PhD thesis proposal - ED397 - Physics and Chemistry of Material

Experimental Molecular Dynamics -
Watching individual liquid molecules moving at solid/liquid interfaces

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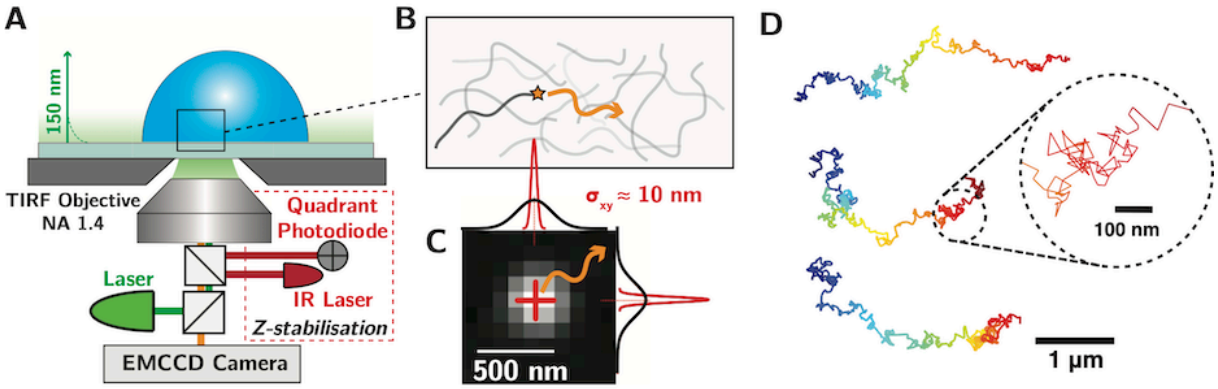

Figure. (A) Schematic of the experimental Single-Molecule fluorescence Microscopy set-up. The solid/liquid interface is selectively excited by an evanescent wave and imaged with a sensitive EMCCD camera. **(B)** Zoom on the local liquid melt structure, made of interacting polymeric molecules. Some polymers are tagged with a single fluorophore, allowing to follow their spatiotemporal trajectories. **(C)** Typical fluorescent signal on the EMCCD camera, with a single diffraction-limited spot related to the emitting fluorophore, localized and tracked with nanometric resolution and high temporal resolution (10 ms). **(D)** Typical trajectories of PEG macromolecules adsorbed at the solid/water interface and dragged by a hydrodynamic flow of solvent.

Molecular-scale interactions between liquids and solid surfaces govern a wide range of processes in soft-matter physics, from wetting and friction, down to confined flows in nanofluidic settings, with broad relevance for a variety of fields from biology to engineering. Under confinement, surfaces can also to the specific emergence of peculiar and dramatic behaviors for liquid transport. Typically, these interactions are probed at an ensemble level and described by averaged phenomenological coefficients accounting for the behavior of the interface, e.g. a slip length in the case of the interfacial solid/friction. However, the molecular foundations behind this averaged vision remain unclear, due to our current inability to experimentally observe the intrinsically nanoscale molecular processes taking place at interfaces and in confinement.

In this PhD proposal, we aim to bridge this gap by developing novel experimental approaches to directly visualize and quantify molecular motion at solid/liquid interfaces, which has been so far exclusive to molecular dynamics simulations. We will rely on state-of-the-art single-molecule and super-resolution fluorescence microscopy techniques which can be used to localize and track the motion of individual fluorophores with nanoscale resolution and high temporal resolution. These single-molecule imaging approaches will be applied to dense polymeric melts (e.g. PDMS molecules), whose relaxation time and viscosity can be tuned over large time-scales through the control of their molecular weight or temperature. As shown in Fig. B, a fraction of these polymeric molecules will be tagged with a fluorophore. By selectively imaging the interface with an evanescent wave, we will be able to directly track the dynamical motion of individual macromolecules and analyze their statistical properties (Fig. C). Note that preliminary results in our group focusing on the interfacial dynamics of flowing polymer solutions have demonstrated the feasibility of this single-macromolecule tracking approach (Fig. D).

These approaches will be harvested to explore a range of questions related to interfacial liquid friction at the molecular scale, playing specifically on polymer-surface interactions through the control of surface physicochemistry, as well as molecular weight and temperature. We will first address the

question of molecular dynamics at the triple-line during low-velocity droplet motion. Probing flow in microfluidic channels, we will then focus on solid/liquid friction, addressing the relation between liquid slippage and macromolecular dynamics. Finally, we will turn to the crucial of question of liquid transport in nanometric-scale fluidic confinement. These single molecule measurements will be coupled with statistical analysis of the dynamics, allowing ultimately for a detailed understanding and modelling of liquid/surface interactions, and revealing a new molecular vision of liquid transport at solid surfaces.

We are looking for a PhD candidate motivated by state-of-the-art experimental work involving custom-made single-molecule imaging and statistical analysis of the dynamics, with a strong a background in physics (soft matter, hydrodynamics, mechanics…) or physicochemistry (polymers…)

References.
- Comtet et al. (2020). ***Nature Nanotechnology***, *15*(7), 598-604.
- Schwartz et al. (2014). **JACS**, 136(4), 1327-1332.