

# Nanoscale imaging of liquid-liquid interfaces using Atomic Force Microscopy

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The precise control of nanoscopic objects and molecules assembly processes at liquid interfaces requires a structural characterization which is conventionally carried out by reciprocal space techniques (X-ray and neutron scattering and reflectivity). While these methods provide high-resolution and statistically significant data, the information obtained is averaged over macroscopic sample regions, preventing detailed characterization of individual nano-scale defects and direct observation and manipulation of localized nano-structures. This characterization can be performed only by microscopies but, in the case of liquid interfaces, it has so far been limited *in-situ* by the low lateral resolution (i.e. fluorescence, Brewster Angle Microscopy). Atomic Force Microscopy (AFM) can also image soft thin films self-assembled at liquid/liquid interfaces *in-situ* [1,2,3]. High-resolution can be achieved making use of a sample preparation protocol reducing the influence of gravity waves, lateral drift and motion characterizing liquid surfaces. In the first part of my presentation, as a case study, I will show images of monolayers of silica nanoparticles (NPs) mixed with CTAB (cetyltrimethylammonium bromide) at the water/hexane interface (Figure 1). NPs, organized in a monolayer with hexagonal packing, can be individually observed in the AFM images. The interparticle distance depends on CTAB concentration as demonstrated by complementary X-rays surface scattering measurements (GISAXS) [1]. The AFM method is versatile and was also applied to image thin layers of a PS-PMMA copolymer at the water/octane interface and extended to the study of the mechanical behavior of the film [2].

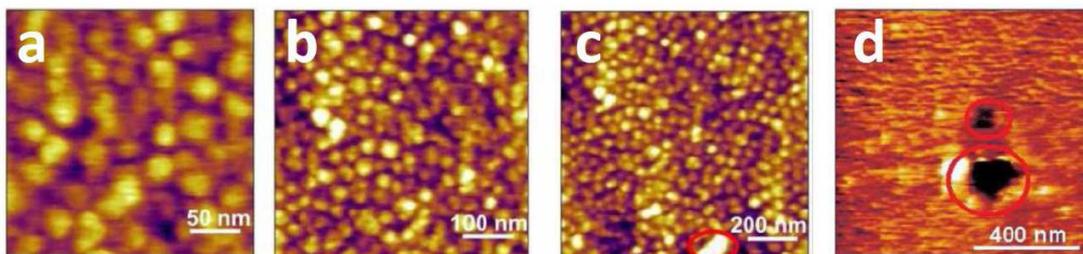
However, AFM still lacks resolution to image very soft samples such as living cells or ultra-soft liquid-liquid interfaces (surface tension  $< 10^{-4}$  N/m) To circumvent this limitation, we employed, as a proof-of-concept, a sensing mechanism based on the energy transfer between a fluorescent nanodiamond (donor) attached to an AFM tip and a metallic substrate (acceptor) [4]. I will present an operational scheme that permits to simultaneously acquire AFM and Fluorescence-lifetime Imaging Microscopy (FLIM) images and does not require mechanical contact between tip and sample, therefore enabling a novel pathway of quench sensing to image ultra-soft samples.

[1] Costa, L., et al. *Nano letters*, 16(9), 5463-5468 (2016).

[2] Costa, L., et al. *Advanced Materials Interfaces*, 4(16), 1700203 (2017).

[3] Chai, Yu, et al. *Science advances* 6.48, eabb8675 (2020).

[4] Fernandes, Thales FD, et al. *Scientific reports* 10.1, 1-12 (2020).



**Figure 1 :** (a-c) In situ AFM images of silica nanoparticles adsorbed at the water/heptane interface at 10 mM CTAB concentration. The same monolayer (ML) is imaged repeatedly at different resolutions. (d) Lower resolution image of sub-mm holes pre-created in-situ with the AFM tip in a solid-like NP ML.