Molecular Scope : watching macromolecular dynamics at solid-liquid interfaces at the single-chain level
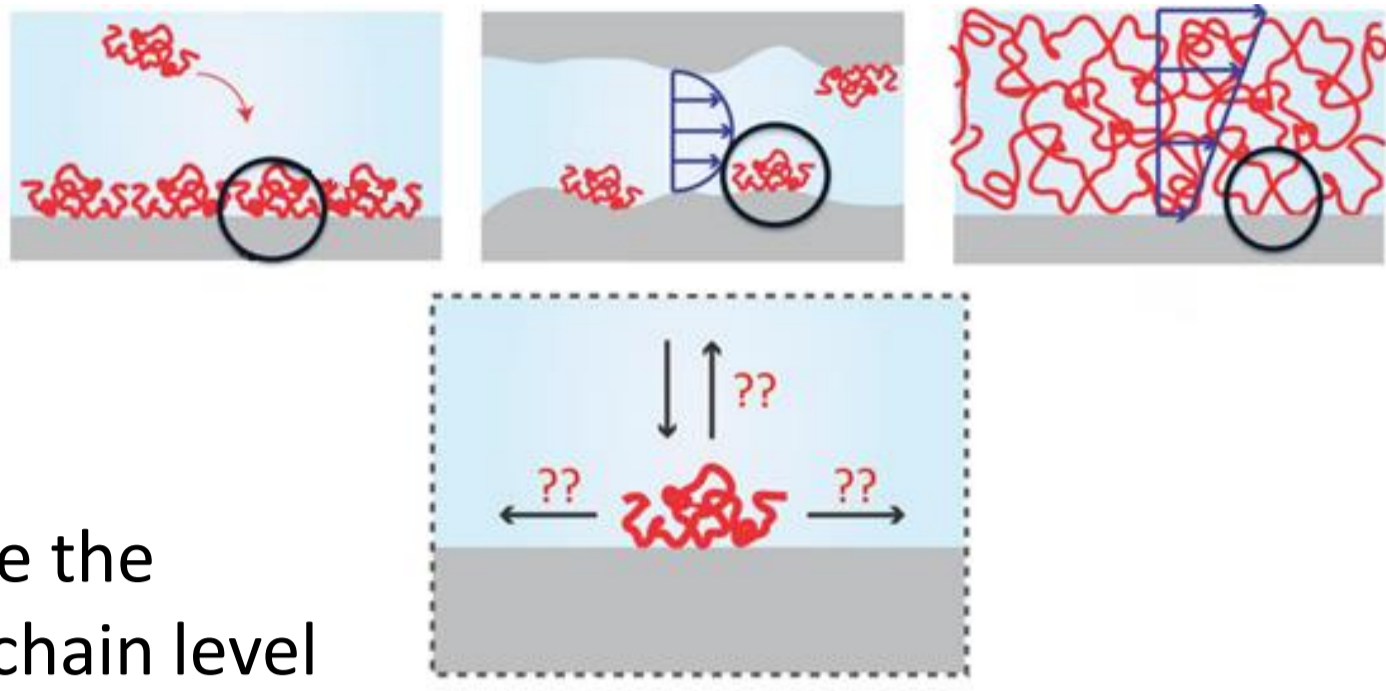
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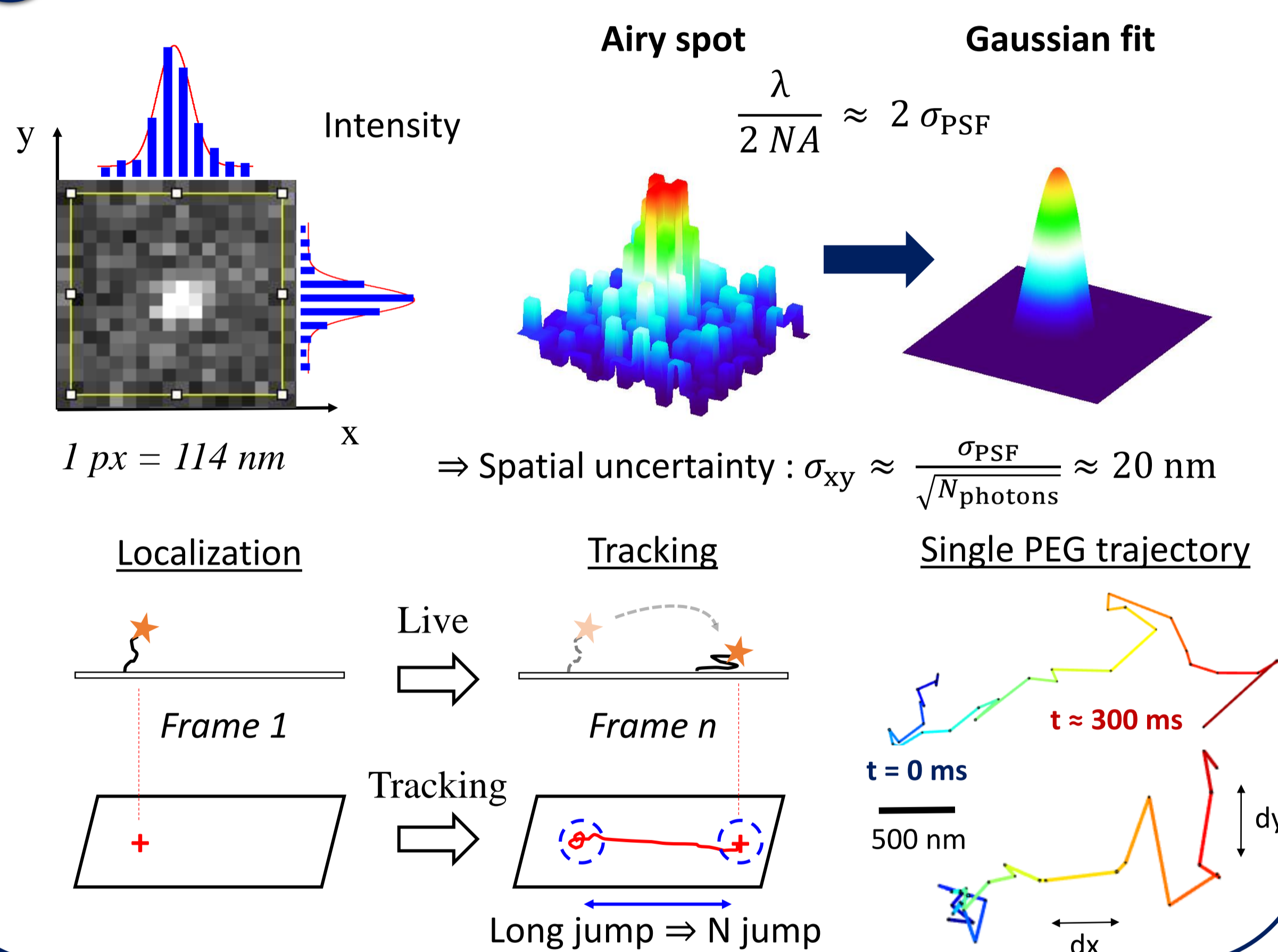
Context & Objectives

→ Macromolecular dynamics at solid-liquid interface is key to a number of surface phenomena like functionalization, transport and adhesion.
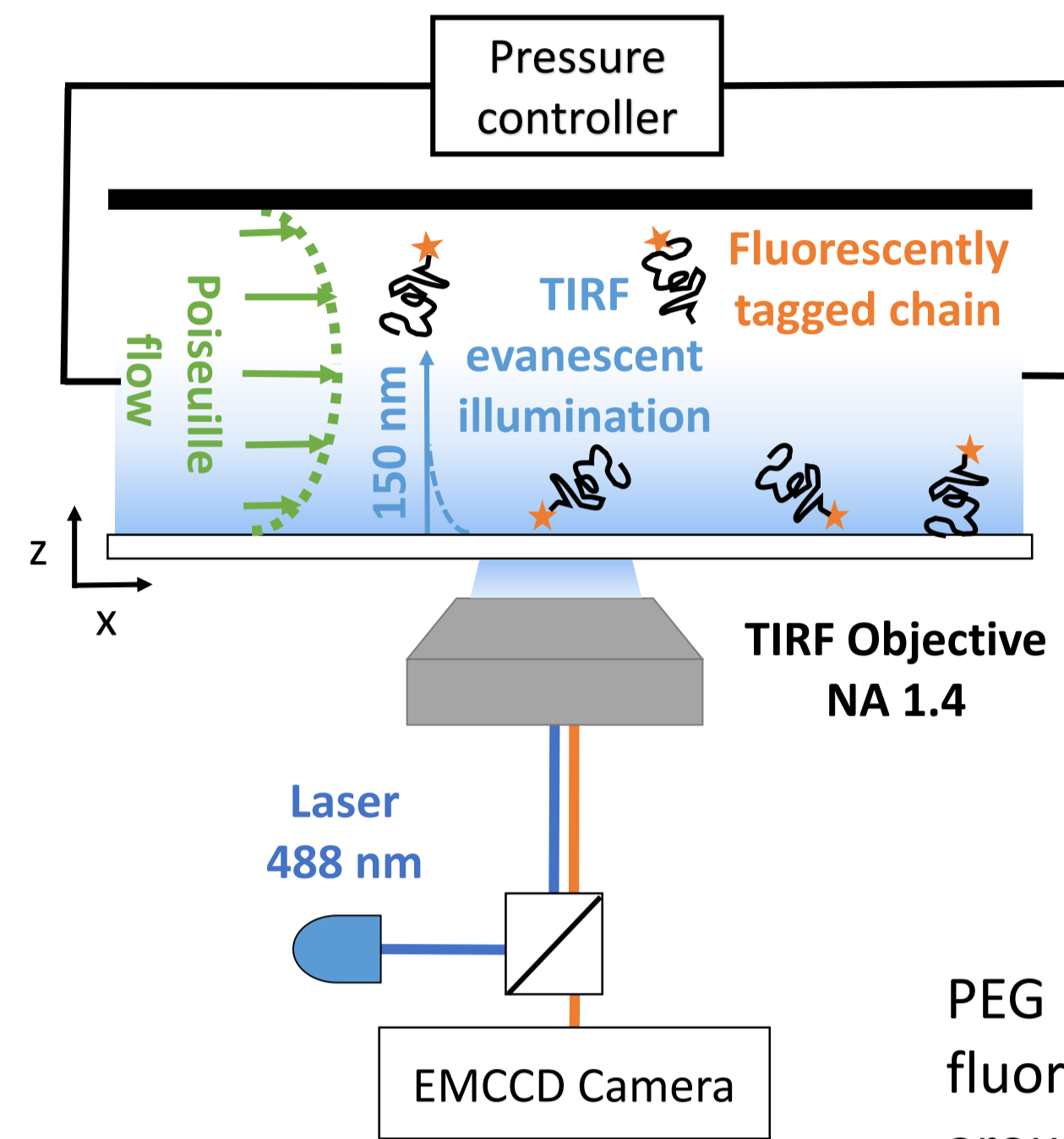
→ We developed a set-up to probe the dynamic under flow at the single-chain level

- What is the behavior of macromolecules at solid/liquid interfaces and how is their dynamics influenced by flow-induced forces ?
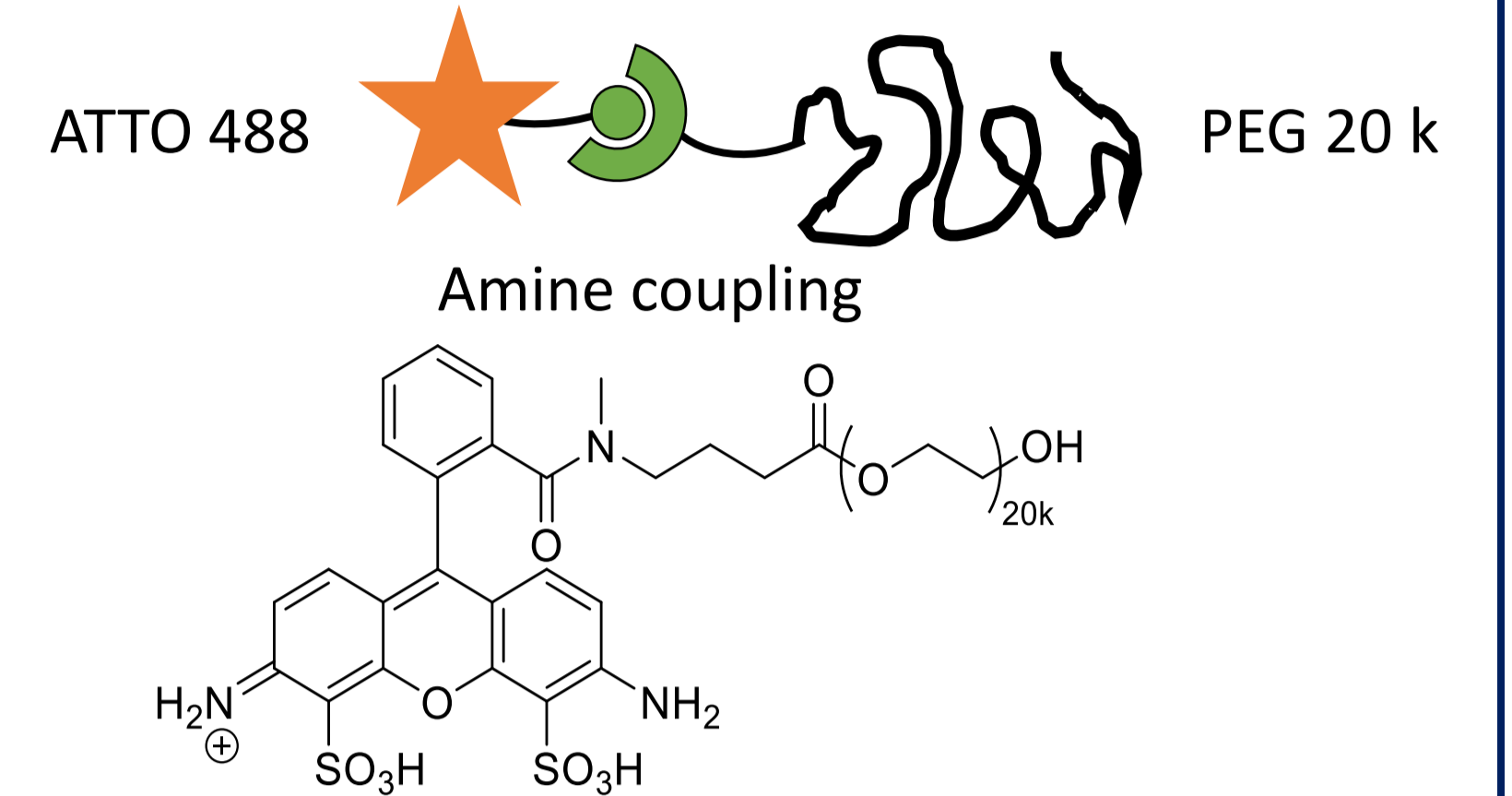
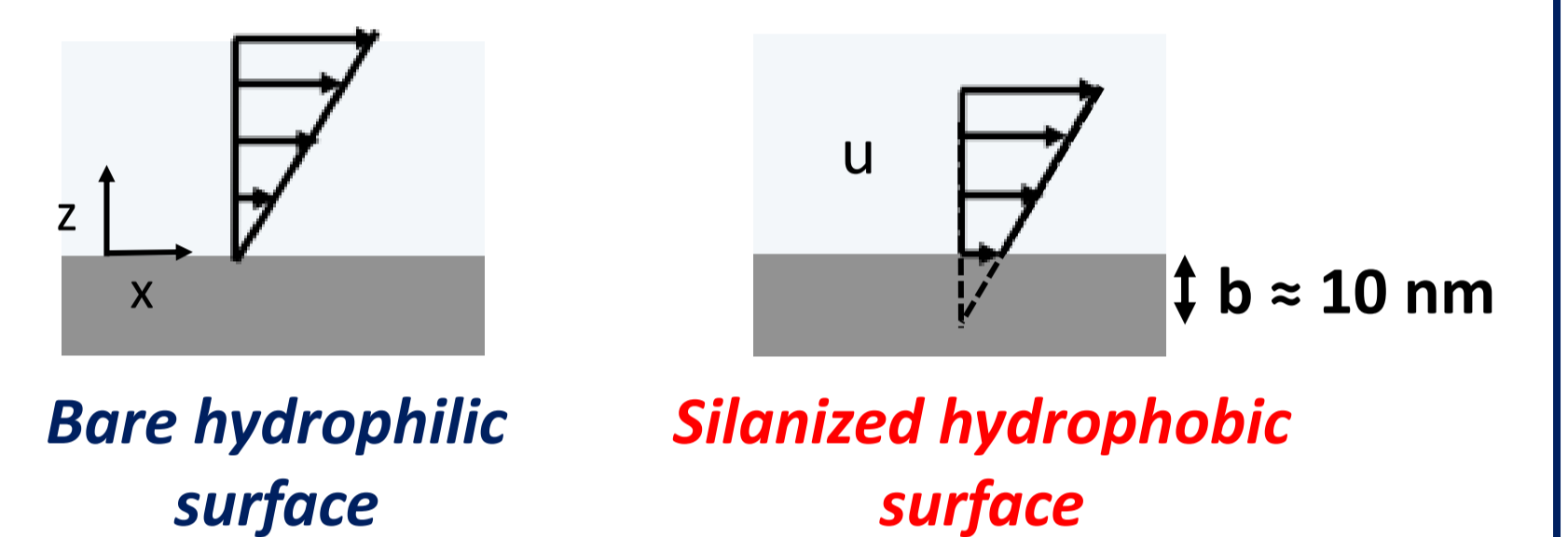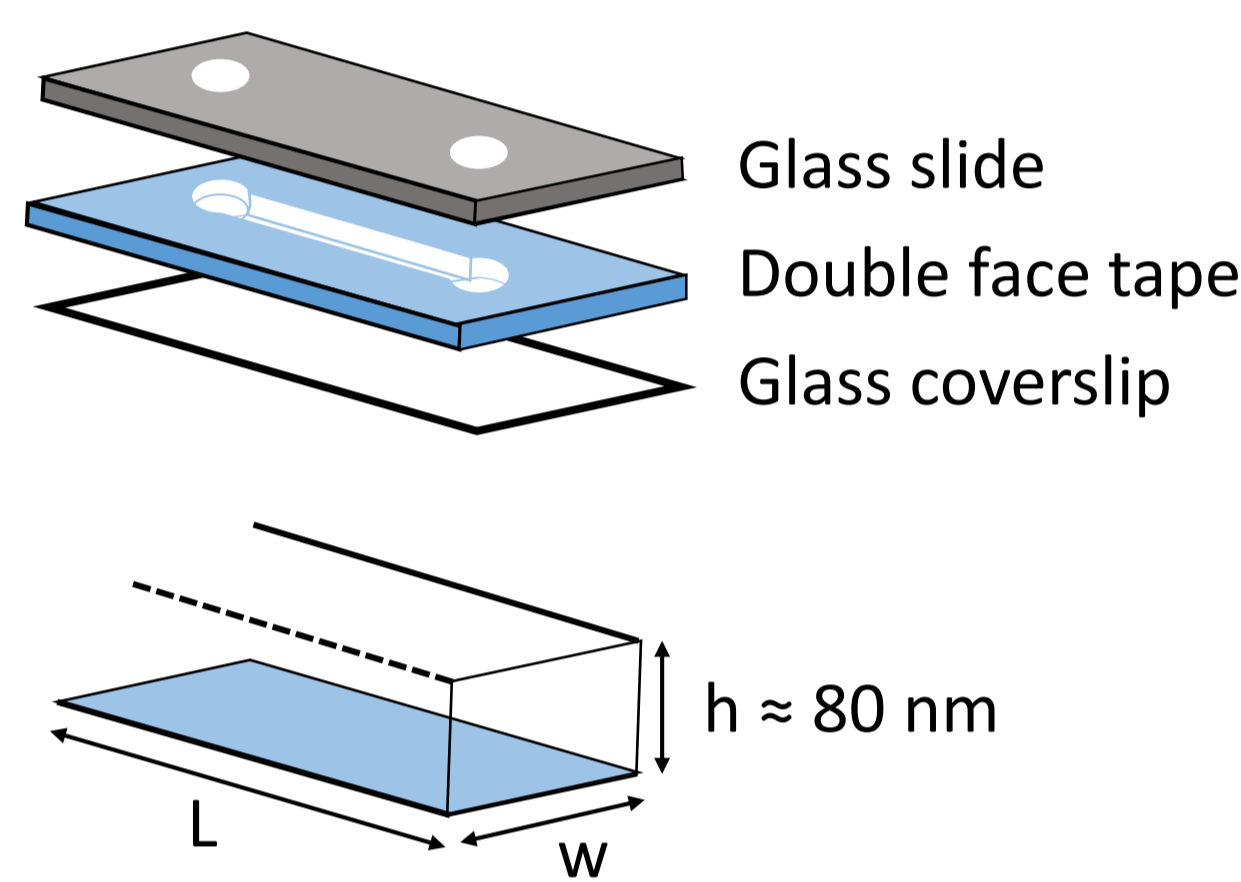## 1 Coupling of Single-Molecule Microscopy with microfluidic…

Total Internal Reflexion Fluorescence allows to illuminate a thin region at the glass/water interface, and image only surface-adsorbed macromolecules.

Pressure controller
Poiseuille flow
TIRF evanescent illumination
150 nm
Fluorescently tagged chain
z
x
TIRF Objective NA 1.4
Laser 488 nm
EMCCD Camera

ATTO 488   PEG 20 k
Amine coupling

PEG is functionalized with ATTO 488, a highly photostable fluorophore absorbing at 488 nm and emitting fluorescence around 520 nm.

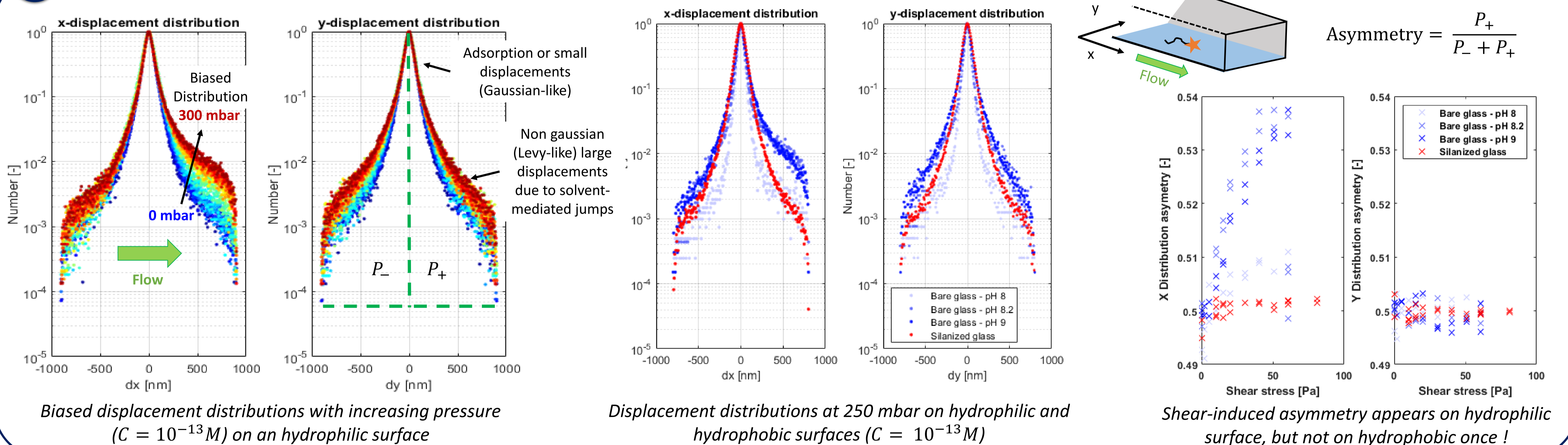Microfluidic channel with hydrophilic / -phobic walls

Cleaned with piranha solution and UV Ozone, the surface is hydrophilic due to the silanol groups. It can be silanized by vapor deposition and so becomes hydrophobic with a finite slip length b.

Glass slide
Double face tape
Glass coverslip

$h \approx 80$ nm
L   w

$b \approx 10$ nm
Bare hydrophilic surface   **Silanized hydrophobic surface**

We assume a fully developed Poiseuille flow in the channel. With geometrical approximations and the boundary conditions, we obtain :
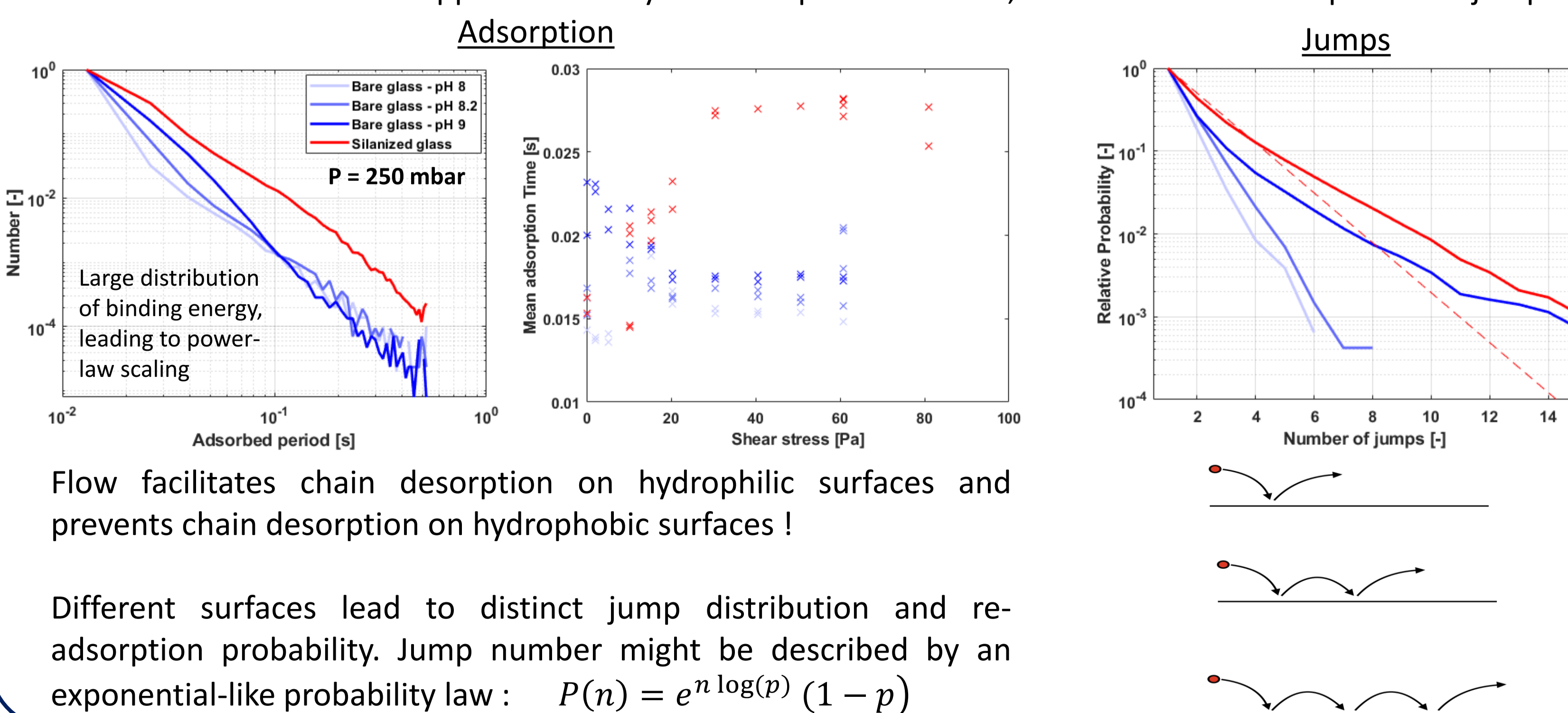
$$\eta \Delta u - \nabla P = 0 \;\Rightarrow\; u_{z=0} \approx \frac{\Delta P \, h \, b}{L \, 2 \, \eta} \text{ and } \sigma_{z=0} = \eta \frac{du}{dz} = \frac{\Delta P}{L}\left(\frac{h}{2}\right)$$

2 allows to track macromolecules under flow,

Airy spot   Gaussian fit
$$\frac{\lambda}{2 \, NA} \approx 2 \, \sigma_{PSF}$$

Intensity
y   x
$1 px = 114$ nm

⇒ Spatial uncertainty : $\sigma_{xy} \approx \frac{\sigma_{PSF}}{\sqrt{N_{photons}}} \approx 20$ nm

Localization   Tracking   Single PEG trajectory
Frame 1   Live   Frame n
Tracking
$t \approx 300$ ms
$t = 0$ ms
500 nm
dy   dx
Long jump ⇒ N jump

3 and to access to single chain dynamics

x-displacement distribution   y-displacement distribution

Biased Distribution
300 mbar
0 mbar
Flow
Adsorption or small displacements (Gaussian-like)
Non gaussian (Levy-like) large displacements due to solvent-mediated jumps
P_- P_+

Biased displacement distributions with increasing pressure ($C = 10^{-13} M$) on an hydrophilic surface

x-displacement distribution   y-displacement distribution

Bare glass - pH 8
Bare glass - pH 8.2
Bare glass - pH 9
Silanized glass

Displacement distributions at 250 mbar on hydrophilic and hydrophobic surfaces ($C = 10^{-13} M$)

y   x
Flow
$$\text{Asymmetry} = \frac{P_+}{P_- + P_+}$$

X Distribution asymetry [-]   Y Distribution asymetry [-]
Shear stress [Pa]
Bare glass - pH 8
Bare glass - pH 8.2
Bare glass - pH 9
Silanized glass

Shear-induced asymmetry appears on hydrophilic surface, but not on hydrophobic once !

4 and to skewed adsorption.

The chain behavior is approximated by a two-step random walk, with successive adsorption and jumps.

Adsorption   Jumps

Bare glass - pH 8
Bare glass - pH 8.2
Bare glass - pH 9
Silanized glass

P = 250 mbar
Large distribution of binding energy, leading to power-law scaling

Mean adsorption Time [s]
Shear stress [Pa]

Relative Probability [-]
Number of jumps [-]

Flow facilitates chain desorption on hydrophilic surfaces and prevents chain desorption on hydrophobic surfaces !

Different surfaces lead to distinct jump distribution and re-adsorption probability. Jump number might be described by an exponential-like probability law : $P(n) = e^{n \log(p)} (1 - p)$

Conclusion and upcoming perspectives

• On hydrophilic surfaces, flow creates an asymmetry in the displacement distribution, increasing the probability for an adsorbed macromolecule to hope over a long distance along the flow. Small displacements, i.e. crawling at the surface are also influence by the flow.

• Such biased random walk are not observed on hydrophobic surfaces, despite higher expected hydrodynamic coupling due to finite slip length…

• The interfacial adsorption time also shows large differences in the response under flow depending on hydrophilic/hydrophobic surface nature. Further investigations are needed to correctly understand the induced modifications of the dynamic.

How does the molecular size affect the dynamic coupling with the flow ? Is there a minimum size, below which flow has no impact ?

Keeping the fluorescent macromolecule concentration constant, it should be possible to increase chain concentration to investigate denser regimes : are similar effects observed in semi-dilute or melt regimes ?

References

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