{Ba}_6\text{Yb}_2\text{Ti}_4\text{O}_{17}$  ( $\text{BaYbTiO}$ ), down to  $50\text{mK}$ .  $\text{BaYbTiO}$  crystallizes in the hexagonal  $P6_3/mmc$  space group, where the six-fold symmetry imposes a perfect triangular lattice occupied by the  $\text{Yb}^{3+}$  magnetic ions. In contrast with  $\text{YbMgGaO}_4$ , **no interplane substitutions are expected** as Ti and Ba occupy very distinct crystallographic sites. Magnetization versus applied field measurements shows a slowly saturating behavior starting from  $4\text{T}$  at  $5\text{K}$ , characteristic of an antiferromagnetic interaction of  $\sim 2\text{K}$ , typical of  $\text{Yb}^{3+}$  rare-earth magnets. In addition, we performed zero-field muon spin relaxation measurements that establish a fluctuating ground state down to  $50\text{mK}$ . Surprisingly, our high-resolution time-of-flight inelastic neutron scattering experiment points to an extremely low exchange interaction, with an energy bandwidth in the paramagnetic state of less than  $0.05\text{meV}$ . The comparison between the low energy dynamics of  $\text{BaYbTiO}$  and  $\text{YbMgGaO}_4$  thus offers the opportunity to draw some conclusions on the effect of the  $\text{Mg}^{2+}/\text{Ga}^{3+}$  interplane substitutions in what has been recently dubbed a “mimicry of a spin liquid” [7].

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[7] Z. Zhu *et al.*, *Phys. Rev. Lett.* **119**, 157201 (2017)

## Neutron Imaging of Paramagnetic Salt Solutions

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Paramagnetic liquids are created by dissolving salts containing transition-metal or rare-earth ions in a solvent<sup>1</sup>. Magnetic levitation of objects immersed in paramagnetic solutions has been used for magnetohydro-static separation since the 1960s<sup>1</sup> and nowadays finds application in biotechnology<sup>2</sup>. Exposing paramagnetic solutions to an inhomogeneous magnetic field gives rise to the magnetic field gradient force.

The method of neutron imaging is for the first time adopted to map the concentration evolution of optically transparent aqueous paramagnetic solutions. In this study, we use neutron imaging to track the concentration distribution of aqueous paramagnetic Gadolinium nitrate ( $\text{Gd}(\text{NO}_3)_3$ ) solution by transmission measurements. This direct method consists of measuring the attenuation of a white neutron beam through a liquid sample. Neutrons interact with the nuclei of the sample, which makes the measurement element-specific. This allows the direct study of liquids that are both miscible and indistinguishable under normal conditions.

The study of the magnetic manipulation of the paramagnetic liquid within a miscible nonmagnetic  $\text{Y}(\text{NO}_3)_3$  solution, is illustrated (see Figure below).

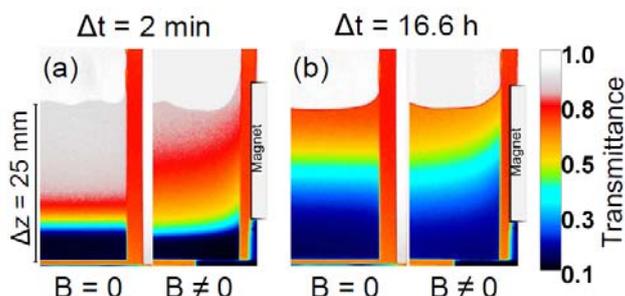


Figure: Kinetic evolution of a paramagnetic solution of  $\text{Gd}(\text{NO}_3)_3$  overlain with  $\text{D}_2\text{O}$  (for the contrast) at  $\Delta t = 2 \text{ min}$  (a) and 16.6 hours (b) respectively. The right cuvettes show the attraction of the liquid to the magnetic pole while the left cuvette is the reference (without magnetic field gradient).

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## Nanoporous alumina membranes studied by neutron techniques

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Nanoporous anodic alumina oxide (AAO) membranes, made of parallel hollow channels with diameters in the range 20-110 nm, are promising host systems for confinement of condensed matter. Characterizing their structure and composition is thus primordial to study the behavior of confined objects. Techniques able to analyze the entering of species and their interaction with the matrix are also necessary. We report here on two studies with neutron techniques coupled to SEM.

In the first approach, Small-Angle Neutron Scattering (SANS) measurements are coupled with Scanning Electron Microscopy (SEM) imaging [1]. A detailed strategy is developed to extract quantitative information on the structure and composition of well-defined AAO membranes: conditions for SANS measurements, channel arrangement, fitting method. We point out that the probed length in the fitting model is a critical parameter related to the longitudinal pore ordering. Applied to several AAOs, this approach indicates the existence of a contaminated shell. This original approach, based on a fine and complete description of the SANS data, can be applied to a variety of confining medium and will allow the further investigation of condensed matter under confinement.

In the second approach, neutron reflectivity is used in combination with SEM to analyze the entering of polyelectrolyte in duplex nanoporous anodic aluminum oxides (nAAO) [2]. Duplex nAAO are promising systems to study the influence of geometrical constriction, i.e. the reduction of pore diameters along the pore channel, on the confinement of condensed matters. Quantitative information about the entering and adsorption of polyelectrolytes (PEs) in nanopores are extracted.

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# Thermodynamic effects of linear peptides on lipid membranes probed with neutrons

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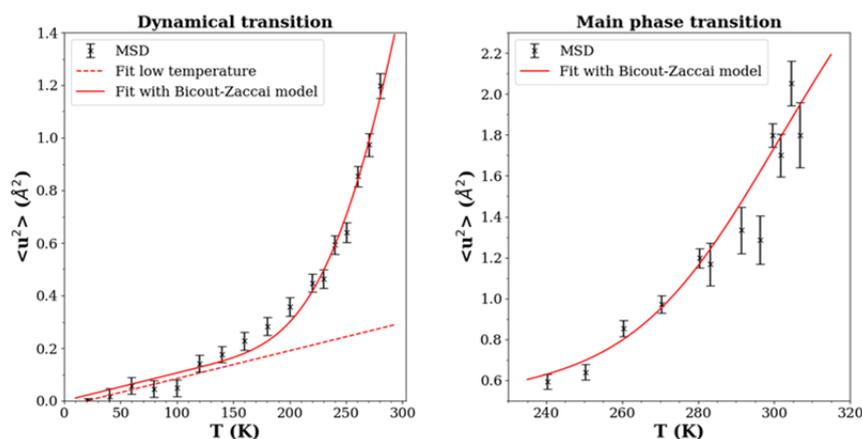
Lipid membranes, in presence or not of molecular components as peptides, undergo a phase transition when temperature is increasing, passing from a gel to a liquid-like state. Above the transition the fluidity of the membrane increases and the lipids become more mobile. Such phases are studied with standard methods, like differential scanning calorimetry (DSC). From there, thermodynamic parameters can be retrieved, like the transition temperature, the excess enthalpy or the heat capacity.

On the other hand, neutrons represent a powerful tool to study hydrogen-containing samples at a nanoscopic level, as the incoherent neutron scattering cross-section is much higher for hydrogen than for other atoms. Biomolecules being composed of around 50% hydrogen, neutrons constitute an ideal probe. Therefore, elastic incoherent neutron scattering (EINS) can elucidate the average dynamics of a large range of biomolecules, like proteins, but also lipid membranes. From the average dynamics, represented by the mean-square displacements of H-atoms, force constants and thermodynamic parameters can be derived through the Bicout-Zaccai two-state model [1] (Bicout and Zaccai, 2001).

For various lipid systems, EINS measurements coupled with this model (see figure below) showed indeed the increase of atomic mobility above the main phase transition (example in [2] Peters et al., JPCB 2017). However, the thermodynamic parameters derived from the same model are rarely compared to classical measurements. As neutron scattering techniques involve very different timescales (ns-ps) compared to classical ones (s-min), the aim of our study is to characterize to what extent thermodynamic parameters extracted from neutron data compare well to calorimetric results.

In collaboration with researchers from the University of Strasbourg, a lipid system composed of POPE/POPG and up to two linear peptides was investigated around its main phase transition (occurring at 20°C), both with DSC and neutrons, at the Institut Laue-Langevin.

We are presenting here first results, and give an outlook about future work.



**Figure :** Mean-Square Displacements derived from EINS measurements on POPE/PG 3:1 fitted with Bicout-Zaccai model. Left : fit on the dynamical transition at lower temperature. Right : fit on the main phase transition at higher temperature, whose extracted parameters were compared to DSC results.

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# Membrane interaction of off-pathway prion oligomers and lipid-induced on-pathway intermediates during prion conversion: a clue for neurotoxicity

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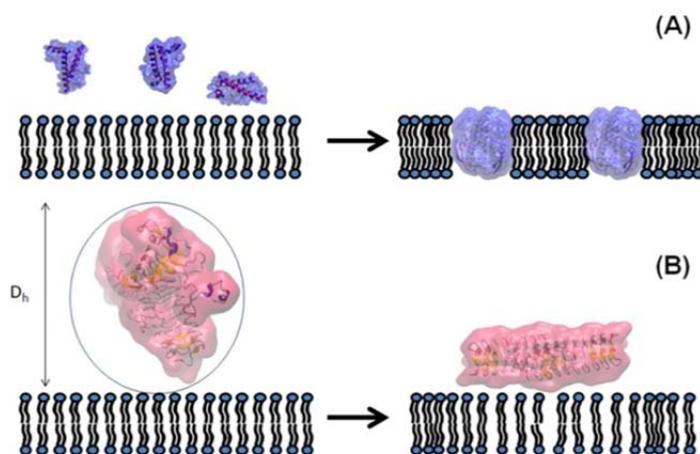
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Prion protein (PrP) misfolding is associated with a range of deadly neuropathological diseases -including bovine spongiform encephalopathy and Creutzfeldt-Jacob in human - characterized by the accumulation of insoluble proteinaceous aggregates inside the infected tissues [1]. Soluble oligomers of PrP, produced during amyloid aggregation, have emerged as the primary neurotoxic species, instead of the fibrillar end-products. However, whether the membrane is among their direct targets, that mediate the downstream adverse effects, remains a question of debate [2]. Recently, questions arise from the formation of membrane-active oligomeric species generated during the  $\beta$ -aggregation pathway, either in solution, or in lipid environment.

In the present study [3], we characterized membrane interaction of off-pathway oligomers from recombinant prion protein generated along the amyloid aggregation and compared to lipid-induced intermediates produced during lipid-accelerated fibrillation. Using calcein-leakage assay, we show that the soluble prion oligomers are the most potent in producing leakage with negatively charged vesicles. The binding affinities and conformational states of the different PrP assemblies were determined by thioflavin T binding-static light scattering experiments on DOPC/DOPS vesicles and FTIR-ATR spectroscopy onto the corresponding supported lipid bilayers. Finally, the modes of interaction of PrP oligomers with supported lipid bilayers were highlighted by specular neutron reflectivity using different contrasts.

Our results indicate that the off-pathway PrP oligomers interact with lipid membrane *via* a distinct mechanism, compared to the inserted lipid-induced intermediates (Figure 1). Thus, separate neurotoxic mechanisms could exist following the puzzling intermediates generated in the different cell compartments. These results not only reveal an important regulation of lipid membrane on PrP behavior but may also provide clues for designing stage-specific and prion-targeted therapy.



*Figure 1.* (A) Membrane-mediated aggregation of the  $\alpha$ -helical monomeric PrP (1tpx.pdb) leading to  $\beta$ -sheeted lipid-induced on-pathway oligomers inserted in lipid bilayers and (B) interaction of  $\beta$ -sheeted off-pathway oligomers at lipid interface for the purpose of size comparison. The 3D structures inside oligomers are drawn to illustrate the conformational change at the membrane.

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[3] Combet S *et al. Biochim Biophys Acta Biomembr* 1861 (2019) 514-523.

## SANS: a powerful tool to probe foams and emulsions

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Foams and emulsions are complex out-of-equilibrium systems whose relevant structural length-scales span from a few nanometers up to millimeters. It is thus necessary to combine several techniques to obtain a refined description of their structure. In this lecture I will show how Small Angle Neutron Scattering can provide such a description at the nanometer scale, although this technique which is widely used in Soft Matter remains poorly used for probing foams and emulsions.

In a first time, I will show how the use of contrast variation enabled to describe the mechanism of stabilization of Pickering emulsions based on cellulose nanocrystals [1]. In a second part, I will discuss the different scattering events that occur when a foam is probed by SANS : the reflectivity from the thin films, which is the main process that occur in dry foams and the bulk scattering from the liquid in the Plateau border, which the main process that occur in wet foams [2]. I will then illustrate how SANS was use to unravel the outstanding properties of foams based on Sodium Dodecyl Sulfate at high concentration [3].

[1] F. Cherhal, F. Cousin, I. Capron, *Biomacromolecules*, 2016, 17(2) (2016) 496–502.

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[3] L. Zhang, A. Mikhailovskaya, P. Yazhgur, F. Muller, F. Cousin, D. Langevin, N. Wang, A. Salonen, *Angewandte Chemie Int. Ed.*, 2015, 127(33) (2015) 9669–9672.

## Hydrogen dynamics in molybdenum compounds

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With an increase in renewable energy production, the problem of energy storage becomes more and more significant. There are different concepts of energy storage techniques and one of the most promising is the “Power-to-gas” concept. Within its scope hydrogen gas is produced from water using the excess of energy and then reconverted when energy is in demand. It is of paramount importance for these processes to be carried out most efficiently with the most readily accessible materials. Therefore, there have been intense studies in the search for catalyst materials for the hydrogen and oxygen evolution reactions, in order to replace the expensive platinum, which is widely used today.

Molybdenum compounds, MoC<sub>2</sub> and Mo<sub>2</sub>S in particular, have shown promising behaviour as a catalyst in hydrogen evolution reaction, but the reason for such behaviour is still obscure. For platinum it is known that it is hydrogen diffusion that plays a crucial role in the activity. Hence it may well be that hydrogen dynamics are also important for molybdenum based catalysts.

The best technique to study hydrogen diffusion is quasi-elastic neutron scattering (QENS). We performed an experiment at the TOFTOF spectrometer at MLZ, Germany, to investigate hydrogen dynamics in MoS<sub>2</sub> crystals electrochemically loaded with hydrogen at a range of temperatures from 3 K to 500 K. Below 100 K no diffusion motion was found within the resolution of the experiment. At 200K a quasi-elastic broadening of the elastic line starts to emerge and then can be clearly seen at 300 K. To accurately fit this broadening, at least two Lorentzians are needed, indicating the presence of both rotational and translational diffusion. After partial desorption at 400 K and above the QENS broadening attributed to translations exhibits Q dependence that is typical for a jump-diffusion process with a continuous distribution of jump distances and can be treated with the Singwi-Sjölander model.

## Ferrofluids in ionic liquids: high temperature study coupling SANS and DLS

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<sup>3</sup> Solvionic SA, Chemin de la Loge, FR-31078 Toulouse, France.

Ferrofluids in ionic liquids are interesting fluids which combine magnetic properties with the advantages of ionic liquids, a broad class of liquids, which consist solely of ions, and can be liquid at room temperature, presenting interesting properties as a low vapor pressure, a large electrochemical window, and possible stability at high temperatures. They are also interesting for thermoelectric materials [1], which convert heat to electricity providing one possible methodology for the recycling of low-grade waste heat. Despite improvements, present thermoelectric solid materials have several limitations. Therefore, investigations in complex liquids (e.g. ionic liquids or nanofluids) have been proposed in recent years [2]. In addition, our recent studies on aqueous dispersions of NPs have demonstrated that the addition of magnetic NPs can influence the TE coefficient [3] and enhance the liquid's TE efficiency [4].

The dispersion of nanoparticles (NPs), here magnetic maghemites of diameter around 8 nm, in an ionic liquid is however not obvious as the usual approaches for colloids in molecular solvent cannot be applied. Our studies at room temperature in EAN [5] and more recently in many other ionic liquids [6] have shown the ability to disperse charged NPs in ILs controlling the solid/liquid interface, i.e. the charge of the surface, the groups producing this charge and the initial counterions of the nanoparticles. The interparticle interactions can vary from weakly repulsive to weakly attractive depending on the precise composition of the systems and long term stable colloidal dispersions can be obtained.

In a second step, understanding how evolve such systems at high temperature, needed for thermoelectrical applications, is crucial. This has been done coupling Small Angle Neutron Scattering (SANS) and Dynamic Light Scattering (DLS) within a furnace up to 200°C. A parallel measurement with Forced Rayleigh scattering completes the analysis of the system in the same temperature range adding a measurement of the diffusion coefficient and of the thermodiffusive properties to the information on interparticle interaction and nanostructure extracted from SANS/DLS.

**Acknowledgements:** We acknowledge funding from Horizon 2020 FET-PROACTIVE project, MAGENTA, associated with the Grant n° 731976.

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- [5] Mamusa, M. et al., Soft Matter 10, 1097 (2014)
- [6] J. Riedl, A. Akhavan Kazemi, F. Cousin, E. Dubois, S. Fantini, S. Loïs, R. Perzynski, and V. Peyre, to be submitted

## New advances on the $\text{RMn}_2\text{O}_5$ multiferroics family

**A. Vaunat**<sup>1</sup>, V. Balédent,<sup>1</sup> S. Petit,<sup>2</sup> M.B. Lepeit<sup>3</sup> and P. Foury-Leylekian<sup>1</sup>

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<sup>2</sup>Laboratoire Léon Brillouin, 91191 Gif sur Yvette, France

<sup>3</sup>Institut Néel, 38042 Grenoble, France

$\text{RMn}_2\text{O}_5$  are a family of magneto-electric multiferroic materials, where the ferroelectricity and magnetism influence each other.

This family presents a great diversity of interesting properties originating from the existence of at least 5 different exchange interactions  $J_i$ , a magnetic frustration and the presence of two different Mn valences.

The structure is built of  $\text{Mn}^{4+}\text{O}_6$  octahedra forming chains along the c direction and  $\text{Mn}^{3+}\text{O}_5$  square-based pyramids. In the (a, b) plane, edge-sharing  $\text{Mn}^{4+}\text{O}_6$  octahedra and  $\text{Mn}^{3+}\text{O}_5$  pyramids form pentagons. There are one antiferromagnetic (AFM) super-exchange interaction  $J_5$  between  $\text{Mn}^{3+}$  ions through a common oxygen, two other AFM super-exchange interactions  $J_3$  and  $J_4$  between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions and two inequivalent AFM super-exchange couplings  $J_1$  and  $J_2$  between  $\text{Mn}^{4+}$ . The pentagonal geometry of the spins and their AFM coupling results in the magnetic frustration which leads to a complex phase diagram with incommensurate magnetic orderings notably. [1]

In addition, for members of the series with magnetic  $\text{R}^{3+}$  ions, another exchange coupling between  $\text{Mn}^{3+}$  and  $\text{R}^{3+}$  has to be considered, as well as the anisotropy term related to the  $\text{R}^{3+}$ . This leads to a more complex panel of magnetic orderings with various propagation wave vectors.

Furthermore, the presence of exotic excitations such as electromagnons is attested for many members of the series, like  $\text{YMn}_2\text{O}_5$ ,  $\text{TbMn}_2\text{O}_5$  and potentially  $\text{GdMn}_2\text{O}_5$ . [2] [3] [4]

The aim of this presentation is to give a brief overview of the properties of  $\text{RMn}_2\text{O}_5$  and to focus on  $\text{GdMn}_2\text{O}_5$  [5]. This compound presents the most prominent properties of the series with a strong electric polarization and a rich magnetic phase diagram. The presence of  $\text{Gd}^{3+}$  ions, with a null spin-orbit coupling is of particular interest to understand the magnetic phase diagram as well as the magnetic excitations. We will thus present our recent inelastic neutron measurements made at the LLB will be presented to illustrate this point.

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[3] S. Petit, «Investigation of the electromagnon excitations in the multiferroic  $\text{TbMn}_2\text{O}_5$ ,» *PHYSICAL REVIEW B* 87, 140301(R), 2013.

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## The iron-based spin ladder BaFe<sub>2</sub>Se<sub>3</sub>: from multiferroic to superconductor

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<sup>3</sup>Institut Laue Langevin, 38000 Grenoble, France

<sup>4</sup>Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1 avenue de la Terrasse, 91198 Gif-sur-Yvette, France.

<sup>5</sup>IRAMIS, SPEC, CEA, 91191 Gif sur Yvette, France

In recent years, Fe-based low dimensional systems have attracted huge interest for the exotic superconductivity they can present. In addition, multiferroics are intensively studied because of their potential applications in technological applications notably. In this context, the spin ladder iron chalcogenides BaFe<sub>2</sub>Se<sub>3</sub> predicted multiferroic [1] and found superconducting under pressure [b] is thus of tremendous interest [2]. We present here the magnetic and structural study of this system as well as the doped analogs. Whereas previous publications suggested that BaFe<sub>2</sub>Se<sub>3</sub> crystallizes in the Pnma space group [3]. We found that the real structure is a Pmn21 polar structure. We also performed a powder neutron diffraction experiment from 1.5 K to 300 K in the pure system and found  $q=(\frac{1}{2} \frac{1}{2} \frac{1}{2})$  magnetic peaks appearing below 175 K in the pure system. The refinement shows that the moment of Fe at 1.5 K is 2.7  $\mu_B$ . Meanwhile, the block-type antiferromagnetic structure proposed by [c] has been confirmed. As for Ba(Fe<sub>0.85</sub>Co<sub>0.15</sub>)<sub>2</sub>Se<sub>3</sub>, preliminary results show that the AFM transition is strongly destabilized by the doping with a TN~30K. We will present the neutron experiment performed on this doped system.

[1] S. Dong, J.M. Liu, and E. Dagotto, PHYSICAL REVIEW L, 113 (2014) 187204.

[2] Jianjun Ying, Hechang Lei, Cedimir Petrovic, Yuming Xiao and Viktor V. Struzhkin, PHYSICAL REVIEW B 95 (2017) 241109(R).

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Monday 16th of September

18:00 BUS departure, Montpellier Saint Roch Station

19:00 Welcome Drink

20:00 Dinner 20:00

Tuesday 17th of September

08:15	Opening	
08:30	Plenary: Arantxa ARBE (CFM, San Sebastian)	
09:15	Keynote: Annie Brûlet (LLB)	Keynote: Mechthild Enderle (ILL)
09:45	Fabien Dutertre	Dalila Bounoua
10:05	Coffee Break 30'	
10:35	Plenary: Markus Braden (Univ. Cologne)	
11:20	Keynote: Urs Gasser (PSI)	Keynote: Jean-Noël Chotard (Amiens)
11:50	Marian Cors	Iurii Kibalin
12:10	Neutrons and Food: Camille Loupiac	
12:30	Lunch 12:30	
14:00	Nathalie Malikova	Morgane Lemaire
14:20	Simeon Minic	Cyrielle Métais
14:40	François Boué	Geoffrey Monet
15:00	Free Time and Swimming Pool	
	Coffee Break 30'	
16:30	Instrum. Frédéric Ott	
16:45	Instrum. Stéphane Rols	
17:00	Instrum. Patrick Judeinstein	
17:15	Instrum. Viviana Cristiglio	
17:30	Instrum. Patrick Baroni	
17:45	Neutron Centers News: ILL, LLB, ESS, PSI, ENSA, 2FDN	
19:30	Dinner 20:00	
21:00	40 years of Science with NEUTRONS from ORPHEE Christiane Alba-Simionesco, Michel Rawiso, François Boué and Frédéric Ott	
22:30		

Wednesday 18th of September

08:30	Plenary: Stéphane Pailhes (ILM Lyon)	
09:15	Keynote: Leonardo Chiappisi, ILL	Keynote: Philippe Bourges (LLB)
09:45	Zijun Lu	Arno Hiess
10:05	Coffee Break 30'	
10:35	Plenary: Giovanna Fragneto (ILL)	
11:20	Julie Wolanin	Diane Rebiscoul
11:40	Yazhao Liu	Jean-Louis Bantignies
12:00	Lunch 12:00	
13h30	José Teixeira (LLB) President of PhD award committee	
13h40	PhD award: Raphael Dos Santos Morais	
14:30	Marion Grzelka	Shelby Turner
14:50	Michel Rawiso	Mickaël Beaudhuin
15:10	Annulé	Romain Viennois
15:30	Posters	
16:30	Coffee Break 30'	
17:00	Aicha Jani	Victor Balédent
17:20	Oriana Osta	Elodie Tailleur
17:40	AG SFN	
19:00	Pre-dinner drinks	
20:00	Gala Dinner 20:00	
23:00		