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MolecularScope: Single Polymer Dynamics at Solid/Liquid Interfaces

PhD thesis proposal - ED397 - Physics and Chemistry of Materials

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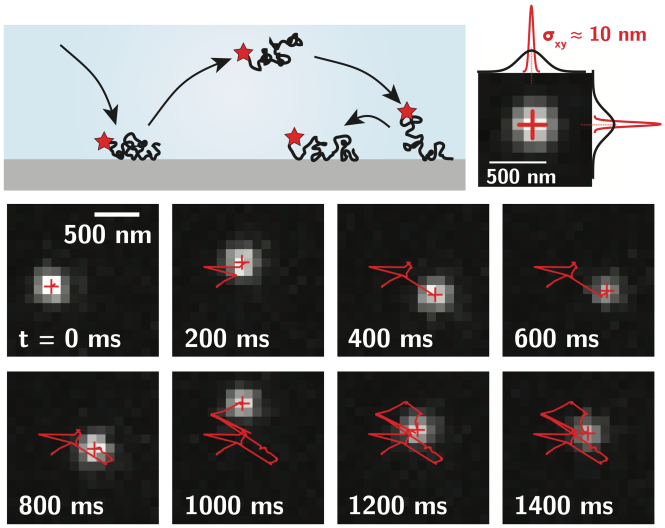
Molecular-scale interactions between polymers in solutions and solid surfaces govern a **large number of macroscopic processes in soft matter**, from surface functionalization with adsorbed or self-assembled polymer layers, polymer flow in porous media, to lubrification, friction and adhesion... These interfacial processes are typically **probed at the ensemble level** and described by averaged phenomenological coefficients, characterizing the mean dynamic response of the interface (surface concentration, slip length, friction coefficient...). However, our **molecular-scale understanding of these complex interfacial responses remains poor,** due to the **difficulties in measuring directly these local molecular processes** (chain adsorption, chain desorption, surface diffusion...).



Nanometrically resolved dynamics of a single fluorescently tagged PEG chain hopping at a solid/liquid interface.

The aim of this PhD is to **bridge this gap between the molecular and the macroscopic scale**, to bring a **new understanding of the out-of-equilibrium interfacial dynamics of polymers at solid/liquid interfaces**. To do so, we will rely on **state-of-the-art optical techniques** based on **single-molecule and super-resolution fluorescence microscopy**, allowing to **track individual chain dynamics at interfaces with nanometric resolution**. Recent application of these techniques to fluorescently tagged polymers have demonstrated their potential for the direct, in-situ and spatially-resolved study of molecular polymer dynamics at solid/liquid interfaces [1-3].

In the first part of this PhD, we will probe the **full out-of-equilibrium interfacial dynamics of single polymer chains, under a hydrodynamic flow of solvent**. In particular, close to attractive interfaces, **polymer adsorption may compete strongly with hydrodynamic flow**, leading to **profound modification of the interfacial dynamics**, with biased chain motion, forced desorption of the chain and modification of the hydrodynamic boundary condition (liquid slip), all of which remain up to now poorly characterized and understood [4, 5]. By coupling the super-resolution microscope with a microfluidic set-up, we will probe in particular the **complex interplay between individual chain dynamics and the flow boundary condition (slip) at the solid/liquid interface.** A fine control of the conformation and molecular-scale interactions between polymer chains and surfaces will be obtained by tuning the physicochemistry of the solvent, polymer and surface. These single molecule measurements will be coupled with statistical analysis of the dynamics, allowing ultimately a **detailed understanding and modelling of polymer and solvent interactions with solid surfaces**. We will also envision innovative ways to access to the internal chain dynamics (e.g. elongation) occurring under flow.

In the second part of this PhD, we will aim at **extending these results to the case of solid friction and adhesion** [6]. The super-resolution microscope will be coupled with a sensitive force measurement set-up to probe the **mechanical response of a confined layer of adsorbed polymer chains**. This configuration will allow us to probe jointly the macroscopic frictional and adhesive response of the contact and the dynamics and statistics of individual chain detachment events, bridging the gap between the **macromolecular dynamics at the interface and the emerging mechanical response at the macroscopic scale**.

The PhD student will be involved in all aspects of this interdisciplinary project: sensitive optical and mechanical set-up development and operation, microfluidics, polymer and surface physicochemistry, signal processing for single-molecule super-resolution microscopy techniques, up to statistical data analysis and modeling.

We are thus looking for a student **strongly motivated by innovative experimental work**, with a background in at least one of the following domains: (soft matter) physics, polymer physicochemistry and polymer physics, optics, mechanics, microfluidics or material science.

Applications should be sent to jean.comtet@espci.fr (include CV and grades).

Bibliography

[1] Granick et al. (2013). ACS nano, 7(11), 9735-9742.
[2] Schwartz et al. (2014). JACS, 136(4), 1327-1332.
[3] Schwartz et al. (2020). The Journal of Physical Chemistry C, 124(37), 19880-19891.
[4] Kumar et al. (2015). ACS Macro Letters, 4(3), 271-274.
[5] Granick et al. (2002). Macromolecules, 35(12), 4658-4663.
[6] Gong, J.P. (2006). Soft Matter 2(7):544–52.

Associated publications :

Comtet et al. (2019). Nano Letters, 19(4), 2516-2523.
Comtet et al. (2020) Nature Nanotechnology, 15(7), 598-604.
Comtet et al. (2021) Science Advances. 7(40), eabg8568.