Experimental Molecular Dynamics -
Watching individual liquid molecules moving at interfaces

PhD thesis proposal (ED397 – Physics and Chemistry of Materials)
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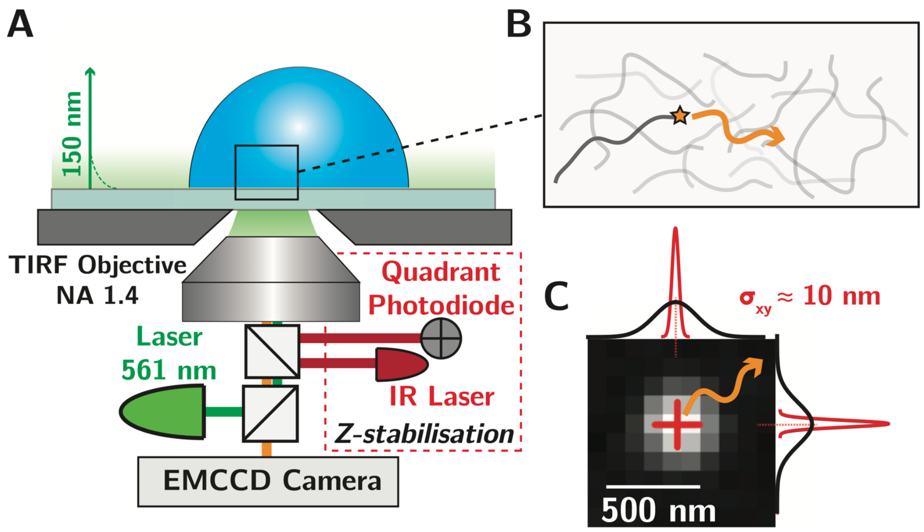

Figure 1. (A) Schematic of the experimental Single-Molecule fluorescence Microscopy set-up. The interface is selectively illuminated by an evanescent wave and imaged with a sensitive camera. **(B)** Zoom on the local polymeric liquid melt, composed of dense interacting molecules. Some polymers are tagged with a single fluorophore, allowing to follow their individual spatiotemporal trajectories at the interface. **(C)** Typical fluorescent signal on the EMCCD/sCMOS camera, with a single diffraction-limited spot related to the emitting fluorophore, localized and tracked with nanometric resolution and high temporal resolution (0.1-1 kHz).

Liquids confined down to nanometric scales can show a range of exotic behaviors, associated among others with molecular ordering, dielectric anomalies, enhanced or hindered transport, reduced friction leading to fast flows, etc… [1]. These peculiar nanoscale phenomena are not only fundamental curiosities but have also macroscopic and practical consequences in diverse fields related to energy storage, energy harvesting, catalysis, water remediation, filtration, or in the biological realm. Many of these effects are intimately related to the short-range interactions arising in the presence of the solid surfaces, and significant experimental progress has been obtained in the recent years, thanks to the advent of exquisite nano-fabrication techniques allowing to confine liquids at the nanoscale [2]. However, our understanding of confined liquid matter still remains partial, due to our current inability to observe the intrinsically nanoscale molecular processes taking place at these interface [3].

This PhD project aims precisely at proposing and developing new experimental approaches based on single molecule fluorescence microscopy for the direct visualization of molecular-scale dynamics at solid/liquid interfaces (Fig. 1A). These state-of-the-art optical techniques allow to localize and track the motion of individual fluorescent molecules with nanoscale resolution and high temporal resolution (0.1 - 1 kHz). Accessing molecular liquid motion at interfaces has been so far exclusive to molecular dynamics simulations, and its opening to real experimental system would represent a clear breakthrough.

As a first route, we will apply these single molecule approaches to dense polymeric liquids (such as PDMS melts), whose relaxation time and viscosity can be tuned over large time-scales through the control of their molecular weight. A fraction of these molecules will be tagged with a fluorophore (Fig. 1B). By selectively imaging the interface with an evanescent wave, we will be able to directly localize their position and follow individual molecular dynamics over time. We will be particularly attentive to the possible slowing down or acceleration of molecular motion at the solid boundary, evidenced here through direct single-molecule visualization and tracking. These measurements will be then extended towards confined and dynamic flow situations, giving unprecedented insights on driven out-of-equilibrium molecular motion at interfaces.

In a second step, we will turn to specific fluorescent defects hosted at the solid surface, whose fluorescence emission allows to reveal molecular interactions with the liquid such as water dissociation/proton chemisorption, or local dielectric screening in organic solvents [4-6]. By revealing surface-specific interactions, these interfacial sensors will provide highly complementary information to the above-mentioned strategy and enlighten our understanding of molecularly confined liquid.

By revealing previously invisible molecular motion, our approach will propel the development of a new molecular vision of liquid dynamics in confinement and at interfaces, with broad impact for a range of fields and materials where interfaces are key.

We are looking for a student strongly motivated by experimental work involving custom-made Single-Molecule Localization microscopy setup and advanced data analysis, micro and nanofabrication and with strong a background in physics (soft matter, hydrodynamics, mechanics) or physicochemistry.

References

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