

Title: What happens at the nanometric scale at the liquid/solid interface? Implementation of an Atomic Force Microscope for 3D-AFM imaging of liquid /solid interface: Application to Biosensors and Tribology	
Scientific field: Atomic Force Microscopy- Instrumentation –Physical-chemistry at interface	
Key words: AFM, force measurements, 3D –AFM , hydration layers, molecules at interface	
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Team: Chemistry and Nanobiotechnology (INL)	Group: ComPETe (Compréhension des Phénomènes Élémentaires en Tribologie)
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Details for the subject:

Background, Context:

A large number of phenomena occurs at the solid/liquid interface, in the first nanometers of liquid in contact with the solid: catalysis reaction, bio recognition on biosensors, tribology, fretting... A fundamental understanding of these processes requires molecular scale knowledge of interfacial solution structures. Surface force apparatus was the first technique to probe the interfacial solution structure between two microscopic mica surfaces immersed in aqueous solution. Since then X-ray reflectivity have proved that ion and solvent distribution within nanometers of a surface differ drastically from the bulk or more recently Second Harmonic Generation technique (SHG) provide vibrational spectra of adsorbed or reactive molecules at interface but all these techniques are limited to large atomically smooth surfaces and do not achieve molecular lateral resolution. Recently, an original technique based on Atomic Force Microscopy (AFM) and called “3D-AFM or 3D FFM” has been developed and has allowed for the first time to generate atomically resolved 3D-images of the organization of atoms, ions and molecules at solid-liquid interface.

Instead of simply measuring the sample height at each x, y position 3D-AFM also record data along the Z direction to probe the whole 3D interfacial space (Figures 1a, 1b [1]). As the oscillating tip interacts with its surroundings, changes in the amplitude, phase or frequency are recorded and then converted into a 3D force map. Previous works have shown that the water molecules adjacent to a membrane strongly interact with the headgroups of adsorbed molecules [2]. The unique capability to visualize hydration structures was also reported (Figure 1c [3]).

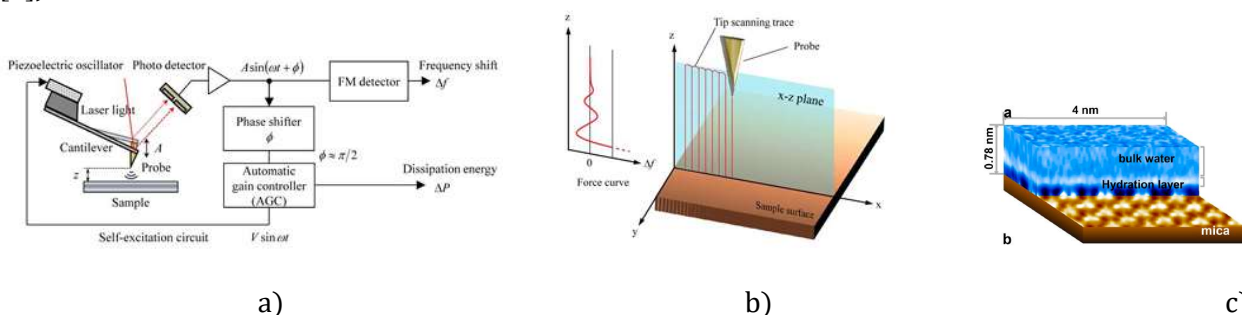


Figure 1: 3D AFM a) Mechanical system and electronic circuit [1], b) Tip scanning Trace on x-z plane c) 3D-AFM map obtained on a mica surface immersed in PBS solution[3].

Research subject- work plan:

The main objective of the PhD is to implement this 3D-AFM technique on an existing recent microscope and to conduct some research on the smart surfaces developed by both labs (INL and LTDS). Indeed, at the INL, some researches are conducted on biomolecular interactions at solid/liquid interfaces and at LTDS, some stimuli responsive polymers brushes are produced to develop smart surfaces. Research topics of both groups are requesting *in situ* characterization of the solid/liquid interface at the molecular scale to measure the density, the organization of the molecules at the surface and their response to the surrounding medium (pH, ionic density, temperature etc ...). There are still some scientific and instrumental challenges for the promotion of 3D-AFM. For instance, the 3D-AFM-based z-depth imaging, with a common value of 1 nm, is ideal for the exploration of the adsorption of ions and solvent molecules on flat substrates, but it is rather small for detecting the hydration structures on non-flat systems, such as isolated proteins, nanostructured surfaces and cells. Thus, it is of great significance to improve the sensitivity, resolution and scanning speed of 3D-AFM for its broader applications, e.g., the study of 3D distribution of flexible surface structures, such as chain polymers or lipid headgroups on a biological membrane surface, and *in-situ* observation.

Mid-term objective of this project is to demonstrate on surfaces with applications in biosensors (INL's project) and tribology (LTDS' project) that this 3D-AFM microscope can be an asset for all the researchers, academic or industrial (Biomérieux, L'Oréal, Saint Gobain, Total, Renault ...), interested in Liquid/Solid Interface.

Scientific environment:

The PhD student will work in the team "Chemistry and Nanobiotechnology" supervised by Prof Magali Phaner-Goutorbe at the INL lab and the group "CompETe" supervised by Dr Frédéric Dubreuil at the LTDS lab, both specialists of AFM since several years in the field of biology and tribology.

INL The Chemistry and Nanobiotechnology group is conducting interdisciplinary research activities focusing on coupling micro/nanotechnology and molecular biology for biology, health care and environmental applications. The role of INL in this internship will be to functionalize the solid surfaces with organic layer and/or isolated biomolecules in the NanoLyon Platform and participate to the 3D- AFM studies (instrumental and experimental) [4,5].

LTDS The CompETe group is working on the knowledge of all elementary friction phenomena and is focused on the usage of nanoparticle, lubricant additives, tribochemistry at the local scale to reduce friction and wear in the contact area. The role of LTDS in this internship will be to prepare some polymeric brushes as surfaces of interest and participate to the 3D- AFM studies (instrumental and experimental)[6,7].

Scientific collaborations with french and international labs will be developed

Candidate skills:

The candidate should ideally have a background in physics or in physical-chemistry of surfaces. The candidate must have a strong taste for instrumentation but also for experimental work (sample preparation, characterization) and must be able to work at the interface between physics, chemistry, mechanics and biology. However, no special skills are required in biology.

Funding:

In the framework of the "Ecole Doctorale Matériaux", the candidate will apply to a PhD grant beginning October 2022 for 3 years. In complement to this grant, the candidate can also participate to the teaching of ECL's students (lab exercices) if desired.

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References :

- [1] T.Hirayama, & N. Yamashita, *Japanese Journal of Applied Physics*, 2020 (59) SN0803.
- [2] H. Asakawa, S. Yoshioka, K. Nishimura and T. Fukuma, *ACS Nano*, 2012, 6 (10), 9013-9020
- [3] T. Fukuma & R. Garcia, *ACS Nano*, 2018, 12(12), 11785-11797.
- [4] F. Zuttion, D. Sicard... M. Phaner-Goutorbe, *Soft Matter*, 2019, 15(36), 7211-7218.
- [5] F. Zuttion, Thèse de Doctorat de l'Université de Lyon soutenue le 24/10/2016 à l'Ecole centrale de Lyon
- [6] M. F. Delcroix, et al, *Biomacromolecules* 2013, 14, (1), 215-225.
- [7] M. Divandari, G. Morgese, S. Ramakrishna, E.M. Benetti *European Polymer Journal* 2019, (110) 301-306.