Porous networks formed by mixtures of lamellar clay particles and nanospheres

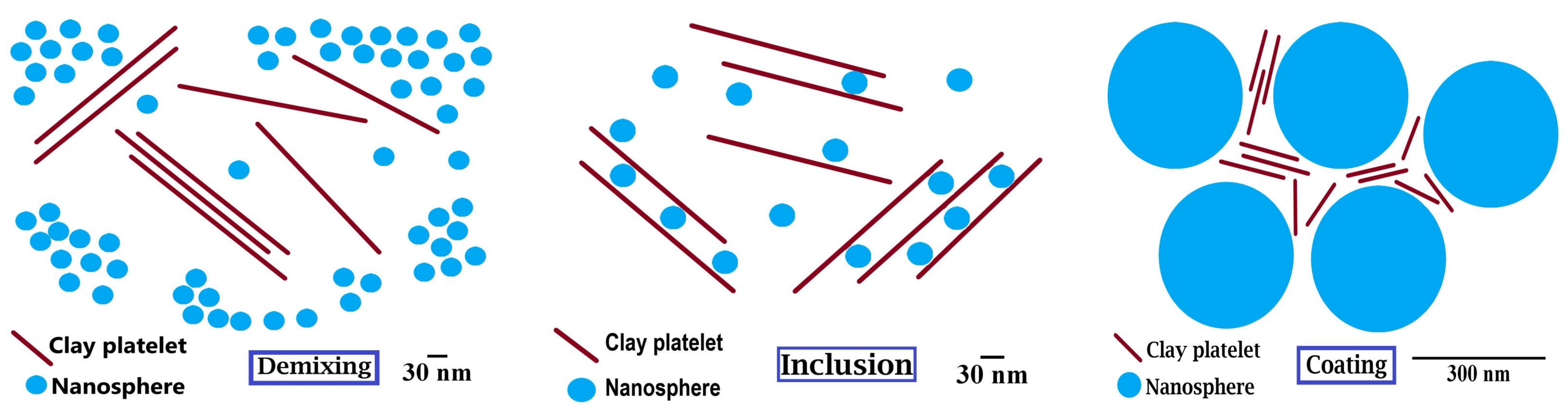
S.VYDELINGUM†[1], P.LEVITZ[1], L.MICHOT[1], N.MALIKOVA[1]

[1]PHENIX Sorbonne University, Paris, France

†sivagen.vydelingum@sorbonne-universite.fr

Introduction

Elementary soil is made of clays, silica and organic matter. Soil porous multi-scale structure depends on every component characteristic [1]. Deposited films* are produced by different deposit methods [2] (passive evaporation, spin coating) from suspensions of clay nano-platelets (200-330 nm in lateral size, 1 nm in thickness, permanent negative surface charge) and spherical nano-particles (30 and 300 nm). By varying relative sizes of the two components, spheres surface charge and number ratio of platelets-spheres different forms of nanoparticles arrangement can be expected:

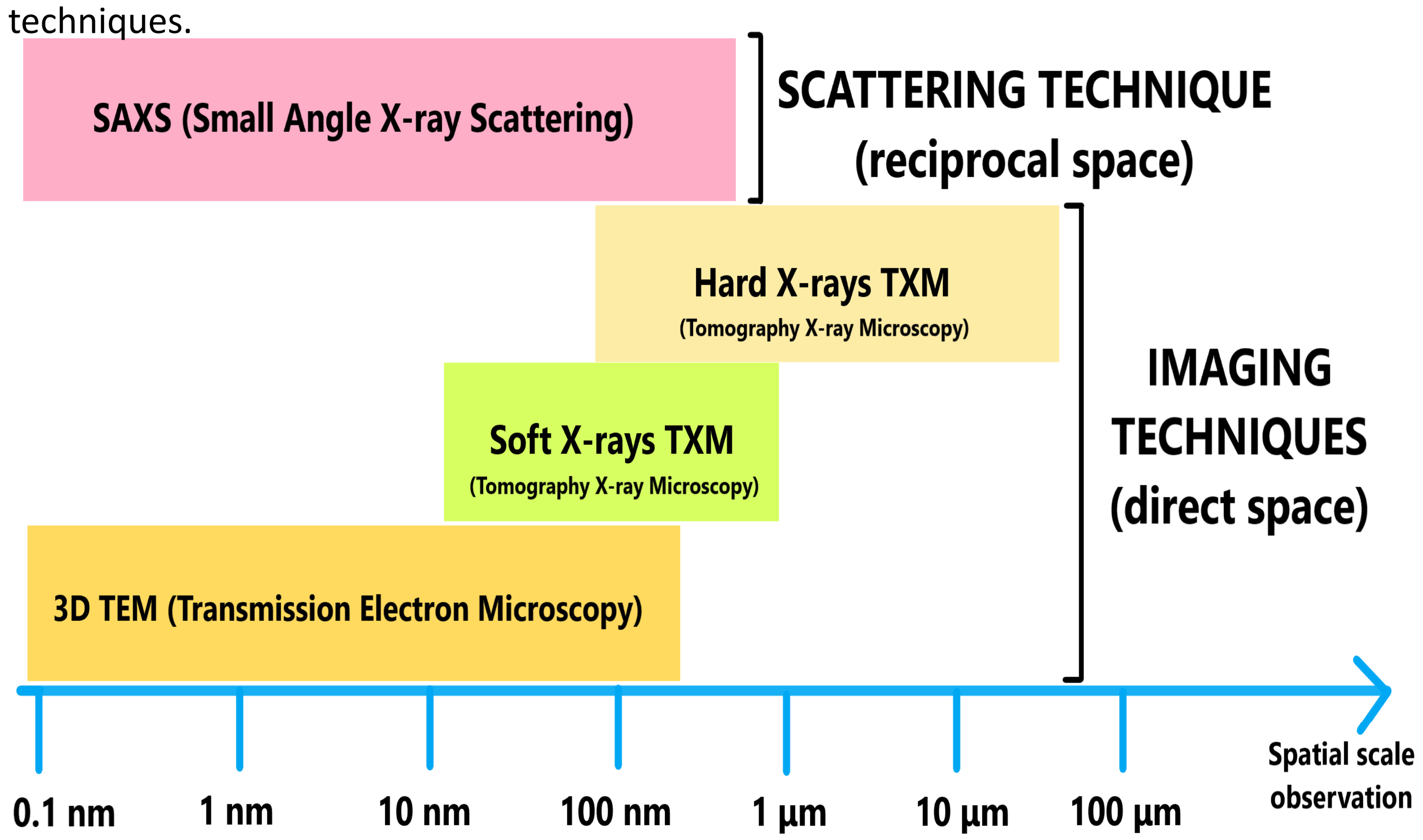


Understanding elementary soil multi-scale structure in relation with molecular and/or colloidal transport has potential interest in soil remediation. Developing a multi-scale structure characterization methodology on this model system* initiate a first step into real soil comprehension. Multi-scale transport of water constitutes the next stage. Suspensions properties are well characterize [3,4]. Only few experiments have been made on clay platelets films without added nanospheres [5].

Characterization methods

Combining several imaging/scattering techniques based on electron and synchrotron radiation allow structural characterization over a large spatial scale.

Comparison between imaging and SAXS data is made in the reciprocal space by working on obtained scattering curves. This permit to know if representative elementary volume (REV) of the sample can be reached by using this different characterization techniques.



Structure characterization techniques

Imaging TEM/TXM observations

Model system :

Beidellite clay platelets (330 nm or 200 nm) + SiO_2 spheres (30 or 300 nm), repulsive interaction.

DEMIXING | **PARTIAL DEMIXING**

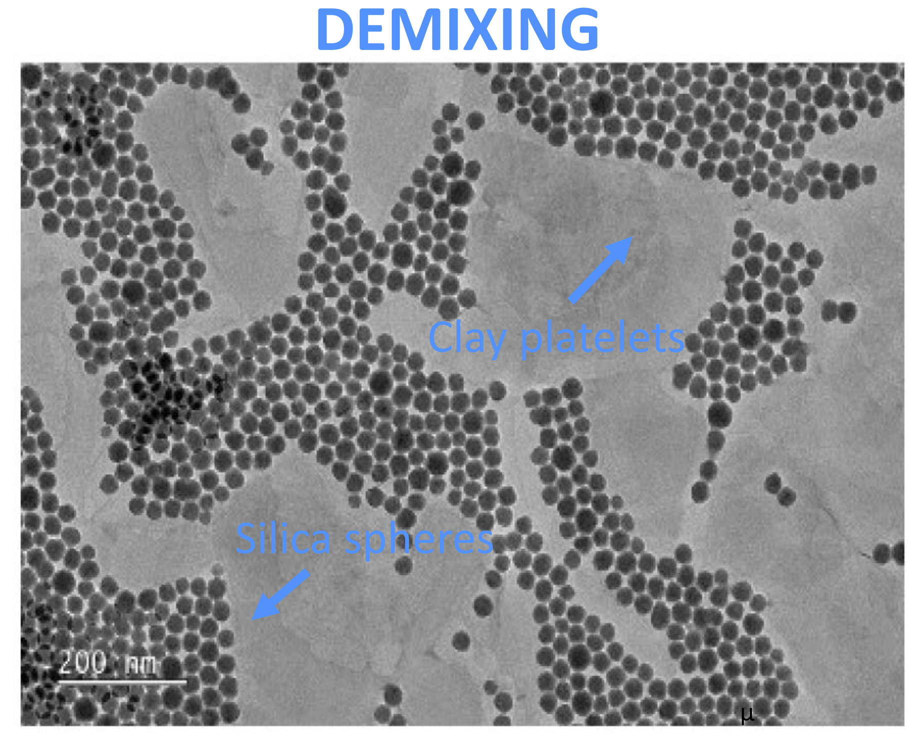


Figure 1 : TEM Spin coated sample, thickness ≈100 nm. 0° projection image. Beidellite 330 nm + 30 nm silica spheres, 1 platelet for 10 spheres (nominal ratio)

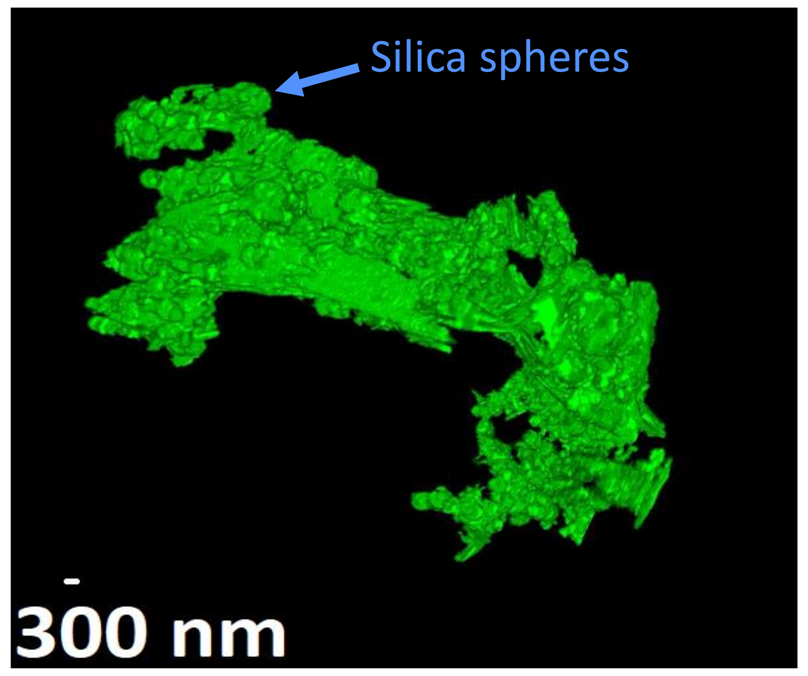
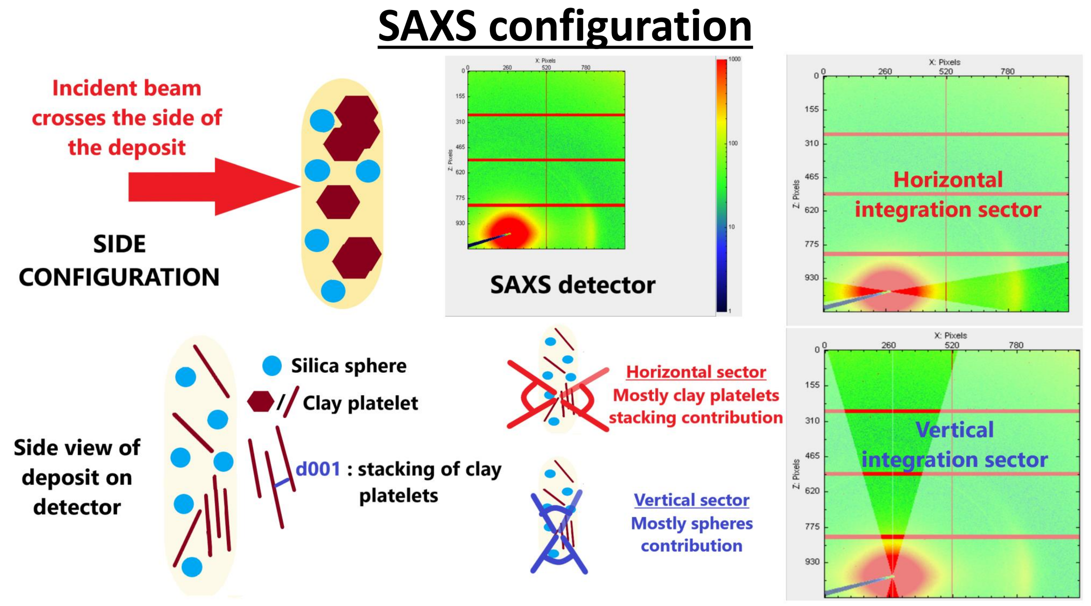


Figure 2 : Soft X-rays TXM 3D model reconstruction: bulk of 200 nm beidellite platelets + 300 nm silica spheres. thickness > 100 nm. Voxel size : 11 nm

SAXS observations

SAXS configuration



Possible demixtion in the deposit is to be confirmed by linear combination (Fig.3).

If linear combination matches with experimental curve of mix in horizontal sector there is demixing (Fig.4). If not a supplementary term is necessary in eq.1 for platelets-spheres interactions.

Linear combination → $$I(q)_{LC} = A \times I(q)_{beidellite} + B \times I(q)_{mix} \quad (1)$$ ← Experimental curves

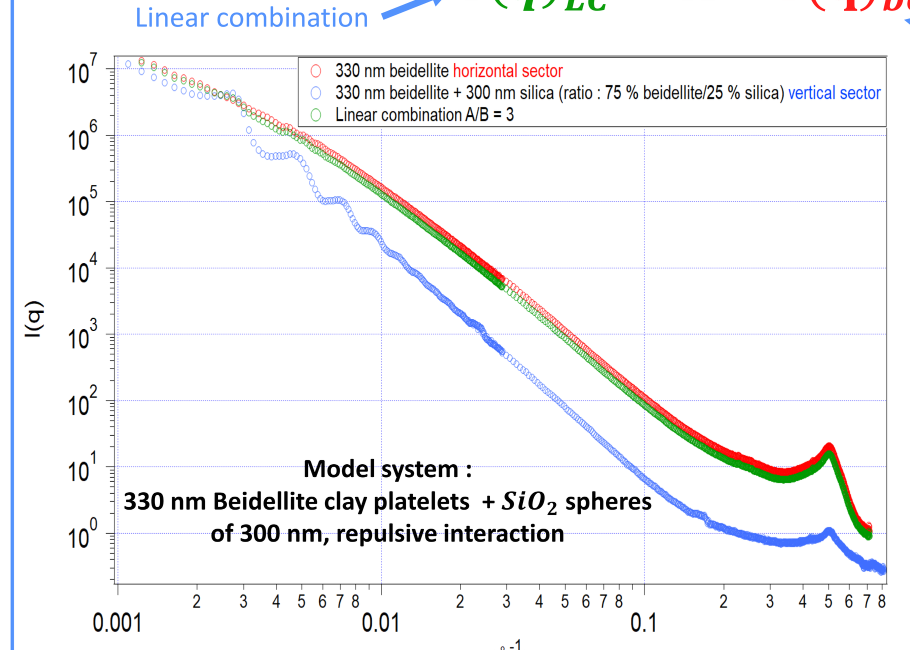


Figure 3 : Construction of linear combination from experimental curves. Linear combination (green curve), sample of only platelets (red curve) and sample of platelets-spheres (blue curve).

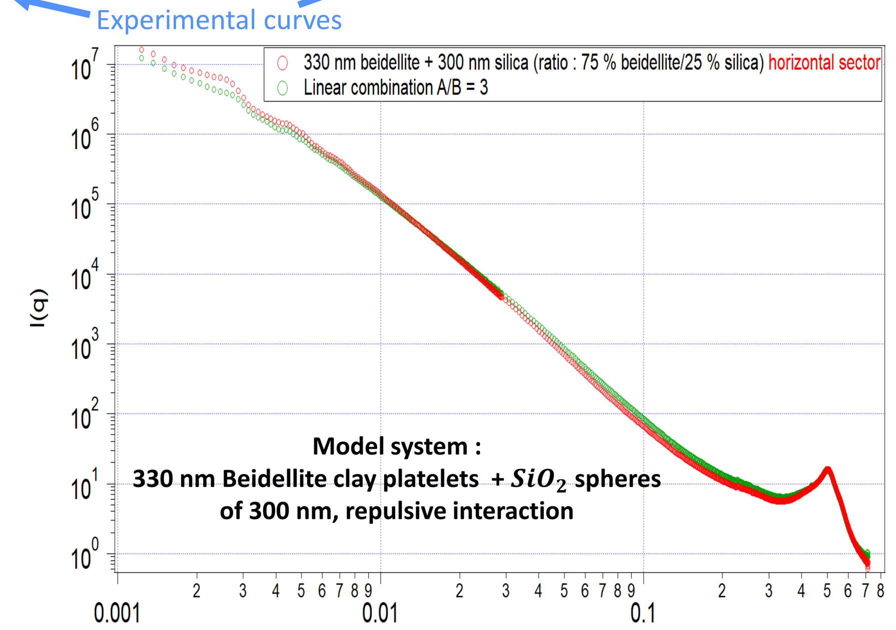


Figure 4 : Linear combination compared to experimental curve of mix platelets-spheres. Matching confirm demixtion in this sample.

Reciprocal space comparaison

Comparison between TEM and SAXS experiment in the reciprocal space for spin coated sample with similar thickness (Fig. 5 a). This permit to see if small areas observed on TEM sample are representative of SAXS experiment with average on larger areas.

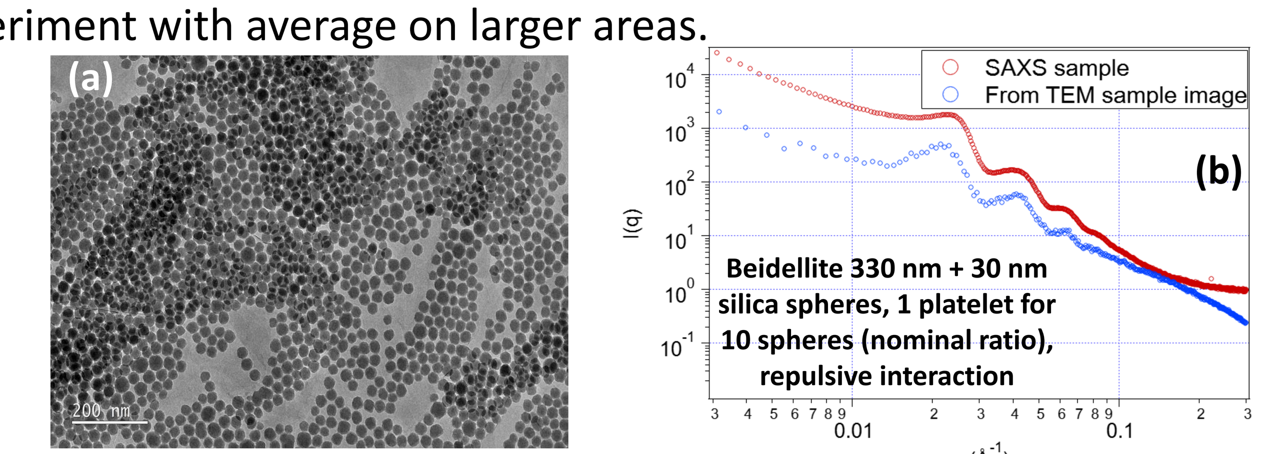


Figure 5 : Imaging and scattering comparison. Spin coated samples with similar thickness : (a) 0° projection image. (b) Intensity in reciprocal space, (red curve) SAXS experiment, (blue curve) TEM experiment.

Attractive interaction

Model system : Beidellite clay platelets (330 nm or 200 nm) + SiO_2 300 nm spheres coated by Al_2O_3 , attractive interaction.

Characterize by Hard X-rays TXM and SAXS :

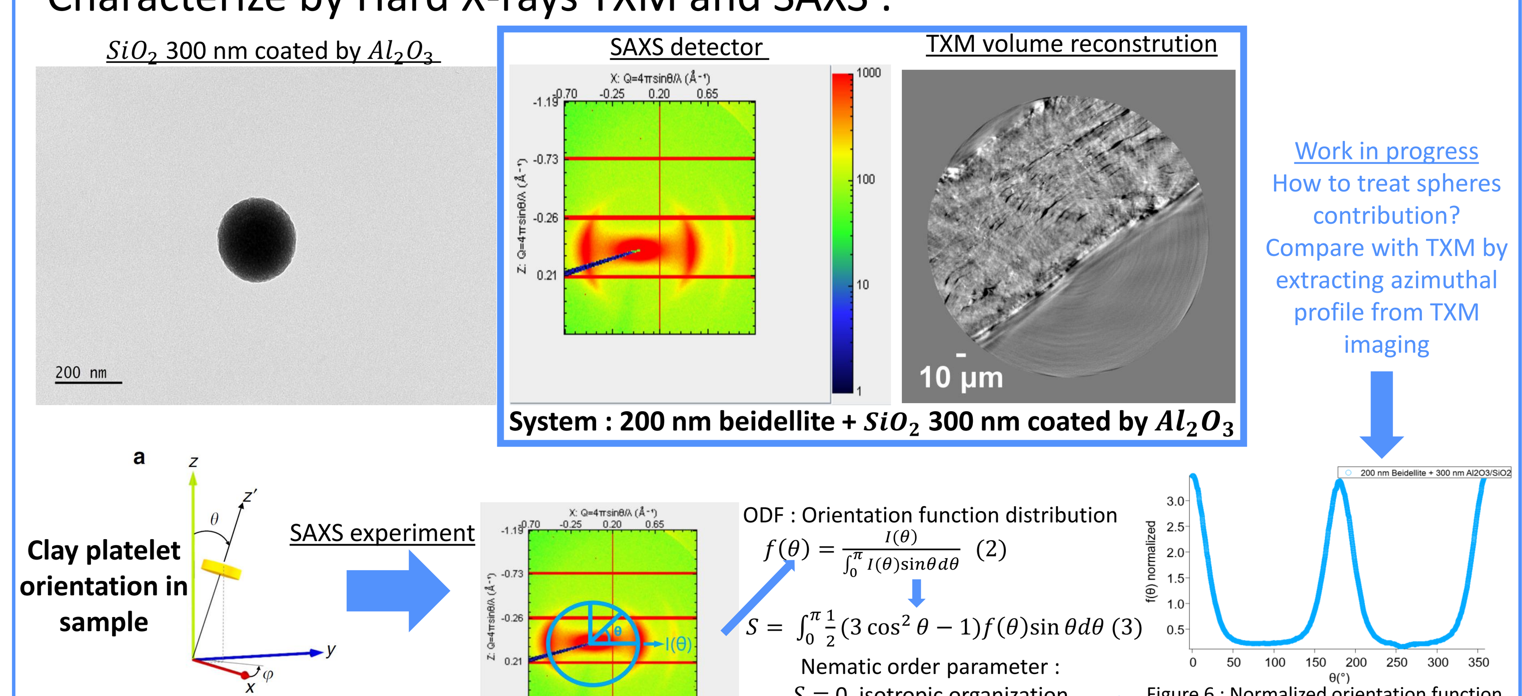


Figure 6 : Normalized orientation function distribution for 200 nm beidellite + SiO_2 300 nm coated by Al_2O_3, $S = 0.404$.

Conclusion

- **Demixing or partial demixing in imaging TEM/TXM and scattering SAXS : using negatively charge silica spheres.**
- **Attractive interaction between platelets-spheres using positively charge SiO_2 300 nm coated by Al_2O_3 in order to observe inclusion and/or coating : work in progress, use also spheres with neutral charge surface.**
- **Linear combination (SAXS), reciprocal space comparison, nematic order parameter are tools that permit to compare imaging and scattering and know how clay platelets orientation is affected by spheres : ratio in the deposit, diameter and surface charge.**

References

[1] F.Attou, "Etude expérimentale d'assemblages squelette-argile. Apport à la compréhension du comportement physique des sols", Thèse soutenue en **1996**.
[2] Zhou, C.-H.; Shen, Z.-F.; Liu, L.-H.; Liu, S.-M. Preparation and Functionality of Clay-Containing Films. *J. Mater. Chem.* **2011.**
[3] Bailey, L.; Lekkerkerker, H. N. W.; Maitland, G. C. Smectite Clay – Inorganic Nanoparticle Mixed Suspensions: Phase Behaviour and Rheology. *Soft Matter* **2015.**
[4] Doshi, N.; Cinacchi, G.; van Duijneveldt, J. S.; Cosgrove, T.; Prescott, S. W.; Grillo, I.; Phipps, J.; Gittins, D. I. Structure of Colloidal Sphere–Plate Mixtures. *J. Phys.: Condens. Matter* **2011.**
[5] Carrier, B.; Vandamme, M.; Pellenq, R. J.-M.; Bornert, M.; Ferrage, E.; Hubert, F.; Van Damme, H. Effect of Water on Elastic and Creep Properties of Self-Standing Clay Films. *Langmuir* **2016** .
[6] Dabat, T.; Hubert, F.; Paineau, E.; Launois, P.; Laforest, C.; Grégoire, B.; Dazas, B.; Tertre, E.; Delville, A.; Ferrage, E. A General Orientation Distribution Function for Clay-Rich Media. *Nat Commun* **2019.**