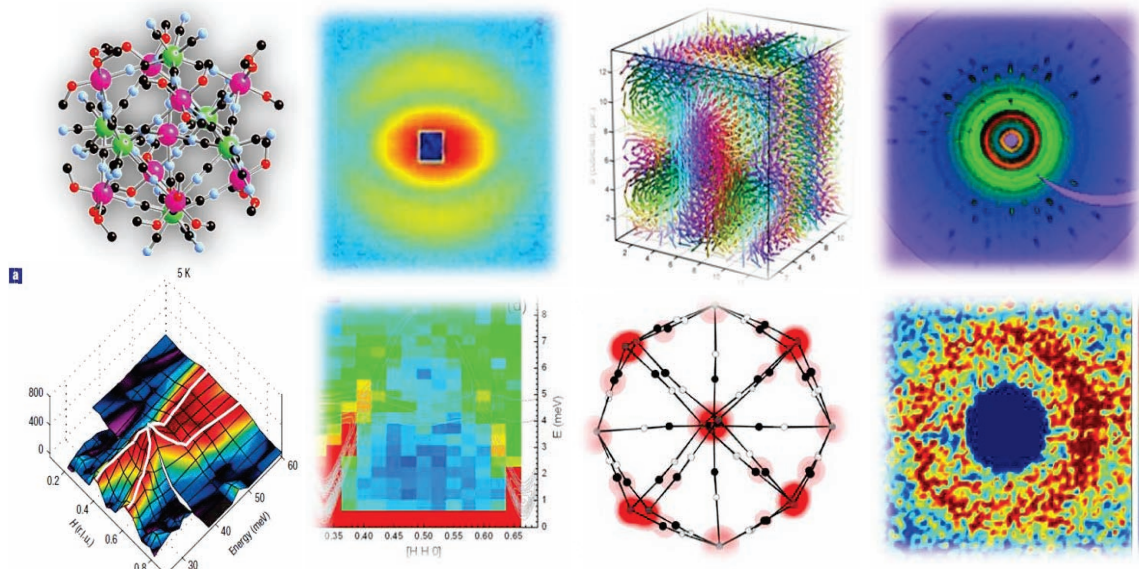


2008~2010

## PART II : SCIENTIFIC RESEARCH



énergie atomique • énergies alternatives



2008-2010



## **AXIS 1 Research: Strongly Correlated Quantum Materials and Magnetism**

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### Keywords:

superconductivity, frustration, multipole orders, Kondo insulators, spin-lattice coupling, magnetoresistance, multiferroics, manganites, cuprates, pnictides, spin ices, molecular magnets.

### **Scope**

This scientific axis encompasses research activities on a large variety of magnetic and/or strongly correlated electron systems (SCES). Included are studies of unconventional superconductors (cuprates, pnictides), geometrically frustrated pyrochlore magnets (spin ices), novel magnetic orders in 4f-electron systems (heavy fermions, Kondo insulators), multiferroic compounds with interplay between electric and magnetic orders, manganites with giant magnetoresistance properties, and molecular magnets. The techniques involved are neutron diffraction and inelastic neutron scattering, with the optional use of polarized neutrons.

During the period from 2008 to 2010, 144 publications have been produced on these topics, and 18 invited reports have been given at international conferences. This scientific area also involves 3 ANR projects, 4 RTRA projects ("Triangle de la Physique"), and 1 JRA project (NMI3-7th Framework Program of the European Commission).



## Current Research

The field of strongly correlated electron systems (SCES) covers a wide range of materials and physical phenomena which go beyond the standard theory of a Fermi gas of non-interacting electrons. The composition of these compounds usually involves transition metals or rare earth oxides, hydrides or intermetallics. The interactions between electrons allow several degrees of freedom such as spin, charge, lattice, or orbital to be simultaneously active. Original features in SCES are studied at LLB, both through experiment and theory. The competition between different phases and interactions induces a great variety of magnetic phenomena, ground states, and phase transitions, ranging from **unconventional superconductivity** or **multipolar orders** to **photomagnetism**. When interactions are short-range, the specific geometry of the lattice plays a crucial role, which raises the possibility of fine-tuning the magnetic states through geometrical frustration or spin-lattice coupling (**spin ices**, **multiferroics**). Because of their complex energy balance, materials from this class can exhibit anomalously large responses to small perturbations, such as the **giant magnetoresistance in manganites**, and open the way to new functionalities (e.g., spintronics and photoswitchable compounds). Interesting states may also occur under extreme conditions (e.g., very low temperatures, high magnetic field or high pressure). The neutron probe is likely the best tool to study their properties from a microscopic standpoint, since it is sensitive to spin and lattice ordered states and low-energy excitations, and its polarization state can further be controlled and monitored by appropriate techniques. The main areas of research studied in LLB are summarized below.

### Unconventional superconductivity: neutron spectroscopy and theory

In the last two decades, new superconducting (SC) compounds, exhibiting surprisingly high critical temperatures ( $T_c$ ), have been discovered. In contrast to conventional superconductors, the SC order parameter is not isotropic, neither in cuprates nor in Fe-based systems. This ignited a search for new SC pairing mechanisms based on the existence of rather strong electronic interactions. These interactions further render the materials extremely unstable against long-range ordering, which can either favor or compete with superconductivity, and thus give rise to extraordinarily rich phase diagrams

## Organization

The experimental work on SCES carried out at the LLB is based on a versatile instrument suite implementing different neutron-scattering techniques.

- I. Inelastic scattering on triple-axis spectrometers: study of the lattice and magnetic excitation spectra. The LLB operates two thermal-neutron (1T, 2T) and three cold-neutron (4F1, 4F2, G4-3) triple-axis spectrometers. The 2T and 4F1 instruments can be equipped with a polarized neutron setup (linear polarization analysis).
- II. Single-crystal neutron diffraction: study of crystalline and magnetic ordered states. These instruments include a four-circle diffractometer on a hot neutron source (5C2); a four-circle diffractometer on a thermal beam (6T2), which can also be operated in a two-axis mode with a lifting detector; and a two-axis diffractometer with polarized hot neutrons (5C1), specially designed for measuring spin density maps. The 6T2 instrument was recently equipped with a 2D multidetector.
- III. Powder neutron diffraction: characterization of crystalline and magnetic orders. This instrument suite consists of one high-resolution diffractometer with thermal neutrons (3T2) devoted to crystalline studies, one diffractometer (G4-1) on a cold neutron guide for the determination of magnetic structures, and one long-wavelength diffractometer (G6-1) optimized for high-pressure studies.

Three groups with specific experimental expertise are in charge of the above spectrometers. This responsibility involves the operation and upgrade of the instruments and their sample environments, as well as providing the technical and scientific support to visitors who perform experiments at the LLB. The research projects described hereafter involve close collaborations between members of the different groups since most studies actually require the use of several types of spectrometers. Collaborations with external teams are also essential. In particular, chemistry laboratories can supply new materials, in the form of powder or single crystal samples. Obtaining large, high-quality, single crystals is generally a prerequisite for undertaking inelastic neutron experiments. Other collaborations make it possible to study or characterize the same samples by probes other than neutrons (e.g., x-rays, bulk magnetization, resistivity, Mössbauer or NMR spectroscopy, etc.). These close relationships both inside and outside LLB, together with a constant effort to optimize the performance of the instruments, are the keys to meeting the standards of top level research in the present international context.

### The spin resonance-mode scenario in high- $T_c$ cuprates

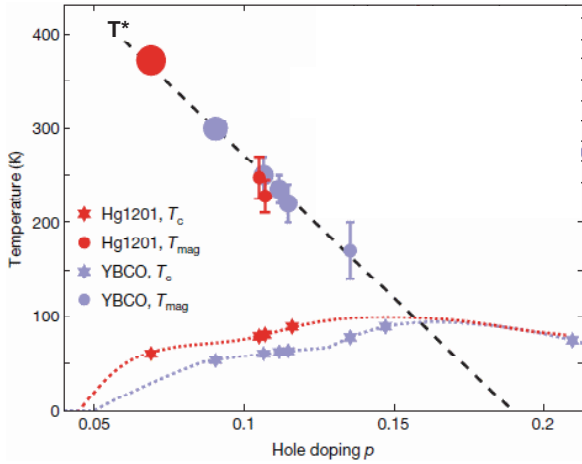
In conventional superconductors, the electron pairing interaction is mediated by an exchange of phonons. In the framework of Eliashberg theory, anomalies in the charge excitation spectrum, probed by tunneling and optical conductivity measurements, were directly connected to the density of phonons, measured by inelastic neutron scattering, thereby providing evidence for the leading role of electron-phonon coupling in these materials. In high- $T_c$  cuprates, on the other hand, the mechanism responsible for superconductivity is still unknown despite 20 years of intensive research. Nevertheless, the observed structure of the low-energy electron spectrum is often considered to be the fingerprint of a strong electron coupling to some boson, which in turn is suspected to be a mediator of the SC pairing. In those materials, strong antiferromagnetic (AF) spin fluctuations, termed “spin-resonance” modes, were observed in the SC state by inelastic neutron scattering. Following early theoretical studies carried out at LLB, these excitations are now well understood as triplet excitons. The theory group has recently developed an improved version of the Eliashberg theory, and has shown<sup>1</sup> that spin-resonance modes could explain significant anomalies observed in the SC high- $T_c$  cuprates: the d-wave SC pairing, the U-shaped angular dependence of the SC gap, the anomalous form of the electron density of states, and the renormalization of the electronic dispersion. This work establishes the scenario of spin-resonance-mediated superconductivity on solid theoretical grounds.

<sup>1</sup> *Superconducting Pairing through the Spin Resonance Mode in High-Temperature Cuprate Superconductors*  
F. Onufrieva and P. Pfeuty, Phys. Rev. Lett. **102**, 207003 (2009).



## Unconventional magnetic order in the pseudogap state of high- $T_c$ cuprates

Whereas ascertaining the origin of superconductivity in cuprates remains one of the major challenges posed to condensed matter physics, the anomalous electronic properties of those materials outside the SC state constitutes another, equally elusive, mystery. In particular, the low-energy electrons become partially gapped well above  $T_c$  in the so-called pseudogap phase (Figure 1.1). Recent, highly accurate, polarized neutron diffraction measurements have demonstrated the existence of a long-range magnetic order developing below the pseudogap-opening temperature  $T^*$ . This pioneering work performed at LLB has stimulated international



**Figure 1.1.** Universal pseudogap phase diagram: dependence on hole doping ( $p$ ) of the superconducting critical temperature  $T_c$  and the ordering temperature  $T_{mag}$  associated with the appearance of an unconventional magnetic phase in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  (YBCO) and  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg1201).  $T_{mag}$  matches the temperature  $T^*$  (dashed line), corresponding to the opening of the so-called pseudogap state, as derived from other types of measurements. From Ref. [2].

collaborations with several groups in the USA (H. Mook, Oak Ridge National Laboratory; M. Greven's group, Stanford University). Our observation was subsequently confirmed in two distinct families of cuprates,  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  and  $\text{HgBa}_2\text{CuO}_{4+\delta}$ <sup>2</sup>. The magnetic phase breaks time-reversal symmetry, but preserves the lattice translation invariance. This implies the existence of staggered magnetic moments within each unit cell. The observed magnetic correlations are distinct from the usual antiferromagnetic spin-correlation, which are well documented from previous inelastic neutron scattering (INS) measurements. Here, in contrast, they are thought to possess an orbital-like character and could originate from nanoscopic current loops, as initially proposed by C.M. Varma in his theory of the pseudogap phase. The neutron scattering measurements indeed provide the first experimental evidence that the pseudogap phase is a long-range-ordered phase, competing with superconductivity in cuprates. The search for this novel magnetic phase is now being extended to other cuprate families, such as  $\text{La}_{2-x}\text{SrCuO}_4$  and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  through new collaborations with other groups in France (I. Laffez, LEMA, Université de Tours) and Switzerland (J. Mesot, Paul Scherrer Institute, Villigen).

## Instability towards a so-called electronic nematic state in cuprates.

Recent INS measurements, carried out in strongly underdoped  $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$  ( $T_c = 35$  K), have demonstrated the existence of quasi-one-dimensional (1D) incommensurate spin fluctuations, developing spontaneously below 150 K<sup>3</sup>. This observation highlights the spontaneous breaking of rotational invariance in the system. On cooling down, the lattice translation invariance is further broken, while incommensurate spin fluctuations freeze at short distance. Static correlations can be enhanced by applying an external magnetic field. In addition to INS measurements, electrical transport properties exhibit a significant 1D anisotropy, while quantum oscillation measurements in high magnetic fields suggest a folding of the electronic band structure, which is associated with a state which breaks the lattice translation invariance. All these findings point toward the existence of an electronic nematic instability, where rotational symmetry is spontaneously broken at long distance as a result of strong electronic interactions. This instability leads to an electronic smectic state when the translation invariance is further broken. Such mechanisms are also regarded as likely candidates for explaining the anomalous electronic properties of cuprates in the pseudogap phase. These results are the fruit of a long-standing collaboration between the LLB and the MPI in Stuttgart.

<sup>2</sup> Unusual magnetic order in the pseudogap region of the superconductor  $\text{HgBa}_2\text{CuO}_{4+\delta}$

Y. Li, V. Balédent, N. Barišić, Y. Cho, B. Fauqué, Y. Sidis, G. Yu, X. Zhao, P. Bourges, M. Greven, *Nature* **455**, 372-375 (2008).

<sup>3</sup> Electronic Liquid Crystal State in the High-Temperature Superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$

V. Hinkov, D. Haug, B. Fauqué, P. Bourges, Y. Sidis, A. Ivanov, C. Bernhard, C. T. Lin, B. Keimer, *Science* **319**, 597 (2008).

## Magnetic superconducting “glue” for Fe-based superconductors?

Non-superconducting  $M\text{Fe}_2\text{As}_2$  ( $M$ : Ca, Fe) shows a crystallographic transition from a tetragonal phase to an orthorhombic phase, accompanied with an AF spin-density wave order. Upon doping with either electrons or holes, the structural and magnetic transitions vanish and the system becomes superconducting. The unconventional “ $s+/-$ ” SC order parameter is believed to reflect an attractive interaction mediated by the exchange of strong AF fluctuations inherited from the spin-density-wave state. Within a collaboration between the MPI Stuttgart (B. Keimer’s group), FRM-II Munich and the LLB, the AF spin excitation spectrum in electron-doped  $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$  was recently mapped out at temperatures spanning the transition from the normal to the SC state. Furthermore, the dynamic spin susceptibility could be determined in absolute units<sup>4</sup>, providing highly valuable information for theories and allowing the coupling strength between electrons and spin fluctuations to be quantitatively evaluated. The role of lattice vibrations in superconductivity was also investigated in non-SC  $M\text{Fe}_2\text{As}$  by the Karlsruhe group at LLB in collaboration with Th. Brückel and his collaborators (Forschungszentrum Jülich, Germany). INS measurements of the phonon dispersions and comparison with density functional theory (DFT) calculations indicate that theory correctly reproduces most phonon frequencies, but fails to account for the anomalous temperature dependence of some modes.<sup>5</sup> The coupling of vibrational and electronic degrees of freedom appears stronger than predicted by DFT and the role of phonons in the superconductivity of Fe-based superconductors could be more significant than anticipated. The importance of both magnetic and lattice degrees of freedom is further supported by first-principle calculations carried out at LLB<sup>6</sup> for FeSe, another newly-discovered iron-based superconductor. Spin-polarized calculations of all frozen phonons at the Brillouin zone center show a significant deformation of the electronic band structure near the Fermi level for several modes involving a displacement of the chalcogen. The particular  $B2u(\text{Se})$  phonon mode shows a strong linear coupling with the AF order parameter, leading to a substantial electron-phonon coupling, which can partly account for the superconducting critical temperature  $T_c$  when the weak coupling BCS theory is used. Nevertheless, the strong linear coupling of this  $B2u(\text{Se})$  mode with the magnetic order parameter strongly suggests that magnetic fluctuations are another necessary ingredient to fully account for the high  $T_c$  observed in this system.

## Novel electronic and magnetic properties in 4f-electron systems

4f electrons are known to be more localized than d electrons and subject to strong spin-orbit coupling. Instabilities of otherwise magnetic 4f states occur mainly in metallic compounds as a result of hybridization with conduction band states, as described in the well-known Anderson model. This approach basically describes a competition between exchange interactions and Kondo-type magnetic fluctuations, producing renormalized Fermi-liquid quasiparticle states, heavy effective masses and, in some cases, “heavy-fermion superconductivity”. Some materials do not fit into this framework, however, because other degrees of freedom (such as the multipole moments) are involved, or because the renormalization leads to a semiconducting ground state (“Kondo insulators”).

## Unconventional ordered states: competing dipole and multipole interactions

Whereas neutron diffraction techniques remain unchallenged in solving intricate magnetic structures, systems in which spin and orbital degrees of freedom are intimately coupled require more diversified approaches. This type of situation occurs in  $f$ -electrons exhibiting various types of “multipole orders” at low temperature, such as skutterudites or hexaborides. The best-known example is  $\text{CeB}_6$ , which shows a mixed order of Ce quadrupole and octupole moments in a narrow temperature range (“phase II”:  $2.3 < T < 3.2$  K in zero field), prior to developing a long-range order of magnetic dipole moments. A field-induced ( $H \parallel [001]$ ) magnetic contribution ascribed to the ordered  $T_{xyz}$  octupole moments was observed

<sup>4</sup> Normal-state spin dynamics and temperature-dependent spin-resonance energy in optimally doped  $\text{BaFe}_{1.85}\text{Co}_{0.15}\text{As}_2$   
D. S. Inosov, J. T. Park, P. Bourges, D. L. Sun, Y. Sidis, A. Schneidewind, K. Hradil, D. Haug, C. T. Lin, B. Keimer, V. Hinkov, Nature Physics **6**, 178 (2009).

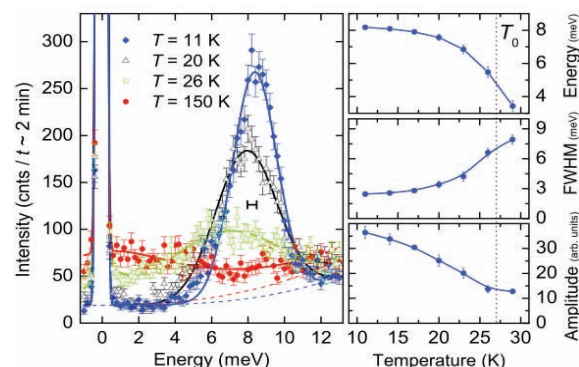
<sup>5</sup> Measurement of Anomalous Phonon Dispersion of  $\text{CaFe}_2\text{As}_2$  Single Crystals Using Inelastic Neutron Scattering  
R. Mittal, L. Pintschovius, D. Lamago, R. Heid, K-P. Bohnen, D. Reznik, S. L. Chaplot, Y. Su, N. Kumar, S. K. Dhar, A. Thamizhavel, and Th. Brueckel, Phys. Rev. Lett. **102**, 217001 (2009).

<sup>6</sup> Strong electron-phonon coupling in  $\text{Be1-xB2C2}$ : ab initio studies  
A.H. Moudden, Eur. Phys. J. B **64**, 173 (2008).

for the first time in neutron diffraction experiments performed at LLB (collaboration with Tohoku University, Sendai and JAEA, Tokai). Substituting Ce by other lanthanide elements with different ground state multiplets ( $^{2S+1}L_J = ^1S_0, ^2F_{5/2}, ^3H_4, ^4I_{9/2}$  for La, Ce, Pr, and Nd, respectively), one can selectively tune the different multipole moments and study the effect on the ordering properties of the material. Studies of the (Ce,Pr)B<sub>6</sub>, (Ce,Nd)B<sub>6</sub>, and (La,Pr)B<sub>6</sub> series, carried out in a collaboration between the LLB (neutron diffraction), Hiroshima University (bulk properties), and Spring-8 (synchrotron x-ray diffraction), led to the characterization of several new ordered phases in the temperature–magnetic field phase diagrams for different compositions, whose relative stability ranges can be traced back to the interplay between multipole interactions of different orders and symmetries.<sup>7,8</sup>

Recently a new material, CeRu<sub>2</sub>Al<sub>10</sub>, became the focus of considerable attention: despite being a seemingly innocuous intermetallic Ce compound, it appears to be on the verge of a semiconducting state, which can be stabilized under a moderate pressure of  $\sim 1$  GPa, but subsequently collapses above 3 GPa. This dramatic effect is directly connected to an elusive phase transition occurring at  $T_0 = 27$  K, whose order parameter remains controversial. Superstructure satellites were observed in a powder diffraction experiment on G4-1,<sup>9</sup> and proven to be magnetic (wave vector  $\mathbf{k}_{AF} = [1,0,0]$ ) using neutron polarization analysis on 4F1. However, the simplest antiferromagnetic structure suggested by the neutron measurements fails to explain the recent results from Al NMR. Furthermore, INS data performed on powder (Figure 1.2) indicate that the main peak developing at about 8 meV below  $T_0$  has a mixed (magnetic + nuclear) character. This suggests that the transition does not reduce to a conventional antiferromagnetic ordering, and more detailed investigations have been undertaken to clarify this important question.

### Kondo insulators and related boride compounds



**Figure 1.2.** Constant-Q scans ( $Q = 1.5 \text{ \AA}^{-1}$ ) measured on CeRu<sub>2</sub>Al<sub>10</sub> powder as a function of temperature, showing a broad excitation peak around 8 meV in the ordered state below  $T_0 = 27$  K, whose spectral weight transfers to a quasielastic signal in the paramagnetic state. Right frames (top to bottom): energy, full width at half maximum, and peak intensity of the inelastic peak. From Ref. [9].

“Kondo insulators” (KIs) form a unique class of strongly correlated *f*-electron compounds, in which the renormalization of electronic states occurring at low temperature causes the opening of a narrow gap in the density of states, rather than an enhancement of Fermi-liquid quasiparticle masses as found in heavy-fermion systems. They are the subject of a long-standing collaboration with the Russian Research Center “Kurchatov Institute” in Moscow. In previous INS studies, the archetype compound YbB<sub>12</sub> was shown to develop a peculiar magnetic response in its KI state below  $T^* \approx 50$  K, dominated by a spin gap and three distinct magnetic excitations. The lower peak, in particular, was ascribed to a spin-exciton (in-gap) mode due to antiferromagnetic correlations and mapped out in *Q* space using both polarized and unpolarized triple-axis measurements. Lutetium dilution experiments subsequently showed that the spin gap opening is not primarily a coherence effect, as assumed in the usual “hybridization-gap” picture, but could reflect the formation of an array of local singlet-states. Recently, substitution of (trivalent) Yb by (tetravalent) Zr was used to probe the contribution of *d*-electron states to the latter mechanism. The results indicate that, at variance with the Lu

<sup>7</sup> *Magnetic order and multipole interactions in Ce<sub>x</sub>Pr<sub>1-x</sub>B<sub>6</sub> solid solutions*

J.-M. Mignot, G. André, J. Robert, M. Sera, and F. Iga, Phys. Rev. B 78, 014415 (2008)

<sup>8</sup> *Effect of Nd substitution on the magnetic order in Ce<sub>x</sub>Nd<sub>1-x</sub>B<sub>6</sub> solid solutions*

J.-M. Mignot, J. Robert, G. André, M. Sera, F. Iga, Phys. Rev. B 79, 224426 (2009)

<sup>9</sup> *Long-range order and low-energy magnetic excitations in CeRu<sub>2</sub>Al<sub>10</sub> studied via neutron scattering*

J. Robert, J.-M. Mignot, G. André, T. Nishioka, R. Kobayashi, M. Matsumura, H. Tanida, D. Tanaka, M. Sera, Phys. Rev. B, Rapid Commun. 82, 100404R (2010).



case, the spin gap is partially filled, entailing a stronger suppression of the exciton peak than with Lu.<sup>10</sup>

Other intriguing aspects of this dodecaborides concern their lattice dynamics. In these materials, the rare-earth ions are rather loosely bound inside a rigid boron network. It was shown previously for YbB<sub>12</sub> that the phonon modes associated with Yb vibrations occur at an energy close to that of the “exciton” peak, and that their intensity is anomalously enhanced on cooling in the temperature region where KI properties develop. This might result from a coupling between low-energy magnetic and phonon excitations. Recently, *ab-initio* calculation and INS measurements performed on superconducting ZrB<sub>12</sub> revealed that similar “quasilocal” Zr vibration modes exist and make an appreciable contribution to the electron-phonon interactions.<sup>11</sup> They might thus play a role in the rather high transition temperature  $T_c = 6$  K of this compound.

### Geometrical frustration in the pyrochlore lattice: spin liquids and spin ices.

In chemically ordered compounds with short-range magnetic interactions, geometrical frustration appears when all interactions cannot be satisfied simultaneously due to the lattice geometry. A well-known example is a triangle of antiferromagnetically coupled spins. This frustration results in a strong degeneracy of the ground state, since many configurations have the same energy. It now appears as a powerful ingredient for designing materials or tuning physical properties, since frustrated magnetic states may be easily switched by small changes in the energy balance. Pyrochlores R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (where R<sup>3+</sup> is a rare earth ion) are model systems showing exotic short-range magnetic orders called “spin liquids” and “spin ices”, with unconventional excitations akin to magnetic monopoles, and a huge sensitivity to perturbations. Various aspects have been studied in collaborations with P. Bonville and A. Forget (IRAMIS/SPEC, Saclay), G. Dhalenne and C. Decorse (ICMMO, Orsay), and H. Mutka (ILL, Grenoble).

### Local susceptibility in R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores (R = Tb, Ho, Yb, Er)

Rare earth titanate pyrochlores of *Fd-3m* space group, where the R<sup>3+</sup> ions occupy the summits of corner-sharing tetrahedra and the Ti<sup>4+</sup> ions are nonmagnetic, show very different ground states, such as spin-liquid (Tb) and spin-ice (Ho) states, short range orders, planar antiferromagnetism (Er), and 2D ferromagnetism (Yb). Their physics is governed by the exchange and dipolar interactions between the R<sup>3+</sup> ions, together with the crystal-field anisotropy along the  $\langle 111 \rangle$  axes. The study of the paramagnetic state under applied fields points to precursor effects of these ground states. Single-crystal polarized neutron diffraction gives access to the local susceptibility tensor in the Gukasov-Brown model,<sup>12</sup> which reduces to 2 components  $\chi_{\parallel}$  and  $\chi_{\perp}$  with respect to the  $\langle 111 \rangle$  local axis, owing to the high symmetry the R<sup>3+</sup> site. This allows one to describe the complex field-induced structures using only two parameters. This tensor cannot be derived from the bulk magnetization due to the equivalent  $\langle 111 \rangle$  axes. Measurements performed in four typical cases where the R-R interactions may be F or AF, and the crystal-field anisotropy either Ising- or XY-type, showed that the local susceptibility is highly anisotropic (Figure 1.3). This is the first determination of the local susceptibility in the Ho<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> spin ice with (F, Ising) behavior. Comparison with a calculation of the non-interacting susceptibility deduced from the crystal-field scheme (measured independently by inelastic neutron scattering) yields the tensor of exchange interactions, which is also found to be anisotropic.<sup>13</sup> As a surprising consequence, in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> with (F, XY) behavior, crystal-field and exchange anisotropies nearly compensate,

<sup>10</sup> *Spin dynamics in the electron-doped Kondo insulator Yb<sub>1-x</sub>Zr<sub>x</sub>B<sub>12</sub> (x=0.2)*

K. S. Nemkovski, P. A. Alekseev, J.-M. Mignot, E. A. Goremychkin, A. A. Nikonov, O. E. Parfenov, V. N. Lazukov, N. Yu. Shitsevalova, A. V. Dukhnenko, Phys. Rev. B **81**, 125108 (2010).

<sup>11</sup> *Lattice dynamics in ZrB<sub>12</sub> and LuB<sub>12</sub>: Ab initio calculations and inelastic neutron scattering measurements*

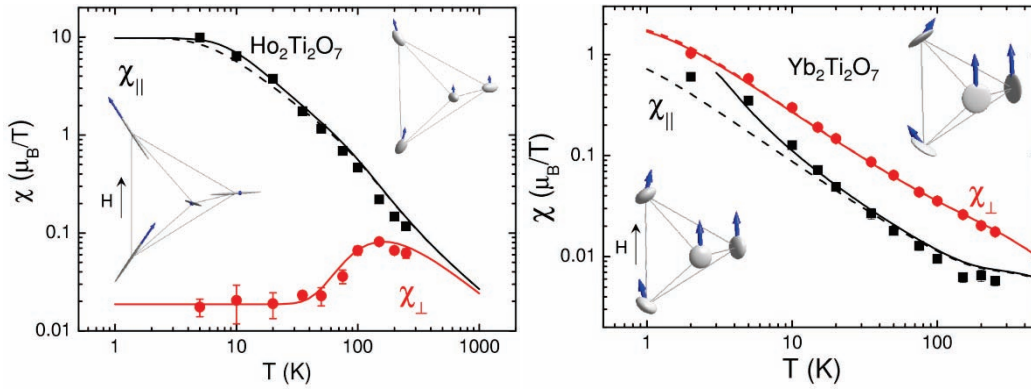
A. V. Rybina, K. S. Nemkovski, P. A. Alekseev, J.-M. Mignot, E. S. Clementyev, M. Johnson, L. Capogna, A. V. Dukhnenko, A. B. Lyashenko, V. B. Filippov, Phys. Rev. B **82**, 024302 (2010).

<sup>12</sup> A. Gukasov and J. Brown, J. Phys. Condens. Matter **14**, 8831, (2002).

<sup>13</sup> *Ising versus XY Anisotropy in Frustrated R<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> Compounds as “Seen” by Polarized Neutrons*

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, C. Decorse, G. Dhalenne, Physical Review Letters **103**, 056402 (2009).

yielding a Curie susceptibility and ground state fluctuations in an original “exchange spin-ice” ground state.<sup>14</sup>



**Figure 1.3.** Susceptibility components  $\chi_{||}$  and  $\chi_{\perp}$  versus  $T$  in  $\text{Ho}_2\text{Ti}_2\text{O}_7$  (left) and  $\text{Yb}_2\text{Ti}_2\text{O}_7$  (right). Dashed lines: CEF-only calculation; solid lines: calculation including an effective exchange. In  $\text{Yb}_2\text{Ti}_2\text{O}_7$ , the anisotropy of the molecular field due to the exchange ( $\lambda_{||} \gg \lambda_{\perp}$ ) is reversed with respect to the crystal field anisotropy (XY type). From Ref. [13]

### Evolution of the spin liquid $\text{Tb}_2\text{Ti}_2\text{O}_7$ ground state under applied field

$\text{Tb}_2\text{Ti}_2\text{O}_7$  realizes the (AF, uniaxial) case with a highly tunable spin-liquid ground state, which is easily destabilized by an applied field, pressure, or magnetic substitution. This tunability results from the peculiar  $\text{Tb}^{3+}$  crystal field scheme, with two low-energy doublets easily populated by temperature, or mixed by the magnetic field, and from  $R$ - $R$  effective (dipolar + exchange) interactions at the border between the F and AF characters. Starting from the spin-liquid ground state, a magnetic field close to a  $\langle 110 \rangle$  axis splits the system into two sublattices ( $\alpha$  and  $\beta$  chains) and induces spin-ice-like local structures with  $\mathbf{k} = 0$  propagation vector, but with different moment values on the two sublattices.<sup>15</sup> Above 2 teslas, magnetic structures with  $\mathbf{k} = 0$  and  $\mathbf{k} = (001)$  propagation vectors coexist. The high sensitivity of the spin structures to a small disorientation of the applied field results from the anisotropic susceptibility. In true spin ices ( $R = \text{Ho}$  or  $\text{Dy}$ ), this feature was used as a trick to tune the concentration of magnetic monopoles.<sup>16</sup>

### An ordered spin ice $\text{Tb}_2\text{Sn}_2\text{O}_7$ under high pressure

Starting from the  $\text{Tb}_2\text{Ti}_2\text{O}_7$  spin liquid, substitution of Ti by Sn yields a lattice expansion and the onset of an ordered spin-ice state. The change in the energy balance is understood as follows: the lattice expansion favors the dipolar (F) Tb–Tb interactions at the expense of the (AF) superexchange interactions, since superexchange depends more strongly on interatomic distances. The ordered or “soft” spin ice, whose anisotropy is reduced in comparison with the true spin ice, has the local spin ice spin structure (mathematically identical to proton order in water ice) but not its degeneracy, since all tetrahedra of the pyrochlore structure have the same orientations. This leads to long-range order, ferromagnetic magnetization, and intricate spin dynamics.<sup>17</sup> What happens when one pressurizes a soft spin ice? We observed three effects: a reorientation of the spin-ice structure, the onset of antiferromagnetic order, and the enhancement of spin-liquid fluctuations.<sup>18</sup> It is worth noting that only the soft spin ice  $\text{Tb}_2\text{Sn}_2\text{O}_7$  is sensitive to pressure (Figure 1.4). In the true spin ice  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , although theory predicts a pressure tuning of the magnetic monopoles, it was not observed up to now. Very high pressures are likely necessary to disturb the crystal-field scheme and exchange interactions.

<sup>14</sup> Anisotropic exchange in frustrated pyrochlore  $\text{Yb}_2\text{Ti}_2\text{O}_7$

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, J. Phys. Cond. Mat. Fast Track, **21**, 492202 (2009).

<sup>15</sup> Field-Induced Spin-Ice-Like Orders in Spin Liquid  $\text{Tb}_2\text{Ti}_2\text{O}_7$

H. Cao, A. Gukasov, I. Mirebeau, P. Bonville, Phys. Rev. Lett. **101**, 196402 (2008).

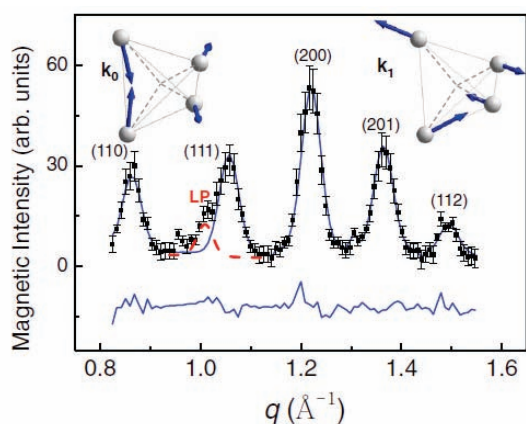
<sup>16</sup> T. Fennell et al. Nature Physics **3**, 566 (2007); D. J. P. Morris et al., Science **326**, 411, (2009).

<sup>17</sup> Investigation of magnetic fluctuations in  $\text{Tb}_2\text{Sn}_2\text{O}_7$  ordered spin ice by high-resolution energy-resolved neutron scattering

I. Mirebeau, H. Mutka, P. Bonville, A. Apetrei A. Forget, Phys. Rev. B **78**, 174416, (2008)

<sup>18</sup> Magnetic order in  $\text{Tb}_2\text{Sn}_2\text{O}_7$  under high pressure: From ordered spin ice to spin liquid and antiferromagnetic order

I. Mirebeau, I. Goncharenko, H. Cao, A. Forget, Physical Review B, Rapid Commun. **80**, 220407R (2009).



**Figure 1.4.** Magnetic diffraction pattern in  $Tb_2Sn_2O_7$  ordered spin ice, at 0.06 K under a pressure of 4.6 GPa. Together with the Bragg peaks of the ordered spin ice [ $k_0 = 0$  propagation vector, fcc lattice], new antiferromagnetic Bragg peaks [ $k_1 = (0,0,1)$  propagation vector, simple cubic lattice] appear under pressure. Top: the spin structures corresponding to the refinement (solid lines). From Ref. [Erreur ! Signet non défini.].

### Strong correlations in CMR manganites

Among the many novel phenomena encountered in strongly-correlated electron systems, specific effects originating from the interplay of different degrees of freedom (lattice, electron charge, spin and orbital angular momentum) have aroused particular interest. One prominent example is the manganites, which are well known for their colossal magnetoresistance (CMR) properties, associated with a phase transition from a high-temperature insulating phase to a low-temperature metallic phase.<sup>19</sup>

In these perovskite manganese oxides  $La_{1-x}B_xMnO_3$  ( $B = Ca, Sr$ ), the number of electrons on each manganese ion can be tuned by the partial substitution of a concentration  $x$  of Ca or Sr atoms on the La site. For  $x = 0$ , there are 4 electrons per manganese site, whose spins are aligned because of a large Hund coupling. The system shows orbital ordering, owing to the  $Mn^{3+}$  Jahn-Teller effect, and is insulating as a result of electronic correlations. In agreement with the Goodenough-Kanamori rules, the spins form ferromagnetic planes that are stacked antiferromagnetically. Upon substitution, the number of electrons per manganese site decreases and the system evolves towards an orbitally disordered ferromagnetic and metallic phase beyond  $x \approx 0.17$ . The latter phase is the one exhibiting the famous CMR properties. The hopping of electrons from site to site leads to a novel type of ferromagnetic coupling ("double exchange"), which is expected to stabilize the ferromagnetic order. However, the way the material evolves towards this new phase is very peculiar and emphasizes the role of charge segregation. The signature of this evolution was characterized by means of inelastic neutron scattering experiments in the course of a longstanding collaboration with the State Steel and Alloys Institute in Moscow (MISIS).

We first showed that, for small  $x$  values, the electronic state can be seen as consisting of hole-rich platelets embedded in a hole-poor matrix within the ferromagnetic planes. Their size ( $\sim 16$  Å) and spatial extension could be determined. As  $x$  increases, these platelets grow and percolate for  $x = 0.12$ , where the antiferromagnetic coupling between layers vanishes.<sup>20-23</sup> The system becomes quasi-metallic at room temperature but, in a small range of concentrations around  $x \sim 1/8$ , the ground state remains insulating owing to charge localization. Our study in this regime revealed very unconventional spin dynamics: the magnetic excitation spectrum consists of a dispersive branch near the zone centre, and several discrete modes at the zone boundary.<sup>24</sup> The former indicates long-range ferromagnetically coupled spins, while the latter were attributed to standing spin waves within small ferromagnetic domains. By assuming that the system forms weakly-coupled ferromagnetic clusters, we were able to explain the data successfully, and to obtain a very good agreement between the experiment and the model (Figure 1.5).

<sup>19</sup> *Nanoscale Phase Separation and Colossal Magnetoresistance*, edited by E. Dagotto (Springer-Verlag, Berlin, 2002).

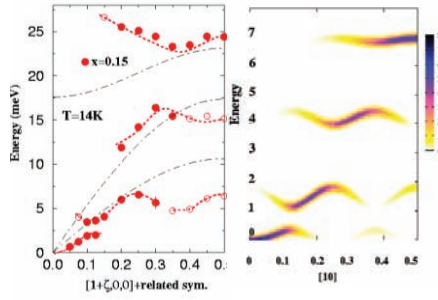
<sup>20</sup> M. Hennion *et al.*, Phys. Rev. Lett. **81** 1957 (1998).

<sup>21</sup> M. Hennion *et al.*, Phys. Rev. B **61**, 9513 (2000).

<sup>22</sup> F. Moussa *et al.*, Phys. Rev. B **67**, 214430 (2003).

<sup>23</sup> M. Hennion *et al.*, Phys. Rev. Lett. **94** 057006 (2005)

<sup>24</sup> M. Hennion *et al.*, Phys. Rev. B **73**, 104453 (2006)



**Figure 1.5.** Experimental (left) and theoretical (right) dispersions obtained at low temperature ( $x = 0.15$ ).

Beyond  $x = 0.17$ , the system enters the ferromagnetic and metallic phase. Pioneering measurements revealed standard cosine laws, although with strong anomalies at the zone boundary, which were described in terms of softening, broadening and flattening of the dispersion. These anomalies were tentatively explained on the basis of a phenomenological Heisenberg model with Mn-Mn magnetic couplings extending up to the fourth neighbors. Subsequently, we revisited these experiments with improved statistics and resolution, and collected data for a number of doping contents ( $x(\text{Sr}) = 0.175, 0.2, 0.3, 0.35, 0.4$  and  $x(\text{Ca}) = 0.3$ ).<sup>25,28</sup> We found that in all cases the spin-wave spectra consisted of a quadratic dispersive branch at the zone centre, characteristic of a three-dimensional (3D) ferromagnetic state, and wave-vector independent (flat) levels at the zone boundary, which were reminiscent of the  $x \sim 1/8$  spectra. The characteristic energies of these levels remain approximately identical, while their intensities show a peculiar temperature and doping dependence. Actually, as the temperature decreases or  $x$  increases, the upper modes become very intense at the expense of the lower ones (

Figure 1.6). At low temperature, this creates the illusion of a cosine law (the quadratic branch) with a softened zone boundary (the upper flat mode), which is in agreement with earlier reports (

Figure 1.7). It is worth emphasizing that, as soon as temperature increases, this effect vanishes as all modes have comparable intensities. Considering the resemblance between the spectra in the  $x \sim 1/8$  region and in the metallic phase, it is tempting to propose a picture where the levels would reflect quantized spin waves in ferromagnetic clusters, embedded in a 3D ferromagnetic matrix. As both insulating and metallic regimes have similar spin-wave spectra, we may speculate that the same physics is at play here and that the existence of such clusters is an important ingredient for the appearance of the CMR phenomenon. However, the stability of these clusters for doping as large as  $x = 0.35$  or  $0.40$  is probably difficult to justify, and casts some doubt on the proposed interpretation. Up to now, the unconventional spin dynamics remain unexplained and new experimental efforts are needed to extend our understanding of these compounds and their puzzling properties.

<sup>25</sup> F. Moussa *et al.*, Phys. Rev. B **76**, 064403 (2007)

<sup>26</sup> Intralayer and interlayer exchange tuned by magnetic field in the bilayer manganite  $(\text{La}_{0.4}\text{Pr}_{0.6})_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$  probed by inelastic neutron scattering

F. Moussa, M. Hennion, A. Gukasov, S. Petit, L. P. Regnault, A. Ivanov, R. Suryanarayanan, M. Apostu, and A. Revcolevschi, Phys. Rev. B **78**, 060406 (2008).

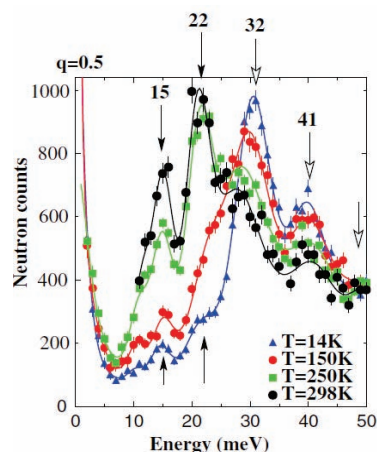
<sup>27</sup> Spin waves and metallic state of magnetoresistive manganites

S. Petit, M. Hennion, F. Moussa, D. Lamago, A. Ivanov and Y. M. Mukovskii, J. Phys. Conf. Ser. **200**, 012159 (2010).

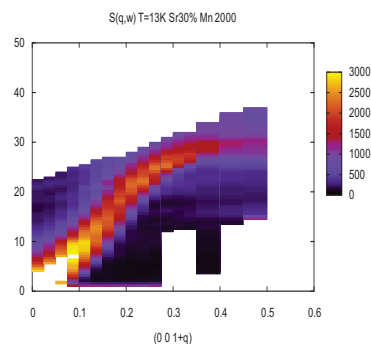
<sup>28</sup> Quantized Spin Waves in the Metallic State of Magnetoresistive Manganites

S. Petit, M. Hennion, F. Moussa, D. Lamago, A. Ivanov, Y. M. Mukovskii and D. Shulyatev, Phys. Rev. Lett. **102**, 207201 (2009).





**Figure 1.6.** Energy scans at the zone boundary  $Q = (1.5, 0, 0)$  for different temperatures ( $x = 0.30$ ). Arrows indicate the different flat modes.



**Figure 1.7.** Color map of  $S(Q, \omega)$  recorded at low temperature ( $x = 0.30$ ).

The bilayer counterpart of the pseudo-cubic manganites,  $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ , is also famous for its colossal magnetoresistance. Here, broad charge-order peaks due to large polarons are found to disappear at the CMR insulator-metal transition. These polarons survive as fluctuations in the metallic phase, which strongly broaden and soften certain phonon modes near the wave-vectors where the charge-order peaks appeared in the high-temperature phase.<sup>29</sup> Again, these findings confirm the amazing entanglement of lattice, charge and spin degrees of freedom in this class of systems.

## Multiferroic materials

Studies conducted over the past few decades came to the conclusion that ferroelectricity and magnetism tend to be mutually exclusive, and interact only weakly with each other when they do coexist. The recent discovery of multiferroic materials, in which ferroelectricity and magnetism are intimately coupled, has completely changed these established views, opened routes to new technological applications, and has forced physicists to reconsider some long-accepted ideas.<sup>30</sup>

Coupling between magnetic and electric orders makes it possible to design promising devices, such as high-speed memories with magnetically and electrically addressable states, magnetically tunable tunnel-junctions, sensors, filters, transducers, etc. For instance, the control of magnetization by an applied electric field via the magnetoelectric coupling offers an opportunity to combine the respective advantages of FeRAMs (ferroelectric random access memories) and MRAMs (magnetic random access memories) in the form of non-volatile magnetic storage bits, which can be switched by an electrical field and thus combine the merits of MRAMs in terms of access time and endurance with a low writing energy.<sup>31</sup>

Meanwhile, a major effort is currently underway to revisit the ferroelectric-ferromagnetic dichotomy and to understand the multiferroic properties on fundamental grounds. The multiferroic compounds are scarce, as symmetry considerations impose severe constraints. Indeed, their space group should be non-centrosymmetric, to accommodate ferroelectricity, but also compatible with a magnetic ground state. Last but not least, all multiferroic materials found to date exhibit a certain amount of magnetic frustration. This, together with a strong spin-lattice coupling, seems to be a basic physical ingredient for multiferroicity. For example, the orthorhombic  $\text{RMnO}_3$  compounds, where R is a rare-earth element ( $R = \text{Eu, Gd, Tb, Dy}$ ), are archetypes of multiferroic materials. Magnetic frustration arises from competing magnetic exchange interactions, yielding an incommensurable spiral magnetic structure. As proposed in the “spin-current” model, the spin-lattice coupling is a result of the Dzyaloshinskii-Moriya

<sup>29</sup> Signature of checkerboard fluctuations in the phonon spectra of a possible polaronic metal  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ . F. Weber, N. Aliouane, H. Zheng, J. F. Mitchell, D. N. Argyriou & D. Reznik, *Nature Materials* **8**, 798 (2009).

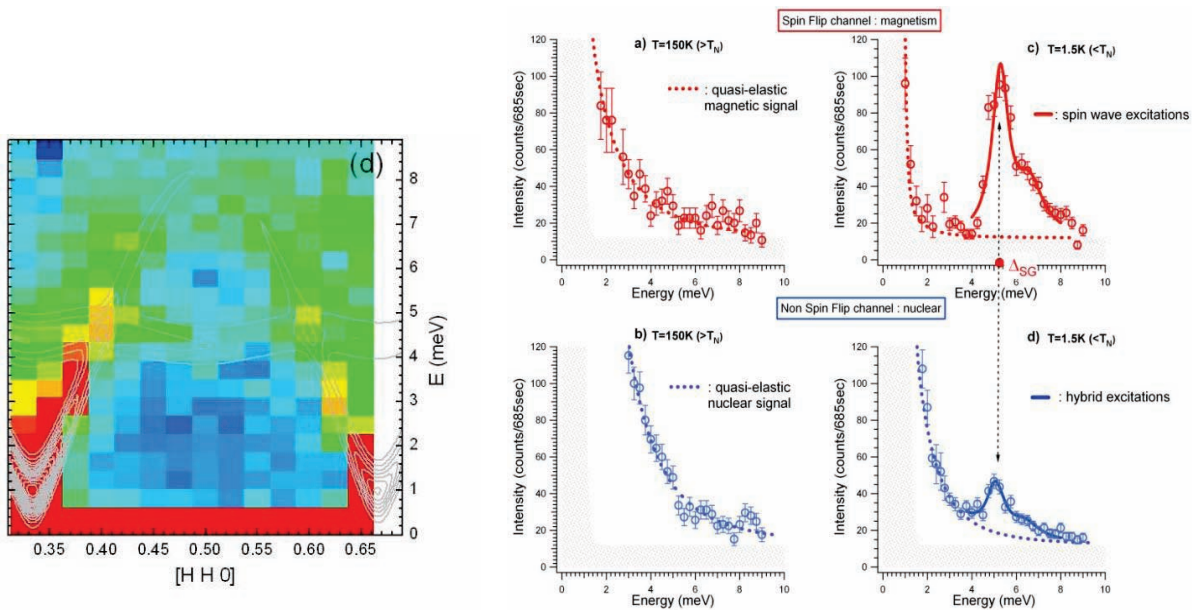
<sup>30</sup> S-W Cheong *et al.*, *Nature Materials* **6**, 13 (2007).

<sup>31</sup> A Barthélemy and M. Bibes, *Nature Materials* **460**, 81 (2009).



interaction: minimizing the corresponding term in the Hamiltonian of the system results in a relaxation of atomic positions and, in turn, in an electric polarization.<sup>32</sup>

A rapid survey of the literature shows that there also exist a large number of multiferroic materials with a triangular-based geometry. Much work at LLB was thus devoted to the study of delafossite-type materials, such as  $\text{CuCrO}_2$  and  $\text{CuMnO}_2$ , in close collaboration with the CRISMAT in Caen (Figure 1.8). These studies showed that the ground state properties of these compounds can be very different, even if the required basic ingredients are present. In  $\text{CuCrO}_2$  the magnetic ground state is an incommensurate  $120^\circ$  magnetic structure, with spin dynamics that is close to that of a 2D Heisenberg triangular lattice; it is multiferroic in its antiferromagnetic phase, but no unambiguous structural distortion was observed so far at  $T_N$ .<sup>33</sup> There are, however, anomalies in the spin-wave spectrum, which can be assigned to additional in-plane interactions, and could be an indication of a magnetoelastic coupling in this material. In contrast, the collinear antiferromagnetic ordering in  $\text{CuMnO}_2$  occurs simultaneously with a symmetry-lowering structural transition, which releases the frustration inherent to the triangular lattice. Below the magnetoelastic transition,  $\text{CuMnO}_2$  is an improper ferroelastic, but is not magnetoelectric.<sup>34</sup> Even though the basic ingredients of multiferroicity (magnetic frustration and spin-lattice coupling) are at play, the balance between the two is subtle and remains unknown. More studies are in progress, focusing in particular on the role of the ligand ions on the magnetic interactions.



**Figure 1.8.** Experimental (color map) and calculated (grey lines)  $S(\mathbf{Q},\omega)$  along the  $[HHO]$  direction in delafossite  $\text{CuCrO}_2$  at 10 K.

**Figure 1.9.** Energy scans performed at the zone center  $\mathbf{Q} = (0,0,6)$  in  $\text{YMnO}_3$ , in the spin-flip (red) and non-spin-flip (blue) channels. Left and right curves correspond to temperatures above and below  $T_N$ , respectively. The spin wave is in reality a hybrid mode, as evidenced by its “lattice” counterpart (bottom right).

Hexagonal  $\text{RMnO}_3$  with  $R$  elements having smaller ionic radii, ( $R = \text{Ho, Er, Yb, Lu, Y}$ ) form another class of triangle-based multiferroic materials, which has been widely studied at LLB in recent years, in collaboration with the Institut de Chimie Moléculaire et des Matériaux d'Orsay (ICMMO University of Paris-Sud 11).<sup>35-38</sup> The Néel order at  $120^\circ$  imposed by the geometric

<sup>32</sup> H. Katsura *et al.*, Phys. Rev. Lett. **98**, 027203 (2007).

<sup>33</sup> Spin dynamics in the geometrically frustrated multiferroic  $\text{CuCrO}_2$   
M. Poienar, F. Damay, C. Martin, J. Robert, and S. Petit Phys. Rev. B **81**, 104411 (2010).

<sup>34</sup> Spin-lattice coupling induced phase transition in the  $S=2$  frustrated antiferromagnet  $\text{CuMnO}_2$   
F. Damay, M. Poienar, C. Martin, A. Maignan, J. Rodriguez-Carvajal, G. André, and J. P. Doumerc, Phys. Rev. B **80**, 094410, (2009).

<sup>35</sup> Spin-Phonon Coupling in Hexagonal Multiferroic  $\text{YMnO}_3$   
S. Petit, F. Moussa, M. Hennion, S. Pailhès, L. Pinsard-Gaudart, and A. Ivanov, Phys. Rev. Lett. **99**, 266604 (2007).

<sup>36</sup> Magnetic order in  $\text{YbMnO}_3$  studied by neutron diffraction and Mössbauer spectroscopy  
X. Fabréges, I. Mirebeau, P. Bonville, S. Petit, G. Lebras-Jasmin, A. Forget, G. André, and S. Pailhès, Phys. Rev. B **78**, 214422 (2008).

frustration is accompanied by an isostructural transition: each ion “moves” inside the unit cell when Mn moments get ordered. This effect provides evidence for a giant magnetoelastic coupling, likely connected with an increase in the ferroelectric polarization. To shed light on these materials, high-resolution neutron diffraction and inelastic neutron scattering were carried out on four  $RMnO_3$  compounds ( $R = Y, Sc, Ho, Yb$ ), with either non-magnetic (Y, Sc) or magnetic (Ho, Yb)  $R$  ions, showing (Ho, Sc) or not (Y, Yb) a spin reorientation at the temperature  $T_{SR}$  (Figure 1.9). We have shown that the isostructural transition is a systematic feature in this series. In addition, we have established a correlation between the atomic positions, the type of magnetic structure, and the nature of the spin-waves, depending on the compound and its magnetic structure. The key parameter is the position of the Mn ions within the triangular plane, which tunes the sign of the exchange interaction. We speculate that, thanks to the magnetoelastic coupling, the atomic motion helps to release the frustration by selecting one particular magnetic structure, depending on the  $x$  value<sup>36</sup>. This process recalls the spin-Peierls states stabilized in several geometrically frustrated 2D or 3D compounds.

Magnetoelastic coupling also results in mixed magnon-phonon excitations, called electromagnons. While their existence has been theoretically predicted a long time ago, their dual lattice and spin nature makes it challenging to observe them experimentally. Due to their dipole electric activity, they could first be detected by optical measurements, especially in  $GdMnO_3$ ,  $TbMnO_3$ ,  $Eu_{0.75}Y_{0.25}MnO_3$ ,  $DyMnO_3$ ,  $YMn_2O_5$ ,  $TbMn_2O_5$  and  $BiFeO_3$ . Recent inelastic polarized neutron scattering experiments provided one of the first direct observations of a hybrid dispersive wave in the hexagonal series of  $RMnO_3$  materials: part of a spin-wave branch is found to be completely dressed by nuclear spectral weight<sup>37</sup>. Again, the Dzyaloshinskii-Moriya interaction could be at the origin of this hybridization.

### Observation of a magnetic “blue phase” in an itinerant magnet

Blue phases often appear in chiral liquid crystals as arrangements of so-called “double-twist cylinders”, characterized by twisting in all directions perpendicular to the cylinder axis.<sup>39</sup> Magnetic moments in chiral magnets tend to form spirals, and one can thus speculate on the existence of magnetic “blue phases”. By combining model calculations with experiments, we show that such a phase does form in MnSi over a large part of the phase diagram, including at ambient pressure.<sup>40</sup>

In chiral magnets, calculations performed in the large-pitch limit show that spirals with a well-defined twist direction (helical order) should have a lower energy in magnets, and that blue phases cannot appear.<sup>39</sup> Despite this result, a blue phase has been suspected to occur in the itinerant chiral magnet MnSi at high hydrostatic pressure, where a so-called partial magnetic order has been observed.<sup>41</sup> In collaboration with A. Hamann, T. Wolf, and H. v. Löhneysen (Karlsruhe Institute of Technology) and D. Reznik (University of Colorado), we have performed calculations starting from magnetic moments of the same fixed magnitude, with random orientations, and placed on simple cubic or B20 lattices. The orientation of each moment was optimized sequentially in random order until the total energy of the system stabilized. A typical spin arrangement obtained by this method is shown in Figure 1.10 (left). The topology is the same as for blue phases of chiral liquid crystals, i.e., with moments twisting away from cylindrical axes. We tested our model via experiments on the 4F cold triple-axis neutron spectrometer and on the PAPYRUS small angle neutron scattering (SANS) diffractometer. The magnetic correlation length is expected to be reduced by Fe-doping similarly to thermal fluctuations. According to our model, Fe doping should allow the blue phase to persist to lower temperatures. Experiments show that this is indeed the case:  $T_c$

<sup>37</sup> Hybrid Goldstone modes in multiferroic  $YMnO_3$  studied by polarized inelastic neutron scattering  
S. Pailhès, X. Fabréges, L. P. Régnault, L. Pinsard-Godart, I. Mirebeau, F. Moussa, M. Hennion, and S. Petit, Phys. Rev. B **79**, 134409 (2009).

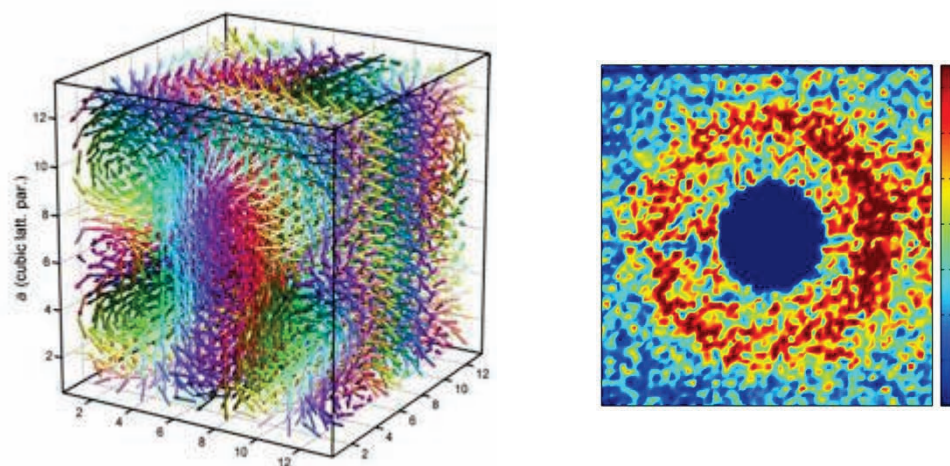
<sup>38</sup> Spin-Lattice Coupling, Frustration, and Magnetic Order in Multiferroic  $RMnO_3$   
X. Fabréges, S. Petit, I. Mirebeau, S. Pailhès, L. Pinsard, A. Forget, M. T. Fernandez-Diaz, and F. Porcher, Phys. Rev. Lett. **103**, 067204 (2009).

<sup>39</sup> D.C. Wright and N.D. Mermin, Rev. Mod. Phys. **61**, 385 (1989)

<sup>40</sup> Magnetic blue phase in itinerant magnet MnSi  
A. Hamann, D. Lamago, H.v. Löhneysen, D. Reznik, (submitted to Nature Materials).

<sup>41</sup> C. Pfleiderer et al., Nature **427**, 227 (2004).

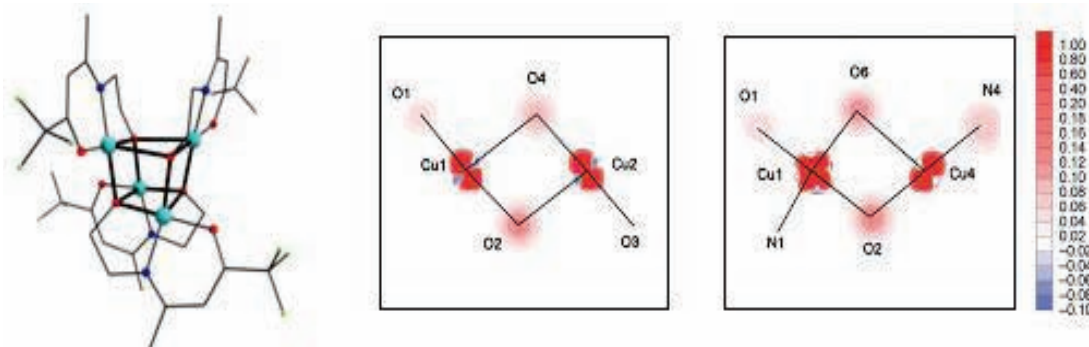
decreases with Fe doping<sup>42</sup> and the SANS spectrum of  $\text{Mn}_{0.8}\text{Fe}_{0.15}\text{Si}$  at 1.5 K is a ring characteristic of the blue phase. The same result was obtained for  $\text{Fe}_{1-x}\text{Co}_x\text{Si}$ ,<sup>43</sup> pointing to a universality of this phenomenon. Our results provide a blueprint for understanding cubic chiral magnets, including MnSi, by showing that the frustrated nature of the magnetic interactions naturally and generically induces complex spin arrangements, which had so far been found only in liquid-crystal blue phases. Controlling special properties of this blue phase with impurities in thin films has a potential for new applications, particularly in electronics and magnetic memory devices.<sup>44</sup>



**Figure 1.10.** (left) Topology of the triple-twist arrangement in a  $12 \times 12 \times 12$  unit-cell cluster containing  $\sim 7000$  spins. (Right) SANS color map for  $\text{Mn}_{0.85}\text{Fe}_{0.15}\text{Si}$  measured at 1.5 K. The scattering intensity ring is characteristic for partial order. The small overall increase in the intensity from left to right results from a sloping background coming from the cryostat.

## Molecular magnetism and photomagnetism

Molecular magnetism is a relatively new field of research, which has attracted growing interest among physicists since the discovery, fifteen years ago, of the first “single molecule magnet” (SMM),  $\text{Mn}_{12}$ -acetate, which behaves as a magnet at the molecular scale below a blocking temperature of 3 K. The present challenges in this field consist in understanding how to control magnetic anisotropy in order to obtain SMM behavior at higher temperatures, and in designing new multifunctional materials possessing other functional properties in addition to magnetism, e.g. magnetic photoswitchable compounds. Optical magnetic switching in the solid state raises questions of fundamental interest as to the mechanisms governing phase separation into magnetic domains or continuous structural changes during photoexcitation.



**Figure 1.11.** Structure of  $\text{M}_4\text{O}_4$  cubane-like complexes.

**Figure 1.12.** Experimental induced spin density in the  $S = 2$  ground state at  $T = 2$  K,  $H = 7$  T, in  $\text{Cu}_4\text{O}_4$  projected onto  $\text{Cu}_2\text{O}_2$  planes with different bridging geometries. Isodensity levels:  $\pm 0.02 \text{ } \mu_B/\text{\AA}^2$

<sup>42</sup>N. Manyala et al., Nature **404**, 581 (2000).

<sup>43</sup>S.V. Grigoriev et al., Phys. Rev. Lett. **102**, 037204 (2009).

<sup>44</sup>X.Z. Yu et al., Nature **465**, 901 (2010).



## Combined analysis of charge and spin densities in molecular magnets

The goal of the CEDA project, supported by the ANR (2008-2010), on the Convergence of Electron spin, charge and momentum Densities Analysis, is to combine data obtained by different techniques on the electron density in order to refine a unique model, thereby allowing the electronic structure of magnetic molecular compounds to be more accurately described. This work involves theoreticians (SPMS, ECP), x-ray (CRM2, Nancy) and neutron (LLB) diffraction specialists, and chemists (LMI, Lyon). The first step devoted to the joint refinement of charge and spin densities from x-ray and polarized neutron diffraction data sets has been completed. In this approach, the multipole model<sup>45</sup> is used to describe the densities of spin up and spin down electrons, the sum (or difference) of which is the charge (spin) density. The software called MOLLYNX was developed by splitting the electron density model into two spin components. Experimental data were collected by x-ray diffraction at CRM2, and polarized neutron diffraction on 5C1 at LLB on two cubane-like  $[M_4O_4]$  complexes ( $M = \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}$ ), synthesized in Lyon (LMI) (Figure 1.11). The joint refinement of these data is expected to ensure a better characterization of the metal-ligand bonds and a more complete understanding of their role in the intramolecular magnetic interactions and the magnetic anisotropy. The first analysis of the PND data alone<sup>46</sup> shows that the experimental spin distribution in the  $\text{Cu}_4$  complex is mainly located in the basal planes of the  $\text{Cu}^{\text{II}}$  ions and visualizes the magnetic interaction pathways via the bridging oxygen atoms (Figure 1.12).

## Light-induced phase separation in a spin-crossover $\text{Fe}^{\text{II}}$ molecular complex

Progress has been achieved in the investigation of the photoexcitation mechanism in the spin-crossover complex  $[\text{Fe}^{\text{II}}(\text{ptz})_6](\text{BF}_4)_2$  in collaboration with the GEMaC (Versailles). The photoinduced structural transformation between the low spin (LS) ground state ( $S = 0$ ) and the high spin (HS) excited state ( $S = 2$ ) was studied on the neutron Laue diffractometer Vivaldi at ILL, equipped by the in-situ photoexcitation setup developed at LLB.<sup>47</sup> In a previous work,<sup>48</sup> we observed a continuous transformation corresponding to randomly distributed LS and HS molecules during the irradiation of a single crystal by a laser beam (470 nm) at  $T = 2$  K. According to a theoretical model based on the competition between photoexcitation (LS  $\rightarrow$  HS) and relaxation (HS  $\rightarrow$  LS), a light-induced phase separation (LIPS) between HS domains and LS domains was expected in an instability region inside the LITH (light induced thermal hysteresis) loop (Figure 1.13, left). We have provided evidence for this process, as illustrated by the evolution of the photoinduced splitting of one reflection as a function of the irradiation time at 53.5 K (Figure 1.13, right).<sup>49</sup>

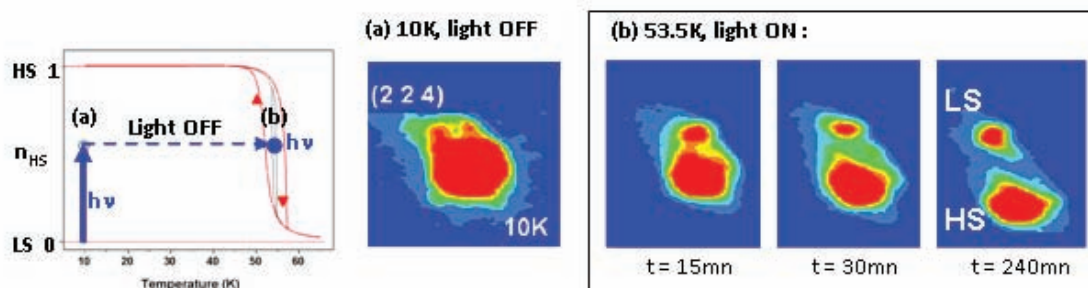
<sup>45</sup> N.K. Hansen and P. Coppens Acta. Cryst. A **34**, 909 (1978).

<sup>46</sup> Structure, Magnetic Properties, Polarized Neutron Diffraction and Theoretical Study of a copper(II) cubane  
C. Aronica, Y. Chumakov, E. Jeanneau, D. Luneau, P. Neugebauer, A.-L. Barra, B. Gillon, A. Goujon, A. Cousson, J. Tercero, E. Ruiz, Chem. Eur. J. **14**, 9540 (2008).

<sup>47</sup> Photoinduced molecular switching studied by polarised neutron diffraction  
A. Goujon, B. Gillon, A. Gukasov, J. Jętic, Q. Nau, E. Codjovi, F. Varret, Phys. Rev. B, Rapid Commun. **67**, 220401(R) (2003).

<sup>48</sup> Neutron Laue diffraction on the spin crossover crystal  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  showing continuous photo-induced transformation  
A. Goujon, B. Gillon, A. Cousson, A. Gukasov, A. Debède, J. Jętic, G. J. McIntyre, F. Varret, Phys. Rev. B **73**, 104413 (2006).

<sup>49</sup> Light-induced phase separation (LIPS) into like-spin phases observed by Laue neutron Diffraction on a single crystal of  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$   
F. Varret, K. Boukheddaden, A. Goujon, B. Gillon and G.J McIntyre, Z. Kristallogr. **223**, 250 (2008).



**Figure 1.13.** Light induced phase separation (LIPS) in the molecular complex  $[\text{Fe}^{\text{II}}(\text{ptz})_6](\text{BF}_4)_2$ . Left: protocol for the LIPS investigation in the LITH loop (in red),  $n_{\text{HS}}$  is the fraction of photoinduced HS state : irradiation by light at  $\lambda = 470 \text{ nm}$  (10mW) at 10 K, then heating up to 53.5 K with light switched off and again light irradiation at 53.5 K. Right : (2, 2, 4) Bragg reflection on the neutron Laue diffraction diagram (a) after partial photoexcitation at 10 K, light off: (HS, LS) random state ; (b) at 53.1 K, light on: evolution of the splitting, as a function of the light irradiation time, towards the LS and HS structural positions.



## Scientific collaborations

The main collaborating institutes in France and abroad are listed below.

| Organization                           | Total |
|--|-------|
| [INST LAUE LANGEVIN GRENoble – FRANCE] | 24    |
| [UNIV PARIS 11 - FRANCE]               | 15    |
| [UNIV BORDEAUX - FRANCE]               | 12    |
| [LAB CRISMAT - FRANCE]                 | 9     |
| [ESRF GRENoble - FRANCE]               | 7     |
| [UNIV STRASBOURG - FRANCE]             | 5     |
| [UNIV GRENoble - FRANCE]               | 4     |
| [UNIV PARIS 6 - FRANCE]                | 4     |
| [UNIV NANTES - FRANCE]                 | 4     |
| [UNIV RENNES - FRANCE]                 | 4     |

| Organization                             | Total |
|--|-------|
| [JULICH - GERMANY]                       | 12    |
| [INST MAX PLANCK - GERMANY]              | 11    |
| [KARLSRUHE INST OF TECHNOLOGY – GERMANY] | 10    |
| [UNIV GOTTINGEN - GERMANY]               | 6     |
| [UNIV MUNICH - GERMANY]                  | 6     |
| [KURCHATOV ATOM INST MOSCOW – RUSSIA]    | 5     |
| [PSI - SWITZERLAND]                      | 5     |
| [RUTHERFORD APPLETON LAB - UK]           | 5     |
| [UNIV DRESDEN - GERMANY]                 | 5     |
| [UNIV COLOGNE - GERMANY]                 | 5     |
| [ARGONNE - USA]                          | 4     |
| [INST ACAD PRAGUE - CZECH REPUBLIC]      | 4     |
| [JAERI IBARAKI - JAPAN]                  | 4     |

## Scientific contracts

ANR: CEDA, MAGD0, NEWTOM,

- CEDA: Convergence of electron spin, charge and momentum densities analysis
- MAGD0: magnetism induced by nonmagnetic impurities
- NEWTOM: new transition metal oxides

RTRA (Triangle de la Physique): EXTREME, GLACEDESPIN, CRISPY, MAGCORPNIC

- EXTREME: high-pressure instrumentation.
- GLACEDESPIN: financial support of post-doc, H. Cao.
- CRISPY: crystal growth of rare-earth pyrochlores.
- MAGCORPNIC: magnetism and electronic correlations in superconducting pnictides.

2 JRA: NMI3-7th Framework Programme of the European Commission

## Other

Theses (2008- 2010)

- **Victor Balédent** (2007-10): *Etude de la phase de pseudo gap dans les oxydes de cuivre supraconducteurs à haute température critique.*
- **Sophie Tencé** (2006-30 sept. 2009) (LLB-université de Bordeaux): *Propriétés et structures magnétiques d'hydrures et de composés magnétocaloriques à base de terres rares.*
- **Xavier Fabrèges** (2007-5 oct. 2010): *Etude des propriétés magnétiques et du couplage spin-réseau dans les composés multiferroïques RMnO<sub>3</sub> hexagonaux par diffusion de neutrons.*
- **Julie Bourgeois** (2008-2011) (LLB-Université de Caen): *Les ferrites de type RFeO<sub>4</sub> à valence mixte.*

- **Sonia de Almeida** (2007-2010) (LLB- Lema Tours- IUT Blois): *Synthèse et études neutroniques de la phase sous-dopée du système  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$*
- **Monica Hatnean** (2009-12): (LLB-ICMMO Paris XI): *Etude du composé magnétoélectrique  $\text{GaFeO}_3$* .
- **Andreas Hamann** ( 2007-10) (LLB-KIT Karlsruhe): *Neutron Scattering on Strongly Correlated Electron Systems:  $\text{MnSi}$ ,  $\text{CeCu}_{5.5}\text{Au}_{0.5}$ ,  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{HgBa}_2\text{CuO}_{4+\delta}$*

#### Post-docs

- **Huibo Cao** (2007-09): Neutron studies of  $\text{R}_2\text{Ti}_2\text{O}_7$  pyrochlores: local susceptibility.
- **Andrew Sazonov** (2009-11): Neutron studies of  $\text{R}_2\text{Ti}_2\text{O}_7$  pyrochlores: symmetry analysis.
- **Sergei Kichanov** (post-doc training in 2009-10): Instrumentation under high pressure.
- **Boris Narozhny** (2007-08): Contribution to the study of spin fluctuations and of their role in the pairing of electrons in high- $T_c$  cuprates.

#### Habilitation à Diriger les Recherches defended

- Sylvain Petit, *Neutrons et dynamique de spin*,

## **AXIS 2 Research : Materials and Nanosciences - Fundamental Studies and Applications**

### Researchers (16):

A. Bataille (CEA), B. Beuneu (CEA), G. Carrot (CEA), A. Cousson (CNRS), M.-H. Mathon (CEA), V. Klosek (CEA), L. Noirez (CNRS), F. Ott (CEA), F. Porcher (CEA), G. Chaboussant (CNRS), B. Gillon (CNRS), F. Cousin (CEA), J. Jestin (CNRS), F. Boué (CNRS), R. Papoulet (CEA).

### Associated Researchers (5):

O. Castelnau (CNRS), J.-M. Kiat (Ecole Centrale), V. Ji (Univ. Paris-Sud), A. Lodini (Univ. Reims), N. Linder (Univ. Paris-Sud)

### PhD Students (5):

T. Maurer (2007-2009), C. Said (2008-2011), A.S. Robbes (2008-2011), S. Zhong (2009-2012), M. Dubois (2009-2012)

### Post-doc Students (5):

R. Dakhiloui (2008), C. Alves Rezende (2008), M. Perut (2007-2009), F. Zighem (2009-2010), F. Muller (2009-2011)

### Keywords

- Thin films, nanoparticles, nanocomposites, textures, strains, dynamics
- Magnetism, polymers, metallurgy, glasses
- SANS, reflectivity, diffraction, synthesis

### **Scope**

This scientific axis covers the activities related to the research in materials science and more generally in hetero-systems (i.e., interfaces, alloys, composites materials, and confined systems). The topics cover the study of the detailed structure of nano-objects, the interactions between nano-objects, and the role of nanostructures in composite materials. The techniques used for these studies range from diffraction to small angle scattering and reflectivity. Other laboratory characterization techniques are also available, including light scattering, rheology, magnetometry (VSM - SQUID), and x-ray reflectivity.

During the period from 2008 to 2010, 152 publications have been produced on these topics (54 in 2008, 59 in 2009, and 39 in 2010). The presented topics have also been the subject of 21 invited conferences and more than 55 oral communications during the last 2 years. Two *Habilitations à Diriger les Recherches* have been defended during the period (2008-2009). One PhD thesis has been defended and 4 PhD students are presently working in the field of Materials Science.

The research in materials science is supported by a number of research contracts: 1 European contract, 1 transverse program CEA-CNRS/DSM-DEN, 7 national ANR contracts, and 3 regional contracts within the RTRA and C'nano organizations.

The studies in the fields of materials and nanosciences range from the detailed study of nanoparticles (structural and magnetic properties) to the study of the role of nanoparticles in composites systems (either metallic or polymer) to the study of materials confined at the nanometer scale. In all these different studies, the scales which characterize the properties of the systems range between 1-100 nm.

The following topics are presently developed at the LLB:

- Magnetic nanostructures
  - Oxide epitaxial layers
  - Nanoparticles
- Composite materials
  - Polymer reinforcement by nanoparticles
  - Metallurgical composites
- Metallurgy (both fundamental and industrial)
  - Textures and strain heterogeneities
  - Nuclear materials
- Confined systems
  - Organized guest-hosts systems and microporous materials
- Amorphous materials
  - Disordered systems – glasses
  - Dynamics in amorphous systems

### **Magnetic nanostructures**

We study the structure and properties of magnetic nano-objects using various techniques: diffraction, SANS, and reflectivity. Five researchers in the laboratory have research topics in this field.

### **Oxide epitaxial layers**

Regular studies of these materials are performed in collaboration with other laboratories on systems, such as  $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$  (with IRAMIS/SPEC – IEF/Orsay – LPMTM/Paris XIII) and  $\text{Fe}_3\text{O}_4$  –  $\text{CoFe}_2\text{O}_4$  –  $\text{MnFe}_2\text{O}_4$  (with IRAMIS/SPCSI<sup>1</sup>), primarily by using Polarized Neutron Reflectometry. More recently, a significant instrumental effort has been made to apply 4-circles diffraction to the study of epitaxial thin films<sup>2</sup>.

During the period of 2008-2009, a concerted effort was made to greatly extend the range of techniques available for studying magneto-electric materials, such as the  $\text{BiFeO}_3$  system. This effort was carried out in collaboration with UMR CNRS-Thalès and IRAMIS/SPEC by applying diffraction, as well as reflectivity techniques<sup>3</sup>.

### **Multiferroic materials: $\text{BiFeO}_3$**

$\text{BiFeO}_3$  is a multiferroic material in which ferroelectric and anti-ferromagnetic orders coexist well above room temperature ( $T_N = 643$  K,  $T_C = 1093$  K), with a high degree of polarization (over  $100 \mu\text{C}/\text{cm}^2$ <sup>4</sup>). We have demonstrated at the LLB, that the magnetization of the material can be modified by the application of an electric field (this was the first direct proof of a magneto-electric coupling). This result opens the way towards implementing this material in spintronic devices in which magnetization might be controlled by a small electrical voltage rather than by currents or magnetic fields.

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<sup>1</sup> *Artificial antiphase boundary at the interface of ferrimagnetic spinel bilayers.* A. Ramos, S. Matzen, J.-B. Moussy, F. Ott, M. Viret, Phys. Rev. B **79** 014401 (2009).

<sup>2</sup> *Biaxial Strain in the Hexagonal Plane of MnAs Thin Films: The Key to Stabilize Ferromagnetism to Higher Temperature.* V. Garcia, Y. Sidis, M. Marangolo, F. Vidal, M. Eddrief, P. Bourges, F. Maccheronzi, F. Ott, G. Panaccione and V. H. Etgens, Phys. Rev. Lett. **99**, 117205 (2007).

<sup>3</sup> *Mechanisms of Exchange Bias with Multiferroic  $\text{BiFeO}_3$  Epitaxial Thin Films.* H. Bea, M. Bibes, F. Ott, B. Dupe, X.-H. Zhu, S. Petit, S. Fusil, C. Deranlot, K. Bouzehouane and A. Barthélemy, Phys. Rev. Lett. **100**, 017204 (2008).

<sup>4</sup> D. Lebeugle et al., Appl. Phys. Lett. **91** 022907 (2007)

The first step consisted of a detailed study of high quality BiFeO<sub>3</sub> single crystals. We confirmed<sup>5</sup> that the spins of the Fe<sup>3+</sup> ions form a circular cycloid with a long period of 62 nm (from powder diffraction data, several magnetic structures were possible).

In a second step, an electric field was applied to the crystal, which was in a single ferroelectric domain state with the polarization along [111] (Figure 2.1). When the electric

## Organization

LLB nanoscience research benefits from a variety of available neutron scattering techniques:

I. SANS (Small Angle Neutron Scattering) - for studying the structure and organization of nanoparticles.

- The laboratory operates 5 SANS instruments: PAXY, PACE, PAXY, PAPHYRUS, and TPA. The latter instrument is specifically used for very small angle scattering studies.

II. Reflectivity - to study thin film structures (polymers, magnetic films, liquid surfaces).

- Two reflectometers are operated: EROS for studies on polymer and liquid systems and PRISM for studies on magnetic thin films.

III. Diffraction - to study the crystalline or the magnetic order of nanostructures.

- The 4-circles spectrometer (6T2) was recently upgraded to be capable of performing diffraction studies on epitaxial thin films.

- The different powder diffractometers are also used to characterize the structural or magnetic properties of nanoparticles.

- Two instruments (6T1 and DIANE) are specifically dedicated to the study of textures and strains in metallurgical materials.

IV. Inelastic scattering - to study dynamic properties of nanosystems.

- The time-of-flight spectrometer, MIBEMOL, is primarily used for these studies.

V. Other characterization techniques are readily available for LLB scientists, including: light scattering, rheology, magnetometry (VSM-SQUID), I.R. spectroscopy, X-ray reflectivity.

The people working on these different topics are organized in groups with specific technical expertise. Each of these groups is in charge of a specific pool of spectrometers (SANS, reflectivity, single crystal diffraction, powder diffraction, or texture/strain). The groups have the duty of operating and upgrading their spectrometers and are in charge of organizing the support for visiting scientists coming to perform experiments at the LLB. This organization allows the laboratory to operate the spectrometers in an efficient way by providing instruments that are constantly upgraded, and by providing a high level of expertise in each technique. These practices strongly benefit our external users.

Though each operational group (see organization chart) has a specific technical expertise, LLB physicists additionally benefit from a variety of different scattering techniques that are available for their research topics. Many of the studies presented here have employed several scattering techniques:

- Magnetic thin film systems have been studied by reflectivity and diffraction techniques.
- Magnetic nanoparticles have been studied by SANS, powder diffraction and inelastic scattering.
- Shape memory alloys are being studied by powder diffraction and on the texture diffractometer.
- ODS steels are characterized by diffraction, texture, and SANS techniques.

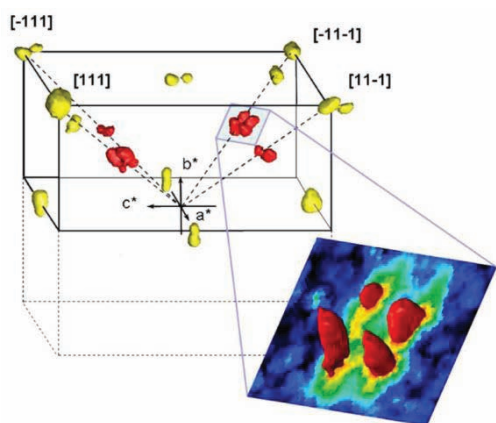
field was applied along the [001] direction, the sample switched to a multidomain ferroelectric state. Using neutron diffraction, we showed that the propagation vector was the same as in the virgin state, but that the spins were lying in two different planes. Applying an electric field thus induced a spin flop of the antiferromagnetic sublattice.

<sup>5</sup> *Electric-Field-Induced Spin Flop in BiFeO<sub>3</sub> Single Crystals at Room Temperature*. D. Lebeugle, D. Colson, A. Forget, M. Viret, A. M. Bataille, and A. Gukasov, Phys.Rev. Lett. 100 227602 (2008).

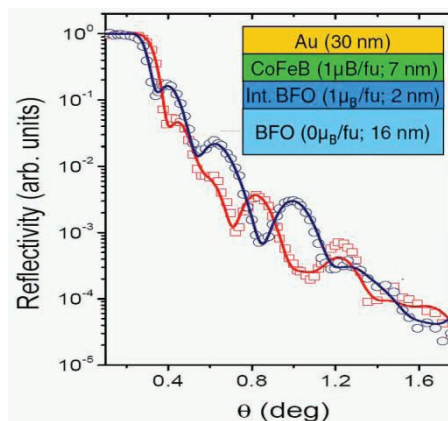


Integration of multiferroics into spintronic devices requires growing thin films. We thus also studied heterostructures grown by pulsed laser deposition by the group of Agnès Barthelemy at the UMR CNRS/Thales. It was first shown using neutron diffraction that the magnetic structure of the BiFeO<sub>3</sub> thin films differs from the bulk one: the cycloidal modulation is not present, and the spins form a simple G-type antiferromagnet<sup>6</sup>.

The next step of the study has consisted of investigating the interaction of a BiFeO<sub>3</sub> thin film coupled to a ferromagnetic layer (CoFeB in our case). In these heterostructures, the two layers are coupled together via the exchange bias mechanism<sup>7</sup>. Furthermore Malozemoff's model suggests that a net magnetization should be observed in BiFeO<sub>3</sub> near the interface with CoFeB. To test this prediction, polarized neutron reflectometry was performed on CoFeB/BiFeO<sub>3</sub> bilayers on the PRISM spectrometer (Fig. 2.2). The data are well reproduced by taking into account a 2 nm thick layer carrying a 1  $\mu_B$  per formula unit magnetic moment. This is far larger than the surface magnetic moment predicted by Malozemoff's model, and suggests that unpinned spins exist in BiFeO<sub>3</sub> near the interface along with the pinned moments predicted by the model. As the ferroelectric domain structure can be easily controlled by an electric field, these results open the route to the electrical manipulation of magnetization at room temperature, in BiFeO<sub>3</sub>-based, exchange-bias heterostructures.



**Figure 2.1** Mapping of the neutron intensity in the reciprocal space, showing the effect of an electric field on a BiFeO<sub>3</sub> single crystal. The magnetic peaks (red spots) are split because of the presence of a magnetic cycloid.



**Figure 2.2** Polarized neutron reflectivity on a CoFeB/BiFeO<sub>3</sub> heterostructure showing the presence of an induced magnetization in the interfacial BFO layer.

This work benefits from the financial support of the RTRA Triangle de la Physique and C' nano, which supported the building of an octupole magnet to perform measurements with arbitrary field directions.

## Nanoparticles

Besides magnetic films, we are also studying the magnetism of objects with even more reduced dimensions, such as magnetic nanomolecules whose magnetic properties in the crystalline state can be studied by diffraction, and small magnetic particles such as nanobeads and nanowires, which can be studied by SANS or powder diffraction. The latter topic was the subject of a PhD thesis by T. Maurer (2007-2009).

## Molecular magnets

Polarized neutron diffraction allows the exact nature of the magnetic interactions that give rise to the ground state in complex molecular magnets to be determined without any ambiguity contrary to SQUID measurements. Such information is important for optimizing the building of new clusters with the highest spin as possible. Tools are also available to reconstruct magnetization density distribution in the molecules from the diffraction data (acquired on the 5C1 spectrometer).

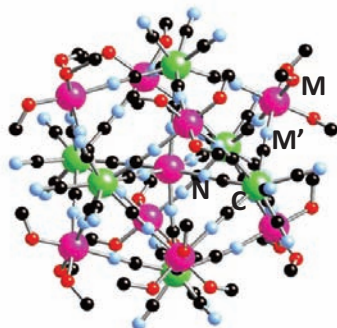
<sup>6</sup> Structural distortion and magnetism of BiFeO<sub>3</sub> epitaxial thin films: A Raman spectroscopy and neutron diffraction study. H. Béa; M. Bibes, S. Petit, J. Kreisel, A. Barthélémy, Philos. Mag. Lett. **87**, 165 (2007)

<sup>7</sup> Mechanisms of Exchange Bias with Multiferroic BiFeO<sub>3</sub> Epitaxial Thin Films. H. Bea, M. Bibes, F. Ott, B. Dupe, X.-H. Zhu, S. Petit, S. Fusil, C. Deranlot, K. Bouzehouane and A. Barthelemy, Phys. Rev. Lett. **100**, 017204 (2008).

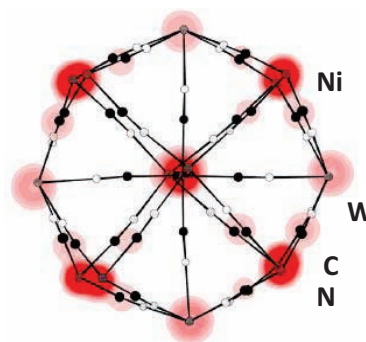
### High-spin molecular clusters

The study of the nature of the spin ground state and interaction mechanisms in paramagnetic molecular clusters is the subject of long time collaborations among the GDR MCM (Montpellier, Lyon)<sup>8,9</sup> and the European network MAGMaNet (Bern, Firenze, Barcelona). Single molecule magnets, such as the Fe<sub>8</sub> cluster<sup>10</sup>, possess high spin in the ground state and strong anisotropy, which produce a high energy barrier to magnetization reversal and behave as magnetic nanoparticles at low temperature.

The octacyanomometallates, such as [M' (CN)<sub>8</sub>]<sup>3+</sup> (M' <sup>V</sup> = Mo<sup>V</sup>, W<sup>V</sup>), have been used in Bern to synthesize a family of high spin M<sub>9</sub>M' <sub>6</sub> clusters, some of which display single molecule magnetic behavior. The M<sub>9</sub>M' <sub>6</sub> core consists of a centered cube of M<sup>II</sup> ions with M' <sup>V</sup> ions capping its six faces (Fig. 2.3). A diffraction study on single crystals had unambiguously demonstrated the AF nature of the Mo<sup>V</sup>-CN-Mn<sup>II</sup> magnetic interactions in the Mn<sup>II</sup><sub>9</sub>Mo<sup>V</sup><sub>6</sub> cluster (*S* = 35/2). The experimental induced magnetization density in the (*S* = 12) ground state of the Ni<sub>9</sub>W<sub>6</sub> cluster (Fig. 2.4) confirms the ferromagnetic nature of the [W...Ni] interaction through the CN bridge predicted by calculations based on DFT (Density Functional Theory)<sup>11</sup>. However, the observed strong spin delocalization from the W<sup>V</sup> ions towards the CN bridges, as reflected by the positive spin density carried by the N atoms, is underestimated by DFT calculations. This delocalization is at the origin of the strong efficiency of the CN groups to transmit magnetic interactions by super-exchange.



**Figure 2.3.** A cyano-bridged M<sub>9</sub>M' <sub>6</sub> molecular cluster.



**Figure 2.4.** Induced magnetization density (1.5K, 5T) in the Ni<sub>9</sub>W<sub>6</sub> cluster (*S* = 12) integrated along a diagonal of the W<sub>6</sub> octahedra (isodensity levels: 0.0 to 0.90 μ<sub>B</sub>/Å<sup>2</sup>)

### Magnetic nanoparticles

These types of magnetic nano-objects form a part of the basis of the work on composite materials combining hard nanoparticles and polymer materials. We have performed extensive studies of the magnetism of anisotropic magnetic particles.

### Magnetic properties of metallic nanowires

The work on this topic began in 2007 with a PhD thesis. Further support was obtained via the ANR contract MAGAFIL (2008-2010) which permitted the hiring of F. Zighem as a post-doc for 2 years (2009-2010). The MAGAFIL network is gathering expertise from various fields, including chemistry at ITODYS Paris VII and LPCNO at INSA Toulouse; magnetism at the LLB; and metallurgy at the LPMTM Paris XIII.

<sup>8</sup> E. Ruiz, G. Rajaraman, S. Alvarez, B. Gillon, J. Stride, R. Clérac, J. Larionova, S. Decurtins, *Angew. Chem. Int. Ed.* **44** (2005) 2711-2715

<sup>9</sup> *Structure, Magnetic Properties, Polarized Neutron Diffraction and Theoretical Study of a copper(II) cubane*. C. Aronica, Y. Chumakov, E. Jeanneau, D. Luneau, P. Neugebauer, A.-L. Barra, B. Gillon, A. Goujon, A. Cousson, J. Tercero, E. Ruiz, *Chem. Eur. J.*, **14** (2008) 9540-9548.

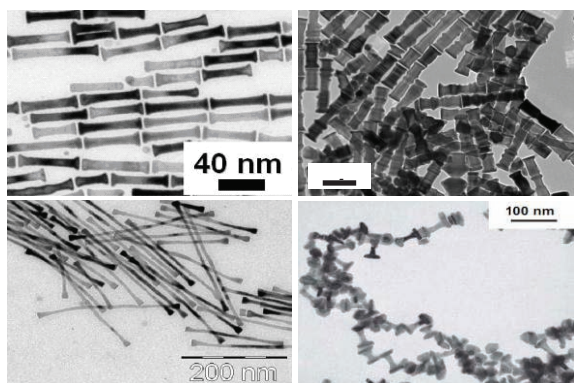
<sup>10</sup> *Experimental spin density in the high spin ground state of the Fe<sub>8</sub>pcl cluster*. B. Gillon, C. Sangregorio, A. Caneschi, D. Gatteschi, R. Sessoli, E. Ressouche, Y. Pontillon, *Inorg. Chim. Acta*, **360** (2007) 3802-3806

<sup>11</sup> *Experimental and Theoretical Study of the Spin Ground State of the High-Spin Molecular Cluster [Ni<sup>II</sup>{Ni<sup>II</sup>(CH<sub>3</sub>OH)<sub>3</sub>}<sub>3</sub>]<sub>8</sub>(μ-CN)<sub>30</sub>{W<sup>V</sup>(CN)<sub>3</sub>}<sub>6</sub>·15CH<sub>3</sub>OH* by Polarised Neutron Diffraction and Density Functional Theory Calculations. B. Gillon, J. Larionova, E. Ruiz, Q. Nau, A. Goujon, F. Bonadio, S. Decurtins, *Inorg. Chem. Acta*, **361**(2008) 3609-3615.

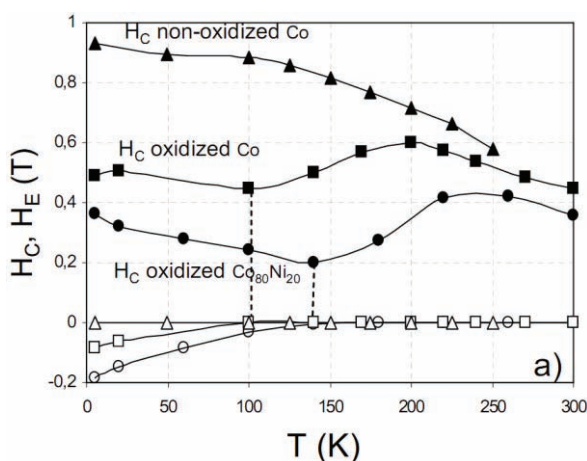
After some initial work on the bulk properties of the systems, which showed the potential utility of these nanowires<sup>12</sup> (Fig. 2.5), the work has since focused on revealing their detailed properties. Complex exchange bias properties have been observed<sup>13</sup> (Fig. 2.6), and because of the specific dimensionality of these systems (1D versus 2D for thin films and 3D for nanoparticles), we have been able to demonstrate a key role for oxide shell superparamagnetic fluctuations in these wires. This work combined powder diffraction measurements, for characterizing the magnetic properties of the oxide shell, with magnetization measurements and micro-magnetic calculations.

Further work has been performed on the detailed micro-magnetic modeling of these nanowires in order to optimize their properties for applications. The magnetic properties of the wires as a function of the detailed shape of the objects (e.g., sphere, rods, cylinders, diabolos, and dumb-bells) have been assessed<sup>14</sup>; and nanowire assembly behavior has been modeled<sup>15</sup>.

*This work was a part of the PhD thesis of T. Maurer.*



**Figure 2.5.** Magnetic nanowires of  $\text{Co}_x\text{Ni}_{1-x}$  alloys.



**Figure 2.6.** Evolution of the coercive and exchange field in different types of nanowires.

## Composite materials

This field of research deals with the combining of several base ingredients in order to create new materials that have properties which are improved over their initial ingredients. Neutron scattering techniques, such as the Small Angle Neutron Scattering for bulk materials and reflectometry for thin film structures, allow us to understand the structures of these new materials at the nanometer scale.

## Polymer reinforcement by nanoparticles

This field of research is a natural extension of the expertise of the LLB in the field of polymer science (see LLB Axis 3: Soft Matter). We benefit from the expertise acquired in the physics of dispersion in a polymer melt, the chemistry of grafting, and rheology. Several types of systems are being investigated at the laboratory.

### **Mechanical properties of grafted nanoparticles dispersed in a polymer melt<sup>16</sup>.**

As shown in LLB Axis 3, dispersions of small ramified aggregates were obtained that were homogenous at scales larger than 1 micron. Under uniaxial elongation, the tensile stress versus

<sup>12</sup> *Magnetic nanowires as permanent magnet materials.*

T. Maurer, F. Ott, and G. Chaboussant, Y. Soumare and J.-Y. Piquemal, G. Viau, Appl. Phys. Lett. **91**, 172501 (2007).  
Selected for Virtual Journal of Nanoscale Science & Technology **16**(19) (Nov. 5, 2007 issue); News in [www.nanotechweb.org](http://www.nanotechweb.org).

<sup>13</sup> *Exchange bias in Co/CoO core-shell nanowires: Role of antiferromagnetic superparamagnetic fluctuations*  
T. Maurer, F. Zighem, F. Ott, G. Chaboussant, G. Andre, Y. Soumare, J.-Y. Piquemal, G. Viau and C. Gatel, Phys. Rev. B **80**, 064427 (2009).

<sup>14</sup> *Effects of the shape of elongated magnetic particles on the coercive field.*

F. Ott, T. Maurer, G. Chaboussant, Y. Soumare, J.-Y. Piquemal and G. Viau Journal of Applied Physics **105**, 013915 (2009).

<sup>15</sup> *Dipolar interactions in arrays of ferromagnetic nanowires: a micromagnetic study.*

F. Zighem, T. Maurer, F. Ott and G. Chaboussant, to appear in Journal of Applied Physics (arXiv: <http://arxiv.org/abs/1008.0172>)

<sup>16</sup> *Direct small-angle-neutron-scattering observation of stretched chain conformation in nanocomposites: More insight on polymer contributions in mechanical reinforcement.*

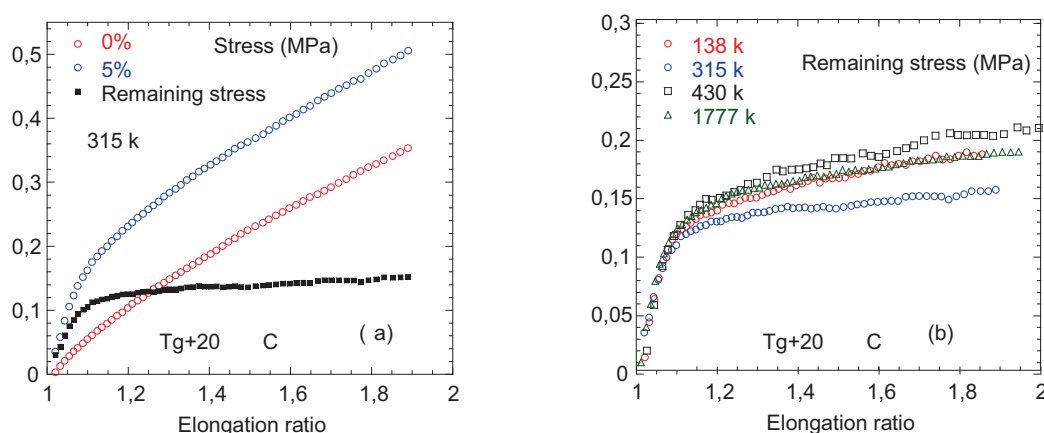
N. Jouault, F. Dalmas, S. Said, E. Di Cola, R. Schweins, J. Jestin, F. Boué, Physical Reviews E **2010**, **82**, 031801.

strain curves (elongation ratio  $\lambda$ ) displayed an important reinforcement (Fig. 2.7). After an initial jump in low  $\lambda$  regime, the curves appear as though the pure matrix curve is shifted by a constant value depending on the silica concentration. This agrees with the fact that the chain deformation remains unaffected by the presence or absence of nanofillers (see LLB Axis 3). Subtracting the pure matrix contribution, we observed that the remaining stress was constant with  $\lambda$  (Fig. 2.7). This implies that existing reinforcement models may need to be revised. Unless they concern only a very small fraction of chains, two main models fail *in our system*, because they both assume that some chains experience a stronger deformation, either by:

- (i) a direct elastic connection of the fillers by the chains<sup>17</sup>, or
- (ii) the existence of a fraction of glassy chains (glassy layer or glassy paths) that would explain reinforcement dependence on  $T - T_g$ <sup>18</sup>.

Therefore, confinement effects do not dominate. The important reinforcement must be due to the response of the filler structure to a combination of filler orientation<sup>19</sup> (along the stretching direction) and filler displacement<sup>20</sup>, which ultimately induces a continuous locking-unlocking process of fillers associations.

*This work was a part of the PhD thesis of N. Jouault.*



**Figure 2.7.** (Left) Stress-strain (elongation ratio  $\lambda$ ) for unfilled polymer (red) and 5% filled nanocomposite (blue) for  $M_w = 315$  k. The remaining stress after subtraction of unfilled polymer stress (black) reaches a plateau above  $\lambda=1.1$ . (Right) Remaining stress versus  $\lambda$  for four molecular weights (from 138 k to 1777 k) at same silica volume fraction 5% v/v.

### **Natural rubber-clay nanocomposites: mechanical and structural properties<sup>21</sup>**

This project relates the mechanical properties of non-vulcanized natural rubber-clay nanocomposites to the morphological and structural aspects of the smectic clay, using TEM and SANS, while paying special attention to the role of non-rubber constituents. Natural rubber latex, apart from polyisoprene, contains non-rubber molecules such as phospholipids, proteins, and a host of inorganic metallic cations, all of which contribute to auto-reinforcement. Pristine natural rubber therefore shows outstanding mechanical properties, with exceptionally high tensile strain and strength at rupture. We have shown that this auto-reinforcement effect is suppressed when non-rubber components are removed by dialysis. On the contrary, for natural rubber-clay nanocomposites, the performance of clay as a reinforcement agent is significantly higher in dialyzed rubber due to the clay's excellent exfoliation and dispersion characteristics during nanocomposite preparation (i.e., the mixing of pre-exfoliated aqueous dispersions of clay with rubber latex). The reinforcement factor of

<sup>17</sup> P.G. Maier, Gummi Kunstst. **2000**, 53. A.S. Sarvestani, Eur. Pol. J. **2008**, 44, 263-269.

<sup>18</sup> D. Long, Eur. Phys. J. E., **2001**, 4, 371-387. J. Berriot, Europhysics Letters **2003**, 644, 50. A. Bansal, Nature Materials, **2005**, 4, 693.

<sup>19</sup> Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network.

J. Jestin, F. Cousin, I.Dubois, C. Ménager, R. Schweins, J. Oberdisse, F. Boué, Advanced Materials, 2008, **20**, 2533-2540.

<sup>20</sup> Y. Rharbi, Europhysics Letters 1999, **46**, 472-478.

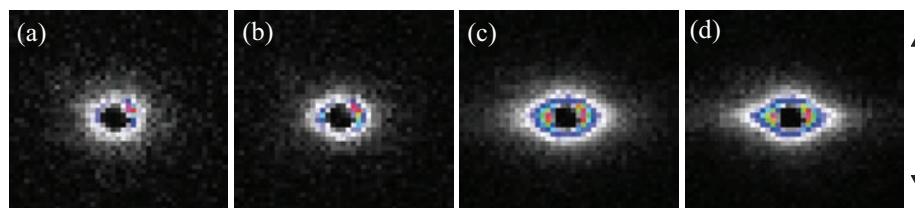
<sup>21</sup> Natural rubber-clay nano-composites: Mechanical and structural properties.

Camila A. Rezende, Fabio C. Bragança, Telma R. Doi, Lay-Theng Lee, Fernando Galembeck, François Boué, Polymer **51** (2010) 3644e3652.



the nanocomposite (from uniaxial deformation) can be modeled by the high aspect ratio of exfoliated clay platelets coupled with immobilized rubber matrix, the latter indicated by SANS and calorimetry data. Correspondingly, the onset of accelerated stiffening of the nanocomposite, attributable to filler network formation, occurs at a very low critical clay concentration that is almost an order of magnitude lower than would be expected for spherical particles. TEM and SANS analyses show completely exfoliated clay lamellae in coexistence with a small fraction of tactoids. Interestingly, the presence of tactoids does not appear to compromise the excellent reinforcement properties of the exfoliated platelet fraction. At high deformations, strain-induced alignment of the clay exhibits anisotropic scattering, with anisotropy increasing with clay concentration and degree of stretching (Fig. 2.8). Thus, enhanced mechanical properties at high uniaxial deformations may also be related to the ordering of the clay network in the nanocomposite.

*This work was a part of the PhD thesis of C. A. Rezende and the work of the post-doc fellow T. Doi.*



**Figure 2.8.** Two-dimensional SANS patterns of natural-rubber clay nanocomposites stretched to  $\lambda = 4$ . Clay concentrations: (a) 0%, (b) 2%, (c) 10%, and (d) 20%. The vertical arrow shows the stretching direction.

### **Crosslinked hybrid multilayer (Polystyrenes / Pt Nanoparticles) thin films<sup>22,23</sup>**

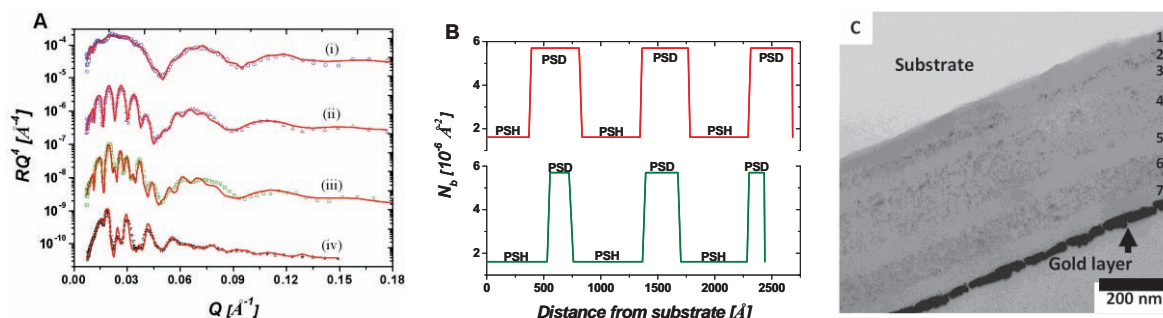
This work has been initiated through collaboration between E. Drockenmuller (Univ. Lyon I) and the LLB, within the ANR “Multiclick” (2007-2009). Organic/inorganic hybrid films made of polymers and inorganic nanoparticles are able to combine two or more desirable properties that can be tuned by particle size, shape and surface chemistry. However, when exposing such hybrid films to solvents, high temperatures, and magnetic or electrical fields, the nanoparticles can undergo aggregation or segregation at the interface. The chemical modification of nanoparticle surfaces, and tuning of the polymer matrix, are therefore of special interest as they enable nanoparticle organization within the thin films to be controlled and directed.

We describe a versatile method of building up well-defined and tunable multilayer thin films based on the combination of polystyrene-grafted platinum nanoparticles with photo-crosslinkable polystyrenes. This approach consists of a straightforward process of sequential spin-coating, UV irradiation, and thermal annealing procedures, which allows the thickness ( $h = 10\text{--}200\text{ nm}$ ) and composition (0-50 wt% of PS-grafted Pt nanoparticles) of each layer to be easily tuned as well as providing precise control over their registration and periodicity. Neutron reflectivity experiments performed on pure organic multilayers with alternated hydrido and deuterated layers provide an accurate characterization of layer thickness and of the limited interdiffusion occurring at each polymer/polymer interface in these multilayer architectures. The homogeneity of the resulting multilayer assemblies, and the high level of dispersion for the PS-grafted Pt nanoparticles among hybrid layers, have been confirmed by transmission electron microscopy (TEM; Fig. 2.9). This work represents a powerful method for the versatile and robust elaboration of (hybrid) multilayer architectures and their subsequent stabilization by UV crosslinking, i.e., through covalent binding.

<sup>22</sup> Design of crosslinked hybrid multilayer thin films from azido-functionalized polystyrenes and platinum nanoparticles. S. Al-Akhrass, F. Cousin, F. Gal, D. Damiron, P. Alcouffe, G. Carrot, E. Drockenmuller, C. Hawker *Soft Matter* 2009, **5**, 586.

<sup>23</sup> Polymer-Grafted-Platinum Nanoparticles: From Three-Dimensional Small-Angle Neutron Scattering Study to Tunable Two-Dimensional Array Formation. G. Carrot, F. Gal, C. Cremona, J. Vinas, H. Perez, *Langmuir* 2009, **25**, 471.





**Figure 2.9.** (A) Reflectivity ( $RQ^4$ ) vs.  $Q$  for PSH/PSD multilayer thin films. (i-iii) correspond to 2, 4 and 6 layers assemblies. The solid lines represent the best fits for each data set. (B) Neutron density length profiles for PSH/PSD multilayers (iii) and (iv). (C) Cross-sectional TEM images of a 7-layer hybrid multilayer assembly with varying layer thickness and a PtH content of 50 wt%.

## Metallurgical composites

In response to industrial needs, steels with very high mechanical characteristics are under continuous development. In particular, the principle of reinforcement, by one or several precipitations of nanometric particles, has attracted considerable interest. The mechanical properties of these composite materials depend strongly on the nature of the nanometer-sized precipitates: i.e., their density, size, and degree of coherence with the matrix. In this research field, Small Angle Neutron Scattering (SANS) allows for very fine characterization of the particles, especially during the first stages of their formation. The LLB is involved in several research contracts for these composite metal alloys.

- **ANR AMARAGE:** Within the framework of this project, the kinetics of the double precipitation of nanometric carbides ( $(\text{CrMo})_2\text{C}$ ) and intermetallic phase (NiAl) was studied in martensitic steels intended for the aircraft industry. The SANS analysis, concordant with observations in TEM (CEMES Toulouse) and tomographic atom probe (GPM Rouen) have demonstrated a synergy between the two types of precipitation. Furthermore, the effect of certain alloying elements, such as cobalt, on the kinetics of precipitation has been clearly demonstrated<sup>24</sup>.

*This work was performed by M. Perrut (post-doc).*

- **ANR AXtREM:** Nanoreinforced steels are being considered for the construction of future nuclear reactors. For higher operating temperatures, Oxide Dispersion Strengthened (ODS) martensitic/ferritic steels exhibit high creep strength as well as potentially high resistance to radiation damage. These materials are being intensively studied with the objective of controlling the evolution of the oxide dispersion during the different stages of the fabrication, which include mechanical alloying, the consolidation processes of extrusion or HIP, and thermal treatments. While these materials are intended for applications up to  $1100^\circ\text{C}$ , reinforcement by nitrides is being considered for applications requiring intermediate temperatures (up to  $700^\circ\text{C}$ ). The development of these new alloys by nitration at the massive state and in comparison with the ODS, constitutes the AxTrem project. The feasibility of the reinforcement by nitride particles was proved, and nanostructures similar to ODS steels were obtained. Subsequently, correlations with their mechanical properties will be investigated.

## Metallurgy from the fundamental to the industrial

The diffractometers associated with metallurgy research activities are DIANE (G52), located in the guide hall, and the 6T1 in the reactor hall. They are respectively dedicated to the analysis of residual strains and to the determination of crystallographic textures. The strong penetrating power of neutrons is used to analyze in-depth metallurgical samples or industrial objects. The instruments are used for both academic and industrial research.

<sup>24</sup> Small-Angle Neutron Scattering of Multiphase Secondary Hardening Steels.  
M. Perrut, MH. Mathon, D. Delagnes. Acta Mat. (submitted).

## Textures and strain heterogeneities

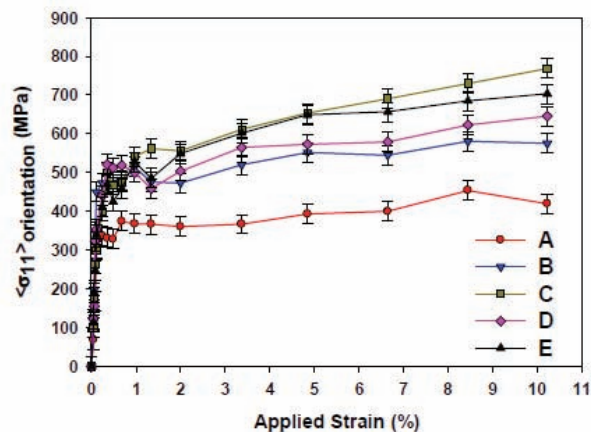
Understanding the macroscopic mechanical properties of polycrystalline materials requires knowledge of the deformation mechanisms at the grain scale. In particular, when a material is subjected to an external macroscopic deformation, the stresses and strains of the crystallites depend on their crystallographic orientation and their environment.

### **Stress fields in polycrystalline materials.**

We have developed a neutron diffraction methodology that associates texture determinations with strain measurements in order to analyze the stress fields within families of crystallites having the same crystallographic orientation in polycrystalline materials<sup>25</sup>. This stress analysis method allows an intermediate approach between a local and a global scale characterization within the bulk of massive samples. It appears promising to use this method in combination with modeling methods that are based on homogenization techniques, due to the statistically representative information it provides. This dual approach has been successfully applied to the vessel steel 16MND5 of pressurized water reactors<sup>26</sup>. The strains measured by *in situ* neutron diffraction during a tensile test (Fig. 2.10) were very heterogeneous among the five analyzed crystallographic orientations (Fig. 2.11). These data were very important for validating a mechanical model developed at CEA/DEN/SRMA, by taking into account both the morphology and crystallography of grains.



**Figure 2.10.** Tensile device adapted on the Euler cradle for *in situ* neutron diffraction measurements.



**Figure 2.11.** Variation of the axial stresses for different grain families (A to E) vs. applied strain. A significant heterogeneity is highlighted.

### **Stress determination in welded materials**

Residual stresses in materials can have significant influence on their mechanical properties, including fatigue behavior, resilience, or resistance. Welding processes typically generate important thermal gradients, due to the localized input of intense heat. Frequently, these gradients create large residual stresses around the weld bead, which can reach the yield point value in some cases. During operation of the considered component, these residual stresses will add to applied stresses, possibly resulting in early cracking or fracture. Thus, knowledge of residual stress is critically important for accurately predicting the service behavior of the component, and hence, for optimizing the welding process and the base materials.

Neutron diffraction is an ideal tool for in depth determinations of the residual stresses distributed within welded components, especially because the size of the region probed by the neutrons is relatively small compared to the size of a “classical” weld bead. At LLB during the past several years, numerous experiments have been successfully carried out on welds produced by various processes that utilized different base materials (e.g., steels, aluminum

<sup>25</sup> *In situ analysis of deformation mechanisms of Cu-based fcc materials under uniaxial loading.*

V. Klosek, M.H. Mathon, M.H. Aouni, R. Chiron, V. Ji, Materials Science Forum, **571-572** (2008) 89-94.

<sup>26</sup> *Orientation stress field analysis in polycrystalline bcc steel using neutron diffraction.*

R. Dakhlaoui, V. Klosek, M.H. Mathon, B. Marini, Acta Materiala, Vol. **58** (2010) 499-509.

alloys, magnesium alloys, titanium alloys, etc.)<sup>27-28</sup>. For instance, residual stress fields within the joints of steel pipes designed for PWR (Pressurized Water Reactor) secondary coolant loops or gaseous hydrogen piping were recently determined in collaboration with CEA/DEN<sup>29</sup>.

### Materials of nuclear interest

Nuclear technologies, such as fission or fusion reactor construction and the storage of accumulated nuclear waste, rely on the development and qualification of advanced structural materials. In particular, the microstructure evolution (precipitation, point defect clusters, etc.) of the materials that constitute the primary water circuit, which must endure important solicitations (e.g., irradiation, thermal aging, hydridation, etc.), is generally responsible for the degradation of their mechanical properties. The knowledge of the aging mechanisms is essential for predicting the behavior of materials under in-service conditions. SANS is a very powerful technique for material characterization and is now usually applied within the framework of research on nuclear materials.

- In Zr alloys (fuel cladding, combustible), the formation of dislocation loops and of  $\beta$  Nb particles induced by neutron irradiation of Zr2.5%Nb alloy, have been revealed in alloys irradiated at different dose rates.
- In martensitic/ferritic alloys, which are candidates for the internal structures of future-generation nuclear reactors, the kinetics of the  $\alpha'$  Cr-rich phase precipitation induced by neutron irradiation has been characterized. After a high dose rate, the deduced Cr threshold concentrations in the ferrite agree with models of the binary Fe-Cr equilibrium phase diagram, and attest to a simple irradiation-accelerated precipitation mechanism<sup>30</sup>.

### Confined systems

#### Organized guest-hosts systems and microporous materials

This topic was originally developed in CRM2, Nancy, with whom a strong collaboration still exists and where all the single-crystal XRD experiments, and most of sample preparations are performed. Collaborations also involve LMPC (ENSCMu, Mulhouse), LRS (Paris VI) and Chimie Théorique (ENS Paris) for the design and modeling of microporous materials<sup>31-32</sup>.

In these studies, diffraction provides the most accurate, though averaged, structural information on the zeolitic system. However, diffraction must also be supplemented by local spectroscopies in order to account for local defects (e.g., “empty zeolites”) or disorder (e.g., “guest-host systems”). In the case of good quality single crystals, XRD allows atomic charges to be estimated, and the resulting values compare well with those used in the modeling of adsorption in these kinds of materials. The resulting structure can also be used as a starting point for molecular dynamics/Monte Carlo studies. This approach was applied to X-type zeolites, for which atomic charges were determined in the simple system, dehydrated Na-X. Structural studies on bicationic Na,Co-X were also performed in order to evidence the cation reorganisation induced by dehydration/rehydration<sup>33</sup>.

Other structural studies concern guest-host systems built by combining a large-channel zeolite with a small, hyperpolarizable molecule, and then exhibiting Second Harmonic

<sup>27</sup> Study of PM2000 microstructure evolution following FSW process

M.H. Mathon, V. Klosek, Y. de Carlan, L. Forest, Journal of Nuclear Materials 2009, 386-388, 475.

<sup>28</sup> Influence of FSSW parameters on fracture mechanisms of 5182 aluminum welds

S. Bozzi, A.L. Helbert-Etter, T. Baudin, V. Klosek, J.G. Kerbiguet, B. Criqui, Journal of Materials Processing Technology 2010, **210**, 1429].

<sup>29</sup> Evaluation of residual stresses in dissimilar weld joints

A. Bonaventure, D. Ayrault, G. Montay, V. Klosek, Materials Science Forum, in press.

<sup>30</sup> SANS Study of Martensitic Steels and FeCr ODS alloys of Nuclear Interest,

M.H. Mathon, Y. de Carlan, M. Ratti, S. Zhong, J. Henry, P. Olier, V. Klosek, V. Ji, in press in Materials Science Forum.

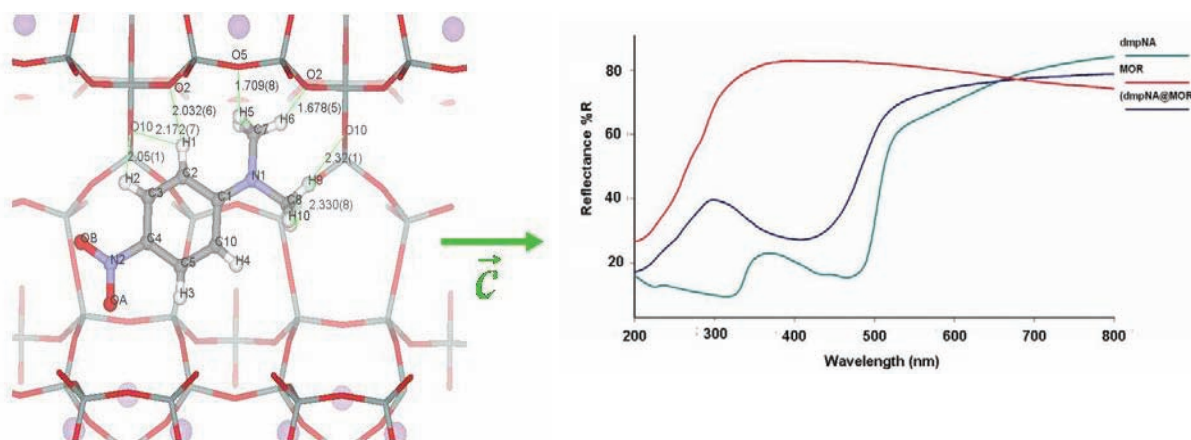
<sup>31</sup> Synchrotron powder diffraction characterization of the zeolite-based (p-N,N-dimethylnitroaniline-mordenite) guest-host phase. F. Porcher, E. Borissenko, M. Souhassou, M. Takata, K. Kato, J. Rodriguez-Carvajal, C. Lecomte, C. Acta Crystallographica B-Structural Science 2008, **64**, 713.

<sup>32</sup> Single crystal structure of fully dehydrated partially Co2+-exchanged zeolite X: Comparison with partially dehydrated partially Co2+-exchanged zeolites

X. E. Borissenko, F. Porcher, A. Bouche, C. Lecomte, M. Souhassou, Microporous and Mesoporous Materials 2008, **114**, 155

<sup>33</sup> F. Porcher, F., Leclercq-Hugeux, F., Lede, B., Kato, K., Takata, M., Hsu, I.-J., Acta Cryst. (2008) **A64**, C504.

Generation. In (dmpNA-MOR), the guest molecules are disordered over 8 sites, but are aligned in the channels with a moderate tilt angle, as requested for SHG. The diffraction explains the stabilization of the guest molecules via H-bonds with the framework (Fig. 2.12 Left). However, due to disorder, it fails to discriminate between different possible local models. UV-visible spectroscopy (Fig. 2.12 Right) gives complementary insight: the blue shift on the dmpNA reflectance window suggests dipolar  $-\text{NO}_2 \cdots (\text{CH}_3)_2\text{N}-$  interactions. Hence, the local arrangement of dmpNA molecules in MOR channels is head-to-tail.



**Figure 2.12.** (Left) Interaction of dmpNA molecule with MOR framework. (Right) UV-Visible reflectance spectra of MOR, dmpNA and (dmpNA-MOR) guest-host system.

## Amorphous materials

### Disordered systems – glasses

Short-wavelength neutrons from the hot source of the ORPHEE reactor offer a decisive advantage for the characterization of short-range order in noncrystalline materials (i.e., liquids and amorphous materials). The LLB's 7C2 diffractometer allows structure factors to be measured over a widely scattered vector range and pair distribution functions to be determined, either directly for simple elements (using isotopic substitution for binary compounds), or by combining the neutron structure factor with other measurements (e.g., X-ray diffraction, EXAFS, or NMR) in the framework of a Reverse Monte Carlo simulation that fits all the datasets simultaneously.

There is considerable interest in phase transition in liquids, and some very accurate studies performed at the LLB have concerned the melting of some simple elements. However, the emerging fields of interest for the structure of liquids and amorphous materials are often related to new problems in materials science, such as those presented by the oxide glasses. The study of Phase Change (PC) materials, which will be developed hereunder, is typical of the connection between materials problems and fundamental properties. The search for better PC materials requires investigating the interplay among electronic structure, atomic structure, and thermal anomalies.

In the metallic or metalloid elements of the 14-16 group, some very accurate measurements of their thermal properties and the anomalous thermal behavior of sound velocity in the materials were carried out by an Israeli team, together with very careful measurement and analysis of the temperature dependence of the structure factor (Y. Greenberg, E. Yahel, E. Caspi, B. Beuneu, C. Benmore, M. Dariel & G. Makov). A temperature-driven structural transformation could be evidenced in liquid bismuth, while the sound velocity maximum was correlated with both the structure and rigidity of the two first shells (*Europhys. Lett.*, 86, May 2009, pp. 36004-9; *J. Chem. Phys.*, 133, Sept 2010, 094506)

### Phase change alloys

Tellurium-based phase-change materials are among the most promising materials for future data-storage applications, including rewritable DVDs and nonvolatile PC-RAM memories. These alloys display optical (DVD) or electronic (PC-RAM) contrasts between their crystalline and



amorphous structures, which permit data storage. A data bit is written by the melting and amorphization of a small zone of a thin layer, while recrystallization erases the bit and is the time limiting step. Improving the properties of the PC-alloys requires an understanding of what drives both the contrast and the crystallization kinetics. Since the liquid state is a precursor to the amorphous state, we have studied by means of neutron scattering, the liquid state of several ternary Te-based alloys, for which the optical contrast had been proven or not, and in which the number of valence electrons ( $N_{sp}$ ) were varied. The latter variable has been shown to be a crucial parameter<sup>34</sup>. With increasing  $N_{sp}$ , the local atomic arrangement changed from a tetrahedral type (bad optical contrast) to an octahedral type. This octahedral atomic arrangement, and its correlation to a pps-type bonding, were also deduced from an *ab initio* molecular dynamics investigation of  $Ge_{0.15}Te_{0.85}$  by the sharp distribution of bond angles at approximately  $90^\circ$ <sup>35</sup>. It has been shown previously that this octahedral local environment is generally distorted at low temperature by a Peierls-like mechanism (trigonal distortion).

An interesting connection could be done using parent alloys that display a negative thermal expansion (NTE), such as Te-rich  $Ge_xTe_{1-x}$  alloys. All these alloys show an octahedral local structure consistent with their large  $N_{sp}$ . An inelastic neutron scattering experiment showed that increased temperatures induced a red shift of the density of vibrational states in the NTE domain due to a gain of vibrational entropy that weakens the Peierls distortion<sup>36</sup>.

## Dynamics in disordered systems

### Finite shear-elasticity in glass formers

On the basis of a Maxwell gas model (1867), it has long been suspected that liquids exhibit a shear elastic effect at sufficiently high solicitation frequencies. Recent experimental improvements carried out at the LLB show that it is in fact possible to reveal shear elasticity at low frequencies. In other words, liquids exhibit long range solid-like correlations at a macroscopic scale away from any phase transition. This result is coherent with studies emerging from different disciplines, such as micro-rheology<sup>37</sup>, NMR<sup>38</sup>, X-ray photon correlation spectroscopy<sup>39</sup>, and voltage effects<sup>40</sup>, which have provided evidence for relaxation modes that are much slower than those described by conventional theoretical models. The consideration of this non-negligible macroscopic component is of primary importance in redefining the relevant parameters that will lead to a better understanding of glass and glass former properties, and more generally, of fluid properties. In these experiments, the shear modulus is measured by applying a mechanical stress to the sample (dynamic relaxation). The stress transmitted by the sample is measured by simple contact between the sample and the surface, which is submitted to small mechanical oscillatory solicitations. Up-to-date progress in instrumentation sensitivity allows access to shear moduli over 6 orders of magnitude<sup>41</sup>. Our developments show that it is also possible to improve the measurement by controlling the boundary conditions between the material and the substrate whereby the stress and the measurement are transmitted<sup>42</sup>. Using this method, we enable the detection of subtle properties that would not have been considered previously, such as the identification of a non-zero low frequency shear elasticity in the liquid state. A new (patented) protocol has been established to measure these elastic properties at the sub-millimeter scale in various materials, such as glass formers (Glycerol, PPG, o-Terphenyl, and alkanes) and polymer melts (polystyrene, polybutylacrylate, polybutadiene, etc.), which have been so far considered as viscous liquids away from any phase transition<sup>43</sup> (Fig. 2.13). These results contrast with the conventional macroscopic description. The solid-like property is usually not considered since

<sup>34</sup> *Characteristic Ordering in Liquid Phase-Change Materials.*

Steimer C., Coulet V., Welnic W., Dieker H., Detemple R., Bichara C., Beuneu B., Gaspard J.-P. Wuttig M., Adv. Mater. **20**, 1-6 (2008).

<sup>35</sup> Bichara C., Johnson M., Raty J.Y PRL **95**, 267801 (2005).

<sup>36</sup> *Dynamics of the Negative Thermal Expansion in Tellurium Based Liquid Alloys*

Otjacques C., Raty J.-Y., Coulet M.V., Johnson M., Schober H., Bichara C., Gaspard J.P., PRL **103**, 245901 (2009).

<sup>37</sup> J. Goyon, A. Colin, G. Ovarlez, A. Ajdari, L. Bocquet, Nature, **454** (2008) 84.

<sup>38</sup> U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, H.W. Spiess, Phys. Rev. Lett. **81** (1998) 2727.

<sup>39</sup> Y. Chushkin, C. Caronna, A. Madsen, A., EPL, **83** (2008) 36001.

<sup>40</sup> E.C. Fuchs, P. Baroni, B. Bitschnau, L. Noirez, J. of Physics D, **43** (2010) 105502.

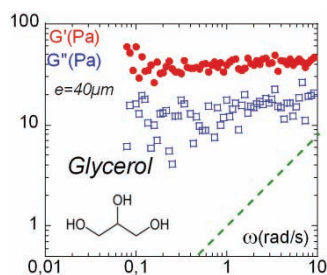
<sup>41</sup> C. Maggi, B. Jakobsen, T. Christensen, N. Boye Olsen, J.C. Dyre, J. Chem. Phys. B **112** (2008) 16320.

<sup>42</sup> Baroni, P., Mendil, H., Noirez, L., Fr. Pat., 05 10988, (2005), P. Baroni, H. Mendil-Jakani, L. Noirez, Techniques de l'Ingénieur, TI Editions, 1 (2010) RE145,

<sup>43</sup> Noirez L., Baroni, P., J. of Molecular Structure, **972** (2010) p.16. Mendil H., Baroni P., Noirez L., Eur. Phys. J. E **19** (2006) 77, L. Noirez, H. Mendil-Jakani, P. Baroni, Polym. Inter. **58** (2009) 962.



this delicate signal, which is observable at low thickness geometry, is hidden in conventional measurements<sup>44</sup>.



**Figure 2.13.** Viscoelastic moduli ( $G'$ ,  $G''$ ) of Glycerol at room temperature (improved boundary condition, Gap thickness: 0.040mm, 2% strain amplitude). The dotted line (---) corresponds to the expected viscous behavior (J. mol. Struct. 2010).

<sup>44</sup> J.D. Ferry, Viscoelastic properties of polymers, Wiley 1971; W. Graessley, Adv. Poly. Sci. **16** (1974) 1.

## Scientific collaborations

The publications are usually the result of close collaborations with other institutes and university. The main collaborating institutes are listed in Table I.

| Collaborators                 | total | Collaborators                      | total |
|-------------------------------|-------|------------------------------------|-------|
| [UNIV PARIS 6 - FRANCE]       | 12    | [INST CIENCIA MAT MADRID - SPAIN]  | 7     |
| [ECOLE CENT PARIS - FRANCE]   | 11    | [UNIV READING - UK]                | 7     |
| [INST LAUE LANGEVIN GRENOBLE] | 10    | [RES INST SOLID STATE PHYS OPTICS] | 7     |
| [UNIV PARIS 7 - FRANCE]       | 10    | [DIAMOND - ENGLAND]                | 5     |
| [UNIV PARIS 11 - FRANCE]      | 9     | [RUTHERFORD APPLETON LAB - UK]     | 5     |
| [UNIV MONTPELLIER - FRANCE]   | 7     | [DESY - GERMANY]                   | 5     |
| [INSA - FRANCE]               | 5     | [UNIV CHEMNITZ - GERMANY]          | 5     |
| [UNIV TOULOUSE - FRANCE]      | 5     | [UNIV TUNIS - TUNISIA]             | 5     |
| [UNIV RENNES - FRANCE]        | 4     | [UNIV TOKYO - JAPAN]               | 4     |
| [UNIV NANCY - FRANCE]         | 4     | [WASEDA UNIV - JAPAN]              | 4     |

## Scientific contracts

The research in materials science is supported by a number of research contracts.

### National support:

- ANR MAGAFIL Magnetic nanowires as permanent magnet materials (2008-2010)
- ANR PROMETFOR Réalisation d' outillage de forge par un matériau à gradient fonctionnel obtenu par projection métallique
- ANR AX TREM Aciers ferritiques/martensitiques renforcés par nanoparticules pour application à haute température en conditions extrêmes (2008-2010).
- ANR AMARAGE Aciers martensitiques alliés de nouvelle génération : vers l'élaboration guidée par la maîtrise de la précipitation secondaire nanométrique (2007-2010)
- ANR NANOHP CUIVRE Recherche Collaborative sur Le Bronze Industriel (2009-2010)
- ANR NSF Structure et Dynamique de Liquides à liaison hydrogène
- ANR BIOSELF Auto-assemblages de nanogels et nano-composites bio-inspirés (2006-2010).

### Regional support

- C' nano FILASPIN Filtres à spins (2007-2009)
- RTRA: OCTUOMETRE: Octupole for 4-circle magnetic diffraction

### Transverse program of our governing bodies (CEA and CNRS)

- CEA/DSM-DAM: Neutron Irradiations
- CEA/DSM-DEN: SANS measurements on steel samples

### Other

- ECO-NET: Magnetic wave guides (2007-2008)

### Industrial contracts

- General Electrics: Determination of residual stresses in crankshafts
- Swiss Neutronics: Reflectivity Measurements on Guide coatings

### Other

### PhD theses defended, and in preparation, during the period 2008-2010

- Thomas Maurer (2007-2009) « Magnétisme de nano-objets anisotropes. »

- Matthieu Dubois (2009-2012) (LLB – Univ. Reims). « Analyse multi-échelle de l' état microstructural et mécanique d' un alliage à mémoire de forme cuivreux par diffraction des neutrons. »
- Shengyi Zhong (2009-2012) « Etude des hétérogénéités de déformation en corrélation avec la distribution de nano-renforts dans des aciers ODS. »
- Cynthia Mohamed-Said (2008-2011) (complete supervision – BDI thesis started October 2008)) Structural and optical properties of PNIPAM-coated gold nanoparticles
- A.S. Robbes (2008-2011) (co-tutelle SOLEIL) « Nanocomposites magnétiques : contrôle de la dispersion par greffage et orientation des charges sous champ externe »
- A. L. Fameau (2008-2011) (co-tutelle INRA Nantes) « 'Vers de nouveaux détergents : assemblages d' acides gras hydroxylés du volume aux interfaces, impact de la structure sur les propriétés moussantes et émulsifiantes' .

#### Post-docs working during the period 2008-2010

- Rim Dakhiloui (2008) (CEA/DEN/DANS/DMN/SRMA). « Contribution à l' étude des hétérogénéités des champs mécaniques dans un acier bainitique à l' aide de la diffraction des neutrons. »
- Francois Muller (2009-2010) l' ANR BIOSELF « Elaboration de nouveaux biomatériaux à base de cellulose »
- Mickael Perrut (2007-2009) Stage post-doctoral dans le cadre des ANR AMARAGE et aXtrem.
- Fatih Zighem (2009-2010). Stage post-doctoral dans le cadre de l' ANR MAGAFIL «Aimants permanents à base de nanofils. »
- Camila Alves Rezende - funded by DRI-CEA (05/2007-04/2008) "Nano-composites: bulk and surface structural properties."

#### Habilitation à Diriger les Recherches defended during the period 2008-2010

- Grégory Chaboussant. *Contribution de la diffusion des neutrons à l'étude des aimants moléculaires.* (Univ. Paris VI)
- Frédéric Ott. *Neutron scattering on magnetic nanostructures.* (Univ. Paris-Sud XI)

## **AXIS 3 Research: Soft Matter and Biophysics**

*Researchers (18):* C. Alba-Simionesco (CNRS), V. Arluison (Univ. Paris VII), F. Audonnet (Univ. Paris XI), M.-C. Bellissent-Funel (CNRS Emeritus), F. Boué (CNRS), A. Brûlet (CNRS), G. Carrot (CEA), S. Combet-Jeancenet (CNRS), F. Cousin (CEA), G. Fadda (Univ. Paris XIII), J. Jestin (CNRS), D. Lairez (CEA), A. Lapp (CEA), L.T. Lee (CNRS), S. Longeville (CEA), N. Malikova (CNRS), N. Brodie-Linder (Univ. Cergy-Pontoise), J. Teixeira (CNRS Emeritus), J.-M. Zanotti (CEA).

*Associated researchers (1):* E. Buhler (Univ. Paris VII)

*PhD students (11):* D. Bhowmik (2008-), G. Chahine (2008-), C. Chevigny (2006-2009), A.-L. Fameau (2008-), F. Gal (2008-), N. Jouault (2006-2009), A.-S. Robbes (2008-), C. Said (2008-), C. Le Coeur (2007-2010), K. Lagrené (2005-2008), J. Jelassi (2007-2010)

*Post-doc students (5):* I. Colinet (2008-2009), C. de Rezende (2007-2008), C. Thibierge (2009-2010), A. Koutsoumpas (2009-), F. Muller (2009-)

### Keywords

- SANS, reflectivity, inelastic scattering, polymer and particles chemical synthesis, rheology
- Complex fluids, polymers, surfactants, colloids, self-assembly, nanoparticles, grafting, nanocomposites, nanopores, multicomponents systems, selfassembly, gels and networks.
- Protein folding-unfolding, protein crowding, protein dynamics, proteins/polyelectrolyte, biocompatible polymers, biopolymers, water properties.
- Polymer dynamics, transport properties, diffusion, anomalous diffusion, slow dynamics, complex fluids dynamics, glass transition, confinement.



### **Scope**

In the field of soft matter, many complex new systems are flourishing. The emergence of these newfound capabilities, many of which marry different technologies and components, and work at the nanometer scale (1-100 nm) has become a major current trend. At LLB, research has progressed in similar directions, though some of the historical specificities of the lab, such as polymer research, are kept as main components. With the advantages of neutron scattering in mind (i.e., labeling and contrast matching), we often marry the reciprocal space (SANS and SAXS) with other techniques, either in real space or at macroscopic scales. The following topics are presently developed: nanoparticles and hybrid systems; organic systems and self-organization; polymer dynamics; and electrostatic complexes. In the following review, we will consider multicomponent systems that involve polymers, while differentiating between: 1) systems where one of the components is intrinsically nanosized (e.g., nanoparticles or nanopores), and the relevant structure and dynamics can be kept at a comparable size, depending on its interactions with the polymer; and 2) systems where the architecture of the basic elements is bound to lead to self-organization at the nano- or micro-scale.

Research at the interface of physics and biology is based on three main topics. 1) Proteins in complex media viewed as model systems for living environments. Experiments here are concerned with macro- or supra-molecular scales and their analysis is strongly influenced by our background in polymer physics, statistical physics, and phase transition physics. 2)

The local dynamics of proteins and hydration water in relation to the dynamic transition of proteins and their enzymatic activity. Neutron scattering techniques, which are very sensitive to protons, are particularly suitable for these studies. 3) Water and its specific properties are fundamentally related to life and to the very peculiar properties of some biological molecules, such as proteins. Here, the properties of water are studied in relation to the dynamics of hydrogen bond networks, and to the notions of hydrophobicity and confinement.

During the period from 2008 to 2010, 138 publications have been produced on these topics (51 in 2008, 36 in 2009, and 51 in 2010). The presented topics have also been the subject of 57 invited conferences. One *Habilitations à Diriger les Recherches* and 5 PhD have been defended.

The research in Soft Matter and Biophysics is also supported by a number of research contracts: 1 bilateral contract with Argentina, 7 national ANR contracts, 2 regional contracts within the RTRA and C'nano organizations, 2 industrial contracts.



## Current research

### Hybrid organic-inorganic systems: nanoparticles plus polymers, nanocomposites, and nanopores

These hybrid systems contain a combination of organic components (mainly polymers) and mineral components, and take the form of nanoparticles. Often such synthesis includes functionalization, or the grafting of polymers onto the surface of particles. This is done with various levels of partnership – from training, to external chemical synthesis in external laboratories, to in-house synthesis, for which our chemistry lab facilities are crucial.

### Direct dispersion of nanoparticles for well-defined structures and related properties

Our aim was to relate the mechanical reinforcement of polymer melts that contain nanoparticles (NP), as a model for nanocomposites (which include the case of filled rubber, as in tires), to the structure of NP dispersion and chain conformation, at rest and under deformation. We synthesized model nanocomposites having dispersions of nanoparticles at the desired levels (i.e. non-aggregated or partially aggregated), in clusters of various compaction/fractalness, and with various degrees of connectivity. The first route to prepare these model nanocomposites was to disperse them directly by mixing them with the solution and evaporating the solvent, which generated homogeneously dispersed fractal aggregates. This method allowed inter-aggregate distances to be controlled, as determined by TEM and SAXS and SANS (N. Jouault, PhD, 2009)<sup>1</sup>, with basically no global glass transition temperature ( $T_g$ ) shift. A first striking result was the strong increase in elastic modulus at low silica concentrations ( $\leq 5\%$ ), although aggregate distances between the NP were still in the non-connected range. If this result was due to the presence of “slowed down” regions around or between the particles, they would be expected to have sizes (between NP) greater than several tens of nm, which would be 10 times larger than the values proposed from fits of mechanical measurements, or than those extrapolated from high-temperature NMR analysis of different polymers.

A second striking result was obtained from deuterated chains under deformation: the behaviors of the chains and the matrix were similar<sup>2</sup>: the labeled chains inside the matrix deformed exactly as they did in the non-reinforced system (Fig. 3.1). Thus, there was no influence of slowing down, or of other interfacial or confinement phenomena.

<sup>1</sup> Well dispersed fractal aggregates as filler in polymer-silica nanocomposites: long range effects in rheology,

N. Jouault, P. Vallat, F. Dalmas, S. Said, J. Jestin, F. Boué, MACROMOLECULES **42**:2031 (2009)

<sup>2</sup> Direct SANS observation of stretched chain conformation in nanocomposites: more insight of polymer contributions in mechanical reinforcement,

N. Jouault, F. Dalmas, S. Said, E. Di-Cola, R. Schweins, J. Jestin, F. Boué, PHYS. REV. E. **82**:031801 (2010);

Direct measurement of polymer chain conformation in well controlled model nanocomposites by combining SANS and SAXS

N. Jouault, F. Dalmas, S. Said, E. Di-Cola, R. Schweins, J. Jestin, F. Boué, , MACROMOLECULES, **43**, 9881-9891 (2010).



## Organization

In essence, research in “ soft matter and biophysics” is interdisciplinary. At LLB, three groups are involved in this domain (“ soft matter”, “ biology and disordered systems”, and “ reflectivity” ). Neutron scattering and a variety of complementary techniques are used to study the structures and dynamics of polymers, complex fluids, colloids, surfactants, and biologically relevant systems. In many cases, the contrast variation capabilities of neutron scattering, as well as its sensitivity to protons, make this technology a very powerful tool for these studies.

Hence, experimental studies are organized around the small angle neutron spectrometers PACE, PAXE and PAXY; the new very small angle spectrometer, TPA; the time-of-flight spectrometer, MIBEMOL; the neutron spin echo spectrometer, MUSES; and the neutron reflectometer, EROS. Many experiments are also conducted using lighter devices.

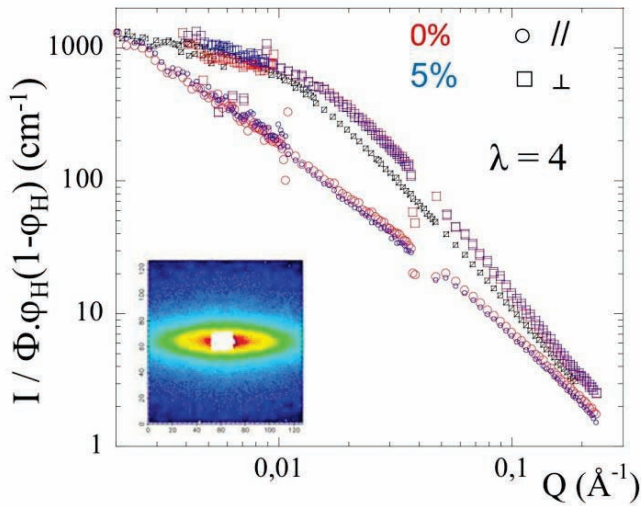
Additionally, these same groups are responsible for operating and upgrading their assigned spectrometers. They are also in charge of organizing the support for external visitors coming to perform experiments at the LLB. This organization allows the laboratory to operate the spectrometers efficiently by providing instruments that are constantly upgraded, and allows it to provide a high level of expertise in each respective technique, both of which greatly benefit all users of these instruments.

1. Small Angle Neutron Scattering (SANS) - to study large length-scale spatial correlations. LLB operates 5 SANS instruments: PAXY, PACE, PAXY, PAPYRUS (to be closed), and TPA (the new, very small angle scattering spectrometer).
2. Neutron reflectivity - for the study of solid/fluid and fluid/fluid interfaces. Two reflectometers are operated for these studies: EROS and PRISM.
3. Inelastic neutron scattering - to study dynamic properties. The Time-of-Flight spectrometer, MIBEMOL; as well as the Spin-Echo spectrometer (Zero Field), are used primarily for these studies.
4. Other equipment:
  - a. Rheometers, shearing and stretching devices, light scattering, opticam microscope, confocal microscope, voltage-clamp measurements.
  - b. Chemistry and physico-chemistry equipment, for synthesis (e.g., fume hoods) and characterization, UV and IR spectroscopy, DSC and TGA, and permeation-adsorption measurements.
  - c. Biology equipment: DNA analysis and production techniques (e.g., thermocyclers, gel migration, and gel imaging); recombinant protein preparation (microbiology equipment); sonicator; protein separation (FPLC) and characterization (SDS-PAGE, Western-blotting); UV and IR fluorescence spectroscopy, centrifugation, cold room, -80° C freezer.

Reinforcement at large deformation can therefore be decomposed into a chain contribution, which is independent from the filler fraction, and a filler contribution, which increases with  $\phi$  but is essentially constant with deformation. This suggests progressive rearrangement of particles when they hit, which is analogous to buckling.

More studies of direct polymer – inorganic mixtures, from a materials science view point, are shown in Axis 2. Examples discussed are Hevea Latex plus clay platelets<sup>3</sup>; latex<sup>4</sup>; and melting that is anisotropically reinforced by magnetic nanoparticles under field.

<sup>3</sup> *Nanoclay natural latex composites: structure and reinforcement under high deformation*, L.T.Lee, C. Rezende, T. Doi, F. Boué, POLYMER 51:3644 (2010)

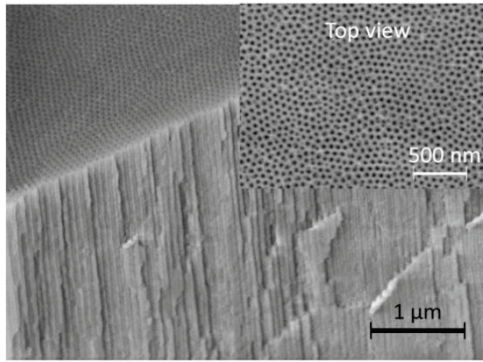


**Figure 3.1.** Comparison of chain deformation between unfilled polymer (red) and nanocomposites (blue): Scattering signal (log-log) of deformed chains in pure polymer and filled with 5%v/v (blue curves) in directions // and  $\perp$  to stretching for elongation ratios  $\lambda=4$ .

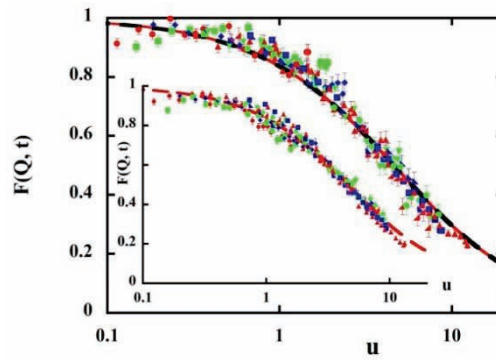
### Single polymer chain dynamics under nanometric confinement

Confinement is thought to deeply modify the dynamic properties of polymers. Recent NMR relaxometry results have suggested that the confinement of a polymer melt in a nanoscopic isotropic porous matrix leads to chain dynamics that are dramatically different from their dynamics in bulk, i.e., the reptation tube diameter under confinement would be only a few angstroms; or one order of magnitude smaller than in the bulk. This would actually correspond to a situation where the chain experiences reptation alongside its own physical contour so that this phenomenon has been called the *corset effect*.

We have challenged the existence of this *corset effect* in a neutron spin-echo (NSE) experiment. We demonstrated how NSE, combined with contrast matching and zero average contrast (ZAC), allowed us to simultaneously (i) match the intense porous detrimental elastic small angle neutron scattering contribution to the total intermediate scattering function  $I_{\text{Chain}}(Q, t)$ , and (ii) measure the  $Q$  dependence of the dynamic modes of a single chain under confinement<sup>5</sup>.



**Figure 3.2.** Scanning electron microscope image of an Anodic Aluminium Oxide membrane<sup>6</sup>. A highly oriented array of cylindrical pores (radius 9 nm) goes from the top down to the bulk of the membrane.



**Figure 3.3.**  $F(Q, t) = I_{\text{Chain}}(Q, t) / I_{\text{Chain}}(Q, t=0) - P(Q) / (1 - P(Q))$  versus reduced time Rouse parameter  $u = Q^2 \sqrt{W t}$ , for the confined and bulk polymer (inset).  $P(Q)$  is the form factor of the reptation tube. The tenfold reduction of the reptation tube diameter predicted by the “corset effect” is not observed.

Our measurements obtained on Poly(Ethylene Oxide) (PEO) chains in Anodic Aluminium Oxide membrane (AAO) (K. Lagrené, PhD 2008) are in contradiction with a tenfold reduction of the reptation tube diameter predicted by the “corset effect”<sup>5</sup> (Figs. 3.2 & 3.3). The method

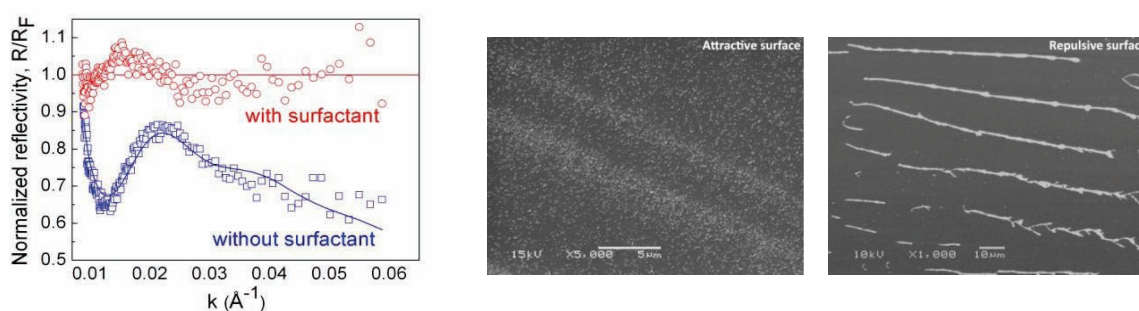
<sup>4</sup> Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network, J. Jestin, F. Cousin, I. Dubois, C. Ménager, J. Oberdisse, R. Schweins, F. Boué, ADV. MAT. **20**:2533 (2008)

<sup>5</sup> Large-scale dynamics of a single polymer chain under severe confinement, K. Lagrené, J.-M. Zanotti, M. Daoud, B. Farago, P. Judeinstein, Phys. Rev. E **81**:060801 (2010)

developed has a general relevance when probing the large scale dynamics of a system of large molecular mass under confinement. The use of the host porous material as an electrolyte for lithium batteries has been extended to a patent<sup>6</sup>.

### Templating nanoparticle surface assembly by polymer dewetting patterns

Here, we used specific interactions between a polymer and nanoparticles to foster self-organization on a substrate. For functional applications, the assembly process must be directed in order to obtain open and complex arrays. Different approaches for this include the use of external electric field force, chemically pre-patterned substrates, and biomolecular templates. Our alternative approach was to use the dewetted morphologies of a polymer solution to template nanoparticle organization. An aqueous solution of non-ionic polymer will dewet a substrate to form different morphologies, which depend on the physicochemical properties at work and the drying conditions. We used elongated dewet patterns to template nanowires / nanoyarns of nanoparticles via a two-stage mechanism: nucleation of an ordered phase by lateral capillary attractions, which confined the nanoparticles in the dewet pattern; and convective transport of the particles towards the ordered region in order to grow the ordered nanoparticle array. The efficiency of this process was diminished, however, due to the presence of particle-substrate attraction, which hinders convective transport such that the formed nanostructures coexist with a non-organized phase. Neutron reflectivity showed that such nanoparticle attachment could be suppressed by adding an anionic surfactant (Fig. 3.4, left). These results, in conjunction with well-controlled drying conditions, enabled us to direct the formation of nanoyarn arrays that were longer than several tens of microns<sup>7</sup> (Fig. 3.4, right).



**Figure 3.4.** Normalized neutron reflectivity showing strong adsorption of polymer-coated silica nanoparticles at a model hydrophobic interface (water-air). Addition of a charged surfactant transforms the attractive surface to a repulsive one, resulting in displacement of the nanoparticles from the surface ( $R/R_F = 1$ ). Similar suppression of nanoparticle adhesion on a solid substrate promotes long range organization of nanoyarns templated by dewetting morphology (SEM images).

### Grafted nanoparticles

Following the pioneering work on nanosilica<sup>8</sup>, the chemistry of grafting has become an important theme in the laboratory. It is now largely developed along new chemical syntheses for each different application. From the thesis work of J. Vinas (PhD, 2008), routes for synthesizing silica and its direct subsequent grafting to hydrosoluble polymers, including a new initiator<sup>9</sup>, have been developed in the CROPS group of Marseille and studied at LLB.

<sup>6</sup> Membrane minérale électrolytes pour dispositifs électrochimiques,

J.-M. Zanotti, K. Lagrené, BREVET n°FR 10/56178

<sup>7</sup> Liquid-templating for nanoparticle organization into complex patterns,

C.A. Rezende, L.T. Lee, F. Galembeck, LANGMUIR **23**:2824 (2007)

Silica nanoparticles at interfaces modulated by amphiphilic polymer and surfactant,

C.A. Rezende, L.T. Lee, Galembeck F., LANGMUIR **24**:7346 (2008);

Surface mechanical properties of thin polymer films investigated by AFM in pulsed force mode,

C.A. Rezende, L.T. Lee, Galembeck F., LANGMUIR **25**:9938 (2009)

<sup>8</sup> Surface-atom transfer radical polymerization from silica nanoparticles with controlled colloidal stability,

A. El Harrak, G. Carrot, J. Oberdisse, C. Eychenne-Baron, F. Boué, MACROMOLECULES **37**:6376 (2004)

<sup>9</sup> SG1-based alkoxyamine bearing a N-succinimidyl ester: A versatile tool for advanced polymer synthesis,

SG1 and BLOCBUILDER® technology: a versatile toolbox for the elaboration of complex macromolecular architectures,

J. Vinas, N. Chagneux, D. Gigmes, T. Trimaille, A. Favier, D. Bertin, Polymer, **49**:3639 (2008) ;

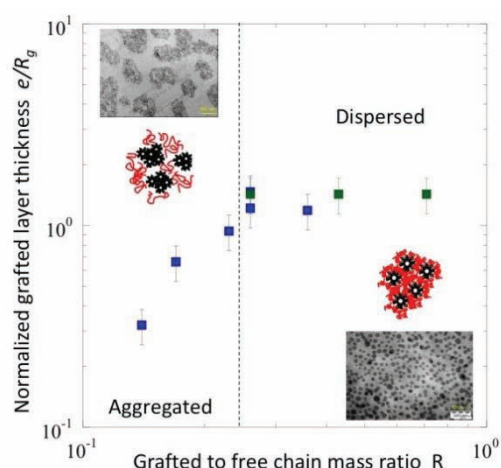


Currently, gold nanoparticles are being grafted by C. Said (PhD) to thermosensitive polymer permitting the distance between particles and the optical properties (plasmon resonance) to be controlled (see “Projects”). In between these efforts, two different grafting approaches were developed, which are detailed in the next section.

### Inclusion of grafted nanoparticles in polymer for mechanical properties

Model nanocomposites for reinforcement studies can also take the form of grafted nanoparticles in polymer. This second route of nanocomposite preparation focuses on using the chemical interactions between the matrix and fillers to influence reinforcement. Nanosilica-controlled grafting was performed through Nitroxide Mediated Polymerization (C. Chevigny, PhD 2009, in collaboration with D. Gigmes & D. Bertin, Univ. Marseille-Aix), using a MAMA-SG1 (BlocBuilder™) -derived alkoxyamine bearing a N-succinimidyl (NHS) ester group, which allowed grafting to silica. This new grafting technique produces well-dispersed single nanoparticles in organic solvent, which are characterized as having an individual core with a polymer corona<sup>10,11</sup>. We are currently extending this method to grafting from the surface of magnetic (maghemite) nanoparticles<sup>12</sup> (PhD of A.-S. Robbes).

One advantage to using these particles is that the various states of dispersion for the particles in the polymer matrix, from lumps to individually dispersed particles, can be controlled by varying the ratio (R) of the grafted chain mass over matrix chain mass, as shown by SAXS and TEM<sup>13</sup>. This is shown in Figure 3.5 below, which also shows an apparent correlation with the thickness of the corona. The latter could be extrapolated from SAXS analysis in all dispersion states, and was subsequently confirmed by direct measurement in the dispersed state using a combination of SAXS and SANS<sup>14</sup>. Corona thickness decreases with respect to its value in solvent, and also decreases when passing into the aggregated state. The same corona form factor measurement could be achieved in the deformed state, so that we were able to follow the effect of the stress on such coronae. Under stretching, corona deformation was found to be comparable to the deformation of the matrix. We also found that particle arrangement in response to deformation is dominated by the local inter-particle interaction. Finally, these mechanical measurements enlighten our understanding of the non-grafted particle dispersion described above.



**Figure 3.5.** Corona thickness versus grafted/matrix mass ratio in model nanoparticles

D. Gigmes, J. Vinas, N. Chagneux, C. Lefay, T. N. T. Phan, T. Trimaille, P. E. Dufils, Y. Guillauneuf, G. Carrot, F. Boué, D. Bertin, ACS Symposium Series, Advances in Controlled/Living Radical Polymerization", Krzysztof Matyjaszewski Ed., 2009.

<sup>10</sup> Polystyrene grafting from silica nanoparticles via nitroxide-mediated-polymerization (NMP): synthesis and SANS analysis with contrast variation method,

C. Chevigny, D. Gigmes, D. Bertin, J. Jestin, F. Boué, SOFT MATTER **5**:3741 (2009)

<sup>11</sup> Controlled grafting of polystyrene on silica nanoparticles using NMP: a new route without free initiator to tune the grafted chain length,

C. Chevigny, D. Gigmes, D. Bertin, R. Schweins, J. Jestin, F. Boué, POLYMER CHEMISTRY, Communication, **2**, 567-571 (2011).

<sup>12</sup> Homogeneous dispersion of magnetic nanoparticles aggregates in a PS nanocomposite: highly reproducible hierarchical structure tuned by the nanoparticles' size,

A.-S. Robbes, J. Jestin, F. Meneau, F. Dalmas, O. Sandre, J. Perez, F. Boué, F. Cousin, MACROMOLECULES **43**:5785 (2010)

<sup>13</sup> Polymer-grafted-nanoparticles nanocomposites: dispersion, grafted chain conformation and rheological behavior,

C. Chevigny, F. Dalmas, E. Di Cola, D. Gigmes, D. Bertin, F. Boué, J. Jestin, MACROMOLECULES **44**: 122–133 (2011).

<sup>14</sup> "Wet-to-dry" conformational transition of polymer layers grafted to nanoparticles in nanocomposites,

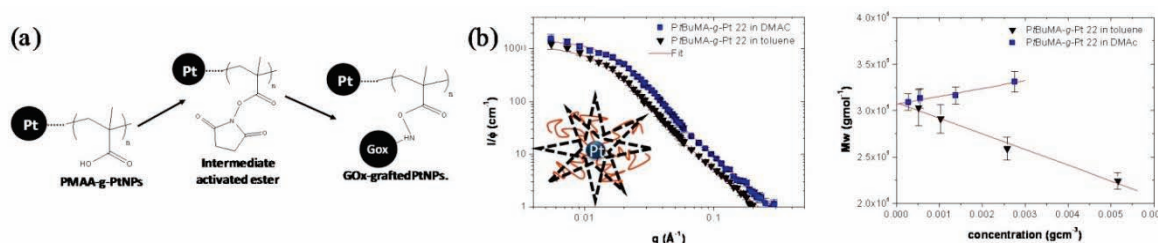
C. Chevigny, J. Jestin, D. Gigmes, R. Schweins, E. Di Cola, F. Dalmas, D. Bertin, F. Boué, MACROMOLECULES, **43**:4833 (2010)



## Nanocomposites for biology

Another development of our pioneering work in grafting of polymers onto nanosilica via controlled polymerization (surface-ATRP)<sup>8, 15</sup>, is now to functionalize platinum nanoparticles (Pt-NPs<sup>16</sup>).

**Enzyme/polymer-grafted platinum nanoparticles: towards construction of glucose probes.** The thesis work of F. Gal (PhD defense, Nov 2010), in collaboration with H. Perez (IRAMIS/SPAM), showed that polymer-grafted-PtNPs could be chemically modified at different stages to form bio-hybrid objects. The first stage involves surface-ATRP, followed by an hydrolysis step to form a poly(methacrylic acid) corona. Finally, the latter is activated in order to bind enzyme (Fig. 3.6)<sup>17</sup>. Using contrast matching data from the Pt core, and the signal from polymer corona, we determined: that the particles were well dispersed (no aggregation); the size and number of grafted chains per object; and the size of the object (Fig. 3.6). Extrapolation at zero concentration yielded the total molecular weight of all chains<sup>16,17</sup>. Then, to study the electrochemical properties of protein/polymer-grafted-PtNPs, it was necessary to transfer these nano-objects onto electrodes, using the Langmuir-Blodgett technique for depositing homogeneous films onto a gold surface. Controls of homogeneity, thickness, and roughness, were attested by neutron reflectivity and TEM.



**Figure 3.6.** (Left) Synthesis of the glucose oxidase (Gox)-poly(methacrylic acid)-grafted-PtNPs: Activation of the PMAA-g-PtNPs with N-hydroxy-succinimide (NHS) and subsequent binding of the glucose oxidase. (middle) Relative scattered intensity  $I/q$  in cm<sup>-1</sup> as a function of scattering wave vector in Å<sup>-1</sup> of PtBuMA-g-Pt 22 in 100% d-toluene and DMAC (95.7% d, 4.3% h). (Right) Molecular weight of the scattering objects as a function of the concentration.

**Grafting biocompatible polymers onto nanoparticles via click chemistry.** The main limitations of the “grafting from” approach (described above) are that our polymerization route is restricted to the use of only vinylic monomers, and that the length of the grafted-from polymer chains is difficult to determine. Due to these limitations, there was great interest in developing a “grafting to” approach for grafting various well-defined preformed polymers, such as the biocompatible polymers PEG and PCL, directly onto PtNPs for their use in biosensor and targeted drug delivery applications. In this scope, the recently developed concept of click chemistry was particularly attractive<sup>18</sup>. The most reliable example of this is copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) that exclusively yields 1,4-disubstituted 1,2,3-triazole linkages. This reaction is highly efficient, tolerant to a wide range of functional groups, and uses mild conditions in protic or aprotic solvents. Our novel “grafting to” approach for the functionalization of PtNPs uses complementary combinations of CuAAC and polymer chemistry<sup>19,20</sup>. For example, tailor-made PtNPs having bromide

<sup>15</sup> Polymer grafting from 10-nm individual particles: proving control by neutron scattering, G. Carrot, A. El Harrak, J. Oberdisse, J. Jestin, F. Boué, SOFT MATTER 2:1043 (2006)

<sup>16</sup> Polymer-grafted-platinum nanoparticles: from three-dimensional small angle neutron scattering study to tunable two-dimensional array formation,

Carrot G., Gal F., Cremona C., Vinas J., Perez H., LANGMUIR 25:471 (2009)

<sup>17</sup> Protein/polymer-grafted platinum nanoparticles: towards the construction of glucose probes, F. Gal, V. Noel, H. Perez, G., POLYMER PREP. 51:216 (2010)

<sup>18</sup> V. Rostovtsev et al., ANGEW. CHEM. INT. ED. 41: 2596 (2002)

<sup>19</sup> Smart combination of “grafting from” and “grafting to” for the design of 2D and 3D hybrid architecture, G. Carrot, S. Al-Akhrass, I. Colinet, F. Gal, D. Damiron, E. Drockenmuller, POLYMER PREP. 51: 220 (2010)

<sup>20</sup> Efficient approaches for the surface modification of platinum nanoparticles via click chemistry, E. Drockenmuller, I. Colinet, D. Damiron, F. Gal, H. Perez, G. Carrot, MACROMOLECULES (2010) (DOI: 10.1021/ma102188d).

functionalities at their surface (Br-PtNPs) were converted to azido-functionalized PtNPs (N3-PtNPs) by substituting the bromide atoms for sodium azide (NaN<sub>3</sub>) groups. In parallel, ω-alkyne PCL and PEG were respectively obtained by esterification of PCL with pentynoic acid, and by alkylation of monomethoxy-PEG with propargyl bromide. After the CuAAC “grafting to” process, we obtained relatively high grafting densities (0.7 to 1.75 chains/nm<sup>2</sup> as determined by thermogravimetric analysis of the organic content). SANS measurements showed that the radius of gyration (R<sub>g</sub>) of the polymer corona increased slightly (5.9 to 7.7 nm) as the molecular weight of the polymer precursors was increased. Moreover, the intensity at low-q values is consistent with the complete grafting of all chains and a non-aggregated state of the hybrid PtNPs. Thus, the CuAAC “grafting to” method successfully functionalized PtNPs with biocompatible polymers. The same strategy is being applied to functionalize silicon nanoparticles with PEG (with N. Herlin, IRAMIS/SPAM). These silicon-based objects are potentially available for use as biomarkers, and have the added advantage being photoluminescent.

## Supramolecular polymer organization

Supramolecular polymers are an increasingly important class of polymers, in which designed intermolecular interactions allow the polymer's properties to be specifically tailored. Numerous studies have focused on the structures and properties of these molecules.

### Dynamic supramolecular polymers

Dynamic supramolecular polymers consist of reversibly associated monomers that connect to each other via reversible covalent bonds or non-covalent bonds (e.g., hydrogen bonds). Due to their dynamic nature, the structure, length, and composition of these polymers are amenable to evolving in response to varied polymerization conditions (e.g., temperature, pH variation, monomer concentration, shear stress, presence of a molecular target, etc.). Due to these constitutional changes, they can be envisaged as smart materials<sup>21,22,23,24,25,26,27</sup>. By altering the reversibility of the monomer connections in response to physical and/or chemical effectors<sup>21,24</sup>, the team of Prof. J.-M. Lehn at ISIS-Strasbourg has developed novel polymer features which ultimately affect their structural ordering and dynamic nature. In addition, the group of Prof. N. Giuseppone at ICS-Strasbourg has developed responsive combinatorial mesophases from libraries of dynamic block copolymers (Dynablocks)<sup>25,27</sup>. These types of studies are opening the way to biologically inspired polymer structuring on the nano- and micro-scales.

### Block copolymers for vesicle-like tunable structures

Polymer vesicles that can be obtained from hydrophilic/hydrophobic diblock copolymers have attracted considerable attention due to an array of beneficial properties (e.g., toughness, stability, tailorable size, and membrane properties<sup>28</sup>), which make them attractive candidates for a number of important applications, including encapsulation, drug delivery, nanoreactors, and templates for micro- or nano-structured materials. Many applications require the ability to control the release of substances encapsulated in the interior compartment and/or in the hydrophobic core of membrane. To address this goal, we developed polymersomes, in which specific external stimuli are able to destabilize the vesicle structure. Diblock copolymer vesicles, studied in collaboration with Dr. M.H. Li (Institut Curie, Paris), are intrinsically responsive to external physical stimuli, such as UV irradiation or a magnetic field. Indeed, the hydrophobic

<sup>21</sup> *Reversible constitutional switching between macrocycles and polymers induced by shape change in a dynamic covalent system*, S. Ulrich, E. Buhler, J. M. Lehn, NEW J. CHEM. **33**: 271 (2009)

<sup>22</sup> *Room temperature dynamic polymers based on Diels-Alder chemistry*,

P. Reutenauer, E. Buhler, P.J. Boul, S. J. Candau, J. M. Lehn, CHEM. EUR. J. **15**:1893 (2009)

<sup>23</sup> *Glycodynamers: dynamic polymers bearing oligosaccharides residues - generation, structure, physicochemical, component exchange, and lectin binding properties*,

Y. Ruff, E. Buhler, S. J. Candau, E. Kesselman, Y. Talmon, J. M. Lehn, J. AM. CHEM. SOC. **132**:2573 (2010)

<sup>24</sup> *Cooperative bottom-up generation of rigid-rod nanostructures through dynamic polymer chemistry*,

J. F. Folmer-Andersen, E. Buhler, S. J. Candau, M. Schmutz, J. M. Lehn, POLYM. INT., published online (2010)

<sup>25</sup> *Dynamic combinatorial evolution within self-Replicating supramolecular assemblies*,

R. Nguyen, L. Allouche, E. Buhler, N. Giuseppone, ANGEW. CHEM. INT. ED., **48**:1093 (2009)

<sup>26</sup> *Dynablocks: structural modulation of responsive combinatorial self-assemblies at mesoscale*,

R. Nguyen, E. Buhler, N. Giuseppone, MACROMOLECULES **42**:5913 (2009)

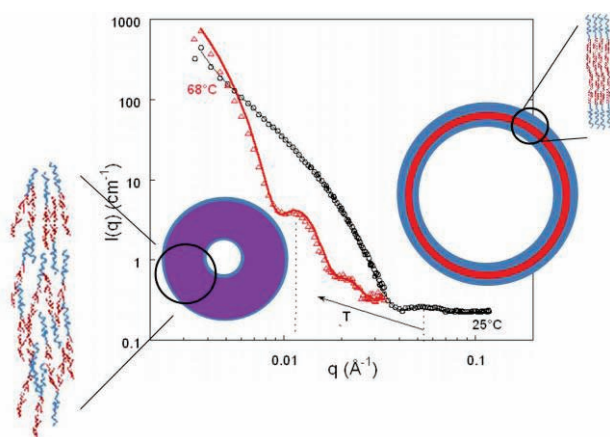
<sup>27</sup> *The hierarchical self-assembly of charge nano-carriers: a highly cooperative process promoted by visible light*,

E. Moulin, F. Niess, M. Maaloum, E. Buhler, I. Nyrkova, N. Giuseppone, ANGEWANDTE **49**:6974 (2010)

<sup>28</sup> *pH and temperature responsive polymeric micelles and polymersomes by self-assembly of poly[2-(dimethylamino)ethyl methacrylate]-b-[poly(glutamic acid)] double hydrophilic block copolymers*,

W. Agut, A. Brûlet, C. Schatz, D. Taton, S. Lecommandoux, LANGMUIR **26**:10546 (2010)

group is an azobenzene-containing liquid crystal (LC) polymer. Upon *in situ* application of a magnetic field and elevated temperature, huge increases in the thickness of the vesicle membrane (Fig. 3.7) caused by partial dehydration of the hydrophilic bloc and mixing with LC polymer have been measured<sup>29</sup>.



**Figure 3.7.** Temperature variation of SANS by vesicular structures obtained with LC block-polyethylene glycol “polymersomes”.

With the group of S. Lecommandoux (LCPO-Bordeaux), we studied new hybrid vesicles made from biodegradable amphiphilic block copolymers and magnetic nanoparticles (NP). SANS experiments performed in different contrast conditions showed that high loading of magnetic NP inside the vesicle membrane could be prepared.<sup>30</sup> These magnetic vesicles have properties suitable for biomedical applications, including: being guided by an external magnetic field gradient; producing local hyperthermia under application of an oscillating magnetic field; and contrast enhancement in Magnetic Resonance Imaging with a nanomolar detection limit.

#### Multiple steps in the organization of alpha-CD/PEO based polyrotaxanes

Polyrotaxanes (PR) comprise another dynamic supramolecular system, which consists of a stable supramacromolecular pearl necklace assembly of macrocycles (here  $\alpha$ -cyclodextrins) on a template polymer chain (here PEO). In a first stage of synthesis, N  $\alpha$ -CDs (N depending on affinity with PEO) are threaded along PEO chains in aqueous solution, resulting in so-called pseudo-polyrotaxane (PPR). In the second stage, capping both ends with bulky groups prevents decomplexation, and leads to the polyrotaxane. If N is high, this allows further functionalization of the PRs, which may include crosslinking to form supramolecular “sliding” gels (S-Gels). Neutron scattering experiments have been performed to describe the kinetics of self-organization of pseudo-polyrotaxanes in water<sup>31</sup>. PPRs are obtained by quenching an  $\alpha$ -CD/PEO mixture in water from 70°C down to  $T < 30^\circ\text{C}$ , and is possible due to favorable interactions between the  $\alpha$ -CD cavities and the PEO chains. At 30°C, the kinetics of formation of the physical gel are slow enough to distinguish:

- In the first step,  $\alpha$ -CDs thread onto PEO chains, forming PPR molecules for which water is a bad solvent, thus, these molecules rapidly aggregate to form threaded  $\alpha$ -CD based nanorods. At a higher length scale, the nanorods associate in a Gaussian way and form precipitated domains.
- After 20 min, the system remains liquid, and reorganizes only after more than 150 min, when the precipitated domains compact and form a physical gel.

At intermediate temperatures, the structure formed is a multiblock copolymer<sup>32,33</sup> with alternating rigid blocks of  $\text{st}_{\text{rod}}$  of  $\approx 7$  nm, and flexible naked

<sup>29</sup> Structural changes induced by temperature variation and magnetic field in liquid crystal polymer vesicle,

S. Hocine, A. Brûlet, L. Jia, J. Yang, A. Di Cicco, L. Bouteiller, M.H. Li, submitted to SOFT MATTER

<sup>30</sup> Dorubicin loaded magnetic polymersomes: a multifunctional nanocarrier for theranostics

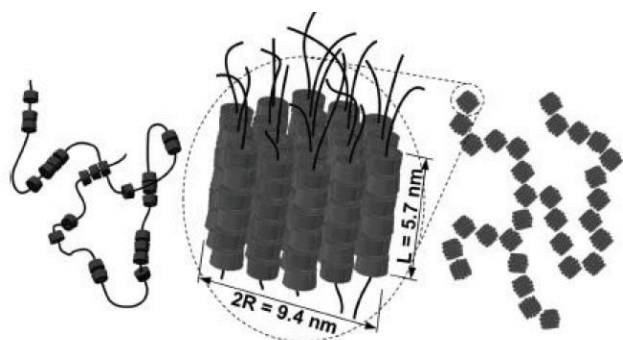
Ch. Sanson, O. Diou, E. Ibarboure, A. Brûlet, S. Miraux, O. Sandre, S. Lecommandoux, submitted to J. AM.CHEM. SOC.

<sup>31</sup> Formation and Self-Organization Kinetics of alpha-CD/PEO-Based Pseudo-Polyrotaxanes in Water. A Specific Behavior at 30°C, C. Travelet, G. Schlatter, P. Hébraud, C. Brochon, A. Lapp, G. Hadzioannou, LANGMUIR 25:8723 (2009)

<sup>32</sup> Multiblock copolymer behaviour of alpha-CD/PEO-based polyrotaxanes: towards nano-cylinder self-organization of alpha-CDs, C. Travelet, G. Schlatter, P. Hébraud, C. Brochon, A. Lapp, D. Anokin, D. Ivanov, C. Gaillard, G. Hadzioannou, SOFT MATTER 4:1855 (2008)

PEO segments. Hence, on cooling to room temperature, the naked PEO segments crystallize, but the  $\alpha$ CD rod-like tubes aggregate to form regular nano-bundles whose size is limited to the nanometric scale because the naked PEO moieties act as a compatibilizer (Fig. 3.8). In this way, the nanometric scale and the gel's transparency are preserved.

Finally, a new class of polymer networks with sliding crosslink points can be obtained, based on the crosslinking of some  $\alpha$ cyclodextrins of the polyrotaxane precursors: the crosslink points created are not fixed but can slide along the chain of polyrotaxane).



**Figure 3.8.** Schematic representation of a PPR molecule showing  $\alpha$ CD rod-like tubes and naked PEO segments; a threaded  $\alpha$ CD based nanorod (at a higher length scale); and the nanorod associated in a Gaussian way.

### Asphaltene aggregates: oil-water emulsions and deposition mechanisms

Transportation of heavy crude oil is facilitated by using emulsions, which abate the oil's viscosity to that of water. Knowing the fine structure of these oil-water interfaces explains their macroscopic stability. With the Institut Français du Pétrole, we developed a protocol for a SANS study of oil macro-emulsions stabilized by asphaltenes. Contrast matching gives access to the composition and the quantity of the interface: it is made of a monolayer of asphaltene aggregates, the thickness of which directly correlates to the size (volume) of the aggregates. Emulsion stability was found to improve when the interactions between aggregates inside the film are strengthened<sup>34</sup>. During transport or production of crude oil, reduced pressure will induce flocculation of asphaltene aggregates, causing adsorption or deposition of aggregate multilayers, which may lead to plugging. To investigate this problem, we used neutron reflectivity to study asphaltene adsorption on various model surfaces. Under static conditions, the aggregates adsorb in a dense monolayer having a thickness close to the size of the aggregates in solution (10 nm)<sup>35</sup>. Following addition of a bad solvent, there is a transition towards an adsorption profile that consists of multiple layers. Under *in situ* shear, we evidenced a critical shear rate, above which multilayer deposition saturates. Thus, it is possible to control local deposition by adjusting the flow rate inside the pipes<sup>36</sup>. We also used SANS to study asphaltene deposition mechanisms inside porous media<sup>37</sup>, and used very dilute solutions to accurately characterize the aggregates using SAXS and SANS<sup>38, 39</sup>.

### Electrostatic-based complexes: the role of the polyion

Electrostatics is a driving force that is frequently used to create complex systems from two components having opposite electrostatic charges. Initially, we used polystyrene sulfonate (PSS), which has been the subject of detailed studies, in either full or partially sulfonated

<sup>33</sup> Temperature-Dependent Structure of  $\alpha$ -CD/PEO-Based Polyrotaxanes in Concentrated Solution in DMSO: Kinetics and Multiblock Copolymer Behavior,

C. Travelet, P. Hébraud, C. Perry, C. Brochon, G. Hadziioannou, A. Lapp, G. Schlatter, MACROMOLECULES **43**:1915 (2010)

<sup>34</sup> A Small Angle Neutron Scattering study of crude oil emulsions. Structure of the oil-water interfaces,

G. Alvarez, J. Jestin, J.-F. Argillier, D. Langevin, LANGMUIR **25**:3985 (2009)

<sup>35</sup> Asphaltene adsorption mechanisms at the local scale probed by neutron reflectivity: transition from mono to multilayer growth above flocculation threshold,

N. Jouault, Y. Corvis, F. Cousin, J. Jestin, L. Barré, LANGMUIR **25**:3991 (2009)

<sup>36</sup> Relation between solution and interfacial properties of asphaltene aggregates,

S. Simon, J. Jestin, T. Palermo, L. Barré, ENER. FUELS, **23**:306 (2009)

<sup>37</sup> Asphaltene multilayer growth in porous medium probed by SANS,

J. Gummel, Y. Corvis, J. Jestin, J. M'Hamdi, L. Barré, EUR. PHYS. J. Special Topics, **168**:171 (2009)

<sup>38</sup> Relation between nanoscale structure of asphaltene aggregates and their macroscopic solution properties,

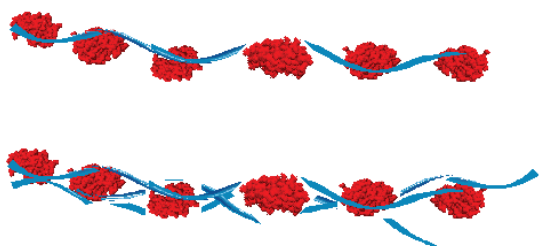
L. Barré, J. Jestin, A. Morisset, T. Palermo, S. Simon, OIL & GAS SCIENCE AND TECHNOLOGY, **64**:617 (2009)

<sup>39</sup> Insight into asphaltene nano-aggregate structure inferred by small angle neutron and X-ray scattering,

J. Eyssautier, P. Levitz, D. Espinat, J. Jestin, J. Gummel, I. Grillo, L. Barré, (submitted to J. AM.CHEM. SOC.)



versions<sup>40</sup> that were complexed with lysozyme, a small globular protein. PSS can be advantageously deuterated for different types of contrast experiments, we were able to characterize the threshold between a gel state and a globular structure. Additionally, we defined the counterions released from the globule<sup>41</sup>, the contents in both components, the relation between the size and the screening length<sup>42</sup>, the polyion chain conformation<sup>43</sup>, and the possible reorganization of these globules<sup>44</sup>. In order to understand the role of the polyion in such complexes, we investigated the effect of increasing the rigidity of the backbone. This led us to use semi-rigid polysaccharides (biopolymers), which have a wide range of applications since such complexes are frequently used in the field of natural materials (food, pharmacy, biology). Unfortunately, deuterated versions of these polymers are not available, but due to the similarities between polysaccharides complexed with lysozyme or pectin<sup>45</sup> and PSS-lysozyme complexes, we have been able to profit from the knowledge obtained from deuterated PSS complexes. Surprisingly, for lysozyme complexed with hyaluronan, a very regular biopolymer, the scattering signals indicate a new structure, namely very well-defined rodlike complexes (Morfin<sup>46</sup> ; see Fig. 3.9). From the point of view of soft matter, data obtained from the latter system suggested the possible existence of “single complexes” leading to phase separation, which is one of the favored hypothesis for “complex coacervation” (see Axis 3: Projects).



**Figure 3.9.** Elementary rodlike complex between lysozyme and Hyaluronan chain, single (up) or multiple (down).

### Protein interactions with DNA<sup>47</sup>

In this area, we have established patterns of interaction between DNA and Hfq, a bacterial protein involved in nucleic acid structuring and whose mechanism remains unclear. We examined the conformation of DNA bound to Hfq by combining vibrational spectroscopy and neutron scattering. Our analysis revealed that Hfq, which preferentially interacts with deoxyadenosine-rich regions (A-tracts), induces partial opening of double stranded dA-dT sequences, which is accompanied by a conformational change in the sugars of the dA strand. We observed that this conformational change correlated with dehydration of the DNA when it is complexed with the protein. By taking into account Hfq's preferential binding to A-tracts, which are commonly found in transcriptional promoters, the biological implications of Hfq binding to DNA are of primary importance. Thus, we are currently trying to analyze the geometry and stoichiometry of complexes of Hfq and DNA, using templates of defined sizes. These results are combined with atomic force microscopy and electron microscopy in order to scan the complexes at different scales (Å to μm).

<sup>40</sup> *Hydrophobic polyelectrolytes in better polar solvent. Structure and chain conformation as seen by SAXS and SANS*, W. Essafi, M.N. Spiteri, C. E. Williams, F. Boué, *MACROMOLECULES* **42**:9568 (2009)

<sup>41</sup> *Counterions release from electrostatic complexes of polyelectrolytes and proteins of opposite charge: a direct measurement*, J. Gummel, F. Cousin, F. Boué, *JACS* (communication) **129**:5806 (2007)

<sup>42</sup> *Finite size and inner structure controlled by electrostatic screening in globular complexes of proteins and polyelectrolytes*, J. Gummel, F. Boué, D. Clemens, F. Cousin, *SOFT MATTER* **4**:1653 (2008)

<sup>43</sup> *Structure transition in PSS/lysozyme complexes: a chain-conformation-driven process, as directly seen by small angle neutron scattering*

J. Gummel, F. Cousin, F. Boué, *MACROMOLECULES* **41**: 2898 (2008)

<sup>44</sup> *Multiscale reorganization of electrostatic complexes of PolyStyreneSulfonate and lysozyme*, F. Cousin, J. Gummel, D. Clemens, I. Grillo, F. Boué, *LANGMUIR* **26**:7078 (2010)

<sup>45</sup> *Spatial structure and composition of polysaccharide-protein complexes from small angle neutron scattering*

I. Schmidt, F. Cousin, C. Huchon, F. Boué, M. A.V. Axelos, *BIOMACROMOLECULES* **10**:1346 (2009)

<sup>46</sup> *Rodlike Complexes of a Polyelectrolyte (Hyaluronan) and a Protein (Lysozyme) observed by SANS*,

I. Morfin, E. Buhler, F. Cousin, I. Grillo, F. Boué. *ASAP Biomacromolecules* DOI: **10.1021/bm100861g**

<sup>47</sup> *Conformational transition of DNA bound to Hfq probed by infrared spectroscopy*,

F. Geinguenaud, V. Calandrini, J. Teixeira, C. Mayer, J. Liquier, C. Lavelle, V. Arluison, *PHYS. CHEM CHEM PHYSICS* (2010, to appear)

## Proteins in complex media

### The effects temperature and high hydrostatic pressure on proteins

Studying the structure and dynamics of the native and denatured states of a protein may shed some light on the mechanism of amino acid sequence folding that results in a functional 3D conformation. Currently, physical parameters, such as temperature and pressure are used for bioconservation and sterilization in food industries and can present different folding pathways for protein. In contrast to thermal sterilization, which can affect the color and taste of food due to the breaking of covalent bonds, sterilization by pressure is gentler and more economic because it can be applied at temperatures below 100°C where only low energy bonds are broken. Proteins require internal flexibility to perform their functions, and include particularly fast conformational fluctuations that occur at the picosecond and nanosecond time scales, and at 1 to 20 Å spatial extension. Quasielastic neutron scattering allows us to access these scales of time and space. Small Angle Neutron Scattering (SANS) experiments have been performed in order to investigate the evolution of the radius of gyration; intermolecular interactions; and the shape of proteins at different states, including in solution in a native conformation, in thermally denatured states at temperatures up to 95°C, and in pressure denatured states at pressures up to 6000 bar. A basic challenge has been to better understand the mechanism of thermal- and pressure-induced unfolding of bovine pancreatic trypsin inhibitor (BPTI)<sup>48,49</sup> and calmodulin<sup>50</sup>. Another protein of interest is beta-lactoglobulin (BLG), which is a sensitive model system for studying denaturation, oligomerization, and nucleation of proteins under destabilizing conditions, which resemble processes known to occur in a number of disease states that involve beta-sheet formation.

As an extension of the previous studies, we are now interested in studying protein denaturation under pressure in relation to cold denaturation (ANR BIOSTAB). The overall goal of the BIOSTAB project is to carry out a research program on the stabilization of biological materials having therapeutic interest. An additional goal is to understand the effects of protectants on biomolecules subjected to different extreme conditions (low temperature, pH, dehydration), making it possible to justify the use of these co-solvents to obtain better stability during the storage of highly active biomolecules. The proteins used for these investigations are lysozyme and lactate dehydrogenase (LDH).

For these studies, small-angle scattering (neutrons or X-rays) has been combined with circular dichroism, fluorescence, and differential scanning calorimetry. Inelastic neutron scattering is combined with Raman spectroscopy and MD simulations.

### Crowded environments

*In vivo*, the cytoplasm and many extracellular compartments are filled with very high quantities of macromolecules that occupy a total volume fraction in the range of 30-40%. As a consequence, interactions between components are significantly enhanced due to their close proximities, which are on the order of 1 nm. The term “crowding” is generally used to describe these environments which affect the thermodynamic equilibria and dynamic properties of proteins with respect to those of proteins in dilute solutions. Neutron scattering techniques are invaluable methods for studying these effects, because they probe the characteristic length and time scales for proteins within the typical ranges of size and intermolecular distance. Secondly, thanks to the scattering length density difference between hydrogen isotopes and contrast variation methods, it is possible to observe the signal of macromolecules at low concentration in the presence of very high concentrations of other components.

Understanding the equilibrium between the different possible conformations of a macromolecule is a fundamental concept in biology. If conformational changes of a molecule

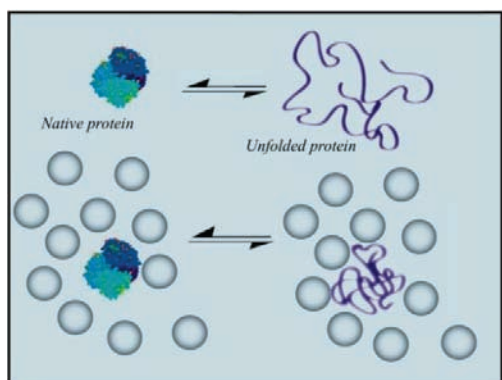
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<sup>48</sup> Influence of pressure on structure and dynamics of bovine pancreatic trypsin inhibitor (BPTI): Small angle and quasi-elastic neutron scattering studies,

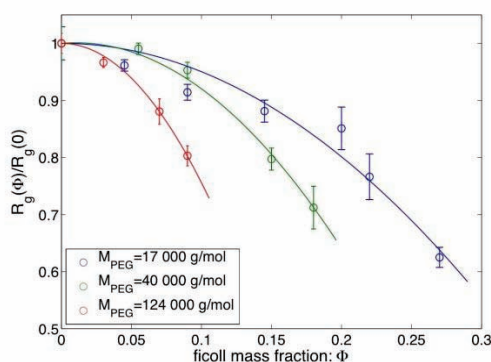
M.-S. Appavou, G. Gibrat, M.-C. Bellissent-Funel, BBA **1764**:414 (2006).

<sup>49</sup> Temperature dependence on structure and dynamics of Bovine Pancreatic Trypsin Inhibitor (BPTI): A neutron scattering study, M.-S. Appavou, G. Gibrat, M.-C. Bellissent-Funel, BBA-PROTEINS & PROTEOMICS **1794**:1398 (2009)

<sup>50</sup> Biophysical studies of thermal denaturation of calmodulin protein: Dynamics of native and unfilded states, G. Gibrat, Y. Blouquit, C. T. Craescu, M.-C. Bellissent-Funel, BIOPHYS. J. **95**:5247 (2008).



**Figure 3.10.** The physical principle of protein stabilization due to macromolecular crowding. The excluded volume tends to destabilize the more extended (unfolded) conformation with respect to more compact ones including the native state. This effect shifts the N $\leftrightarrow$ U equilibrium to favor the native state.



**Figure 3.11.** Evolution of the radii of gyration of Gaussian chains due to the presence of Ficoll (crowding agent), obtained for polymer chains of different molecular weights.

alter its effective volume, then its structural equilibrium inside the cell is shifted with respect to this equilibrium in dilute solution. Protein folding-unfolding falls into this category. It was predicted<sup>51</sup> that inert co-solutes stabilize the native state (N) of proteins against unfolding mainly by destabilizing the unfolded state (U). Osmotic pressure induced by the co-solutes diminishes the volume of a protein's unfolded state, shifting its N $\leftrightarrow$ U equilibrium towards the native state. We undertook a detailed SANS experiment to quantify the effects of inert co-solutes on the structure of a "model" unfolded chain. We first observed the compaction of a gaussian chain due to the presence of inert cosolutes. Using contrast methods in SANS experiments, the contribution of the crowding agent was matched and the conformation of a linear polymer chain was studied as a function of the crowder concentration. It was shown that when the free volume is reduced by the crowder (300 mg/ml of cosolutes), the polymer chain is compressed and its radius of gyration is reduced by 30%<sup>52</sup>. To compare our results with the predictions of excluded volume theory, we studied the effect of varying the size ratio between the random coils and the crowder<sup>53</sup>. We then studied the temperature dependence of protein unfolding in a presence of macromolecular crowder. Preliminary results show that protein stability correlated to compression of the unfolded state.

In some cases, macromolecule diffusion is the key parameter that controls the kinetics and/or the mechanism of a biological process. Thus, a protein's mobility in crowded surroundings plays a major role in its activity. A typical example of this concept occurs in the oxygen transport system of vertebrate organisms, in which transport is mediated by oxygen-binding proteins. Neutron Spin-Echo spectrometry is a powerful technique for studying the reduced mobility of oxygen-binding proteins in crowded or concentrated solutions because it is able to probe protein motions over appropriate intermolecular distances. We studied the details of myoglobin diffusion in solution when protein concentration was varied. It was thus possible to compare these experimental results to theoretical models developed for colloidal solutions<sup>54</sup>. We showed that, by rescaling the hydrodynamic volume that accounts for the hydration shell, the theories are mostly applicable up to substantial volume fraction<sup>55</sup>. It was also possible to measure the diffusion of hemoglobin *in vivo*, inside red blood cells (RBC),

<sup>51</sup> A. P. Minton, BIOPHYSICAL J., 88, 971 (2005)

<sup>52</sup> Compression of random coils due to macromolecular crowding,

C. Le Coeur, B. Demée, S. Longeville, PHYS. REV. E. **79**: 031910 (2009)

<sup>53</sup> Compression of random coils due to macromolecular crowding: Scaling effects,

C. Le Coeur, J. Teixeira, P. Busch, S. Longeville, PHYS. REV. E. **81**:061914 (2010)

<sup>54</sup> Myoglobin in crowded solutions: structure and diffusion,

S. Longeville, W. Doster, G. Kali, CHEM. PHYS. **292**: 413 (2003)

<sup>55</sup> Microscopic protein diffusion at high concentration by neutron spin-echo spectroscopy,

C. Le Coeur, S. Longeville, CHEM. PHYS. **345**: 298 (2008)

which is not directly possible using other experimental approaches<sup>56</sup>. For a long time now, hemoglobin diffusion has been recognized as facilitating the rate of oxygen uptake by RBC in the lungs. Using a simple model, we have shown that the hemoglobin concentration observed in human RBC (330 mg/ml) corresponds to an optimum for oxygen transport, if we account for: 1) the trivial increase in transport capability that occurs with increasing hemoglobin concentration; 2) the reduced mobility of hemoglobin caused by increased protein-protein interactions; and 3) the limited time that RBC spend near the alveolar sac in the lungs to capture oxygen.

Another example of a crowded environment is the extra cellular matrix (ECM). The ECM resembles a gel that consists mainly of proteins, such as collagen, and serves to embed internal organs. It plays a central role in cancer metastasis, as both cellular invasion and tumor vascularization imply that cells must pass across this solid barrier. Cells are able to migrate through the ECM by producing proteinases. As a result, these enzymes are potential targets in cancer therapy, however, they have not been well-studied with respect to the phase transition (from a gel to a liquid state) they are able to catalyze. Cell motion responds to physical properties of the ECM at the cellular length scale, which is three orders of magnitude larger than that of typical macromolecules. These properties are governed by the physical mechanism of the phase transition (i.e., its universality class). We pointed out that this mechanism is inherently controlled by the diffusion of enzymes within the gel<sup>57</sup> that introduce correlations in broken bond loci. From kinetics measurements on the gelatin/thermolysin system, and by varying solvent viscosity as well as gel and enzyme concentrations, we proposed scaling relations and reduced variables that account for the experimental results, and demonstrated that the random walk of enzymes in this system is self-attracting, leading to a continuum percolation model for gel degradation<sup>58</sup>. We intend to pursue this pioneering work in the framework of two collaborations (with Univ. Cergy-Pontoise and INRA Reims).

Cells are organized in closed compartments that are usually surrounded by lipid bilayer membranes. This organization requires communication between compartments, i.e., the passage of nucleic acids or proteins across the membranes that separate the compartments. In many cases, this “translocation” process is achieved via proteins or peptides that self-organize within the lipid bilayer to form nanochannels having diameters that are typically between 2 nm and 5 nm. The ability to perfectly control translocation in *in vitro* studies has given rise to increasing research activity.

Many small peptides, either natural or synthetic, are known for their ability to make holes in cell membranes and for their ability to transfect DNA<sup>59</sup> efficiently, which allows them to have potential applications in gene therapy. Using voltage-clamp measurements, we focused<sup>60</sup> our attention on ionic current fluctuations observed at the onset of pore formation. The dynamics in this regime might provide clues to the trigger of pore opening. Indeed, the time autocorrelation function of the ionic current exhibited a slow power law decrease, from which no average lifetime could be computed. This is reminiscent of many-body problems near a jamming transition, such as the one occurring in Random Sequential Adsorption (RSA), rather than single particles dynamics. We have shown that four different peptides exhibit this generic feature. The exact mechanism of the membrane damage they produce is still being debated, but at least one point is established: prior to pore formation, peptides adsorb in parallel onto the membrane surface up to a high surface density at which pores begin to be observed. Our results tend to indicate that the dynamics of pore formation is controlled by fluctuations in the peptide concentration at the crowded surface. Also, they give a new insight into how these pores could be viewed as quenched or jammed structures.

Ionic current recording through single nanopores gives rise to hopes of using this technique for the study of biological macromolecules. Notable applications include DNA sequencing and

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<sup>56</sup> *Microscopic diffusion and hydrodynamic interactions of hemoglobin in red blood cells*, W. Doster, S. Longeville, BIOPHYS. J. **93**: 1360 (2007)

<sup>57</sup> *catalyzed gel proteolysis: an anomalous diffusion-controlled mechanism.*, G. C. Fadda, D. Lairez, B. Arrio, J.-P. Carton, and V. Larreta-Garde, Enzyme BIOPHYS. J. **85**:2808 (2003); *Percolation model for enzyme gel degradation.*,

T. Abete, A. de Candia, D. Lairez, and A. Coniglio, PHYS. REV. LETT. **93**:228301 (2004)

<sup>58</sup> *Scaling and continuum percolation model for enzyme-catalyzed gel degradation*,

D. Lairez, J. P. Carton, G. Zalczer, and J. Pelta, PHYS. REV. LETT. **98**:228302 (2007)

<sup>59</sup> M. Martin and K. Rice, Peptide-guided gene delivery, AAPS Journal **9**:E18 (2007)

<sup>60</sup> *Fluctuations of ionic current through lipid bilayer at the onset of peptide attacks and pore formation.*, G.C. Fadda, D. Lairez, and G. Zalczer, PHYS. REV. LETT. **103**:180601 (2009)



protein folding-unfolding studies at a single molecule level<sup>61</sup>. Initially concerned with biological nanopores, recent reports have considered artificial nanopores because of their versatility. Nanopore sensing of macromolecules is based on the idea that individual chain translocation causes a resistive pulse in the ionic conductance of the channel and, more generally, current fluctuations. Analysis of these fluctuations is expected to be a signature of the solute. While quite promising, progress in this domain has been impeded by a low frequency (1/f) noise of the current spectrum that is observed even for nanopores filled with solvent alone. We studied single artificial nanopores (obtained by chemical etching of heavy ion track on irradiated polymer film) with the goals of understanding and reducing this noise, which will be crucial to making the most of translocation studies<sup>62</sup>. We found that the relative noise amplitude is virtually independent of concentration and pH for KCl solutions, but varies strongly for ionic liquids. We have shown that whether the transport of charge carriers is either strongly facilitated (low noise and higher conductivity than in the bulk) or jammed depends on the ionic liquid. These results show that the origin of the 1/f noise cannot be ascribed to fluctuations in the properties of the pore, but rather to a cooperative effect on ion motion in a confined geometry.

### Local dynamics of proteins

The sudden change at 220 K in the slope of the temperature dependence of the mean-square displacement for hydrated proteins has been extensively studied (for a review see ref. <sup>63</sup> and references therein). The reason for such focus on this so-called dynamical transition is twofold. First, this transition is intimately connected to protein function. Second, and this is even more interesting, this connection can be made for a wide variety of systems, from small soluble globular proteins<sup>64</sup> to membrane proteins. In the early steps, the role of the solvent surrounding the proteins<sup>65</sup> was recognized, i.e., in the absence of hydration, the 220 K dynamical transition vanishes. Also, the transition temperature is controlled by the viscosity of the solvent, i.e., the transition temperature increases in the presence of co-solvents, such as sugar<sup>66,67</sup>. A consensus has now emerged for the idea of a deep interplay between protein motion, and therefore function, and the surrounding solvent<sup>68</sup>.

Dynamic processes at play in water physics are now well understood, at least in bulk water. In bulk, a water molecule is hydrogen bonded, on average, to slightly less than four neighboring molecules. If, due to thermal energy, a hydrogen bond O---H-O deviates from linearity by an angle larger than 25°, the bond breaks. When several H-bonds engaged by a molecule are simultaneously broken, the molecule is free to experience a rotational diffusive motion until several hydrogen bonds are formed again leading to the formation of a transient localization “site”. It is a key point to note that within this mechanism, long range translational dynamics can only occur if rotational dynamics is present. In other words, translation is driven by rotations. Therefore, while the notion of “water dynamics” appears to be a convenient shortcut, it is actually rather vague and imprecise. Gaining real insight into the physics of water and hydration-related phenomena requires us to be able to distinguish between rotational and translational contributions.

In interfacial water, when dealing with just a monolayer of water molecules, the mechanism above is still at play even when the average number of H-bonds per molecule is

<sup>61</sup> *Unfolding of proteins and long transient conformations detected by single nanopore recording,*

G. Oukhaled, J. Mathé, A. L. Biance, L. Bacri, J.-M. Betton, D. Lairez, J. Pelta, and L. Auvray, *PHYS. REV. LETT.* **98**:158101 (2007)

<sup>62</sup> *Pink noise of conductance through single nanopores,*

C. Tasserit, A. Koutsoubas, D. Lairez, G. Zalczer, M.-C. Clochard, preprint <http://arxiv.org/abs/1007.3850v2>

<sup>63</sup> W. Doster, S. Longeville, Protein dynamics and function, *Dynamics of Soft Matter: Neutron applications*, V. Garcia Sakai, C. Alba-Simionesco and S.-H. Chen, Series Eds: R. McGreevy, I. Anderson, A. Hurd Eds, Springer (2010)

<sup>64</sup> *Temperature dependence on structure and dynamics of bovine pancreatic trypsin inhibitor (bpti): A neutron scattering study.*

M. S. Appavou, G. Gibrat, M. C. Bellissent-Funel. *BBA-PROTEINS AND PROTEOMICS*, **1794**:1398 (2009)

<sup>65</sup> *Dynamics of hydration water in proteins,*

J. Teixeira, *GEN. PHYSIOL. BIOPHYS.*, **28**:168 (2009)

<sup>66</sup> *C-phycoerythrin hydration water dynamics in the presence of trehalose: An incoherent elastic neutron scattering study at different energy resolutions.*

F. Gabel, M. C. Bellissent-Funel. *BIOPHYS. J.*, **92**:4054 (2007)

<sup>67</sup> *Dynamics of C-phycoerythrin in various deuterated trehalose/water environments measured by quasielastic and elastic neutron scattering.*

I. Koepfer, S. Combet, W. Petry, M. C. Bellissent-Funel. *EUR. BIOPHYS. J.*, **37**:739 (2008)

<sup>68</sup> *Hydration water in dynamics of a hydrated beta-lactoglobulin,*

K. Yoshida, T. Yamaguchi, M. C. Bellissent-Funel, S. Longeville, *EUR. PHYS. J.* **141**:223 (2007)

reduced to three<sup>69</sup>. We have been able<sup>70</sup> to discriminate between the rotational and translational contributions of water molecules in such a monolayer situation at a hydrophilic surface (Vycor glass). The originality of this work was not only to discriminate between the translational and rotational water components, but also to perform this decomposition over a wide range of temperature, from 70 to 280 K. We have recently extended these results to the very active field of biophysics, which is devoted to understanding how the function of a bio-molecule can be shaped by the structural and dynamic properties of the surrounding solvent.

We have shown that interfacial water at the surface of Vycor (a hydrophilic, but chemically and dynamically inert material) experiences different dynamical crossovers. As far as rotational motion of water is concerned, transitions are detected at 150 and 220 K. At 150 K, the H-Bond becomes softer<sup>71</sup>. But no change in the H-Bond strength has been detected at 220 K. The 220 K dynamical crossover could then be associated to a large-scale structural change in H-Bond connectivity. We have shown<sup>72</sup> a strong parallel evolution at 150 and 220 K between the mean-square displacements related to (i) interfacial water rotational dynamics, and (ii) proton dynamics of a hydrated protein. This connection is made at the local scale (few Angstroms) and in the nanosecond timescale. We interpret these observations as evidence that the rotational dynamics of interfacial water is the real source of entropy that drives protein dynamics.

All together, we reach this final view of the protein-hydration water interaction<sup>73</sup> and how this interaction can drive protein function: the short time motions of a protein's external side-chains<sup>74</sup>, induced by fast, water-reorientational motion, propagate in a hierarchical way along the protein structure, from the residue side chains down to the protein core to induce the longer the timescale motion of the protein backbone that is necessary for its function. The dynamical crossovers experienced by water at 150 and 220 K are also detected on the protein dynamics, even though the timescales of the crossover can be different (longer times for protein than interfacial water).

Finally, it should be noted that LLB has started an ambitious program to routinely couple, online, a neutron experiment with other experimental techniques - not to simply make two different measurements simultaneously, since the final result is often disappointing - but in the sense of a pump-probe approach. A key point is that the excitation must be triggered by the neutron spectrometer. The performances of the next generation of neutron spectrometers (Fa#, MultiMuse) give indeed the possibility to envision time-resolved inelastic experiments following an external stimulus (laser, electric field...). To gain expertise in this new way of using neutron scattering, we have developed such an experiment, in the field of biology. The sample was a light harvesting protein under excitation with a laser<sup>75</sup>. The goal was to detect a possible correlation between the light harvesting process and specific dynamical modes of the protein (Figure. 3.12).

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<sup>69</sup> *Water in confined geometries,*

J. Teixeira, J.-M. Zanotti, M.-C. Bellissent-Funel, S. H. Chen, *PHYSICA B* **234**:370 (1997)

<sup>70</sup> *Experimental evidence of a liquid-liquid transition in interfacial water,*

J.-M. Zanotti, M.-C. Bellissent-Funel, S.-H. Chen, *EUROPHYS. LETT.* **71**:91 (2005)

<sup>71</sup> *Phase transitions of interfacial water at 165 and 240 K. connections to bulk water physics and protein dynamics.*

J.-M. Zanotti, M.-C. Bellissent-Funel, A. I. Kolesnikov. *EUR. PHYS. J.* **141**:227 (2007)

<sup>72</sup> *Hydration water rotational motion as a source of configurational entropy driving protein dynamics. crossovers at 150 and 220 K.*

J.-M. Zanotti, G. Gibrat, and M.-C. Bellissent-Funel. *PCCP* **10**:4865 (2009)

<sup>73</sup> *Water hydrogen bond analysis on hydrophilic and hydrophobic biomolecule sites,*

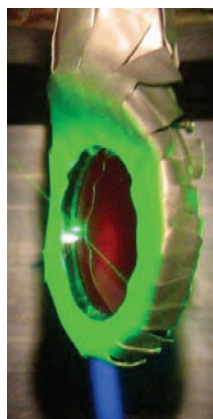
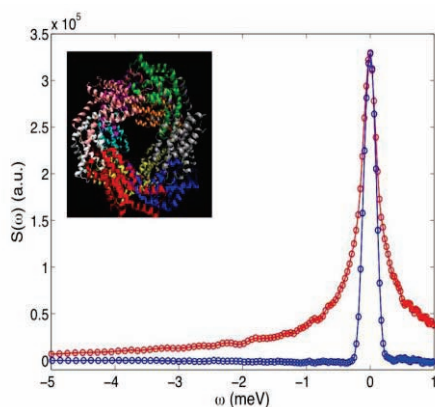
D. Russo, J. Ollivier, J. Teixeira. *PCCP* **10**:4968 (2008)

<sup>74</sup> *The impact of hydration water on the dynamics of side chains of hydrophobic peptides: From dry powder to highly concentrated solutions.*

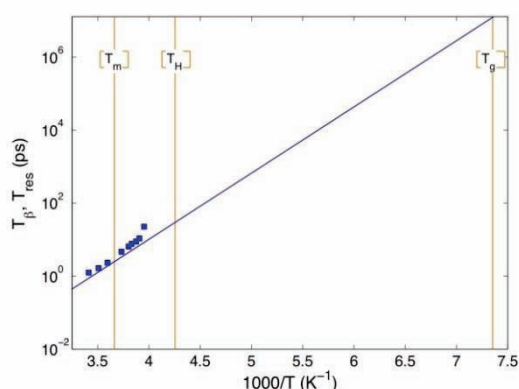
D. Russo, J. Teixeira, J. Ollivier. *J. CHEM; PHYS.* **130**:235101 (2009)

<sup>75</sup> *Coupling of laser excitation and inelastic neutron scattering: attempt to probe the dynamics of light-induced c-phycocyanin dynamics.*

S. Combet, J. Pieper, F. Coneggo, J.-P. Ambroise, M.-C. Bellissent-Funel, J.-M. Zanotti. *EUR. BIOPHYS. J.* **37**:693 (2008)



**Figure 3.12.** Measurement (left) (Mibémol spectrometer) of the internal dynamics of the light harvesting protein C-phyococyanin (hexamer, inset) under excitation by a green laser (right).



**Figure 3.13.** Arrhenius plot of dynamic processes in supercooled water. Squares are residence times,  $T_{res}$ , obtained from neutron scattering experiments at temperatures above  $-20^{\circ}\text{C}$ <sup>78</sup>. The solid blue line represents  $\beta$  processes, in this case, the dynamics of hydrogen bond dynamics, which follows Arrhenius temperature dependence. Above  $-20^{\circ}\text{C}$  this characteristic time,  $T_{\beta}$ , is obtained from the same experimental results.  $T_m$ ,  $T_H$  and  $T_g$  are the temperatures of melting, homogeneous nucleation and glass transition, respectively.

## Water properties

Water and its specific properties are fundamentally related to life and to the very peculiar properties of biological molecules, such as proteins (cf. previous topic). Here, water properties are studied in relation to the dynamics of the hydrogen bond network, as well as the notions of hydrophobicity and confinement.

The properties of bulk liquid water in the very large temperature domain extending from the lowest accessible metastable states (approximately  $-25^{\circ}\text{C}$ ) to the glass transition ( $-138^{\circ}\text{C}$ ), are always the object of speculation, such as those based on extrapolations of simulations, or on the hazardous interpretation of the properties of confined water. Efforts to explain the polyamorphism of water; in particular, the large difference in density between the low and high density forms of amorphous ice, have led to the reappearance of mixture models<sup>76</sup> despite the large amount of experimental evidence against their validity. In order to clarify this controversy, we performed a careful analysis and interpretation of small angle X-ray scattering experiments, and showed that the small angle scattering intensity of water at

<sup>76</sup> C. Huang et al PNAS **106**: 15214 (2009)

low temperature is completely explained by enhanced density fluctuation, which ruled out the existence of clusters<sup>77</sup>.

In our view, the main unresolved problem of metastable bulk water derives from the poor knowledge of intermolecular directional hydrogen bonds. While definitions of an intact or broken bond, and its lifetime, are somewhat arbitrary, in our experiments we separate two types of dynamics in bulk water: that of the bonds and that of the molecules. The latter depends dramatically on the number of intact bonds, which increases with decreasing temperature. Its temperature dependence is non-Arrhenius with an apparent divergence at the homogeneous nucleation temperature, while the hydrogen bond dynamics depicts a simple Arrhenius temperature dependence<sup>78</sup>.

While the coordinance of ions in aqueous solutions is well established, studies of the water structure in highly concentrated solutions are scarce and can be achieved only by a combination of scattering techniques, taking advantage of isotopic substitutions, and computer simulations. Actually, the structure of water in NaCl solutions, namely the hydrogen bond-related partials HH and OH, is not significantly modified by the presence of ions. Instead, as expected, the number of intermolecular hydrogen bonds decreases with increasing salt concentration<sup>79</sup>, explaining the smaller thermodynamic anomalies as compared to bulk water.

Among the puzzling phenomena observed with pure water, the “water bridge” is one of the most spectacular. A bridge of water is formed and remains stable over long times between two glass beakers filled with water and submitted to a differential electrical voltage of 15 kV<sup>80</sup>. Although the understanding of this phenomenon is more likely to be in the macroscopic properties of liquid water, a diffraction study showed that air microbubbles are likely present in the bridge accompanying the steady flow established between the beakers<sup>81</sup>.

Beyond such fundamental problems of the physics of bulk water, the effects of confinement are also important, and make up the largest part of the present research. Generally speaking, the behavior of fluids confined within nanometric pores (the size of a few molecular diameters) differs significantly from that of the bulk fluid. In the case of liquid water, as pointed out above, confined water shows a rich variety of behaviors depending on essentially all the properties of the substrate. Size, roughness of the interface, wetting, hydrophobicity, and the presence of charges are some of the parameters that any detailed study must consider. Some materials are prototypes, either because of their homogeneity (e.g. porous silica or carbon nanotubes) or because of the importance of their applications (e.g. clays or cement pastes).

A comprehensive view is emerging from experiments where the confinement is due to silica nanotubes, which have a well-defined diameter and surfaces that can be grafted in order to monitor their hydrophobicity. Differential Scanning Calorimetry allows the phase diagram of confined water to be established as a function of the pore diameter and the nature of the interface. The dynamics of the liquid form persists at temperatures that decrease with the size of the pore and with the hydrophobicity of the interface, reaching 206 K in the extreme conditions. For diameters below 2.3 nm, only amorphous ice is formed<sup>82</sup>. These results raise important questions about the relation between structure and dynamics, the extension of the interfacial effects, the validity of thermodynamic laws for mesoscopic systems, and the significance of the surface area/volume ratio.

Globally, the behavior of water under hydrophilic confinement is better understood despite a large variety of situations related to the arrangement and dynamics of hydrogen bonds, while the behavior of water confined under hydrophobic conditions remains at the center of fundamental and applied research. As briefly mentioned above, its roles in biological systems, protein folding, hydration, energizing technologies, nanofluidic devices, are indeed crucial. Intrusion of water inside hydrophobic porous materials is naturally difficult. We intend to profit from recent progress in the synthesis of nanomaterials<sup>83</sup>, surface treatments, and high pressure experiments, to develop the study of water confined in hydrophobic nanopores in order to evaluate a thermodynamic limit for the melting/crystallization of water.

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<sup>77</sup> A. K. Soper, J. Teixeira, T. Head-Gordon, PNAS 107:E44 (2010); G.N.I. Clark, G.L. Hura, J. Teixeira, A.K. Soper, T. Head-Gordon, PNAS 107:14003 (2010)

<sup>78</sup> J. Teixeira, A. Luzar, S. Longeville, J. PHYS.: COND. MATTER, 18: S2353 (2006); J. Swenson, J. Teixeira, J. CHEM. PHYS. 132:014508 (2010)

<sup>79</sup> S. Bouazizi, F. Hammami, S. Nasr, M.-C. Bellissent-Funel, J. MOL. STRUCT. 892:47 (2008)

<sup>80</sup> E.C. Fuchs et al., J. PHYS. D: APPL. PHYS. 40:6112 (2007)

<sup>81</sup> E. C. Fuchs, B. Bitschnau, J. Woisetschlager, E. Maier, B. Beuneu, J. Teixeira, J. PHYS. D: APPL. PHYS. 42:065502 (2009)

<sup>82</sup> C. Alba-Simionesco, B. Coasne, G. Dosseh, G. Dudziak, K.E. Gubbins, R. Radhakrishnan, M. Sliwinska-Bartkowiak, J. PHYS.: COND. MAT. 18:R15 (2006)

<sup>83</sup> N. Brodie-Linder, G. Dosseh, C. Alba-Simionesco, F. Audonnet, M. Impérator-Clerc, MAT.CHEM. PHYS. 108:73 (2008)



Clays are an example of situations where the lamellar periodicity of water layers and alumino-silicates generates a complex array of quasi two-dimensional water slabs that can be studied only through complementary information coming from experiments and atomic-scale computer simulations<sup>84</sup>. Incoherent quasi-elastic neutron scattering has been used to probe the water motion in these systems<sup>85</sup>. Unconventional data analysis is necessary to highlight the signal of low-dimensional water diffusion in clays which, in the majority of cases, exist in a powder form and cannot be easily oriented macroscopically<sup>86</sup>. Clay-confined water molecules form the first hydration shells of ions in these systems. The ionic diffusion coefficients are difficult to obtain experimentally, and thus parallel atomic-level simulations are exploited to provide this kind of information<sup>87</sup>. Information on ion and water motion is of crucial importance in light of the role of clays in soil and their numerous applications (catalysis, radioactive waste-disposal, etc.).

The isotopic effect, i.e., the different affinity of H<sub>2</sub>O or D<sub>2</sub>O to forming bonds with a substrate, is another complex effect observed under confinement. We studied the kinetics of cement-water mixtures during their evolution towards the gel phase. Due to specific chemical reactions that take place in different time scales, the behaviors of mixtures prepared with H<sub>2</sub>O or D<sub>2</sub>O are completely different from each other. The cement paste exhibits well-known temporal oscillations. These oscillations are in phase with the formation of hydration products only in the case of H<sub>2</sub>O<sup>88</sup>, while they are asynchronous when hydration takes place with D<sub>2</sub>O. This observed isotopic effect results from small differences in water diffusion on the rough interface of the cement due to the increased stability of hydrogen bonds in the case of D<sub>2</sub>O. Small angle scattering experiments measure the fractal dimension of the interface in both cases, which can be correlated with the kinetics of the sol-gel process.

<sup>84</sup> N. Malikova, E. Dubois, V. Marry, B. Rotenberg and P. Turq, Z. Phys. Chem **224**: 153-181 (2010);

B. Rotenberg, V. Marry, N. Malikova and P. Turq, J. Phys. Cond. Matter **22**: 284114 (2010).

<sup>85</sup> N. Malikova, A. Cadène, E. Dubois, V. Marry, S. Durand-Vidal, P. Turq, J. Breu, S. Longeville, and J.-M. Zanotti, J. PHYS. CHEM. C, **111**: 17603 (2007);

V. Marry, N. Malikova, A. Cadène, E. Dubois, S. Durand-Vidal, P. Turq, J. Breu, S. Longeville, and J.-M. Zanotti, J. PHYS.: COND. MATTER, **20**: 104205 (2008);

<sup>86</sup> N. Malikova, S. Longeville, J.-M. Zanotti, E. Dubois, V. Marry, P. Turq, J. Ollivier, PHYS. REV. LETT. **101**, 265901 (2008).

<sup>87</sup> N. Malikova, V. Marry, J-F. Dufrêche, C. Simon, P. Turq and E. Giffaut, Molecular Physics **102** (18), 1965-1977 (2004).

<sup>88</sup> S. Mazumder, D. Sen, J. Bahadur, J. Klepp, H. Rauch and J. Teixeira, PHYS. REV. B **82**: 064203 (2010)

## Scientific collaborations

The main partner organisms in France and abroad are listed in the two Tables hereafter:

| Organization                          | Total | Organization                               | Total |
|---------------------------------------|-------|--|-------|
| [INST LAUE LANGEVIN<br>GRENOBLE -...] | 25    | [JULICH - GERMANY]                         | 6     |
| [INRA - FRANCE]                       | 11    | [UNIV BERLIN - GERMANY]                    | 6     |
| [UNIV PARIS 6 - FRANCE]               | 11    | [RUTHERFORD APPLETON LAB -<br>UK]          | 4     |
| [UNIV PARIS 11 - FRANCE]              | 9     | [UNIV ROME - ITALY]                        | 4     |
| [ESPCI PARIS - FRANCE]                | 6     | [UNIV TUNIS - TUNISIA]                     | 4     |
| [UNIV AIX MARSEILLE -<br>FRANCE]      | 5     | [UNIV COMENIUS - SLOVAKIA]                 | 4     |
| [UNIV MONTPELLIER - FRANCE]           | 5     | [NIST - USA]                               | 3     |
| [UNIV PARIS 7 - FRANCE]               | 5     | [UNIV MESSINA - ITALY]                     | 3     |
| [UNIV BORDEAUX - FRANCE]              | 4     | [UNIV REGENSBURG GERMANY]                  | 3     |
| [UNIV STRASBOURG - FRANCE]            | 4     | [CANADIAN NEUTRON BEAM -<br>CANAD...]      | 3     |
| [INST FRANCAIS PETR -<br>FRANCE]      | 4     | [DESY - GERMANY]                           | 3     |
| [UNIV ORLEANS - FRANCE]               | 4     | [HELMHOLTZ ZENTRUM BERLIN<br>- GERMANY...] | 3     |
| [UNIV RENNES - FRANCE]                | 3     | [INST OF ATHENS -GREECE]                   | 3     |
| [UNIV LYON - FRANCE]                  | 2     | [UNIV BAYREUTH - GERMANY]                  | 3     |
| [UNIV PAU - FRANCE]                   | 2     | [UNIV MUNICH - GERMANY]                    | 3     |
| [UNIV TOULOUSE - FRANCE]              | 2     | [UNIV PATRAS - GREECE]                     | 3     |
| [ENS PARIS - FRANCE]                  | 2     | [UNIV AMSTERDAM<br>- NETHERLANDS]          | 2     |
| [INSERM - FRANCE]                     | 2     | [UNIV CALIF BERKELEY USA]                  | 2     |
| [UNIV GRENOBLE - FRANCE]              | 2     | [INST BUCHAREST - ROMANIA]                 | 2     |
| [UNIV REIMS - FRANCE]                 | 2     | [UNIV BRUSSEL - BELGIUM]                   | 2     |
|                                       |       | [UNIV BUDAPEST - HUNGARY]                  | 2     |
|                                       |       | [UNIV RUTGERS - USA]                       | 2     |

## Scientific contracts

Our research activities are supported by a number of different research contracts:

- ANR-PNANO BIOSELF «Auto-assemblages de nanogels et nanocomposites bioinspirés », coordonné par L. Heux, CERMAV (MAcromolécules Végétales), Grenoble(F. Boué, F. Cousin, L.-T. Lee)
- ANR-PNANO 2006-2010: projet LISSIL “ Développement d’ une nouvelle famille d’ électrolytes solides nanohybrides. Dynamique moléculaire en milieu liquide ionique nanoconfiné”, coordonné par J. le Bideau, Univ. Nantes
- ANR “ MULTICLICK” (E. Drokenmuller, G. Carrot, F. Cousin)
- ANR-PCV 2007-2011: projet BIOSTAB “ Optimisation de la stabilité de matériaux biologiques pour de nouvelles stratégies thérapeutiques”, coordonné par A. Hedoux, Univ. Lille 1.
- ANR-programme blanc international 2009-2012: projet TEMPLDISCO “ Template confinement effects on discotic liquid-crystals”, coordonné par D. Morineau, Univ. Rennes.
- ANR-programme blanc 2008-2011: projet TRANSFOLDPROT, Dynamics and mechanics of protein transport, interaction and folding through different protein channels at the single molecule level, coordonné par J. Pelta, Univ. Evry.
- ANR-jeune chercheur 2009-2012: project DYPOLYPO, Modelling the dynamic properties of polyelectrolytes in charged porous media, coordinated by M. Jardat (University Paris VI)

- RELAXAN: RTRA, A Langmuir trough common to neutron and X-Ray reflectivity technique, F. Cousin, Ph. Fontaine.
- PA 20 building: RTRA + C' nano (A. Brûlet)
- CIFRE for PhD in partnership with MICHELIN Reinforced rubbers, (J. Jestin, F. Boué).
- OSEO-programme GENESIS 2008-2011, " Nanomatériaux", coordonné par ARKEMA.
- Programme bilateral Ecos Sud A09B02 2010-2013: " Etude interdisciplinaire et multi-échelle de l' interaction entre la couche-S des bactéries lactiques et les protéines de la membrane externe des bactéries Gram(-)", Univ. Paris Diderot (V. Arluison, E. Fort, C.mayer, C. Ricolleau)/Univ. de La plata - Argentine (A. Gomez Zavaglia, P. de Urzaa)

## Other

### PhD theses defended, and in preparation, during the period 2008-2010

- J. Vinas, " Matériaux hybrides polymères-particules de silice: synthèse et caractérisation", 2005-2008.
- K. Lagrené, " Etude dynamique de polymères sous confinement quasi-uniaxial", 2007-2010.
- C. Chevigny, " Nanocomposites polymères-particules greffées: de la synthèse à l' étude des propriétés macroscopiques", 2006-2009.
- N. Jouault, (LLB-Univ. Bretagne Sud). " Nanocomposites Silice/Polymère. Structure des charges, Renforcement mécanique, Conformation des chaînes, Evolution sous deformation", 2006-2009.
- C. Le Coeur, " Influence de l'encombrement cytoplasmique sur la stabilité et la diffusion des protéines", 2007-2010.
- C. Mohamed-Said (2008-) " Structural and optical properties of PNIPAM-coated gold nanoparticles".
- A.-S. Robbes (2008-) (LLB-SOLEIL) " Nanocomposites magnétiques : contrôle de la dispersion par greffage et orientation des charges sous champ externe".
- F. Gal " Nanoparticules de platine greffées polymère", 2007-2010.
- A.-L. Fameau (2008-) (LLB-INRA Nantes) " Vers de nouveaux détergents : assemblages d' acides gras hydroxylés du volume aux interfaces, impact de la structure sur les propriétés moussantes et émulsifiantes".
- L. Shi (2009-) (LLB-Univ Paris VII) " Assemblages électrostatiques macromoléculaires et supramoléculaires".
- D. Bhowmik (2008-) (LLB - Paris VI) " Dynamics in complex fluids"

### Post-docs working during the period 2008-2010

- Colinet (2008-2009) " ANR MULTICLICK"
- F. Muller (2009-2010) l' ANR BIOSELF " Elaboration de nouveaux biomatériaux à base de cellulose"
- C. Rezende (funded by DRI-CEA 05/2007-04/2008) nanoparticles: bulk and surface properties. Nanocomposites latex and clay: from structure to mechanical properties.

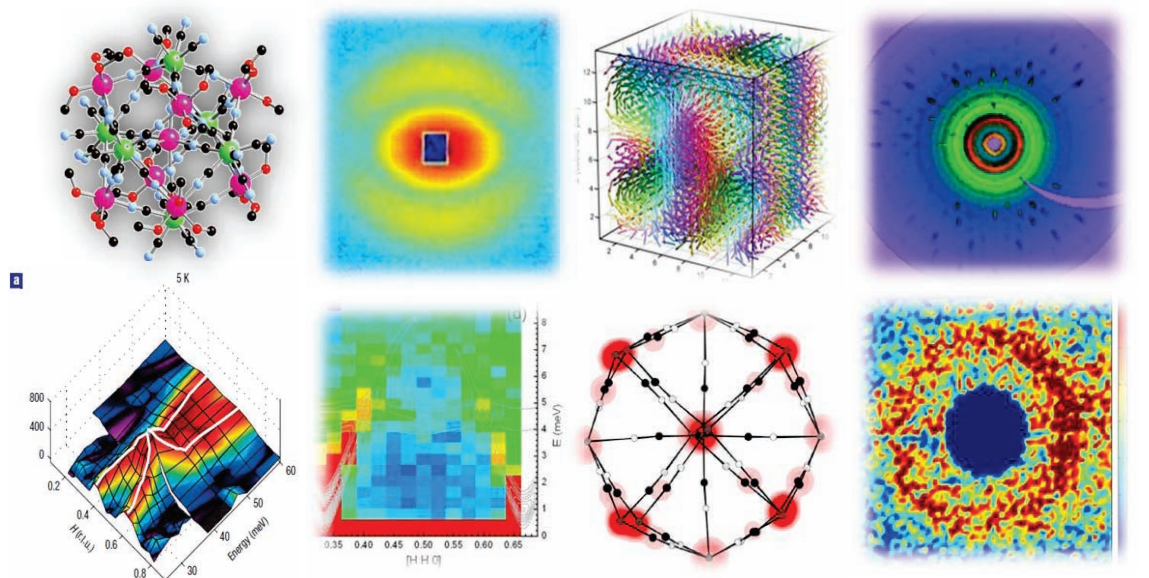
### Habilitation à Diriger les Recherches defended during the period 2008-2010

- S. Longeville (Univ. Paris VI), 2009





# SCIENTIFIC PROJECTS



énergie atomique • énergies alternatives





## AXIS 1 Projects: Strongly Correlated Quantum Materials and Magnetism

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superconductivity, frustration, multipole orders, Kondo insulators, spin-lattice coupling, magnetoresistance, multiferroics, manganites, cuprates, pnictides, spin ices, molecular magnets.



### Scope

The field of strongly correlated electron systems (SCES) covers a wide range of materials and physical phenomena going beyond the scope of standard Fermi gas theory for non-interacting electrons. The interactions between electrons allow several degrees of freedom such as spin, charge, lattice or orbital ones to be simultaneously active. The competition between different phases and interactions induces a great variety of magnetic phenomena, ground states and phase transitions, ranging from **unconventional superconductivity** or **multipolar orders** to **photomagnetism**. When interactions are short-range, the specific geometry of the lattice plays a crucial role, which raises the possibility of fine-tuning the magnetic states through geometrical frustration and spin lattice coupling (**multiferroics**, **spin ices**). Due to their complex energy balance, materials from this class can exhibit anomalously large responses to small perturbations, such as the **giant magnetoresistance in manganites**, which open the way to new functionalities (e.g., spintronics and photoswitchable compounds). Interesting states may also occur under extreme conditions (e.g., very low temperatures, high magnetic field or high pressure).

Neutron scattering has proved the tool of choice for studying these compounds at a microscopic scale, as exemplified by the recent breakthroughs presented in the Axis 1 Report chapter. Most of the work presented there focuses on novel, rapidly developing subjects. Keeping pace with the international competition thus requires current projects to be continuously updated. This section outlines some of the most promising directions along which major effort will be placed in the months and years to come.

### Unconventional superconductivity

In copper oxide superconductors, theoretical studies have emphasized the role that spin fluctuations (in particular, resonant collective modes) could play in the appearance of unconventional *d*-wave superconductivity. Future developments will focus on the anomalous low-doping regime, the combined effect of spin fluctuations with phonons, and on direct exchange interactions with spin fluctuations. In addition, neutron scattering studies have brought to light the existence of a new orbital-like magnetic phase in the pseudogap state, and have provided evidence for an electronic liquid-crystal phase at low doping level. The study of the new orbital magnetic order will continue with the generalization of its observation in other cuprate families (including electron-doped materials), the search for its collective excitation modes, and the study of its interplay with the electronic liquid-crystal phase.

In the new iron-based superconductors, neutron scattering studies have provided a quantitative description of spin fluctuations, which are believed to play a crucial role in the superconducting pairing mechanism. The study of the spin excitation spectrum will be extended to the low-doping regime where superconductivity and a spin density wave phase coexist. Furthermore, commensurate magnetic excitations have been observed by neutron scattering, whereas incommensurate excitations were expected according to local probe measurements: future works will aim at shedding light on this controversial issue. Besides spin fluctuations, there are serious experimental and theoretical indications that the role of phonons should be reconsidered in these materials. To improve our understanding of the role of lattice degrees of freedom, the current plans are to follow the phonon evolution in systems where superconductivity can be induced under hydrostatic pressure, to look for new magneto-elastic excitations, and to improve the simulation of phonon dispersion by using real *ab initio* calculations without relying on pseudo-potentials.

### Low dimensional and frustrated topologies

The physics of low-dimensional and/or frustrated magnetic systems requires understanding unconventional spin excitations, which cannot be described as classical spin waves. Two decades of intensive research have yielded a fairly complete understanding of the most basic one-dimensional models, whose milestones include the discovery of the famous Haldane gap and the observation of the fractionalization of standard magnons in spinon pairs. The latter can be seen as domain walls between reversed antiferromagnetic domains moving freely and independently along the chain. Today, the general trend in low-dimensional magnetism is to move on to more complex problems. Amongst them, new research directions will focus on randomness or doping effects, but also on the crossover regime from “quantum” to “classical” magnetism. In that context, and in close collaboration with the CRISMAT in Caen, we intend to study a new family of Cr-based materials, which could be a possible experimental realization of a frustrated spin 3/2 chain. Its peculiar zig-zag topology and its complex incommensurate cycloidal magnetic ground state were reported recently. Preliminary inelastic neutron scattering experiments have revealed that the spin excitation spectrum of this material shows strong deviations from standard linear spin wave theory, which are interpreted as arising from the fractionalization effects.

### Magnetic ground states and spin excitations in pyrochlores

The rare-earth pyrochlore family  $R_2\text{Ti}_2\text{O}_7$  is the source of a large variety of magnetic behaviors, bringing up fundamental questions as well as new phenomena. The spin-ice compounds ( $R = \text{Dy}$  or  $\text{Ho}$ ), which combine an Ising anisotropy of the  $R^{3+}$  ion and an effective ferromagnetic  $R$ - $R$  exchange, recently showed the existence of “magnetic monopoles”, namely punctual sources, or sinks, for the magnetic field similar to point charges for the electric field. The monopoles interact via magnetic Coulomb interactions, arising from the dipolar interactions between the magnetic moments. The question whether the monopole description is mainly an elegant representation of more conventional approaches or brings about entirely new physics is an open debate, which may be clarified by investigating other compounds from the same family. The spin liquid  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , with weaker uniaxial anisotropy, is a good case and its fluctuating ground state has been a long-standing mystery. Work is underway at LLB to understand this



ground state in zero and finite applied fields using single-crystal neutron diffraction. Starting from  $\text{Tb}_2\text{Ti}_2\text{O}_7$ , Ti/ Zr substitution should allow us to tune the magnetic interactions from spin liquid to soft spin ice by expanding the lattice (single-crystal synthesis is in collaboration with the ICMMO, *Crispy* project). Alternatively,  $\text{Er}_2\text{Ti}_2\text{O}_7$ , with planar anisotropy and AF exchange, offers the possibility to study the physical counterpart of the spin ices and to investigate a field-induced transition considered, up to now, to be a quantum critical point. Other projects concern  $\text{Yb}_2\text{Ti}_2\text{O}_7$ , which we found to behave as an “exchange spin ice” in the paramagnetic regime, and whose 2D short-range ferromagnetic ground state is unclear. The investigation of all compounds in the zero-field and field-induced ground states benefits from the conceptual tools recently developed both at LLB (local susceptibility models, symmetry analysis) and through collaborations with the SPEC (self-consistent calculations on a tetrahedron, precise knowledge of the crystal field). Our recent results bring up the importance of anisotropic exchange interactions, not considered by theoreticians up to now, which need to be included in models of the cooperative orders. Especially, the study of the spin excitations in the long-range ordered states by inelastic neutron scattering requires measuring the spin waves in a zero magnetic field and by crossing the field-induced critical points. These studies should be associated with new analytical developments, in order to combine the descriptions of the crystal field and the spin waves; to integrate several types of interactions, such as dipolar and anisotropic exchange; and possibly to compare these calculations with a direct evaluation of the neutron cross section using Monte Carlo algorithms. Such projects will allow, in turn: (i) the crystal-field and spin-waves excitation to be described with respect to other “exotic” ones (e.g., monopole excitations in spin ices, deconfined spinons or closed-loop fluctuations in spin liquids, and fluctuations related to a quantum critical point); and (ii) new tools to be developed, which can be generalized to the analysis of other rare-earth or intermetallic compounds on frustrated lattices, including the large class of multiferroics.

### Multiferroics

Despite a huge amount of experimental and theoretical studies, the microscopic mechanism responsible for the spin-lattice coupling and the precise role of magnetic frustration in multiferroic materials, are still matters of debate. As mentioned above, the “spin current” model is one of the most plausible scenarios. Via a Dzyaloshinskii-Moriya interaction, the non-collinear magnetic structure induces a relaxation of the atomic positions, which accounts for the rise of an electric polarization. Other mechanisms have also been proposed, such as a spin-dependent variation of the hybridization between the transition metal oxide and the bonding atoms. This mechanism would distort the electronic wave function and in turn induce a polarization. To contribute to the understanding of these phenomena, we plan to continue our efforts, but also to diversify our activities by studying new materials in close collaboration with different solid-state chemistry institutes, such as CRISMAT (in Caen) or ICMMO (Paris XI). Neutron techniques are a most powerful tool for investigating such materials, as they make it possible to study both nuclear and magnetic contributions, be they static (neutron diffraction) or dynamic (inelastic neutron scattering). Let us emphasize here that we also expect a strong outcome from neutron polarized experiments. Appropriate upgrades of the spectrometers are currently under consideration. The search for, and characterization of, possible hybrid excitations is one of our main goals, and experiments will be performed alongside numerical simulations of coupled spin and lattice dynamics (which we hope to develop through a joint RTRA project between LLB, ICMMO and IPHT). As an example, we intend to carry out investigations of the spin-lattice coupling in the delafossite oxide system, in which multiferroicity is still controversial. We will also extend this study to related materials having different anion ligands, so as to chemically modify orbital hybridization and investigate its impact on the multiferroic properties. We also plan to investigate non-multiferroic-but still magneto-electric-materials, such as  $\text{GaFeO}_3$  (PhD thesis) or  $\text{LiMPO}_4$ .

### Unconventional orders in *f* electron systems

Numerous ordering phenomena occurring in *f*-electron systems remain unexplained, especially those involving higher-order multipole moment interactions. Neutron scattering experiments, together with other experimental microscopic probes such as synchrotron x-ray diffraction, optical spectroscopy, NMR or  $\mu\text{SR}$ , have proven to be invaluable tools in sorting out the interplay between the different degrees of freedom, both in the static and dynamic

properties. Neutron diffraction studies are underway on the hexaborides family, in particular, to characterize the order parameters of recently discovered high-pressure phases in  $\text{PrB}_6$  and  $\text{CeB}_6$ . In the latter compound, it has been suggested that a uniform (i.e., ferromagnetic-like) order of the Ce dipole moments could occur at high pressure as an indirect effect of higher multipole interactions, without an actual FM dipole exchange coupling between the Ce ions. Unpublished  $\mu\text{SR}$  experiments have observed a transition to a new high-pressure phase at  $P = 1.3\text{--}1.4$  GPa, which seemingly possesses an FM component. However, no depolarization attributable to FM domains could be detected in our polarized-neutron test experiment. More detailed measurements are therefore necessary to resolve this issue. We also plan to investigate magnetic and quadrupole order phenomena occurring in  $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ , in collaboration with the TU Wien. The  $R_3\text{Pd}_{20}\text{Si}_6$  family is interesting because the rare earth ions occupy two sites of different symmetries, which can order separately, either magnetically ( $R = \text{Nd, Sm, Gd, etc.}$ ), or in a mixed state (AFM + antiferroquadrupolar) as suspected for the case of Ce. This study was initiated a few years ago but crystals of sufficient quality have become available only recently.

The novel family of compounds  $\text{Ce}M_2\text{Al}_{10}$  ( $M = \text{Fe, Ru, Os}$ ), already discussed in this report, attracts growing interest because of its unusual electronic and magnetic properties, in particular, the long-range order occurring below  $T_0 = 27$  K. Whereas we could demonstrate a clear AFM signature in the low-temperature phase, the AFM order alone does not seem to explain either the local fields measured by Al NMR or the anisotropy of the bulk magnetization, especially at high magnetic fields. Further polarized neutron diffraction experiments must be performed to ascertain the orientation of the ordered magnetic moment within the orthorhombic ( $a, c$ ) plane. Inelastic neutron scattering experiments will also be undertaken on an assembly of several small single crystals. The important point is that, in the powder results, the broad inelastic peak, at  $\sim 8$  meV, which appears above the spin gap below the ordering temperature, exists *both* in the magnetic (spin-flip) and in the nuclear (non-spin-flip) channels. It is thus essential to study the  $Q$  dependence of this mode in the Brillouin zone to see how these two components are related. We also plan to study the high-field phase diagram of  $\text{CeRu}_2\text{Al}_{10}$ , as well as the effects of hydrostatic pressure (enhancing the Kondo-insulator character) and Rh substitution (favoring a more conventional AFM-type order).

Other projects concerning Kondo-insulators, which is still one of the major unsolved issues in correlated-electron physics, include spin-dynamics experiments on  $\text{YbB}_{12}$  at the highest possible magnetic field (previous attempts were unsuccessful owing to various technical problems and limitations). The aim is to search for incipient changes in the magnetic spectral response reflecting an enhancement of AFM correlations as the KI state becomes gradually suppressed. A new study of low-temperature spin correlations in  $\text{FeSi}$  will also be undertaken using polarized neutron INS experiments at the ILL. This compound may represent a transition-metal analog of  $f$ -electron Kondo insulators. The dramatic redistribution of electronic spectral weight taking place below room temperature suggests that the opening of the charge gap in this compound is dominated by many-body effects. Early polarized neutron scattering results obtained by Tajima *et al.*, back in 1988, were interpreted in terms of temperature-induced paramagnetism with a narrow-band-gap model, but the quality of the data was still rather poor. We intend to check this interpretation with better accuracy and to search for spin correlations close to the band gap energy of approximately 50-60 meV at low temperatures, in possible analogy with  $\text{YbB}_{12}$ , where the emergence of a spin-exciton mode is associated with the formation of a sharp insulating gap. This will help us to understand the formation of the unusual narrow gap existing in  $\text{FeSi}$ .

### High-pressure magnetism

Many magnetic systems undergo pressure-induced transitions through a variety of mechanisms which are sensitive to a change in interatomic distances. Pressure-induced structural transitions or lattice distortions usually modify the magnetic order. While keeping the same crystal symmetry, pressure changes the magnetic order by changing the crystal field or the magnetic interactions through, for example, localized-to-itinerant, insulator-to-metal, high-spin-low-spin, or valence transitions. When several interactions are competing and vary differently with interatomic distances (such as superexchange and dipolar interactions), pressure tunes the energy balance. Geometrically frustrated magnets and multiferroic compounds are especially sensitive to pressure, which affects both the spin-lattice coupling and the competition between interactions. Neutron diffraction experiments under high pressure were developed at LLB, beginning in the 1990s. They strongly suffered following the early passing of I. Goncharenko in November 2007, but recently restarted thanks to a collaboration with Russian scientists

(Kurchatov Institute in Moscow, Dubna neutron center) and the funding of a new CNRS engineer position obtained in 2010. The experiments performed at LLB in 2009-10 involve multiferroic compounds, with different kinds of interactions and lattices. These measurements, whose analysis is now underway, showed a pressure-induced antiferromagnetic order to occur in  $\text{BiMnO}_3$  (ferromagnetic multiferroic with an orbital order at ambient pressure), a crossover transition towards a 2D or spin-liquid behavior in  $\text{YMnO}_3$ , an incommensurate-to-commensurate transition in  $\text{TbMnO}_3$ , and a decrease of the ordered magnetic moment in  $\text{LuFe}_2\text{O}_4$  (multiferroic with charge order). Other projects involve studies of  $\text{RCO}_2$  and  $\text{RMn}_2\text{D}_x$  Laves phase compounds and hydrides, combining the influence of 3d-4f interaction, lattice frustration, and localized-itinerant magnetism of the transition metal ion.

As noted above, the study on other materials such as rare-earth hexaborides also requires measurements under pressure, some of which will be performed using new medium-pressure devices (He-gas pressure, liquid pressure medium) currently under development at the LLB within the framework of the "Sample Environment" Joint Research Activity (FP7/NM13).

### Spin dynamics in thin films and super-lattices

In the last decade, artificially structured magnetic materials like films, super-lattices, or dot arrays have aroused a growing interest amongst the condensed matter physics community because of their unusual properties and their promising potential as novel devices or sensors, especially in spintronics. Among several elaboration techniques, molecular beam epitaxy (MBE) makes it possible to grow such nanometer size objects with single crystal properties. The possibility to vary the elaboration parameters of these objects opens a very rich field of investigation, which encompasses tailoring structural properties, creating new interfaces, or introducing super-periodicity or artificial strains. X-ray and elastic neutron scattering experiments, carried out on magnetic films and super-lattices, have unveiled invaluable information, as these objects exhibit novel ground states and magnetic structures compared to the bulk material. To get more insight into this problem, our aim is to use inelastic neutron scattering experiments to determine the microscopic quantities (e.g., force constants, electronic interactions, magnetic anisotropy, and spin-lattice couplings) that may explain the observed properties. Observing the dispersion of magnetic excitations in such nanoscale materials represents a formidable challenge for the neutron scattering experimentalist but, if successful, should open a whole new field of research. Feasibility studies on Dy films, whose main advantage is their large magnetic moment, are planned in collaboration with the institute Jean Lamour in Nancy.

### Molecular magnetism and photomagnetism

A key problem for future applications of Single Molecule Magnets (SMM) in information data storage is controlling the magnetic anisotropy for increasing the blocking temperatures. In order to characterize the magnetic anisotropy of the molecular building blocks used for the synthesis of SMMs at the atomic level, we plan to apply the local susceptibility tensor approach for the analysis of polarized neutron diffraction data. This method allows one to visualize the ellipsoids of induced magnetic moments on each atomic site of the molecule, and therefore provides direct information on the local anisotropy directions. We demonstrated this recently in a study of the strongly anisotropic dinuclear molecular complex  $[\text{Co}_2(\text{sym-hmp})_2](\text{BPh}_4)$ . A project developed in collaboration with R. Lescouezec (IPCM, Université P. et M. Curie) is devoted to the study of the magnetic anisotropy in the **fac**- $[\text{Fe}^{\text{II}}(\text{Tp})(\text{CN})_3]^-$  block\*, which is a precursor of single-chain magnets (SCM). Another part of this project consists of a multi-techniques approach for the spin density determination (NMR in solid state, EPR and PND).

The mechanisms responsible for photomagnetism in molecular compounds are of several types: spin transition due to LIESST effect in transition metal complexes and/or interatomic charge transfer in Prussian Blue Analogs. Explorations by various experimental techniques, such as SQUID, EPR, x-ray absorption spectroscopy, and x-ray magnetic circular dichroism (XMCD), do not always permit the exact nature of the photoinduced magnetic state to be determined. This is the case for the molecular compound  $\text{MoCu}_2\text{en}$ , which belongs to the family of photoswitchable  $[\text{Mo}(\text{IV})\text{Cu}(\text{II})_n]$  clusters synthesized by V. Marvaud at the IPCM. Different mechanisms may be involved: charge transfer from low-spin  $\text{Mo}(\text{IV})_{\text{LS}}$  to one  $\text{Cu}(\text{II})$

\* (Tp = tris-pyrazolyl-borate)

atom producing a  $\text{Cu(II)Mo(V)Cu(I)}$  state and/or spin transition located on Mo leading to the configuration  $\text{Cu(II)Mo(IV)}_{\text{HS}}\text{Cu(II)}$ . The determination of the spin distribution in the excited state is aimed at characterizing the magnetic nature of this state and thereby elucidating the photoexcitation mechanism. This experimental study on a very thin crystal with a volume of less than  $1 \text{ mm}^3$  is now possible on the polarized neutron diffractometer, Super-6T2.

### Instrumentation assets

The research projects outlined above will benefit from a number of new technical developments already underway or which form part of the current instrumentation roadmap that is presented in another section of this document. Most relevant to the present field of research are the improvements that were made to the suite of single-crystal diffractometers by implementing new position-sensitive detectors (Super-6T2 and VIP) and supermirror polarizers (Super-6T2). The new detector of G6-1 will provide even higher performance for measurements of very small powder samples, especially at high pressures. For the study of magnetic excitations, high magnetic fields up to 10 T have been commissioned on the cold neutron TAS 4F2, and a refurbishment of the thermal-beam instrument 2T will follow, in order to replace magnetic or field-sensitive elements and make it possible to use the cryomagnet there too. As shown above, a growing fraction of the experiments performed on the TAS instruments now require neutron polarization analysis. The analyzer shielding on 4F2 will be enlarged to accommodate the (larger) Heusler alloy analyzer of 2T, whereas new, higher-quality crystals will be installed on the latter spectrometer. Taken together, these improvements will provide users with extended opportunities to carry out cutting-edge research on superconductivity and magnetism at the LLB neutron beam lines.



## **AXIS 2 Project : Materials and Nanosciences - Fundamental Studies and Applications**

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### Keywords

- Thin films, nanoparticles, nanocomposites, textures, strains, dynamics
- Magnetism, polymers, metallurgy, glasses
- SANS, reflectivity, diffraction, synthesis

### **Scope**

This scientific axis covers the activities related to the research in materials sciences and, more generally, in hetero-systems, such as interfaces, alloys, composites materials, and confined systems. The topics cover the study of the detailed structure of nano-objects, the interactions between nano-objects, and the role of nanostructures in composite materials. The techniques used for these studies range from diffraction to small angle scattering and reflectivity. Other laboratory characterization techniques are also available: light scattering, rheology, magnetometry (VSM-SQUID), and X-ray reflectivity.

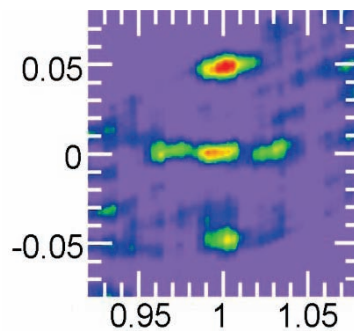
### **Scientific Projects**

#### **Magnetic nanostructures**

##### **Interface magnetism in epitaxial Cr layers and Cr/MgO/Cr tunnel junctions**

We recently became interested in epitaxial Cr/MgO heterostructures. In particular, Cr/MgO/Cr trilayers exhibit a peculiar magnetic behavior which cannot be understood from the properties of the individual Cr layers, and we ascribe this to a tunnel coupling between the two Cr layers across the ultrathin MgO barrier (Fig. 2.1). During the PhD thesis of M.-A. Leroy, starting in Sept. 2010, we will expand this work toward the external control of the ordering parameter of Cr. These studies will be part of an emerging trend, consisting of using antiferromagnets as active layers in spintronics devices. This work will be realized in close

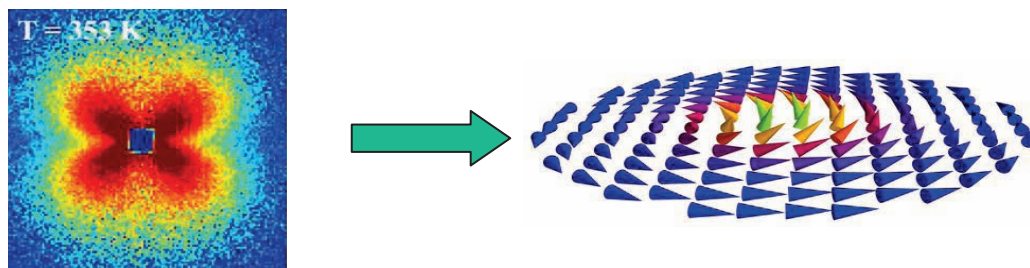
collaboration with IJL/P2M (Univ. Nancy I), and will combine neutron scattering studies (diffraction - reflectometry) together with X-ray diffraction spectroscopy (XMCD - XRMS).



**Figure 2.1.** Neutron diffraction pattern of a Cr/MgO/Cr trilayer. The position and relative intensities of the peaks allow us to determine the magnetic structure of the whole stack.

### Vectorial imaging of magnetic nanostructures

We are presently developing new methods for the study of non-collinear magnetic structures in thin and small particles. The first objective is to expand the possibilities of SANS to be able to reconstruct vectorial magnetization distributions in nanoparticles. We will develop tools to calculate the magnetic form factors of nano-objects having complex geometrical shapes, and compare the results with experimental polarized SANS scattering spectra (Fig. 2.2). Note that this 3D vectorial mapping technique has no equivalent in existing techniques. Magnetic imaging techniques (Kerr, MFM, X-PEEM) are essentially surface techniques which probe only the very outer surface of samples. Electron holography has limitations in that it measures only field integrals, so that volume reconstruction is very difficult.



**Figure 2.2.** The objective is to reconstruct the magnetic structure of a nano-object from SANS scattering patterns (left picture, Michels, et al., PRB 74, 2006, 134407).

In parallel, we are developing a new method to image non-collinear structures in magnetic thin films. We have dubbed this new technique “precessional spectroscopy”, and have performed a demonstration experiment in collaboration with the CEA/Le Ripault (P. Thibaudeau, thesis of V. Dubuget) and the Laboratoire de Physique des Solides (A. Thiaville). In the coming years, we will develop the technique so as to make it available to mainstream users. It will be complementary to reflectivity in the case of long range magnetic structures. Its advantages will be that: (i) it is a direct beam technique, which is therefore intrinsically, one of high flux; (ii) it is only sensitive to the magnetic structure, so that structural details (roughness - flatness) do not interfere with the determination of the magnetization profile; and (iii) it can be extended to 2 planar structures.

The project will benefit from the support of the RTRA “Triangle de la Physique” (Project IMAMINE) to hire a post-doc student in 2011. We have also sought European support for these projects within the NMI3 initiative.

### Molecule-based magnetic layers

In the general framework of nanomagnetism, the fundamental properties of new magnetic materials (e.g., molecular magnetic clusters and magnetic nanoparticles), which display very interesting functional properties, such as photo-commutation or the precise control of magnetization at the molecular level (data storage), are of prime interest. These switchable molecular solids are promising materials for high-density optical memory devices, especially since current synthesis and deposition techniques now allow thin-film organization or nanoscale

control of the size and shape of magnetic particles, such as Prussian Blue Analogues (PBA; ICMO, in collaboration with T. Mallah; Fig 2.3). These compounds, having the formula  $A(I)_xM(III)_y[M'(II)(CN)_6]_n \cdot zH_2O$  (where  $A = Cs, K, Rb$  and  $M, M' = 3d$  transition metal ions), display a wide variety of magnetic behaviors, among which  $CsNiCr$  becomes ferromagnetic below 90K and  $KCoFe$  displays a photoinduced ferrimagnetic behavior below 20K.

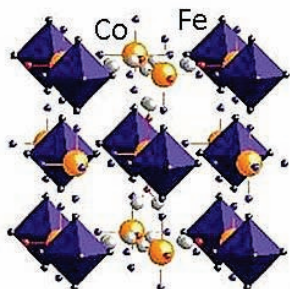


Figure 2.3. KCoFe Prussian Blue Analog

Light-coupled neutron diffraction will be applied to study photoinduced long-range magnetic ordering below 20K in a thin layer of the KCoFe analogue at the bulk limit. As first steps, the crystallinity of  $CsNiCr$  and KCoFe layers of different thickness will be tested by X-ray diffraction, and the feasibility of the magnetic structure determination will be checked for the ferromagnetic  $CsNiCr$  analogue. In a second step, the same procedure will be applied to study the ferrimagnetic metastable state induced by light irradiation in a KCoFe layer.

## Composite materials

### Magnetic composites

In the field of composite materials, we are capitalizing on the expertise acquired from work on anisotropic magnetic nanoparticles (PhD of T. Maurer) and from the long-term work on mechanical reinforcement by nanoparticle dispersion in a polymer matrix (see Axis 3).

#### Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network

In a recent work<sup>1</sup>, we have evaporated aqueous mixtures of maghemite nanoparticles (8 nm) and nanolatex polymer particles of similar size to obtain a “ferrolatex” film, as done previously for nanosilica-latex. In films prepared under magnetic fields, SANS and SAXS reveal a different structure of the particles. Elongation along, or transverse to, the applied magnetic field axis leads to differences in both evolution of this structure and its mechanical behavior, and suggests a strong link between them (Fig. 2.4). This topic corresponds to the PhD work of A.S. Robbes (joint thesis LLB-SOLEIL).

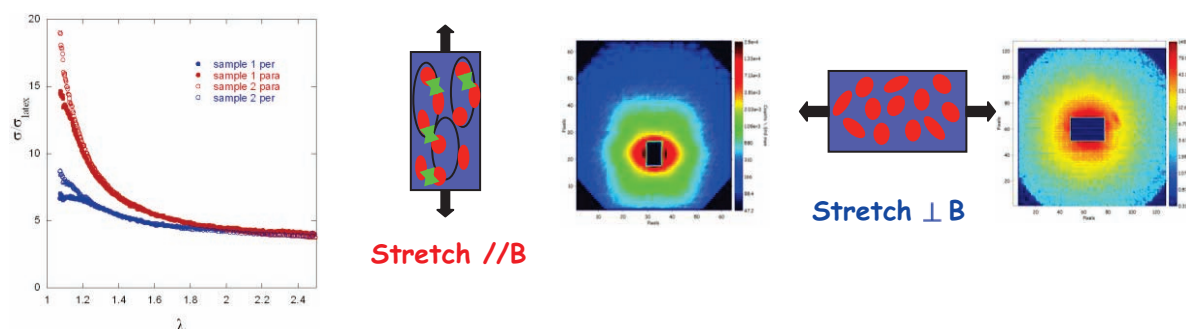


Figure 2.4. (Left) Stress vs. elongation for samples stretched parallel (red) or perpendicular (blue) to the magnetic field used during drying. (Right) SANS intensity contours.

<sup>1</sup> Anisotropic reinforcement of nanocomposites tuned by magnetic orientation of the filler network.

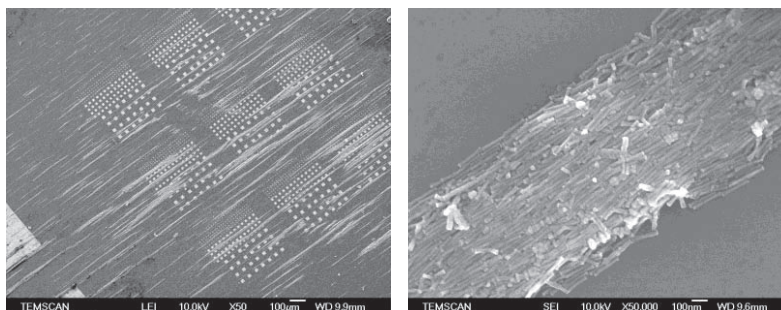
J. Jestin, F. Cousin, I. Dubois, C. Ménager, J. Oberdisse, R. Schweins, F. Boué, *Advanced Materials*, 2008, **20**(13), 2533-2540.

### Magnetic nanocomposites for permanent magnets

We have acquired extensive knowledge in the synthesis and magnetism of 3D metal nanowires during the past few years (Fig. 2.5). A new PhD thesis project (W. Fang, Oct. 2010), in collaboration with magnetism and polymer scientists at the LLB, will focus on developing new composite materials by combining anisotropic magnetic nanoparticles with polymer and/or metallic matrices in order to fabricate new types of permanent magnets. The project consists in creating lightweight magnets having strong coercive  $H_c$  fields, but without involving rare earth metals such as neodymium.

The crucial step pertains to the soft matter domain, i.e., to effectively disperse these strongly attracting objects. This will require developing new methods, and we will start this work in the context of a narrow interaction with the synthesis laboratory of ITODYS. The physics of these systems is closely related to that of polymer confinement, which depends on the structure of dispersed filler. Depending on the extent of this confinement, polymer dynamics is slowed down by an increase in the glass transition temperature, without changes in structure, but with strong effects on reinforcement properties.

This work will be conducted in collaboration with ITODYS (Univ. Paris VII), INSA Toulouse, and LPMTM (Univ. Paris XIII), who will provide expertise in chemistry and metallurgy, and we continue to gather proficiency in fields ranging from solid state chemistry, polymer science, magnetism, and powder metallurgy.



*Figure 2.5. Aligned CoNi nanowires in a polymer matrix.*

### Metallurgy

In the field of metallurgy, several projects are under development.

#### Shape memory alloys

The LLB has accumulated a great deal of experience in studying the deformation and recrystallization behaviors of copper alloys. This research field will be extended to a Cu-based shape memory alloy (Cu-11%Al-0.62%Be), which presents a stable austenitic phase at ambient temperature, while a martensitic transformation can occur under cooling or external mechanical loading. Our main objective is to understand the relation between macroscopic deformation and phase transformation in polycrystalline samples. This work requires a broad approach that simultaneously encompasses phase transformations, microstructure, deformation textures, and residual stress distribution; but that also considers the strain heterogeneities between grains that appear during deformation. This topic corresponds to the PhD work of M. Dubois (started March 2009).

#### Strain heterogeneities in composite materials

The experimental approach to evaluating strain heterogeneities will be developed through an application on composite materials: the Oxides Distribution Strengthened (ODS) steels. The correlation between the nanometric  $Y_2O_3$  oxides size distribution and the strain heterogeneities will be analyzed (PhD of S. Zhong, 2009-2012).

#### Micromechanical modeling

In parallel with ongoing experimental work, micromechanical modeling is currently being developed at the LLB by means of scale transition methods within mean field approaches. The main aim is to establish a strong relationship between modeling and determinations of internal



stress and texture established by means of neutron diffraction experiments, especially through the identification of constitutive law parameters. In the coming months, this double approach will be applied to anisotropic polycrystalline materials (copper alloys and ODS steels) to measure and simulate their elastic and/or viscoplastic responses under external loading. Special attention will be devoted to correctly taking into account the crystallographic texture and microstructure of these materials. These efforts will provide new insights into the plastic deformation mechanisms (especially slip and twinning) of polycrystals.

### Nuclear materials

Finally, we will continue to study materials of nuclear interest. Firstly, concerning the development of ODS and NDS alloys, the correlation between the elaboration parameters and the size distribution will be analyzed in detail. Secondly, several materials of great interest for future nuclear reactor construction (Zr-Nb alloys, ODS steels, and martensitic steels) will be investigated by SANS in order to determine the microstructure evolution effects induced by neutron irradiation.

### Confined systems - Mesoporous materials

#### Synthesis of mesoporous materials having hydrophilic and hydrophobic surfaces for a targeted study of confined water behavior in the presence of inorganic ions ( $\text{Cu}^{2+}$ , $\text{NO}_3^-$ , $\text{PO}_4^{3-}$ , $\text{SO}_4^{2-}$ , $\text{CO}_3^{2-}$ ).<sup>2-3-4</sup>

The processes that shape our environment have many origins, including physical (volcanic eruptions), chemical (acid rain), and biological (colonization by organisms, such as fungus). A common denominator in all these processes is water, which can both nourish as well as destroy in its environmental actions. For example, a nourishing chemical process, such the adsorption of nutrients by soil, can also be destructive, as in the context of inorganic salt adsorption in rock formations. Adsorption in rock structures by transport in pores of under confined conditions can cause cracking and fissuring, which can possibly have very dangerous results.

In order to understand some of the confined water processes which help as well as hinder the well-being of our environment, we have targeted the study of water and inorganic salts in confined conditions. The project will be organized in the following manner:

- Preparation of mesoporous materials, with both hydrophilic and hydrophobic surfaces and their characterization;
- Study of ion uptake into mesoporous materials under various conditions;
- Determine the structural and dynamical differences between confined pure water and confined water containing ions by using neutron diffraction while varying parameters such as temperature and pressure to define the differences.

### Materials with induced disorder.

#### Searching for hidden solid-like properties in liquids – correlations with microstructural organization.

The physics of liquids is not simple. Spectacular phenomena, such as the suspension of water between two containers by applying a high voltage is a typical unforeseeable effect<sup>5</sup>

<sup>2</sup> *SBA-15 synthesis: Are there lasting effects of temperature change within the first 10 min of TEOS polymerization?*

N. Brodie-Linder, G. Dosseh, C. Alba-Simionesco, F. Audonnet, M. Imperor-Clerc, Marianne (2008) Materials Chemistry and Physics, **108**, 73-81.

<sup>3</sup> *The key to control Cu II loading in silica based mesoporous materials.*

N. Brodie-Linder, R. Besse, F. Audonnet, S. LeCaer, J. Deschamps, M. Imperor-Clerc, C. Alba-Simionesco, (2010) Microporous and Mesoporous Materials, **132**, 518-525.

<sup>4</sup> *A thermodynamic limit of the melting/freezing processes of water under strongly hydrophobic nanoscopic confinement.*

J. Deschamps, F. Audonnet, N. Brodie-Linder, M. Schoeffel, C. Alba-Simionesco, (2010) Physical Chemistry Chemical Physics, **12**, 1440-1443.

<sup>5</sup> *The floating water bridge.*

E.C. Fuchs, J. Woisetschlager, K. Gatterer, K. et al. J. Of Physics D – Applied Physics **40** (2007) 6112-6114.

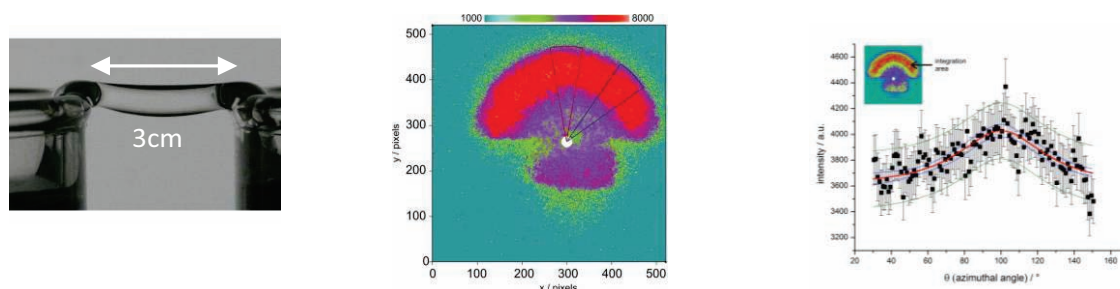
*Neutron scattering of a floating heavy water bridge.*

E.C. Fuchs, Brigitte Bitschnau, Jakob Woisetschlager, Eugen Maier, Brigitte Beuneu and José Teixeira. J. Phys. D: Appl. Phys. **42** 065502.

*Two-dimensional Neutron Scattering in a Heavy Water Bridge.*

E.C. Fuchs, P. Baroni, B. Bitschnau, L. Noirez, J. of Phys. D **43** (2010) 105502.

("Waterbridge" experiment, see Fig. 2.6a). In collaboration with E. Fuchs (Leuwarden, Netherlands), and using a 2D high resolution detector developed in-house (BAROTRON<sup>6</sup>, see instrumental section), the spatial distribution of molecules in the water-bridge was determined for the first time. Using this detector, a slight orientation of the molecules, mainly along the bridge was observed (see Fig. 2.6c).



**Figure 2.6.** (Left) Submitted to a high voltage, a string of water forms between two glass beakers. (Middle) A 2D neutron scattering pattern from the bridge. (Right) Angular dependence of the intensity in the first structural peak of the molecules in the water bridge.

We would like to extend these types of experiments to not only to characterize the microstructure of organized materials such as anisotropic fluids, liquid crystals, polymers, semi-crystalline polymers, and all materials expected to exhibit a molecular scale change in response to external stresses (shear induced deformation, stretching); but also to study the distribution of the intermolecular interactions that are responsible for the macroscopic elasticity described above. *In situ* experiments designed to couple 2D neutron measurement to shear or flow conditions will be a priority.



## Instrumentation Projects

### Single Crystal Diffraction

Work is in progress to extend the possibilities offered by the 6T1 single crystal diffractometer for the study of epitaxial thin films. Among the foreseen developments are:

- A new "octupole" magnet to provide the capability to apply high magnetic fields in any direction
- A dispex - furnace will be fitted into the octupole magnet

This project is supported by the RTRA Triangle de la Physique and the Network C'nano.

### Small Angle Scattering

In order to improve the capabilities of the laboratory in the field of SANS, a new SANS spectrometer is being built (PA20). The actual construction phase will start 2011. All studies on composite materials (polymer and metallic) will benefit from this new instrument. The PA20 will be equipped with polarized neutrons which will provide additional capabilities for the study of magnetic nanomaterials.

This project is supported by the RTRA Triangle de la Physique and the Network C'nano.

### Reflectometry

The time-of-flight reflectometer, EROS, is being upgraded within the CAP'2015 program. Significant gains in flux (5-fold) are expected when the spectrometer is installed at a guide end (G6).

### Texture and strain diffractometer

The "texture" diffractometer 6T1 is being refurbished to upgrade its capabilities within the CAP'2015 project. It will soon allow measurements of internal strains and crystallographic textures on a beam of thermal neutrons. Micro- and macrostrains can be measured from several Bragg peak shifts and broadenings, while studies that couple stress and texture determinations

<sup>6</sup> Détecteur 2-D pour Rayonnement Neutrons.

P. Baroni & L. Noirez, n°0502379 (2005) – Brevet PCT (international).

Two dimensional neutron scattering study of the bulk microstructure of polytetrafluoroethylene under uniaxial stress,

L. Noirez, P. Baroni, A. Phys. Lett. **90** (2007) 243111.

(including *in situ* measurements under load) will be achievable with shorter acquisition times. In 2011, a new sample stage will be mounted, including a new Eulerian cradle equipped with small translation tables. In 2012, a position-sensitive detector will be added in order to speed-up measurements of diffraction line profiles. Finally, in 2013, new vertically-focusing monochromators will be set up to increase the flux significantly, and to allow strain measurements at various wavelengths.

#### **Hot Neutron, 2-Axis Diffractometer 7C2**

This spectrometer is being upgraded within the CAP'2015 project. New detectors, to be installed in 2011, should boost the performance of the instrument by a factor of 25 in terms of flux (by both increasing the detection efficiency and by increasing the detection solid angle).





## AXIS 3 Project : Soft Matter and Biophysics

### Researchers (18):

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### Associated Researchers (3):

F. Audonnet (Univ. Paris XI), N. Brodie-Linder (Univ. Cergy-Pontoise), E. Buhler (Univ. Paris VII, )

### PhD Students (7):

D. Bhowmik (2008-), A.-L. Fameau (2008-), A.-S. Robbes (2008-), C. Said (2008-), Z. Guinnouni (2010-), A. Bouty (2010-), W.Q. Fang (2010-).

### Post-doc students (2):

A. Koutsoumpas (2009-), F. Muller (2009-).

### Keywords

- SANS, reflectivity, inelastic scattering, polymer and particles chemical synthesis, rheology
- Complex fluids, polymers, surfactants, colloids, self-assembly, nanoparticles, grafting, nanocomposites, nanopores, multicomponents systems, self-assembly, gels and networks.
- Protein folding-unfolding, protein crowding, protein dynamics, proteins/polyelectrolyte, biocompatible polymers, biopolymers, hydrophobicity, water properties.
- Polymer dynamics, transport properties, diffusion, anomalous diffusion, slow dynamics, complex fluids dynamics, glass transition, confinement.

### Scope

In the field of soft matter, many complex new systems are flourishing. The emergence of these newfound capabilities, many of which marry different technologies and components, and work at the nanometer scale (1-100 nm) has become a major current trend. At LLB, research has progressed in similar directions, though some of the historical specificities of the lab, such as polymer research, are kept as main components. With the advantages of neutron scattering in mind (i.e., labeling and contrast matching), we often marry the reciprocal space (SANS and SAXS) with other techniques, either in real space or at macroscopic scales. The following topics are presently developed: nanoparticles and hybrid systems; organic systems and self-organization; polymer dynamics; and electrostatic complexes. In the following review, we will consider multicomponent systems, many of them –not all of them- involving polymers. In some systems, the architecture of the basic elements is bound to lead to self-organization at the nano- or micro-scale, in other systems one of the components is intrinsically nanosized (e.g. nanoparticles or nanopores), which acts on the relevant structures at a comparable size, in particular for the polymer, and the corresponding dynamics. These effects can be present in bulk (3 d) or at interfaces (2d). Increasing the degree of complexity, specific original dynamics can be studied in glasses, in particular involving species – liquids, polymer melts- hosts – porous media- and local structures – clusters, heterogeneities often encountered in soft matter.

Research at the interface of physics and biology is based on three main topics. 1) Proteins in complex media viewed as model systems for living environments. Experiments here are concerned with macro- or supra-molecular scales and their analysis is strongly influenced by our background in polymer physics, statistical physics, and phase transition physics. 2) The local dynamics of proteins and hydration water in relation to the dynamic transition of proteins and their enzymatic activity. Neutron scattering techniques, which are very sensitive to protons, are particularly suitable for these studies. 3) Water and its specific properties are fundamentally related to life and to the very peculiar properties of some biological molecules, such as proteins. Here, the properties of water are studied in relation to the dynamics of hydrogen bond networks, and to the notions of hydrophobicity and confinement.



## Projects

### Complexes and assemblies in volume and on surfaces.

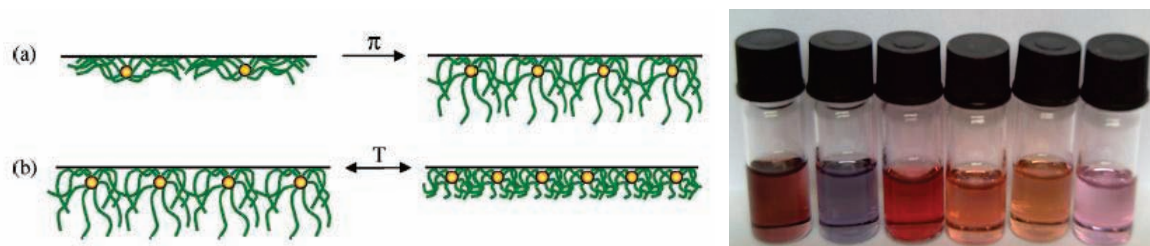
The systems studied here all involve assemblies of different objects and different environments. For the sake of brevity, we will limit the discussion in this part to projects already in progress (primarily a PhD thesis for each of them). On the one-hand, in the real-life conditions of use of several systems such as for two nanocomposites under study, the environments are hydrophobic. The corresponding studies, which start along our former theme of dispersion in a polymer, are now extended to the industrial point of view for the first (car tyres) and to the practical one for the second (advanced magnets): they will be detailed at the end of this section. On the other hand, aqueous environment for water soluble or water dispersible components can give us very interesting systems in physicochemistry of soft matter, as well as in systems that are more biological in nature: this prompted projects on nanocomposites with hydrophilic environment, which we describe first. A frequent trend in the use of dispersants is to employ materials of biological origin, or polymers, including biological ones. These more complex, larger structures may be more robust than typical dispersant materials, and this opens questions of their survival at interfaces, and of their properties, so that some studies concern 2 dimensional systems. But even in 3 d nanocomposites, surface aspects are present in the interactions between filler and the matrix.

### Gold-grafted thermosensitive nanoparticles: tailoring optical signature at a surface.

This PhD work of C. Said is in collaboration with Prof. H. Tenhu (Univ. of Helsinki); N. del Fatti, and F. Vallée (LASIM, Univ. Lyon 1); and G. Zalczer (CEA/DSM/IRAMIS/SPEC). The collective oscillation of conduction-band electrons in noble metal nanoparticles induced by an electromagnetic field (Localized Surface Plasmon Resonance) gives rise to an absorption band at approximately 520 nm in the UV-vis spectrum, thus conferring to these gold sols their characteristically intense colors; an attribute that has been, and continues to be, exploited for numerous applications. LSPR depends on shape factors and the dielectric environment, such as the solvent refractive index and the properties of stabilizing ligands. Our current project aims at tailoring this optical signature by using a graft layer of thermosensitive polymer, poly(N-isopropylacrylamide) (PNIPAM), that undergoes coil-globule transition at around 34°C. The structure of the polymeric shell, and thus the local dielectric environment of the gold nanoparticle, can be conveniently controlled by temperature.

The Au-PNIPAM nanoparticles are synthesized by a “grafting-to” technique in a “one-step” reaction, in which the grafting of well-fractionated polymer chains and the growth of the gold cores occur simultaneously. They are colloidally stable and their plasmonic properties in aqueous sol can be modulated, such that an increase in temperature induces a significant red-shift, with complete or partial thermal reversibility, depending on salinity (Fig. 3.1). Determining whether this plasmon shift is due to polymer collapse and/or to dipole coupling is our on-going work. Another notable feature is that, beyond a critical chain length, the surface plasmon mode

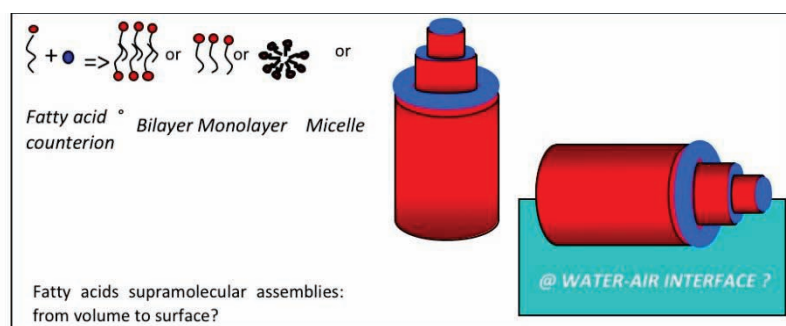
is “frozen”: the gold core sees only the polymer layer and becomes insensitive to the solvent refractive index. We will focus on two principal aspects of this phenomenon: ligand diversity and interfacial properties. In the first case, we plan to increase the flexibility of the thermosensitive behavior by grafting co-polymers that exhibit structural transition at lower temperature. This permits using a wider range of temperatures to induce the optical shifts. Secondly, the nanoparticles are surface-active by virtue of the amphiphilic nature of the polymer shell. Straddling a polar/non-polar interface, we predict that, due to their polar asymmetry, these nanoparticles will exhibit optical properties different from those observed in bulk. At the liquid-air interface, we plan to apply isothermal compression to investigate the optical properties of these gold nanoparticle monolayers at controlled interparticle distances, and to characterize the accompanying effects of changes in the polymer layer conformation.



**Figure 3.1.** (Left) Conformational changes of PNIPAM-AuNP monolayers: (a) compression-induced pancake-to-brush transition, (b) reversible temperature-induced contraction-expansion of polymer-graft layer and interparticle distance. (Right) Colors of suspended NP having different coatings.

### Self-assembled biosurfactants at the surface

In this PhD project of A.-L. Fameau, studies also range from those in volume to those at the interface, and employ SANS and NR (neutron reflectivity). The use of agricultural resources for industrial purposes is a major challenge of the 21st century, due to depletion of fossil fuel resources and the need for environmentally friendly molecules. We seek potential contributions from biological compounds of plant origin for use as surface active agents. Fatty acids are potentially good candidates, but are limited because long chain fatty acids and their hydroxylated derivatives are insoluble in aqueous solution. A simple solution to realizing their full dispersion is to produce salts of the fatty acids by using specific counterions. Then, when dispersed in water, fatty acids can form various supramolecular architectures, such as micelles, tubes, twisted ribbons, and vesicles, according to the nature of the counterion (Fig.3.2). It is reasonable to suggest that the interfacial, emulsifying and foaming properties of these systems will certainly be affected by their polymorphism in bulk. The aim of the present work is therefore to determine how the structures of fatty acid supramolecular assemblies impact their interfacial properties, as well as the formation and stabilization of foams and emulsions.



**Figure 3.2.** Fatty acid self-assemblies.

### Bioinspired self-assembly of nanogels and nanocomposites from vegetal origins.

This project (F. Muller, postdoc; ANR BioSelf) follows a former collaboration with Centre d' Etudes et de Recherche sur les Macromolécules Végétales (CERMAV) and uses reflectivity to study cellulose whiskers on surfaces. Here, the idea is to use controlled dispersion to build two kinds of materials from elementary bricks of cellulose nanocrystals (whiskers) (Fig. 3.3).

- Controlled dispersion in a polymer melt takes advantage of opportunities in their organization, particularly those offered by liquid crystalline phases, such as cholesteric ones, as shown in Figure 3.3. The first step has been achieved, namely the dispersion of the whiskers using a natural surfactant. We are currently characterizing the layer formed around each whisker using SANS. The next step is orienting this suspension using an electric field, for which we have recently built an electric field cell for SANS.
- Controlled dispersion using added xyloglucane components (e.g. “hemicellulose”), which are known to associate inside the primary wall of plant cells, forms a gel-like material for which the macroscopic properties will be investigated; first, as a model for plant wall elasticity, which controls plant growth.

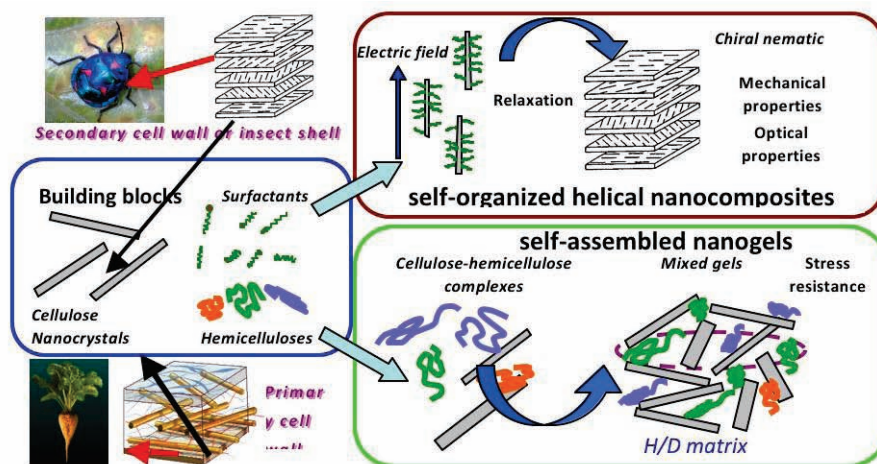


Figure 3.3. Steps of the BIOSELF-ANR project

### Electrostatic complexes: effect of polyion rigidity

In the PhD thesis work of Li Shi, we seek to extend the theme of electrostatic complexation involving polyelectrolyte and colloids of opposite charge (see Axis 3 Report), which is attracting considerable interest, to include a new system that incorporates a semiflexible chain. Indeed, many theoretical works have been reported on the problem of such chains interacting with oppositely charged spheres, but much remains unknown. In the dilute regime, most of these studies have focused on the local interaction between a short segment of chain and a single oppositely charged sphere, while the effects of the total polyelectrolyte length and the total number of particles per chain have rarely been taken into account. Moreover, some predictions on the effect of the sphere diameter or salt concentration have yet to be confirmed experimentally, probably due to the paucity of experiments performed on a model system. In this context, our first aim is to study the electrostatic complexation between chitosan, which is a well-known polyelectrolyte that has a semi-flexible backbone ( $L_p \approx 10$  nm) and bears a positive charge, and negatively charged model nanoparticles of size either larger or smaller than this value, made of silica or gold (for the smaller ones). Here we can fulfill different interesting conditions: (i) relatively dilute ones, which allow better monitoring of liquid-liquid phase separation; and (ii) very asymmetric conditions, such as chains and small spheres (as described by Shklovskii, et al.), in which “single complexes” consisting of a large component “decorated” by smaller ones can appear before coexisting with larger and more compact “condensates”.

### Hydrophobic ions and polyelectrolytes in aqueous solution

In collaboration between the LLB and the University of Ljubljana (Prof. V. Vlachy and S. Cebasek), we study a less well-known family of cationic hydrophobic polyelectrolytes: ionenes. Building upon LLB's experience regarding the conformation studies of the well-known



hydrophobic polyelectrolyte, partially sulfonated polystyrene<sup>1</sup>, we turn to ionenes as a class of materials which provides simpler and more well-defined structures. More precisely, the charge is situated on the polyion backbone (as opposed to a side-group), while the regularity and tunability of the charge separation on the backbone can be defined during synthesis. We intend to study the conformation of such chains in aqueous solution as a function of chain hydrophobicity (or linear charge density), and to continue with a dynamic study under conditions of zero average contrast, to access the dynamics of a single ionene chain, in analogy to previous studies of uncharged polymers already performed at LLB<sup>2</sup>. Ionenes have been studied extensively by Prof V. Vlachy in terms of their macroscopic properties, such as heats of dilutions, osmotic coefficients, conductivity, etc. They show interesting trends resulting from a mixture of hydrophobic effects and counterion (halide ions)-specific effects<sup>3</sup>.

A closely related project, probing the static and dynamic behavior of tetra-alkyl ammonium (TAA) salts in aqueous solution, is also underway (PhD of D. Bhowmik). TAA salts can be thought of as the monomer building blocks of ionenes, and they are considered to be the archetypal hydrophobic cation. The motions of the ions themselves and of the water molecules surrounding them are both of particular interest. A combination of the two main quasi-elastic techniques (time-of-flight and neutron spin echo) is enabling the study of not only the individual ionic motion (from the incoherent signal), but may also allow the coherent motion of several such ions in concentrated aqueous solution (0.5-1.0 M) to be studied as well. With the aid of atomic-scale simulations, these signals can be properly decoupled.

In a second phase, TAA and ionene solutions will be studied under confinement (see “Dynamics under confinement” below). Such systems will mimic, for example, the many organic species (be they pollutants or nutrients) present in the confinement of soil particles (clays), and thus will be relevant to understanding the retention and release of these species by soil.

### Polymer nanostructures metallized by radiolysis and/or photoreduction

In the PhD thesis work of Zineb Guinnouni, in collaboration with M. Goldmann (Soleil and Univ. Paris V), we use an original method combining self-assembly of amphiphilic organic molecules to form hybrid nano-objects. Here also, synthesis is undertaken to permit new specific properties (e.g., plasmon resonance, nonlinear optics) to emerge as a function of the metal nature. Functionalization is obtained by using these organic structures as “templates”, which are coated with a nm-thin metallic layer either through radiolysis or chemical reduction. We obtained metal nanoplatelets anchored below a Langmuir film (2D geometry) and nano-shells (3D geometry). We will extend this approach to diblocks of hydrophilic-hydrophobic copolymers. For those macromolecules, it is possible to tune the surface charge density and, consequently, the adsorption of metal precursor ions at the interface. At the air-water interface they organize and form brushes or surface micelles, some of which, for example, may serve as original templates for metal plots networks. The structure of these systems at the interface will be determined by neutron reflectivity, combined with X-rays for characterization of the metallic parts, as well as physicochemical techniques. Optical properties will be characterized by visible and UV spectroscopy.

### Nanocomposite systems: towards improved applications

**Reinforcement of tire rubber.** Along the theme of polymer nanocomposites (see also Axis 2), one PhD “CIFRE” (Contrat Industriel de Formation par la Recherche, A. Bouty) is now beginning, in collaboration with Michelin, on the dispersion of silica inside the rubber used for tires. The silica used will be either the one currently used in the tires, or better defined silica particles, as were used in our previous measurements. There is a twofold interest in these measurements, similar to what was done for silica/PS: the industrial problem, and using the data in the expert in computer simulations of M. Couty’s group in Michelin. We will apply the understanding gained previously from the PhD theses of N. Jouault and C. Chevigny to a new situation. Focus will be placed on the mixing methods (milling, flat rolling), as well as on

<sup>1</sup> *Pearlnecklace - like chain conformation of hydrophobic polyelectrolyte: a SANS study of partially sulfonated polystyrene in water*,

M.N. Spiteri, C. E. Williams, F. Boué, *Macromolecules*, **40**(18), 6679-6691 (2007).

<sup>2</sup> *Diffusion in semidilute polymer solutions. A complementary experiment*,

T. Csiba, G. Jannink, D. Durand, R. Papoular, L. Auvray, F. Boué, J.P. Cotton, R. Borsali, *J. Phys. II*, **381**-396 (1991).

<sup>3</sup> M. Luksic et al. *J. Phys. Chem. B* **114**:10401 (2010).

the type of chains used. For example, we showed recently (in a collaboration with the LCVN Montpellier) that mixing first with surface active short chains, and then with long ones, resulted in different dispersions than those predicted by *ab initio* simulations. We plan to follow the mutual movements of the fillers (using X-rays for the lowest  $q$ s), and to follow chain deformation directly in the deformed industrial system, both of which present significant challenges.

The PhD work of W. Fang (co-directed by the Soft Matter Group and the Materials Group) aims at building light magnets with strong coercive  $H_c$  fields from polymer/nanorod composites. The crucial step, namely to effectively disperse these strongly attracting objects, is a joint effort with the synthesis team (ITODYS), and pertains to the soft matter domain. Details are given in projects of Axis 2.

To conclude this part, we note that physics of these systems are closely related to polymer confinement: the latter depends on the structure of dispersed filler. It could result in a slowing down of polymer dynamics (ultimately, an increase in the glass transition temperature), without changes in structure, but with strong effects on reinforcement properties.

### **Viscous slowing down and glass transition**

The aim of the present projects is to identify and understand the nature and the role of static and dynamic length scales in determining the relaxation times in glassy systems, specifically glass forming liquids, by addressing specific questions through coordinated theoretical, computational and experimental investigations. In an ANR project (DynHet) ending in march 2011, we have provided direct evidence from experimental data for an increase of spatial correlations in the dynamics of glassforming liquids as one approaches the glass transition; we used the recently introduced three-point dynamic susceptibility, from which can be extracted a number of molecules dynamically correlated during the structural **relaxation**,  $N_{corr}$ <sup>4</sup>. Although the precise relation to a lengthscale is not straightforward, this nonetheless shows the existence of a length that grows as the glass transition is approached (PhD Thesis of C Dalle-Ferrier, july 2009, and S Eibl, dec 2009). The systems of interest are simple molecular liquids considered as model systems from which general trends should be transferred. Among them van der Waals and hydrogen bonded liquids are archetypical ones; however the same approaches were recently proposed for polymers as well

### **Viscous liquids: local structural heterogeneities versus dynamical heterogeneities**

Our goal is to understand the behavior of hydrogen-bonded liquids, which are essential to all biological applications and to technologies relevant to soft matter or liquid physics. Our question is how H-bond strength and lifetime may drive transformation from chainlike to ring aggregates, and how water molecules can be associated with and can move within such structures. Monoalcohols are of special relevance, due to the competition between the hydrophobic interactions of the alkyl chains and those of the hydrophilic OH groups. In the presence of water, these interactions are either enhanced or disturbed, and their study becomes particularly informative. Our approach here is based on merging our expertise in dielectric relaxation, solvation dynamics, calorimetry, elastic and inelastic neutron scattering, and MD computer simulations in collaboration with B. Rousseau from the LCP, Paris 11. The synergy of these techniques will allow us to probe, in relation to their size and occurrence, the structure and dynamics of the preferred local structures, such as clusters (rings, micelles, or chains) induced by the H-bonds, and to examine the impact of nanoscale structural heterogeneities on the overall description of the slow dynamics in glass-forming liquids. An international ANR project Strudynal will start in 2011 supported by an ANR-NSF program in chemistry in collaboration with the Professor R Richert from Arizona State University.

### **Aging and stable glasses**

Glass is often considered to be a snapshot of its liquid form frozen at  $T_g$  where flow events are no longer expected and the glassy state is formed. The particular arrangements of liquid molecules (or monomers for polymers), which number is quantified by the number of dynamically correlated molecules frozen at  $T_g$ , exert a determining influence on the properties of the solid. The properties affected include the existence of characteristic low-frequency

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<sup>4</sup> *Spatial correlations in the dynamics of glassforming liquids: Experimental determination of their temperature dependence*, C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hôte, and G. Tarjus Phys. Rev. E **76**, 041510 (2007)

vibrations, the so-called boson peak<sup>5</sup>, and the particular values of the Poisson ratio. In turn, knowledge of the latter properties will help to understand the local organization of the molecules in melts and could lead to the definition of structural length scales. Moreover, they could be analyzed during the aging process in view of the fact that glass becomes denser and more stable, both thermodynamically and kinetically, as it ages. Unfortunately one of the main goals in understanding aging is to prepare glasses that have aged a very long time; it is time-consuming and requires specific procedures. Recently, stable glasses having apparent ages estimated to be on the order of centuries were obtained by vapor deposition<sup>6</sup> by Professor M Ediger (Wisconsin University) and its group. This raises fundamental questions about the existence of an underlying phase transition deep in the viscous liquid and opens applications for new materials. We have started a collaboration to characterize the properties of these new glasses in particular by looking at the vibrational density of states, the best way to get the heat capacity and the entropy differences between the normal and the stable glasses and their corresponding crystal.

### Dynamics of molecular liquids under confinement

The emergence of nanosciences has recently given new breath to the field of physics under confinement. This renewed interest has been mainly shaped by the numerous technological developments for studying the complex interplay of surface/volume ratio, confinement topology, and dimensionality (3D to 1D). At LLB, with our expertise in this domain and the major advantage that many materials are transparent to neutrons, we intend to develop this research axis in two main directions.

### Hydrophobic confinement of water

Confining liquid water at nanoscale is of special interest due to the fact that experiments on water in the bulk liquid state cannot be carried out at temperatures below 240K. While this so-called “no-man’s land” of temperature can indeed be explored under confinement conditions, water and H-bonded liquids are perturbed by the presence of a surface, which can modify water’s hydrogen-bonding network and thus alter its energy, entropy, and phase transformations. As a result, questions persist as to whether the confined liquid water (or any other confined fluid) is an extension of the “bulk” supercooled regime, or whether it adopts specific behaviors controlled by external parameters, such as finite size and/or surface effects. Despite the obvious fundamental interest in understanding bulk water, the issues addressed here also correspond to many cases in biological and geological systems, and deserve particular attention *per se*.

Water confined under hydrophobic conditions is at the center of many basic and applied research areas, including the study of biological systems and energizing technologies, where the stability of compact native protein structure is of interest; the storage or dissipation of mechanical energy; nanofluidic device technologies; and in understanding the fundamental properties of water. Intrusion of water inside hydrophobic porous materials is possible. Our approach is based on the principle of intrusion and extrusion of water in nanopores, and combines recent progress made in the synthesis of nanomaterials, surface treatments, and high-pressure experiments. By trapping water in small nanopores and avoiding the process of extrusion, we should be able to define a new phase diagram of water (including crystalline and amorphous states), and perhaps shed light on crystalline phases that are exotic for the bulk state but realistic for water found in geological or biological systems.

The mesoporous silicate matrices prepared here permit the hydrophobicity of the confining surface to be tailored at will (see Axe 2 project). Together with clays (See “Axis 3 Report: Current research/Water properties” and “Projects/Hydrophobic ions and polyelectrolytes in aqueous solution”) and carbon nanotubes (see below), they provide a useful framework of confining media spanning 1-, 2-, and 3-dimensional confinement. The effect of silicate wall hydrophobicity on the dynamics of water can also be compared and

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<sup>5</sup> Pressure dependent neutron-scattering experiments :A study of the link between slow and fast dynamics of glass-forming molecular liquids,

K Niss, C Dalle-Ferrier, B Frick, D Russo, J Dyre and C Alba-Simionesco, Phys. Rev. E **82**, 2 (2010).

<sup>6</sup> Swallen SF, Kearns KL, Mapes MK, et al. Science **315** 5810, 353-356 (2007);

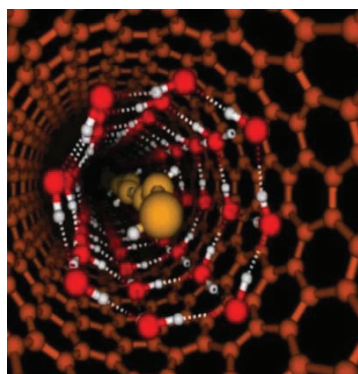
Kearns KL, Whitaker KR, Ediger MD, et al. J. Chem. Phys. **133**, 014702 (2010.)

contrasted with the effects that hydrophobic ions exert on hydration water. In the latter case, the coulombic and hydrophobic effects are by definition convoluted.

### Quasi-1D confinement: a multiscale approach

For many new technologies, such as the development and improvement of single molecule probing; nanoporous membranes; and electrical batteries and cells, the use of 1D-confined geometries has become increasingly frequent. For all these applications, the underlying fundamental issue is to understand the transport properties of liquids under quasi-1D confinement.

So far, many contradictory experimental results, simulations, and theoretical expectations have been reported for the transport of molecules in confined structured liquids such as water or ionic liquids. Findings range from molecular transport being facilitated to it being impeded or “jammed”. On one hand, experimental studies show exceptional transport properties for water through carbon nanotube (CNT) membranes: water flow measurements exceeded by more than two orders of magnitude the values derived from continuum hydrodynamics models<sup>7</sup> (Fig. 3.4). Molecular dynamics (MD) simulations support these results, but a satisfactory theoretical explanation has failed to emerge<sup>8</sup>. On the other hand, at LLB, from ionic current recordings through single nanopores<sup>9,10</sup> filled with ionic liquids, we recently observed either facilitated or jammed transport behavior, depending on the liquid. In any case, interplay of the liquid dynamics and the reorganization of the liquid structure due to confinement is widely expected<sup>11,12</sup>. We intend to address this question using a multiscale approach.



**Figure 3.4.** Proposed structure of water confined in a Single Wall Carbon NanoTube (SWCNT) with 1.4 nm internal diameter. The interior “chain” water molecules have been colored yellow to distinguish them from the exterior “shell” water molecules (colored red). Here the real sample consisted of a “powder” of SWCNT, so that dynamical observables were averaged out (powder average). It was therefore not possible to disentangle the radial and longitudinal (perpendicular and alongside the SWCNT axes respectively) contributions to the overall dynamics<sup>11</sup>.

The vast majority of research on confinement has been conducted using samples with no specific macroscopic orientation. This leads to the loss (or at least a “blurring”) of detailed orientational, structural, and dynamical quantities. While the associated data analysis is possible, it becomes more challenging, as we have shown on liquids confined in a quasi-2D environment<sup>13</sup>. The most direct way to lift this “powder average” limitation is to take advantage of macroscopically ordered confining systems (see PhD of K. Lagrené). Unfortunately up to now, the minimum pore diameter that has been achieved is 10 nm. Such a dimension is convenient for macromolecule confinement, but is too large to change the

<sup>7</sup> J. K. Holt et al. *Science* **312**: 1034 (2006)

<sup>8</sup> G. Hummer et al. *Nature* **414**:188 (2001);  
H. Verweij et al., *Small* **3**:1996 (2007).  
S. Joseph et al. *Nanoletters* **8**:452 (2008)

<sup>9</sup> *Unfolding of proteins and long transient conformations detected by single nanopore recording*  
G. Oukhaled, J. Mathé, A. L. Biance, L. Bacri, J.-M. Betton, D. Lairez, J. Pelta, and L. Auvray. *Phys. Rev. Lett.* **98**: 158101 (2007).

<sup>10</sup> *Pink noise of conductance through single nanopores*,  
C. Tasserit, A. Koutsoubas, D. Lairez, G. Zalczer, M.-C. Clochard. *Physical Review Letters* **105** (2010), 26060, and references therein.

<sup>11</sup> *Anomalously soft dynamics of water in a nanotube: A revelation of nanoscale confinement*,  
A. I. Kolesnikov, J.-M. Zanotti, C.K. Loong, et al, *Phys. Rev. Lett.* **93**:35503 (2004).

<sup>12</sup> S. Perkin et al., *PCCP* **12**:1243 (2009)

<sup>13</sup> *Signature of low dimensional motion in complex systems*,  
N. Malikova, S. Longeville, J.-M. Zanotti, E. Dubois, V. Marry, P. Turq, J. Ollivier. *Phys. Rev. Lett.* **101**:265901 (2008)



properties of most molecular liquids. Recently, M. Mayne and colleagues (CEA/DSM/IRAMIS/SPAM) have produced a system that demonstrates quasi-perfect macroscopic order in addition to nanometric pore size. It is based on aligned CNT membranes, consisting of a dense array ( $10^{10}$  CNT/cm<sup>2</sup>) of narrow and long (tens of  $\mu$ m) CNT.

Molecular dynamics simulations and neutron scattering are wonderfully complementary probes for the dynamical phenomena at stake here, but the retrieved physical insight is limited to the local scale (up to few tens of Å) and to relatively short times (few tens of ns). As an attempt to bridge this detailed microscopic view to the macroscopic transport properties (at least in the  $\mu$ s and  $\mu$ m ranges), the same samples will be challenged using Pulsed-Field Gradient NMR (in collaboration with P. Judeinstein, ICMMO, Orsay) and NMR relaxometry (in collaboration with P. Levitz, LPMC/Ecole Polytechnique). Recent developments in CNT chemistry, manipulation, assembly, and their use in electronic devices<sup>14</sup>, allow us to consider the possibility of performing ionic current measurements through a single CNT (in collaboration with G. Zalczer and P. Chenevier, CEA/DSM/IRAMIS/SPEC). Beyond the simple access to transport properties at a macroscopic scale, and thanks to the “single channel feature” of CNTs, recordings of the noise will give access to the correlation function of the current (Fourier transform of the spectral density of the signal) from 0.1 ms up to 1 second, and longer (see PhD of C. Tasserit and post-doc of A. Koutsoumpas). We hope that this experimental multiscale approach will be the route to a full understanding of the unexpected transport properties under 1D-confinement.

### **Biomacromolecules in crowded or confined environments**

In the continuity of the pioneering work of S. Longeville (see Axis 3 Report/Proteins in complex media/Crowded environments), who has studied the collapse of a polymer chain caused by the osmotic pressure exerted by a crowding agent, we intend to pursue this research by using biologically relevant macromolecules such as polypeptides, proteins, or nucleic acids. Different methods will be explored in parallel, on a variety of systems, but with the same central idea that confinement lowers the conformational entropy of random assemblies, which may favor the formation and the stabilization of structures.

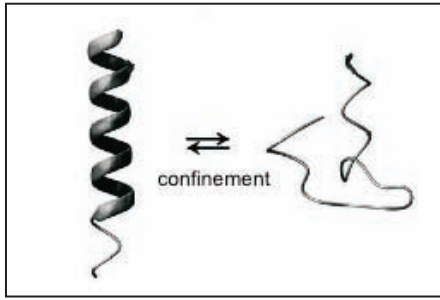
In order to make the most of contrast variation techniques for these multicomponent systems, the key point is to have at our disposal for any given compound, either the deuterated species or the natural one. For small angle scattering, the most favorable case in terms of optimizing the signal-to-noise ratio is to match the crowding agent using a deuterated solvent. Different possibilities must be explored and optimized with respect to their constraints, including: finding the best contrast between solvent and protein; matching of the crowding agent while minimizing incoherent scattering; and ensuring the absence of specific interactions between the protein and the crowding agent so that excluded volume interactions remain unobscured.

### **Coil-helix transition of polypeptides**

The ultimate 3-dimensional structure of a protein results from different levels of structuration of the linear polypeptide chain. In the first level, the linear polypeptide chain organizes itself into the so-called “alpha-helix” and “beta-sheet” secondary structures. A first step to understanding protein complexity, therefore, could be to study the coil-helix transition of a homopeptide under crowded or confined environments. In particular, we aim to study the coil-helix transition of poly-L-glutamic acid (PGA). At low pH, PGA forms helices that are destabilized at high pH due to the dissociation of the carboxylic groups, which introduces repulsive forces between the glutamic acid residues. This easily tunable parameter (pH) allows us to approach the very point of the coil-helix transition. For homopeptides, each turn of the alpha-helix structure is stabilized by periodically spaced hydrogen bonds between neighboring residues, wherein the entropy cost per residue decreases with the degree of alpha-helicity. This leads to a highly cooperative mechanism for the transition. In this context, the confinement or crowding effect should be particularly interesting, as not only a shift of the transition but also a change in the mechanism is expected (Fig 3.5).

<sup>14</sup> V. Derycke et al., *C.R. Physique* **10**:330-347 (2009)





**Figure 3.5.** Confinement of a polypeptide chain lowers the conformational entropy and may favor the formation of a helix.

### ***In vivo* conformation of DNA-protein complexes**

DNA condensation plays a major role *in vivo*, in particular, by ensuring the efficiency of DNA repair. In eukaryotic and prokaryotic cells, the condensation of negatively charged DNA is driven by proteins which behave in a manner similar to polycations. In bacteria, HU (heat-unstable nucleoid protein), H-NS (histone-like nucleoid structuring protein), and Hfq (host factor Q) have been identified as playing key roles in DNA condensation (Fig. 3.6).



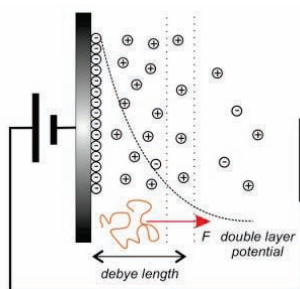
**Figure 3.6.** Effect of HU, H-NS and Hfq on plasmid structure

It is clear that the study of DNA condensation in dilute solution reveals only a partial understanding of the process as it occurs in a crowded *in vivo* environment. We intend to take advantage of small angle neutron scattering, with its versatility for contrast matching, combined with macromolecule labeling in order to perform studies of DNA condensation *in bacteria*. For this purpose, hydrogenated plasmids will be added to deuterated bacterial extracts. Different mutant strains of bacteria lacking some nucleoid proteins will also be used to characterize the specific functions of these proteins.

### **2D confinement**

In soft matter, 2-dimensional systems display special properties due to many factors. The reduction of dimensionality reduces translational entropy and magnifies the effects of excluded volume interactions and concentration, and thus allows molecular associations to be increasingly favored. *In vivo*, 2D interfaces are ubiquitous: from the cellular plasma membrane to membranes that separate intracellular compartments. These interfaces are naturally crowded or confined environments, which we intend to address using different strategies.

- In the case where an electrolyte solution is in contact with a charged solid surface, counterions ensure electrical neutrality, and the electrostatic potential is correspondingly screened. However, the thermal energy in the solution prevents this screening from occurring at close proximity to the surface, but rather it occurs within a range roughly equal to the Debye length (Fig. 3.7). Depending on the magnitude of this potential, a repelling or attracting force can be exerted on charged macromolecules. The use of a metallic surface at a given electrical potential with respect to the electrolyte solution would allow us to fine tune this force and the corresponding confinement strength. We intend to develop this general idea by using neutron reflectivity to study protein adsorption. For instance, this system is particularly suitable for the study of adsorption kinetics (with its many open questions in relation to slow dynamics of molecules in jammed systems), or protein stabilization due to confinement at the surface.



**Figure 3.7.** Schematic representation of a double layer formed near a negatively charged surface. Also the force that is exerted on a negatively charged chain is shown.

- Understanding how interactions between membrane proteins and the lipid bilayer control the organization and dynamics of membrane proteins is a significant current challenge for modern biology. At LLB, we have the opportunity to address this problem using a “multiscale approach” (see “Quasi-1D confinement: a multiscale approach”) to study hemolytic peptides or porins. For instance, recording the ionic current through a lipid bilayer allows us to sense the dynamics of insertion and association of hemolytic peptides in the bilayer. Once formed, the internal dynamics of the pore can be probed with the same techniques, from 0.1 ms up to 1 second and more. We intend to study these dynamics as a function of lipid fluidity by varying the temperature near the “gel” temperature of an appropriate lipid (e.g. DPPC). Small angle neutron scattering on similar systems, but with the bilayer in the form of vesicles, would give access to the membrane thickness or to the pore scattering function depending on contrast matching conditions. Finally, in conditions where the lipid bilayer is fully matched, neutron spin echo at a scattering vector corresponding to the first oscillation of the pore scattering function, would give access to internal modes of protein dynamics in a time scale comparable to the characteristic times of the lipids in the liquid state ( $\sim 1$  ns).
- S-layer structures are macromolecular arrays that cover the prokaryotic cell envelope, in particular, that of *Lactobacillus*. They are attached to the underlying cell wall by non-covalent bonds and have been reported to perform several specific functions, such as protective coats, ion traps, cell adhesion, and surface recognition. That several species harboring S-layer structures play essential roles in probiotics has made the study of *Lactobacillus* S-layers increasingly important, especially with respect to the adherence of enteropathogens. It has been demonstrated that *Salmonella* strains pre-treated with S-layer proteins are unable to invade eukaryotic cells *in vitro*, which suggests a protective role for these proteins against pathogenic bacteria. The corresponding mechanism and the origin of the interaction between the S-layer and membranes of pathogenic bacteria are still open questions. The aim of this project is to investigate the interactions between S-layers and pathogen-like membranes using neutron reflectivity that would allow us to access the structure of membranes whose compositions can be varied through genetic means.

