PAPYRUS: A DEDICATED TOOL TO STUDY SURFACES AT THE NANOSCALE

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PAPYRUS, formerly PAPOL [1], is a spectrometer that has been modified to perform Grazing Incidence Small Angle Neutron Scattering (GISANS). It is primarily devoted to the study of surface and interface at the nanometer scale [2,3,4].

GISANS (and SANS) can be performed using a $\lambda=8\pm0.5$Å neutron beam $(3.10^5$ n/cm^2/s) with polarization option (94% polarization, 45% transmission). It allows to work in the Q-range 0.02-3 nm^{-1} thanks to a 64x64 cm BF$_3$ detector grid (128x128 cells) and an adjustable sample-to-detectors distance (min 80cm, max 380cm).
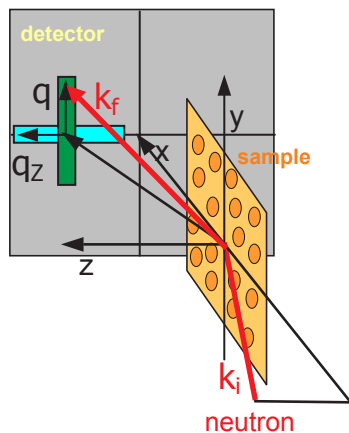

Figure 1. GISANS geometry. The accessible Q range is $10^{-2} < q_y < 3$ nm^{-1}. Scattering in the off-specular GISANS plane (green area) allows to probe objects with typical size between 5 and 100 nm. In the specular direction (q_z), typical sizes between 600 nm and 60 μm can be probed (blue area).

PAPYRUS can also be used as a standard polarised neutron reflectivity instrument, probing structural and magnetic depth profile.

The GISANS configuration, schematically represented in Figure-1, is particularly useful for the study of domain formation in magnetic thin films, organized nanostructures (nanowires, nanodots) and soft matter materials. By detecting off-specular scattering perpendicular to the incident plane (q_Y direction, green area in Figure-1) one can bring information on the lateral (planar) correlations between nanometer scale objects deposited on a surface or confined at interfaces with typical size between 5 and 100 nm. Off specular scattering in the incident plane (light blue area) also brings information about lateral

structures (in the plane of the surface) but with typical length scales from 600nm to 60μm [5,6,7]. The period 2003-2004 has seen a refit of the instrument with several new features. The 7m long collimation has been improved, a 3m neutron guide and a new slit system are now in place, leading to a best q_Z resolution of about 0.02 nm^{-1}, essentially limited by the resolution of the detector grid. The sample table area is now motorized in four directions (vertical, rotation, translation, tilting) and allow accurate reflectivity measurements as well as GISANS measurements in horizontal geometry which is the most convenient for liquid samples.
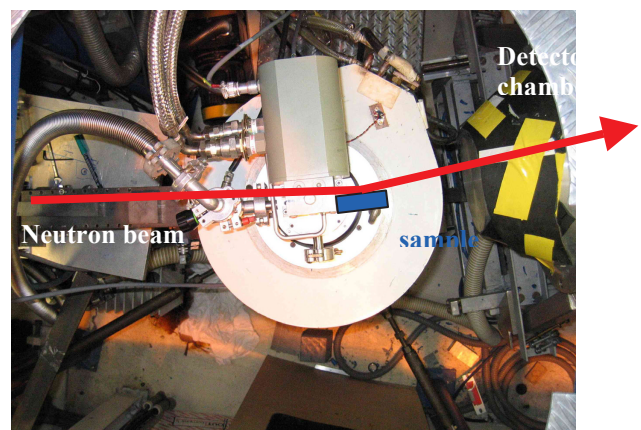

Figure 2. Partial view of PAPYRUS with the neutron guide on the left hand side and the detector chamber on the right hand side.

A variety of sample environment (cryomagnet, displex, electromagnet, etc.) can now be accommodated (see Figure 2). The background noise from the detector chamber has been reduced (0.5 count/cell/hour). In addition, new instrument developments in 2005 will include a new beam stop system and a polarization analysis option.

To illustrate the GISANS capabilities, a selection of recent achievements using PAPYRUS are given below.

Domain formation in AFM Fe/FeF2 bilayers

Neutron off-specular scattering is a technique which can be used for the study of the formation of magnetic domains at the interfaces of bilayer systems like Fe/FeF$_2$. This material consists of a 100nm FeF$_2$ layer, deposited on a Mg0 substrate and capped with a 80nm Fe layer and a thin non-magnetic Al layer. We show that it is possible to

study the exchange coupling within the single magnetic interface between the Fe layer and the antiferromagnetic FeF_2 layer (T_N = 80K).

Figure-3 shows two polarised neutron scattering intensity maps obtained with UP and DOWN polarisations, close to the critical angle and at low temperature (13K) and weak negative magnetic field (-30G) after Zero field cooled under a positive magnetic field of H=+1kG.

Beside the specular reflectivity which is identical for "up" and "down" configurations, a strong off-specular peak is observed at higher Q_z values. This off-specular intensity is strongly temperature dependent (not shown) and suggests that it is of magnetic origin. It is also visibly strongly dependent on the polarisation as illustrated in the horizontal slice shown in Figure-4.
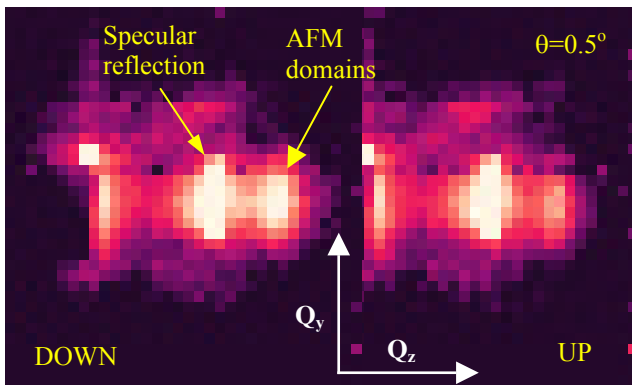
Figure 3. Scattering intensity maps with "up" and "down" neutron polarisation of Fe/FeF_2 layers obtained with θ_i = 0.5°, T=13K and H=—30G applied field.
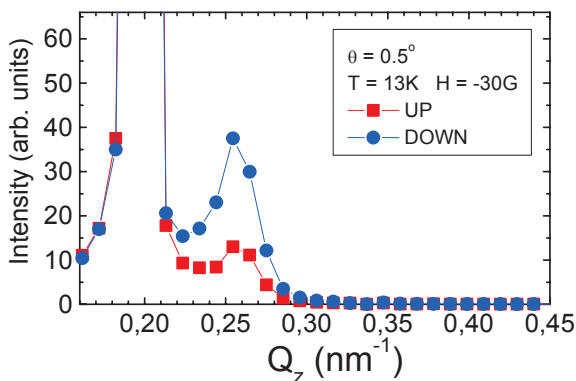
Figure 4: Scattering intensity maps with "up" and "down" neutron polarisation of Fe/FeF_2 layers obtained with θ_i = 0.5°, T=13K and H=—30G applied field.

Magnetic off-specular scattering in the Q_z direction is attributed to the formation of magnetic domains at the interface between the two magnetic layers [8,9] while reducing the magnetic field from a fully polarized state to the remanent state.

Magnetic (Fe) nanodots in insulating matrix

Figure-6 shows an example of a GISANS measurement taken at T=210K and H=1T on an array of Fe nanodots (60 nm in diameter and 100nm separation) grown on porous Al_2O_3 membranes (Figure 5).
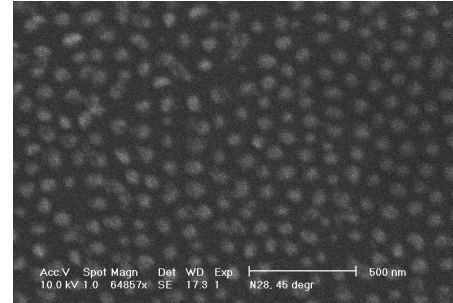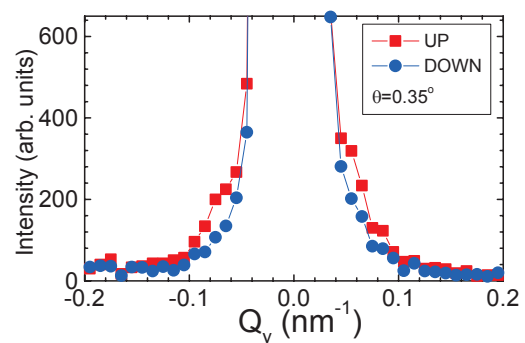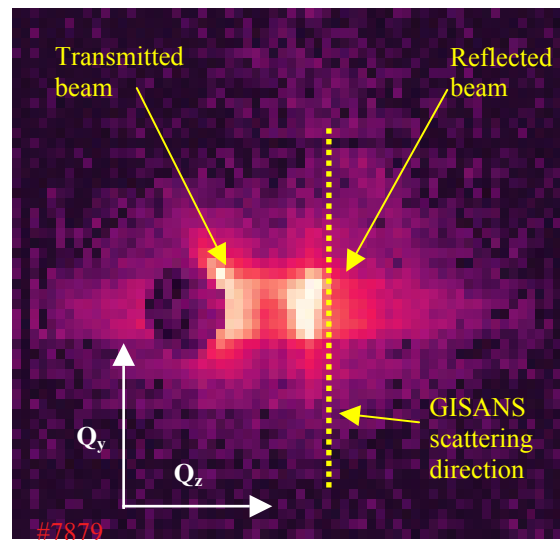
Figure 5. Fe (60nm) nanodots observed by SEM

Figure 6: Top: Colour image of Fe nanodots scattering at θ=0.35°, T=210K and H=1T applied field. Bottom: Slice along Q_y close to the specular reflection for UP and DOWN polarisation.

Off-specular scattering is observed in the Q_y direction corresponding to in-plane properties of the sample. Up and Down polarisation measurements at remanence and under 1T (Figure 6) shows that some extra scattering of magnetic origin develops o symmetrically on each side of the specular reflection. It is thus possible to

measure the local magnetization of nanodots deposited on a surface. It also shows that the magnetisation of the Fe dots is close to saturation as expected at low temperature. In principle one could infer the magnetic form factor of such dots and to determine their vortex state. However, more work is needed to improve the resolution and signal-to-noise ratio I order to quantitatively study such nanostructures.

PAPYRUS for soft matter

GISANS can also be a powerful tool for soft matter applications to study the structure of objects weakly organized on a surface, especially for systems whom surface properties are driven by the bulk properties (micelles adsorption for example) [10]. We present here an experiment **in liquid environment** that allow to get both the signal from the objects organized on the surface and the signal from the objects in bulk solution.
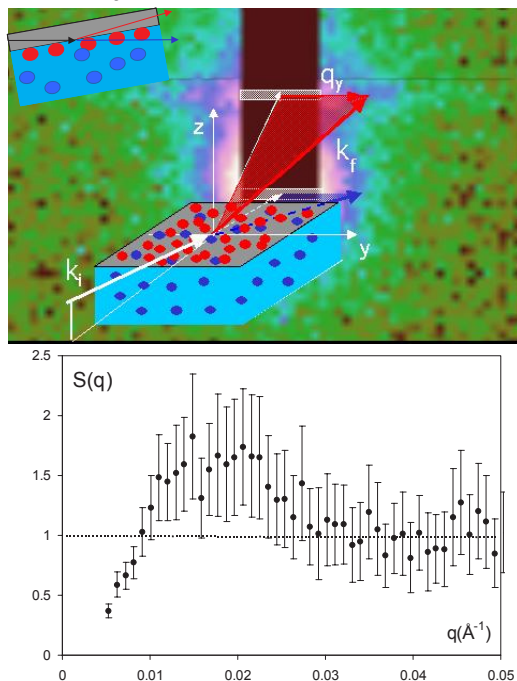

Figure 7. Top: principle scheme of GISANS in liquid environment : the signal of the red spheres attached on surface (GISANS) is located in the plane of specular reflectivity. The signal of the blue spheres in bulk solution (SANS) is located around the direct beam. Bottom: Structure factor of spheres at the surface.

We have designed for this purpose a model system to test the experiment feasibility on PAPYRUS. A layer of monodisperse nanospheres of SiO_2 ($<R>=135\text{Å}$) has been grafted on a silicon wafer.

The surface of the wafer is in a first step functionalized by terminal amines functions that provide positive charges to the surface at neutral pH. The silica nanospheres, negatively charged at pH 7, interact then electrostatically with the surface. As this interaction is irreversible, it is possible to place the wafer containing the same nanospheres in bulk solution without degrafting the surface nanospheres. The system enables thus to continuously tune the ratio of spheres at the surface to the spheres in volume.

The nanospheres layer at the silicon surface has been characterized by neutron specular reflectivity on EROS spectrometer (LLB). It was shown that the layer is homogenous and rather dense with a surface fraction Φ_s of about ~ 0.4.

The GISANS measurement has been realized at the silicon/ D_2O interface and is presented in figure 7. The neutron beam crosses through the silicon and is partially reflected by the silicon/ D_2O interface. The signal from the spheres at surface (red spheres on picture) is located in the plane of the specular reflectivity and the signal from the spheres in the bulk (blue spheres on picture) around the direct beam as in classical SANS.

In the experiment described here, the spheres in bulk were diluted enough to identify the signal of SANS to the form factor of spheres ($\Phi = 0.001$). Dividing the GISANS signal by the one of SANS provides then the structure factor of spheres at surface (figure 7, bottom). The structure factor show a repulsive liquid-like order of the nanosphere at the surface. This is in accordance to our expectations as spheres mutually electrostatically repel in solution during the grafting stage. The correlation peak enables to get the mean distance between spheres (~ 370 Å) and to recover the same surface fraction as (Φ_s about ~ 0.4) as obtained by specular reflectivity.

This experiment has revealed the feasibility of soft matter experiment on PAPYRUS. Especially the typical acquisition time (about 12 hours) is reasonable regarding to the volume of spheres at surface (about 0.01 mm^3). Plus, this is to our knowledge the first time that both the structure of objects at interface and the structure of objects in bulk are simultaneously measured.

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