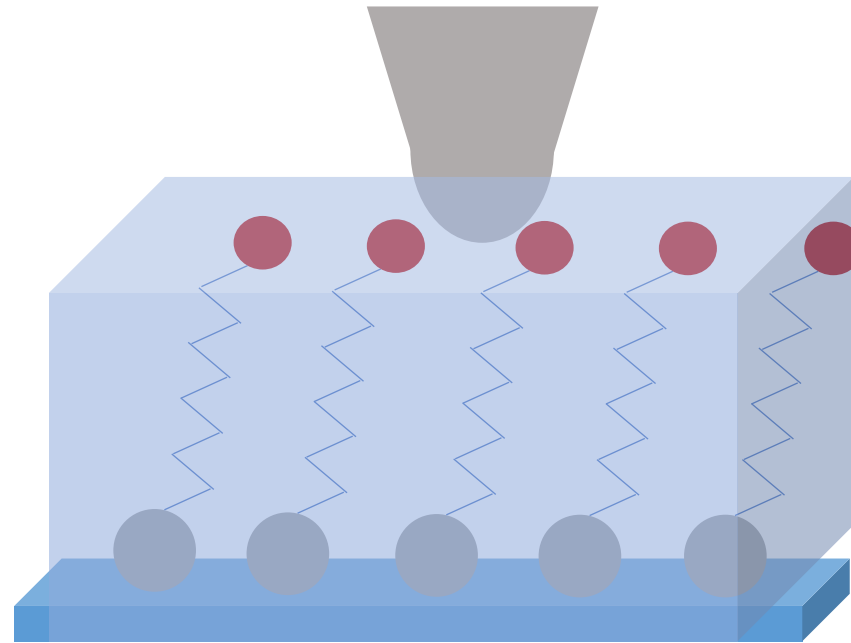


# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

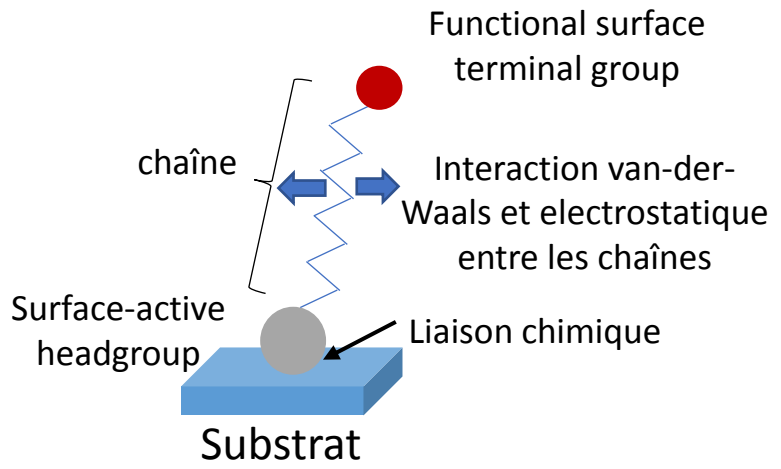


Présentée par Dahlia SAAD

# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Brosses de polymère



Régime mushroom

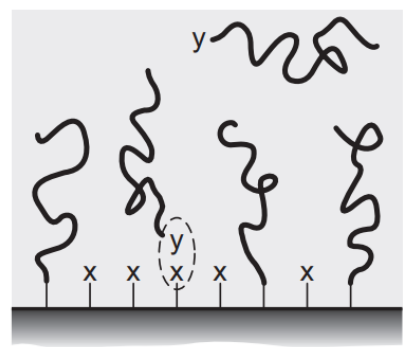


Régime brosse

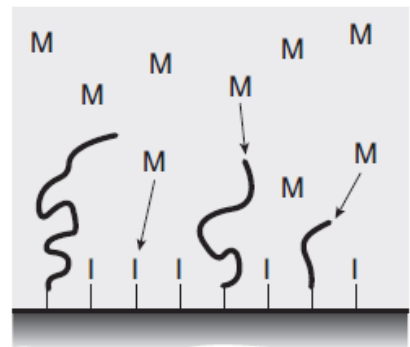


N. Akkilic *et al.* Elsevier, 2015, pp. 119–146.

Grafting onto



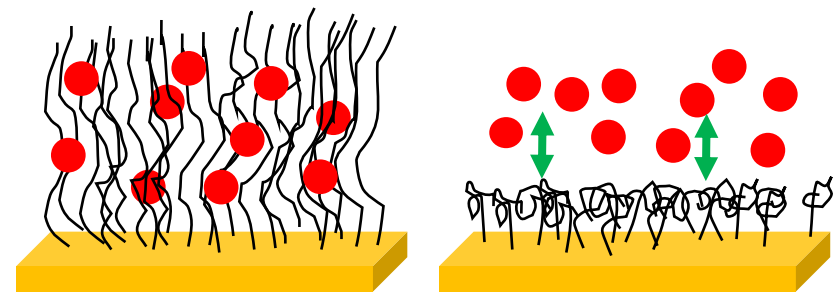
Grafting from



N. Akkilic *et al.* Elsevier, 2015, pp. 119–146.

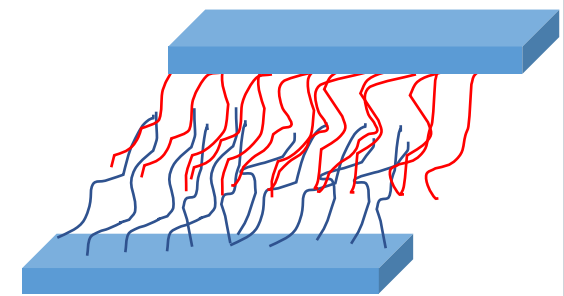
### Applications

Biomédicale



Adsorption sélective des protéines

Tribologie



Couche protectrice

# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



ÉCOLE CENTRALE LYON

## Objective

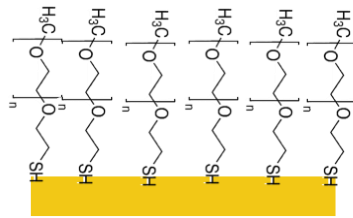
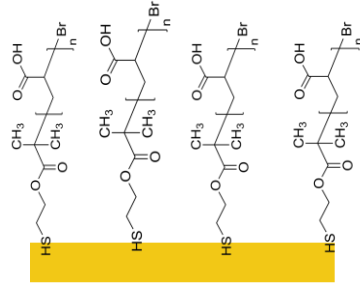
Biocapteurs (INL)

Tribologie (LTDS)

## 1D-AFM ou Spectroscopie de force

Liquide/Couche de thiol/Or

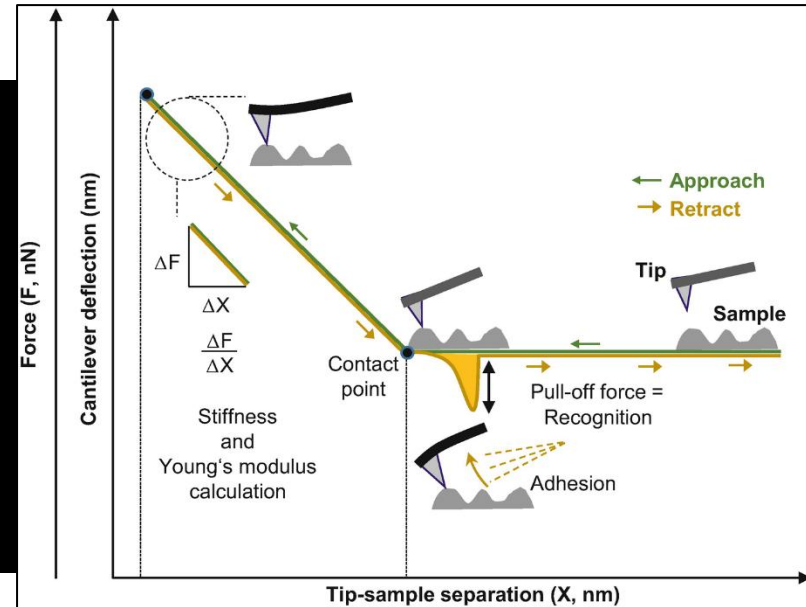
$C = 1,5 \text{ g/L}$   
Dépôt pendant 4 heures



Or

Acide polyacrylique  
PAA /Or  
 $M_n = 2000$   
*Annealed polymer*

Poly(oxyéthylène)  
PEO/Or  
 $M_n = 2000$   
*Neutral polymer*



Liashkovich, I., Rosso, G., Shahin, V. (2022). In: Goldberg, M.W. (eds) The Nuclear Pore Complex. Methods in Molecular Biology, vol 2502. Humana, New York, NY.

Solutions

- Eau pure + HCl (pH = 4)
- Eau pure (pH = 5,5)
- $10^{-4} \text{M}$  PBS (pH = 7,4)

+ 2M NaCl

- Eau pure + HCl + NaCl ( $C \approx 0,18 \text{M}$ )
- Eau pure + NaCl ( $C \approx 0,18 \text{M}$ )
- PBS + NaCl ( $C \approx 0,18 \text{M}$ )

# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

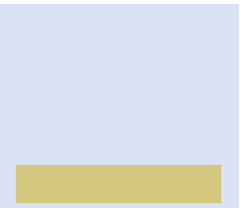
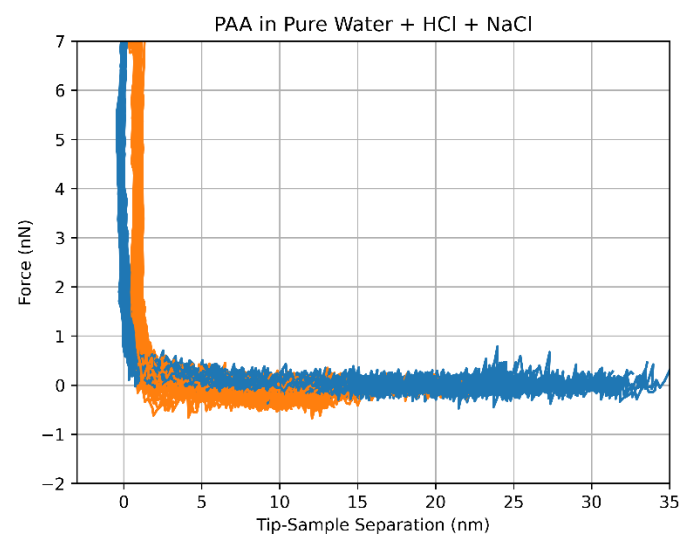
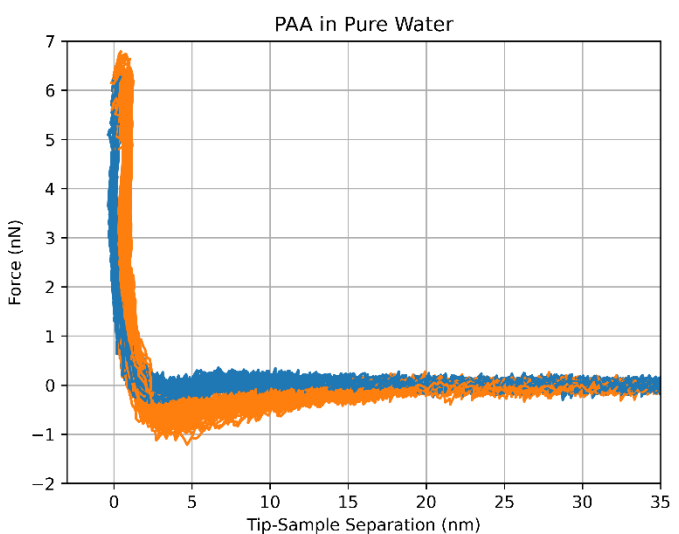
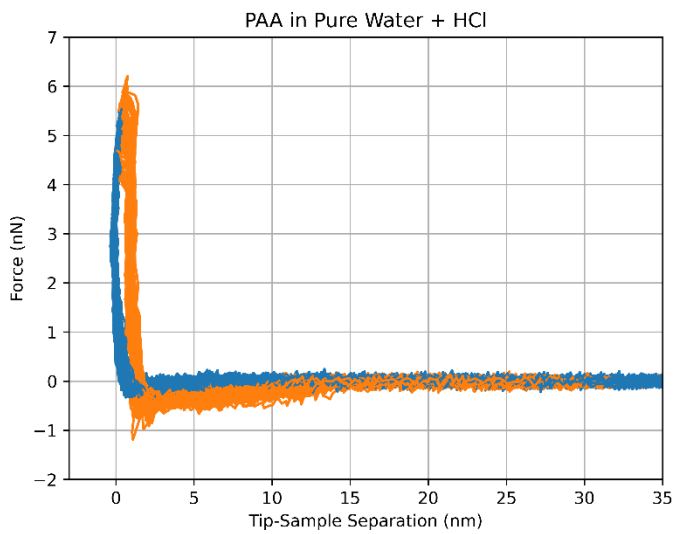
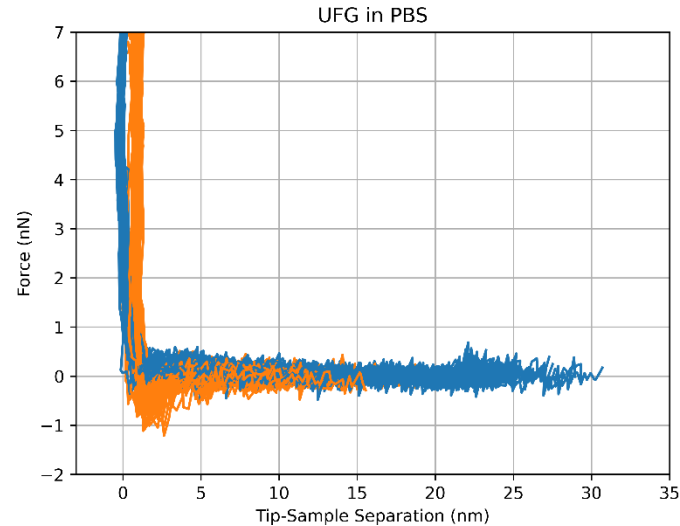
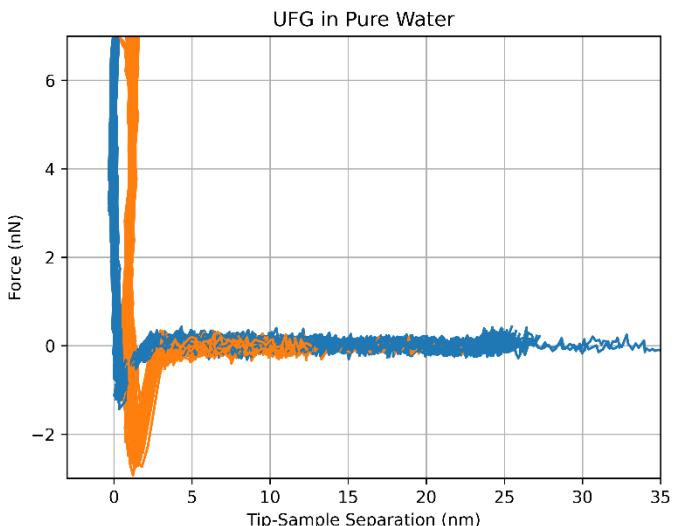
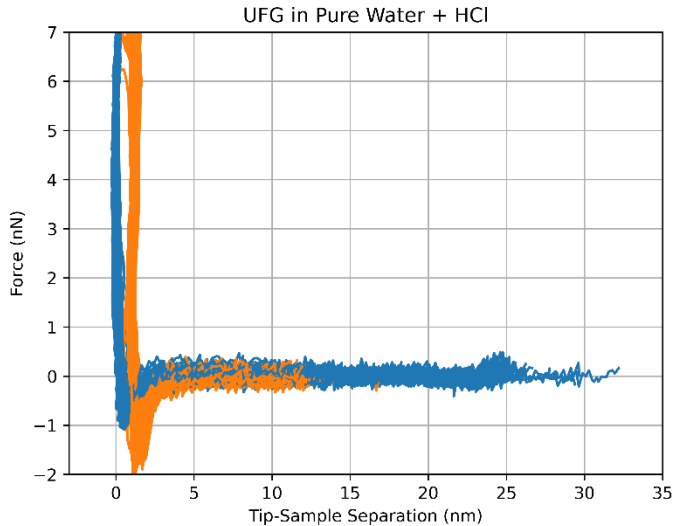


## Courbes des Forces

Eau pure + HCl pH = 4

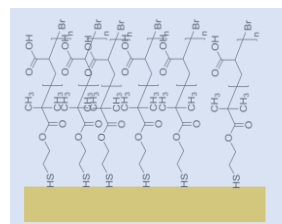
Eau pure pH = 5,5

PBS pH = 7,4



or

1024 courbes/mesure  
10 mesures/solution



PAA

# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

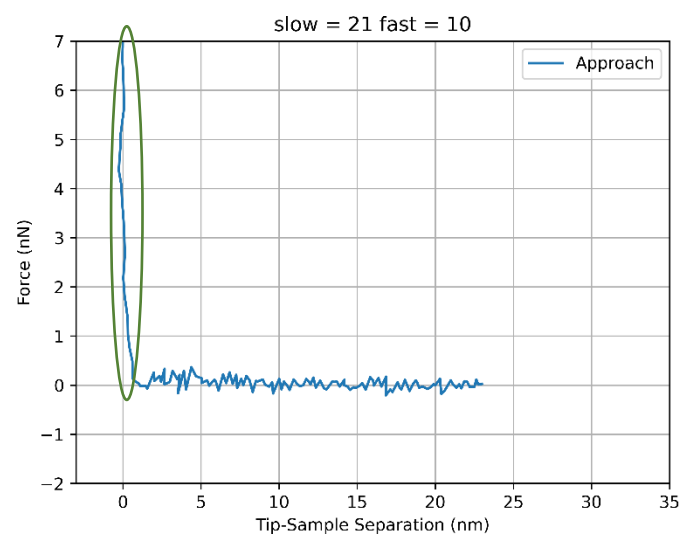
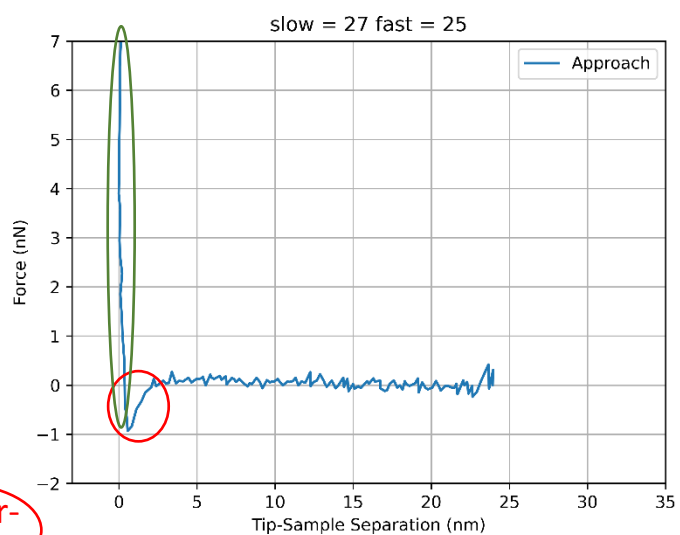
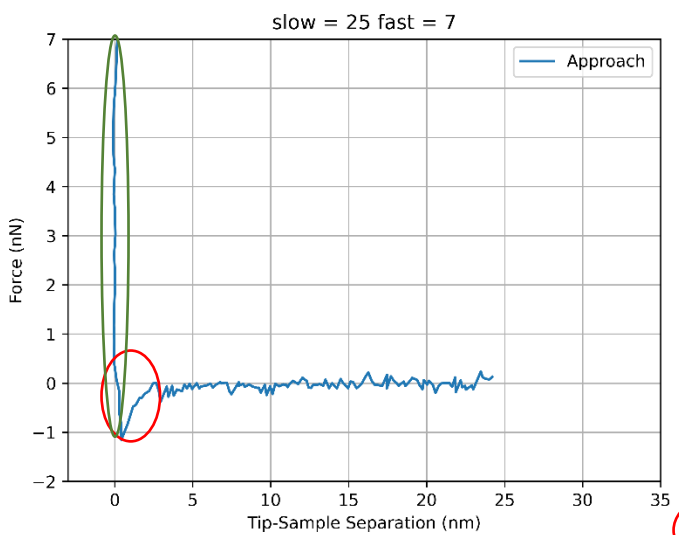


## Courbes des Forces

Eau pure + HCl (pH = 4)

Eau pure (pH = 5,5)

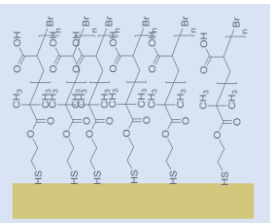
PBS (pH = 7,4)



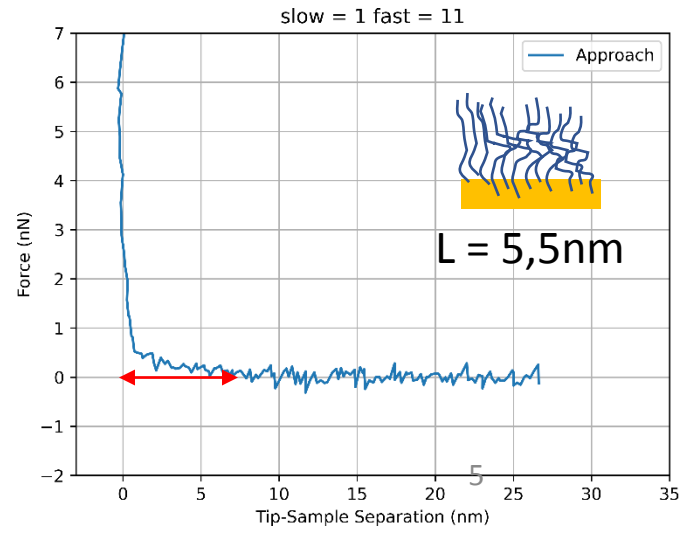
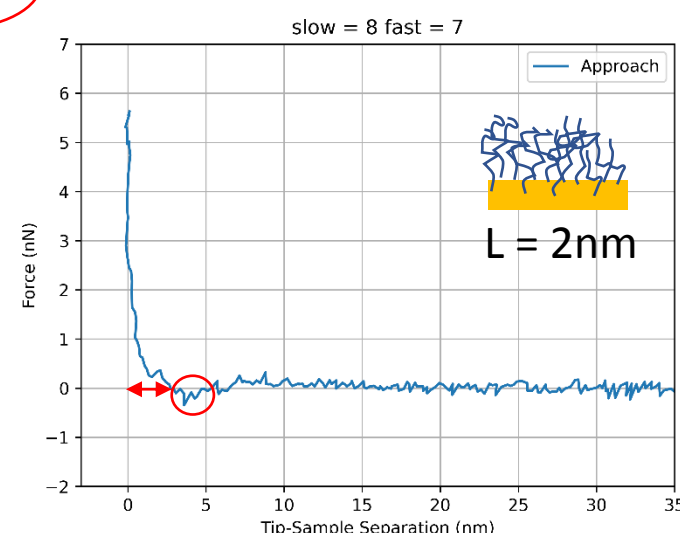
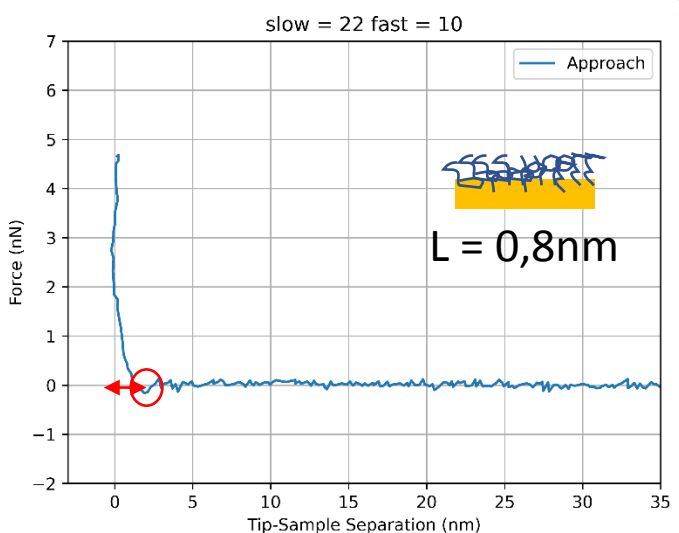
Van-der-Waals



or



PAA



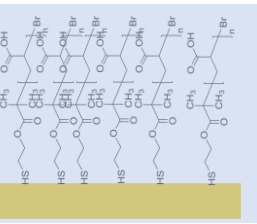
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Courbes des Forces

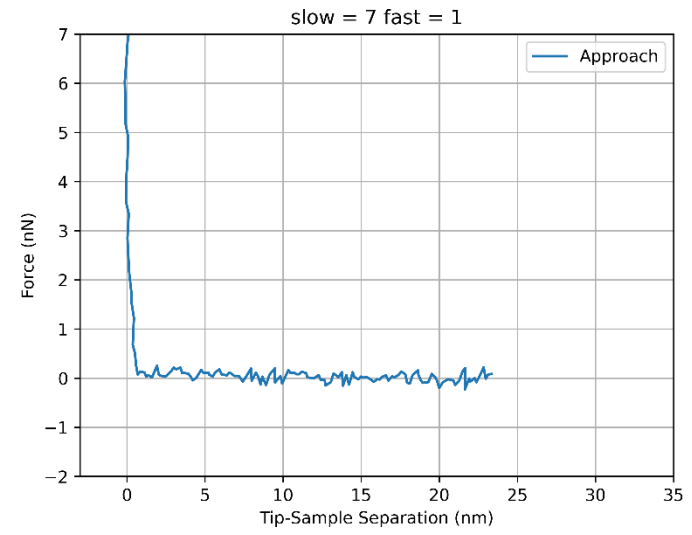


or

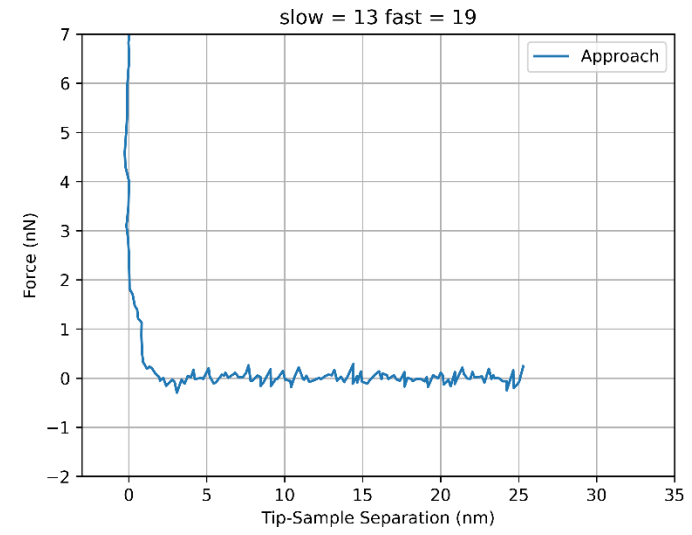


PAA

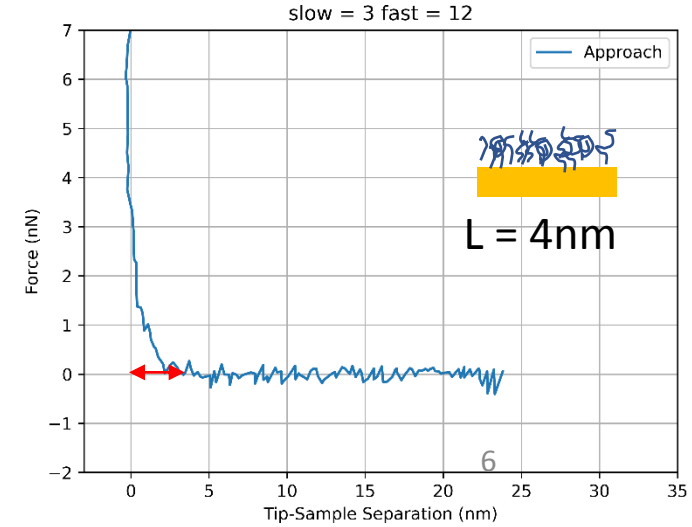
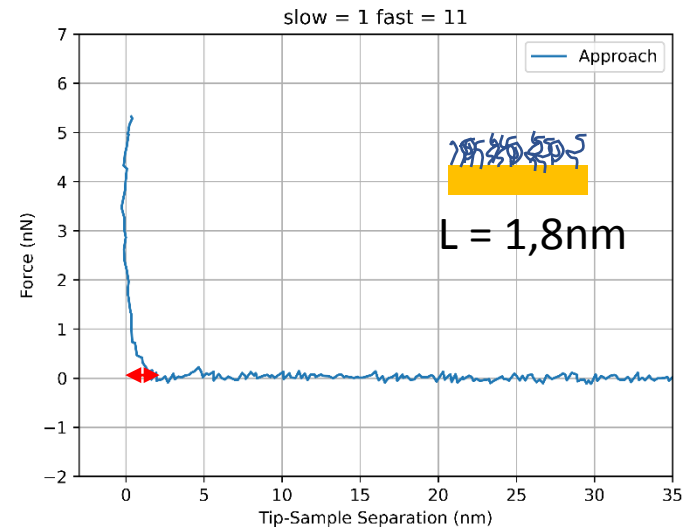
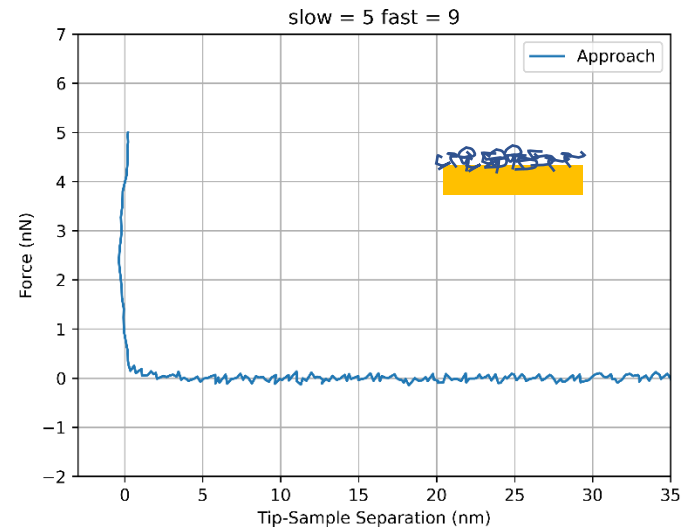
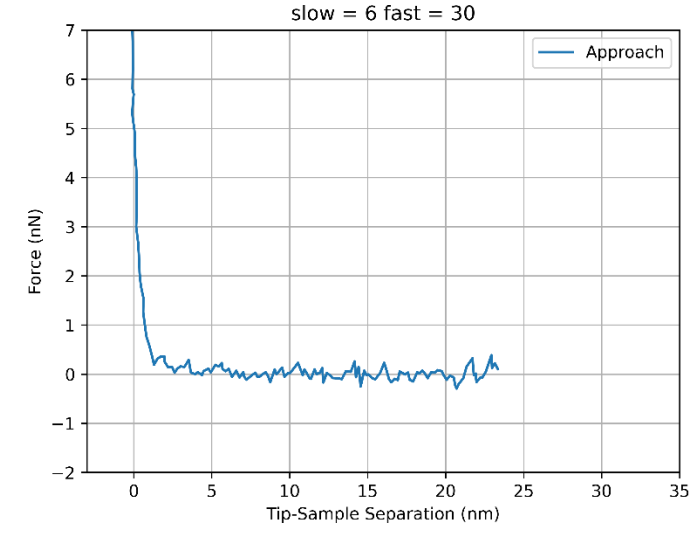
Eau pure + NaCl + HCl (pH = 4,5)



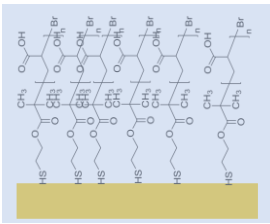
Eau pure + NaCl (pH=5)



PBS + NaCl (pH = 7,4)

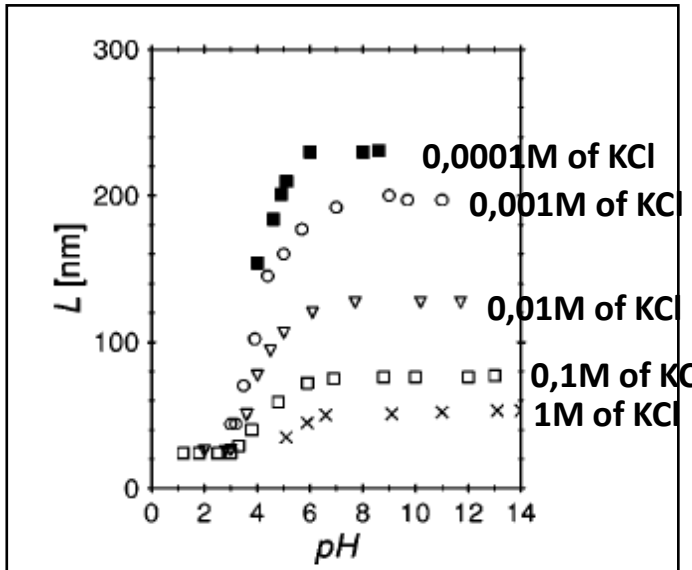
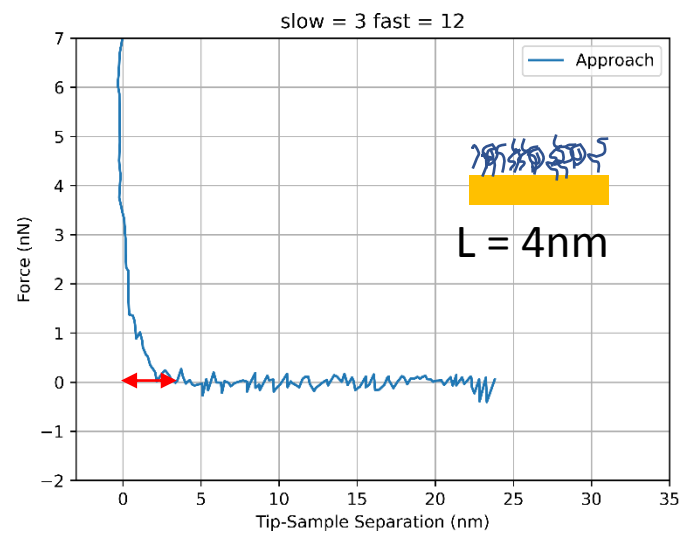
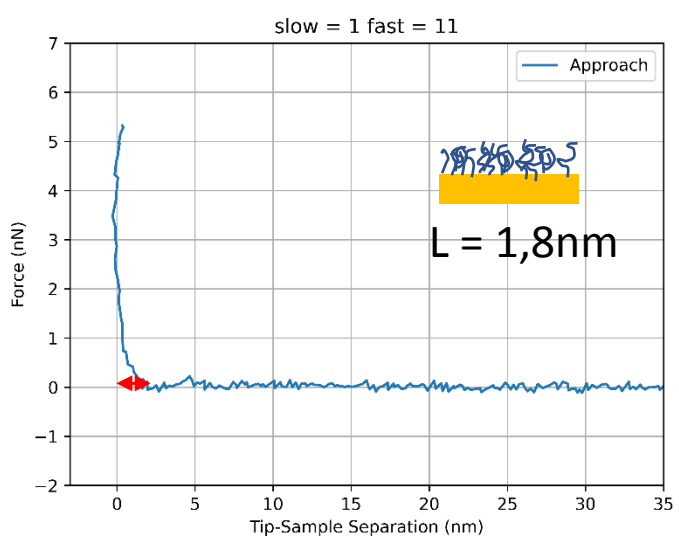
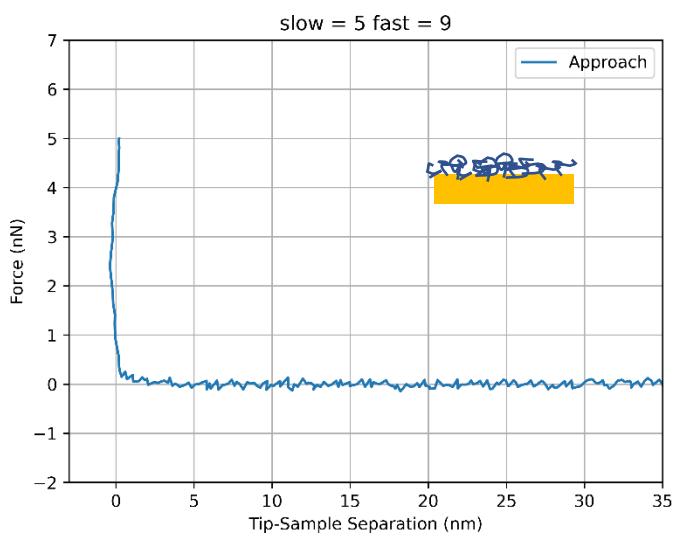


# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



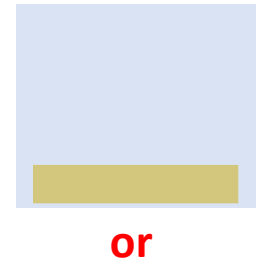
**PAA**

## Courbes des Forces

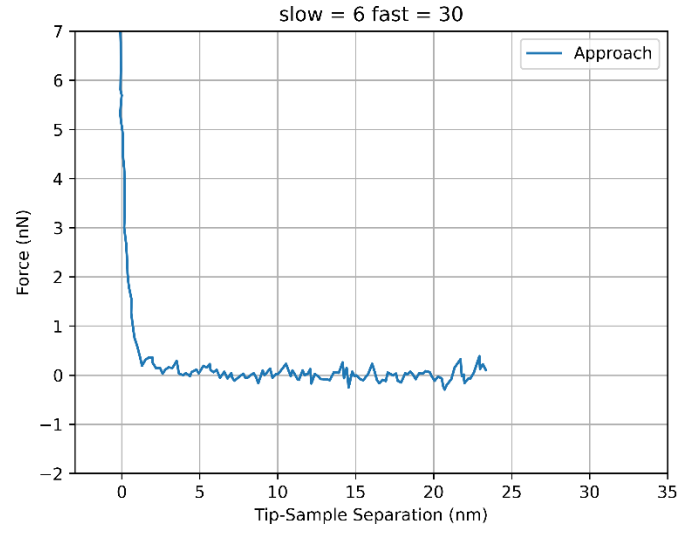
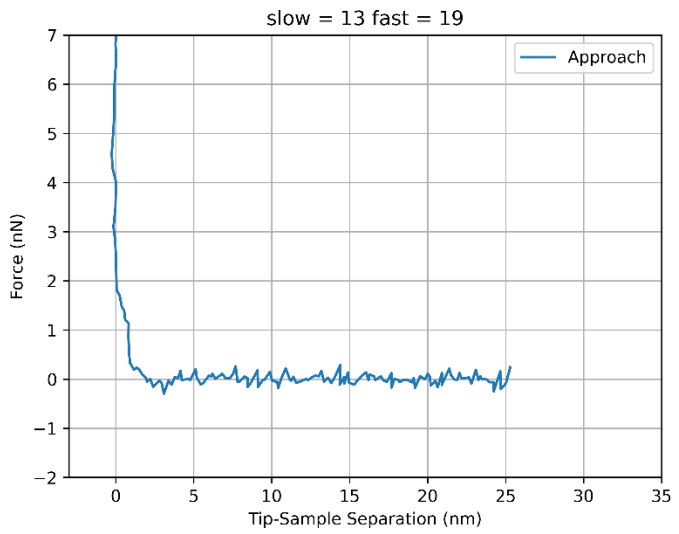
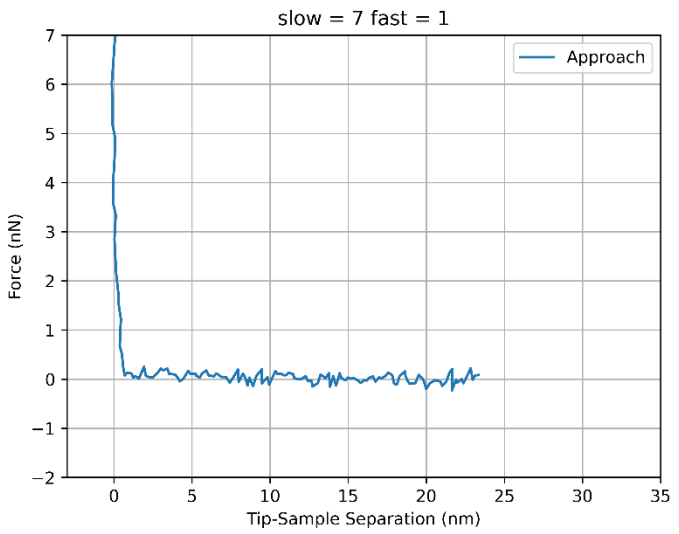


X, Guo and M, Ballauff, *Physical Review E* **2001** 64,051406

# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Courbes des Forces



DOI: 10.1002/cphc.200900700

### Physical Properties of Water Near a Gold Surface: A Nanorheological Analysis

David Mendez Soares,\* Mário Alberto Tenan, Andreza Barbosa Gomide, and Wyllerson Evaristo Gomes<sup>[a]</sup>

*Dedicated to the memory of Konrad G. Weil, one of the pioneers in the use and applications of the quartz crystal microbalance*

Water at room temperature is not simply a medium for which uniform properties can always be assumed. Water close to solid hydrophobic or hydrophilic surfaces has elasticity, which is measured by monitoring the quartz crystal microbalance (QCM) resonant frequency and resistance. Small additions of

salt are shown to modify this elasticity. Furthermore, near the hydrophobic QCM gold electrode, undersaturated aqueous NaCl solutions present a high concentration of ion pairs, which is confirmed by atomic force microscopy through force versus distance measurements.

1. Dépôt de sel
2. Pairs d'ions NaCl

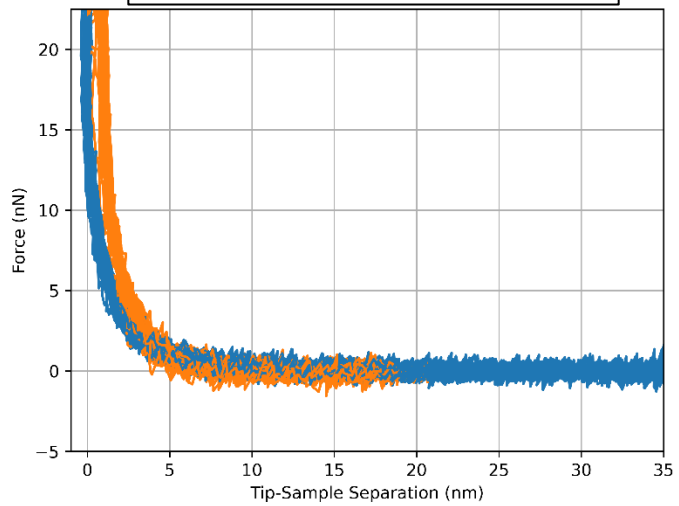


# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

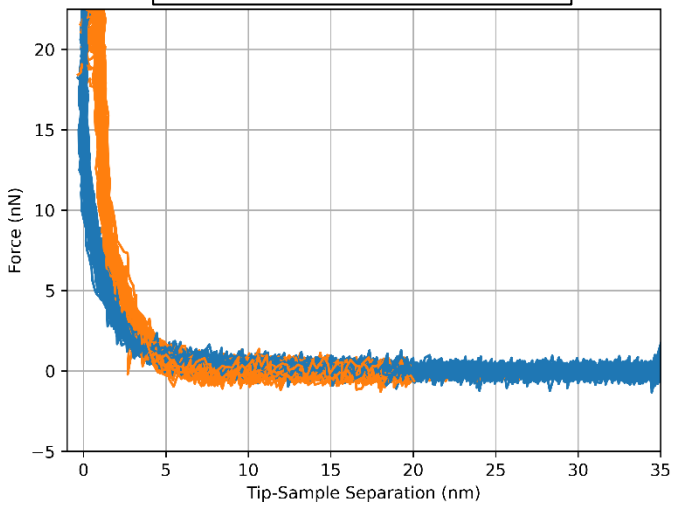


## Courbes des Forces sur le PEO

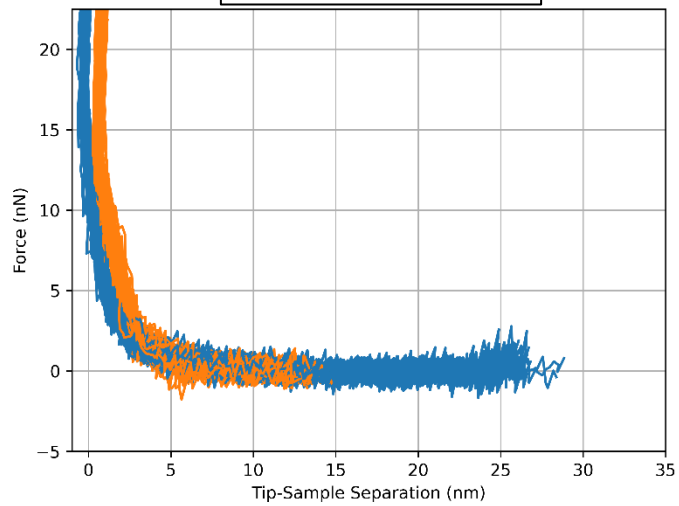
Eau pure + HCl (pH = 4)



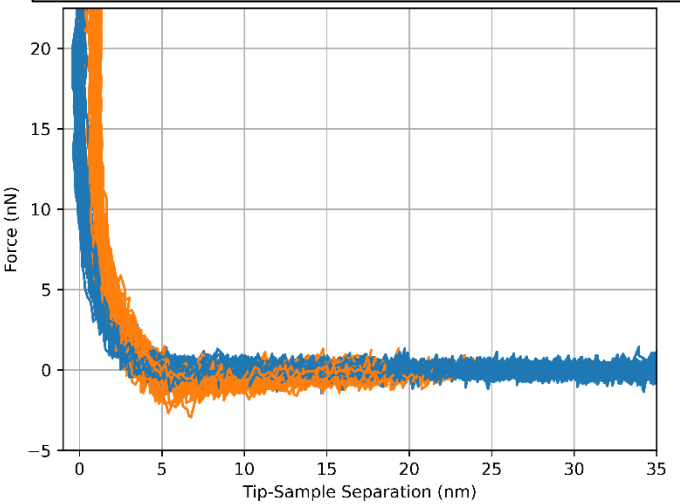
Eau pure (pH = 5,5)



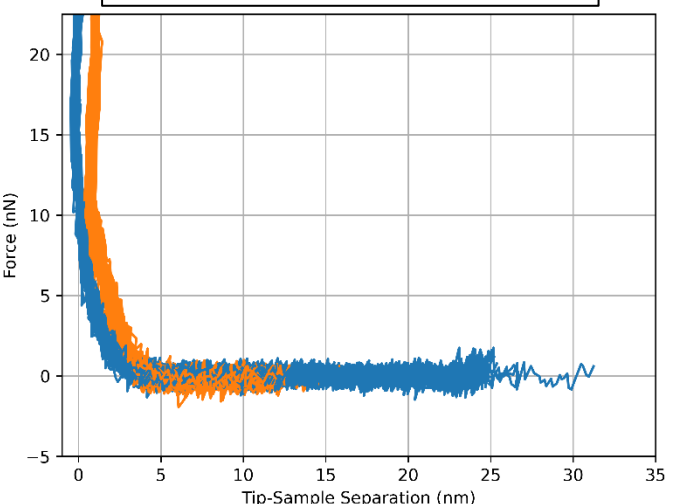
PBS (pH = 7,4)



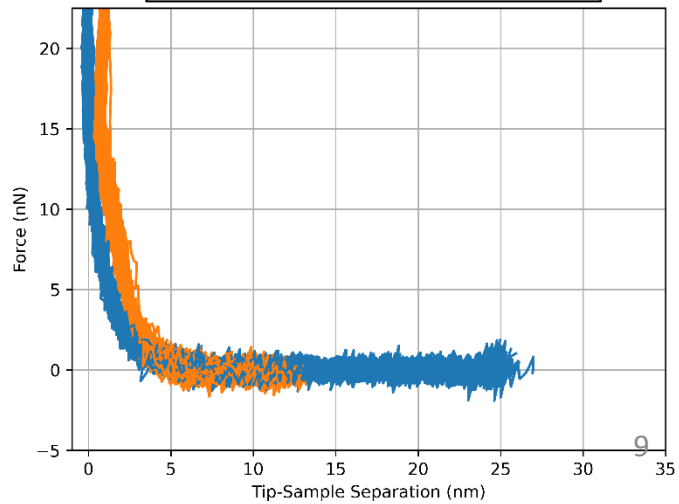
Eau pure + NaCl + HCl (pH = 4,5)



Eau pure + NaCl (pH=5)



PBS + NaCl (pH = 7,4)



# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

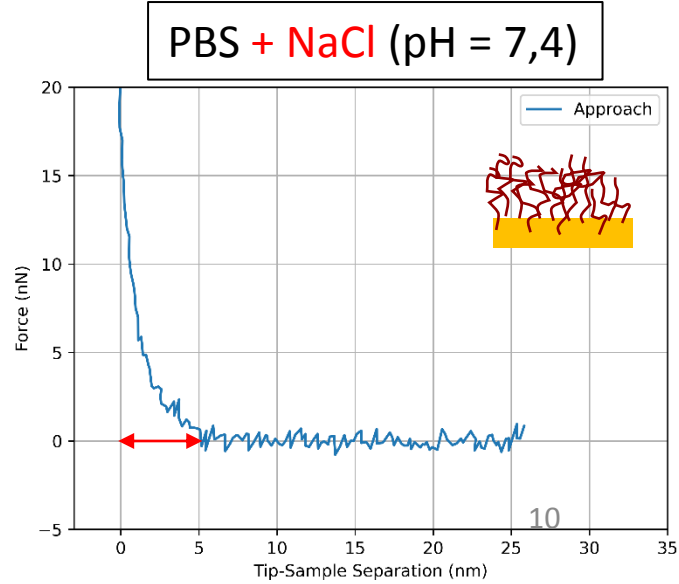
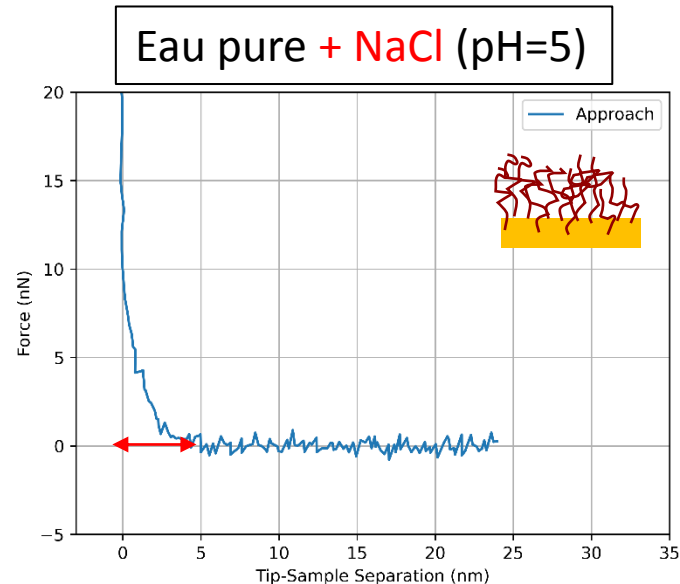
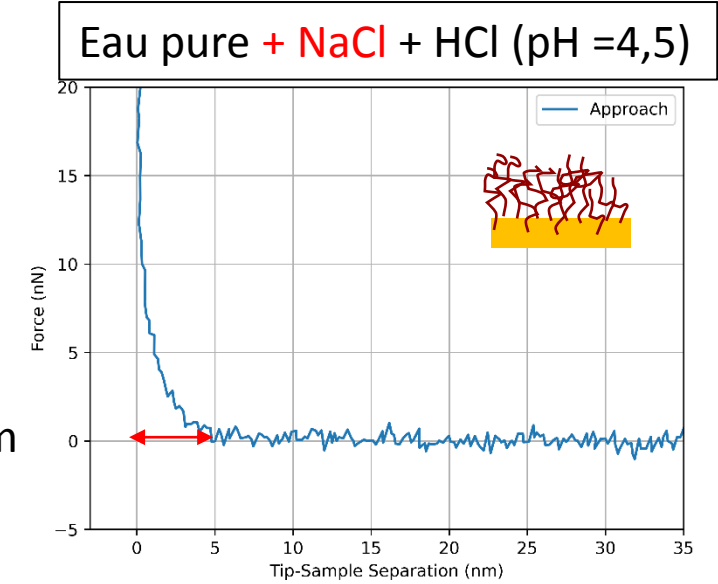
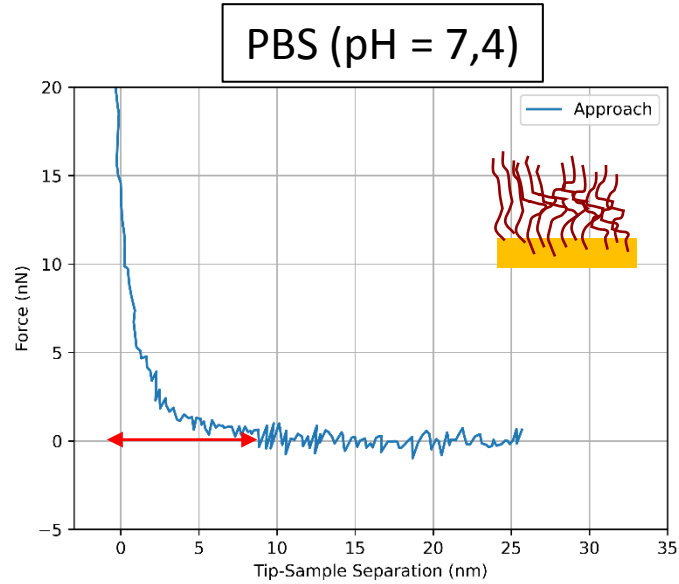
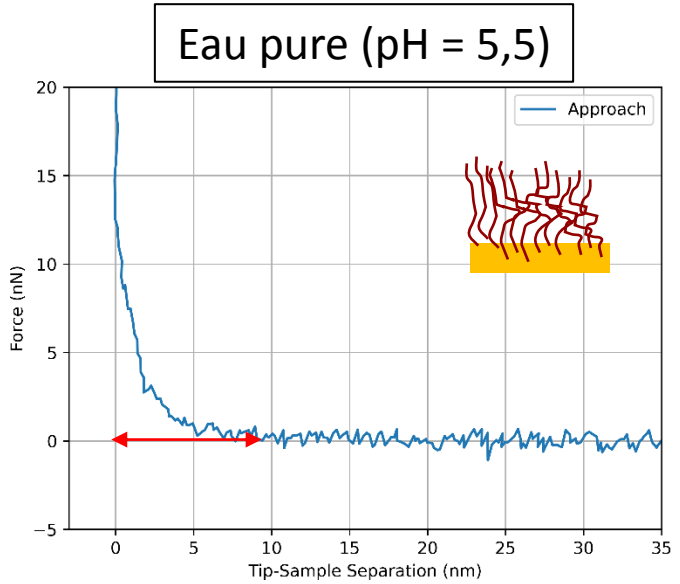
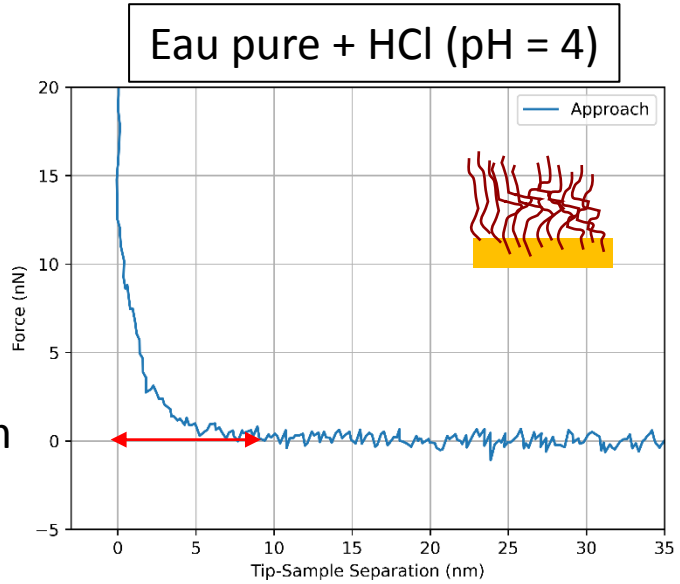


## Courbes des Forces sur le PEO

$L = [8 - 9] \text{ nm}$

$C \approx 0,18 \text{ M}$

$L = [4 - 5] \text{ nm}$

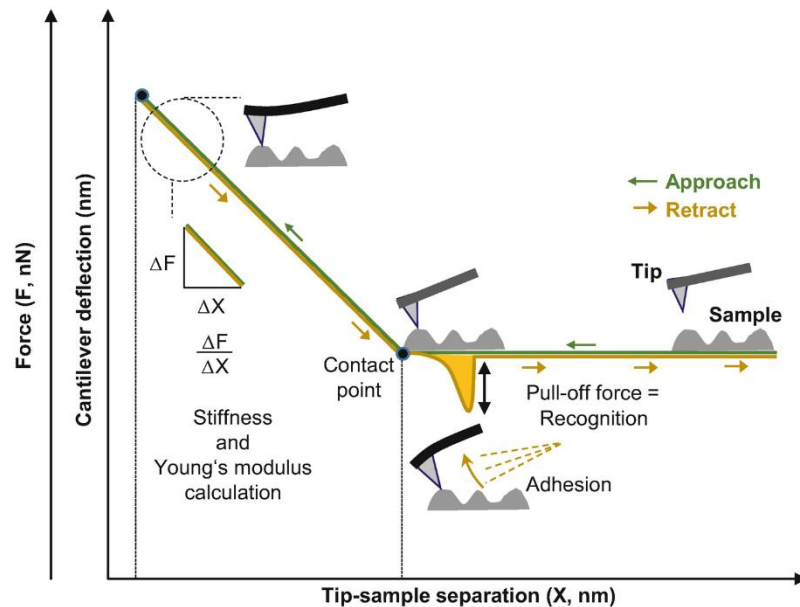


# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



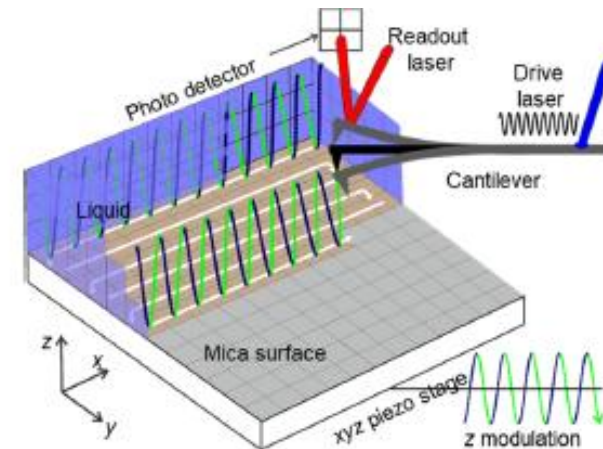
## Interface Solide/Brosse/Liquide

### 1D-AFM ou Spectroscopie de force Organisation des brosses sur la surface Interface Solide/Brosse



Liashkovich, I., Rosso, G., Shahin, V. (2022). In: Goldberg, M.W. (eds) The Nuclear Pore Complex. Methods in Molecular Biology, vol 2502. Humana, New York, NY.

### 3D-AFM Organisation du liquide sur les brosses Interface Brosse/Liquide



J. Hernández-Muñoz, M. R. Uhlig, S. Benaglia, E. Chacón, P. Tarazona, and R. Garcia, *The Journal of Physical Chemistry C* **2020** 124 (48), 26296-26303

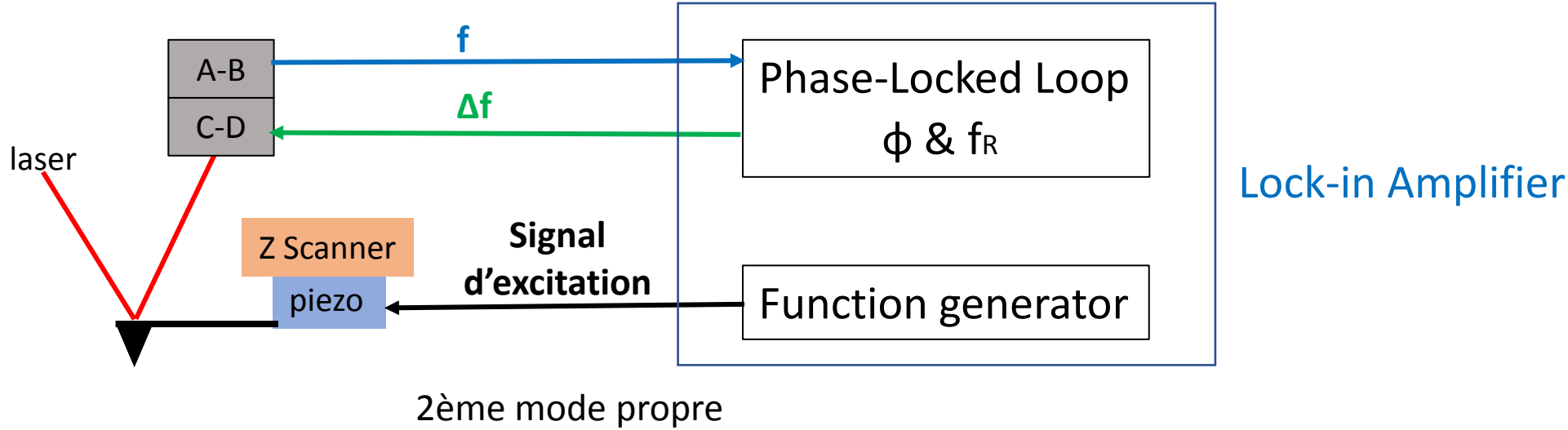
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Mesures 3D-AFM

- Implémenter 3D-AFM dans notre AFM

PinPoint™ mode

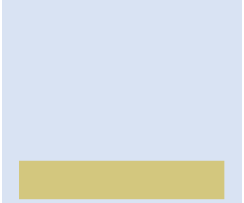


# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Mesures 3D-AFM

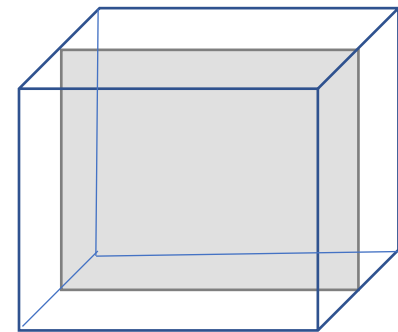
Echantillon



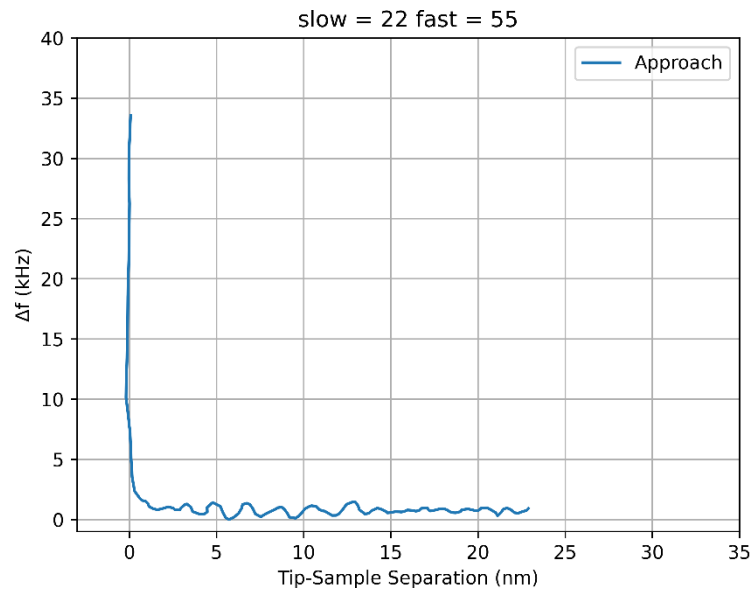
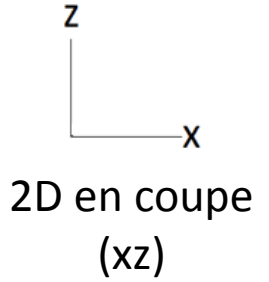
25 nm x 25 nm  
64-pixel x 64-pixel



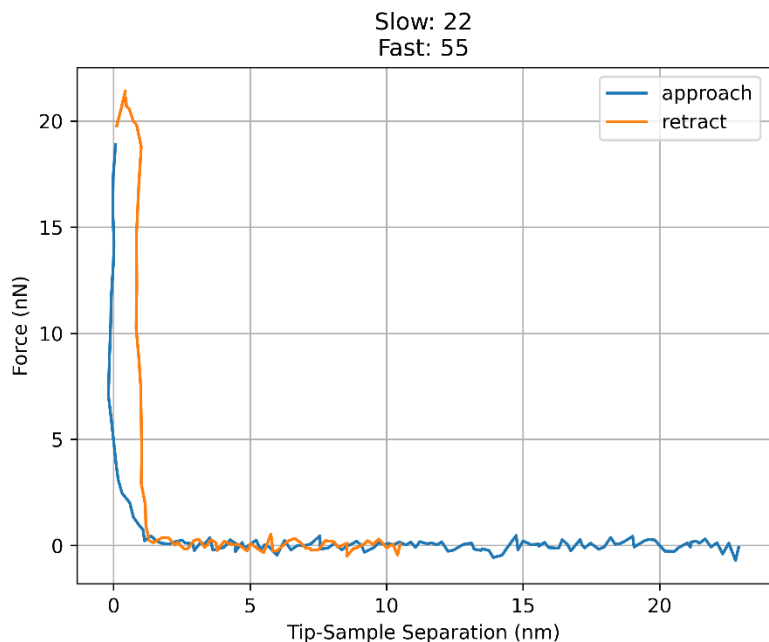
1  $\Delta f$  courbe/pixel  
 $\approx$  500 points/courbe



3D  $\Delta f$  map



PAA



Tip-sample separation calculé des courbes de forces correspondantes

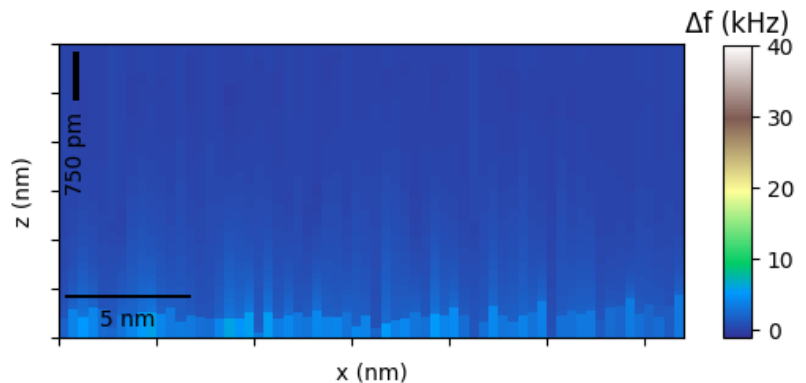
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



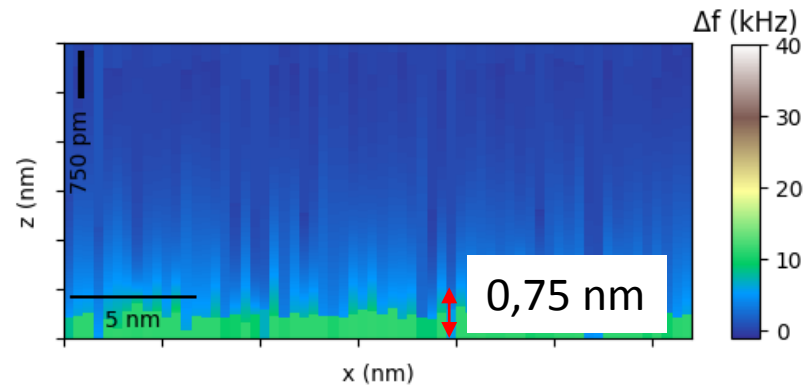
## Mesures 3D-AFM

### PAA

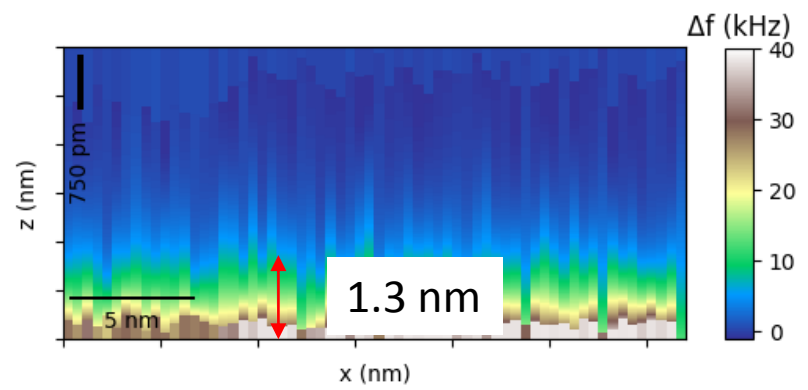
Eau pure + HCl (pH = 4)



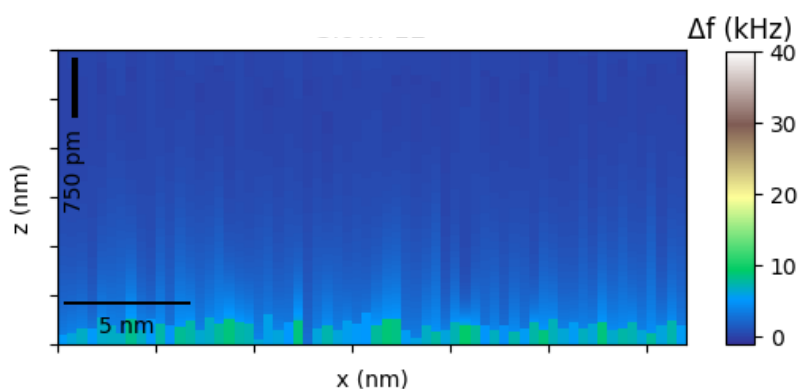
Eau pure (pH = 5,5)



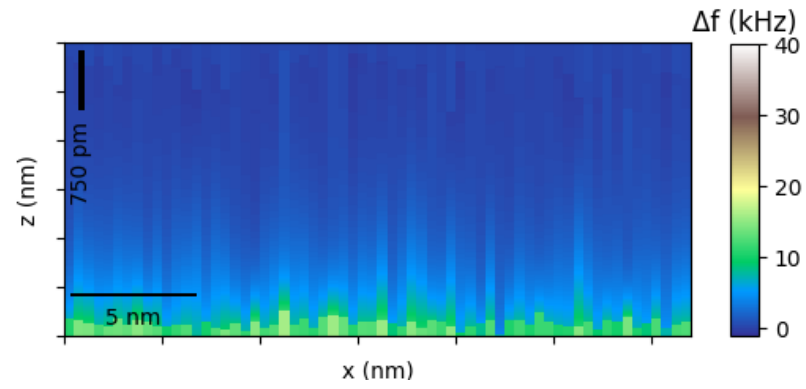
PBS (pH = 7,4)



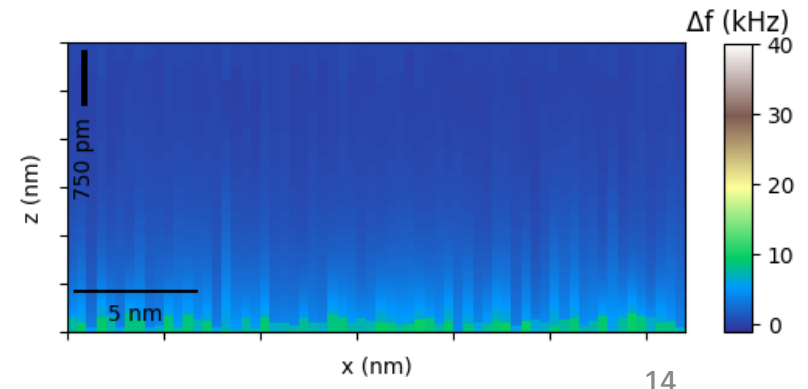
Eau pure + NaCl + HCl (pH = 4,5)



Eau pure + NaCl (pH=5)



PBS + NaCl (pH = 7,4)



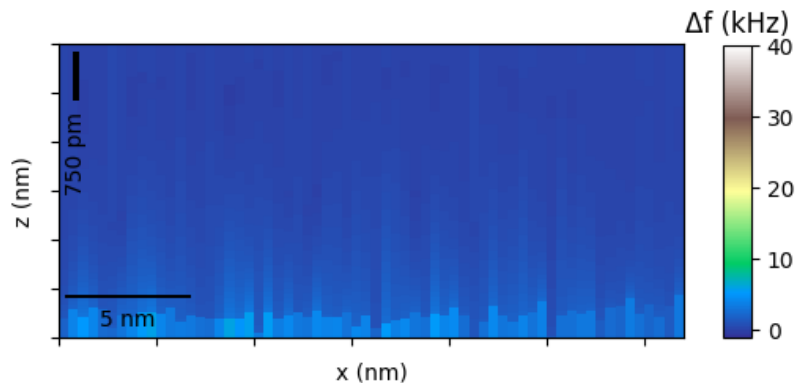
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



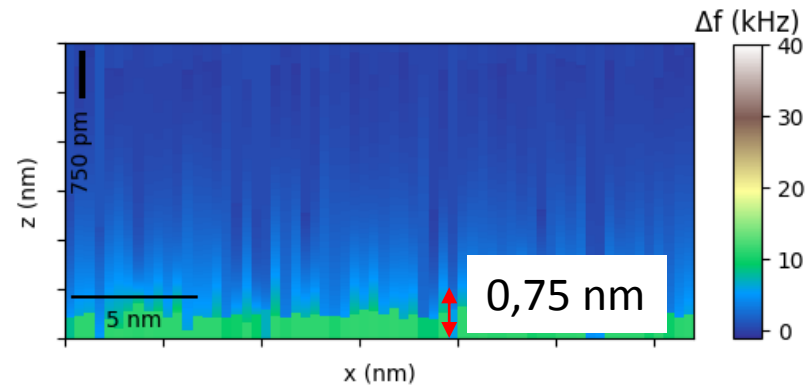
## Mesures 3D-AFM

### PAA

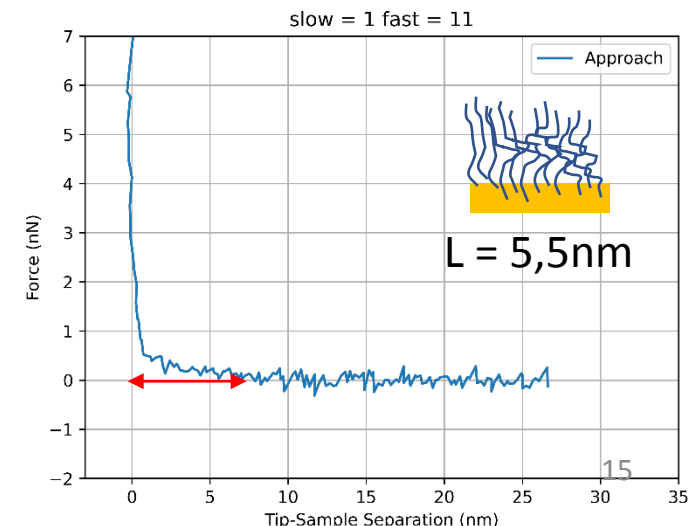
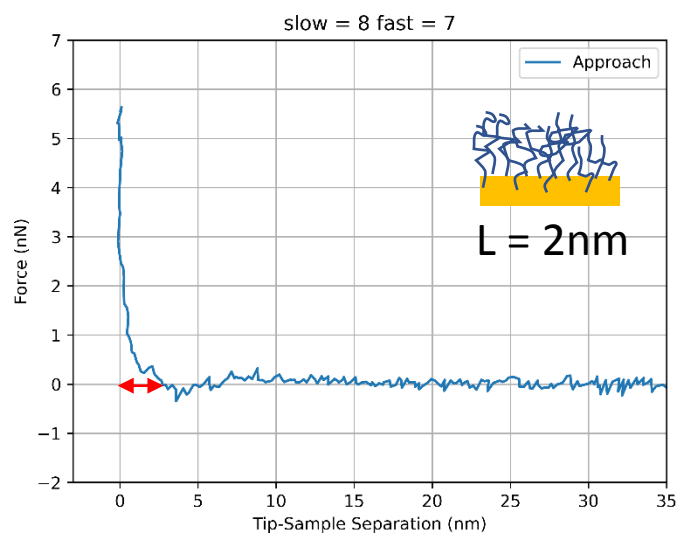
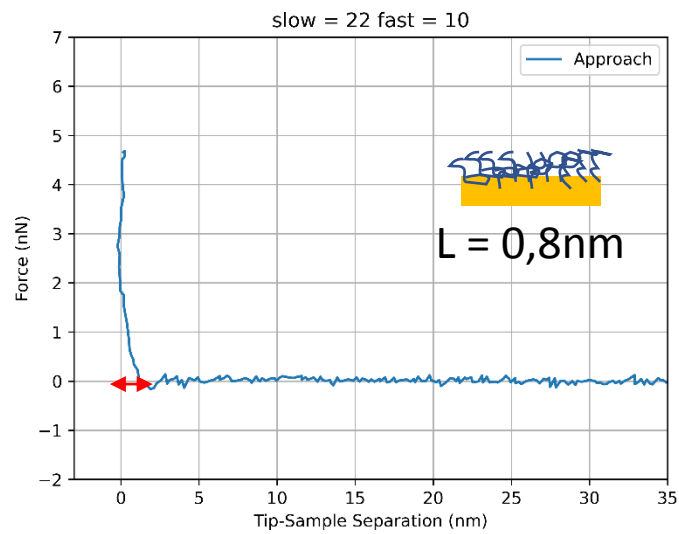
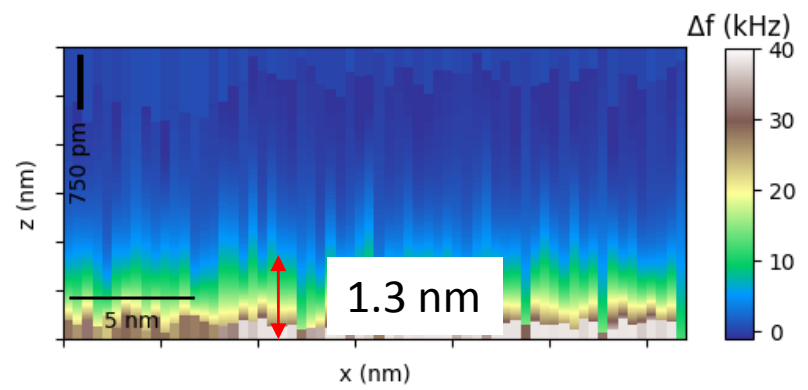
Eau pure + HCl (pH = 4)



Eau pure (pH = 5,5)



PBS (pH = 7,4)



# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



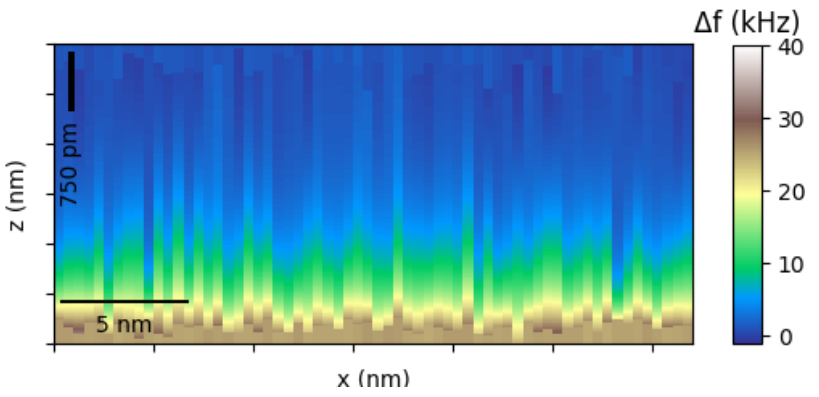
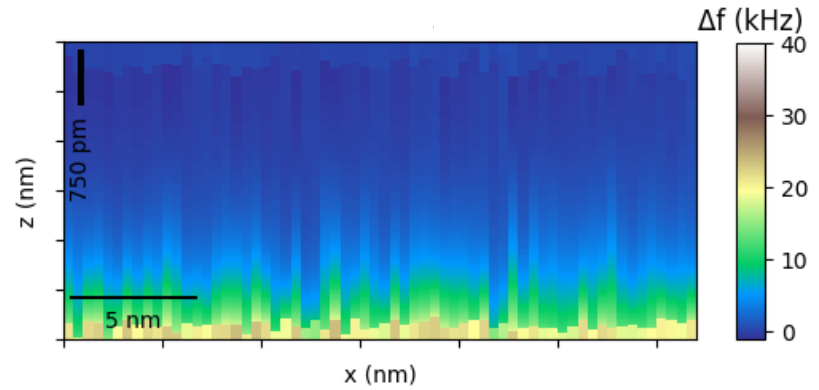
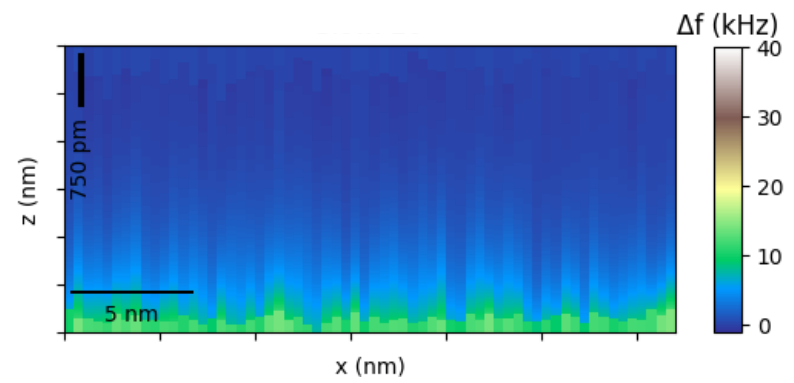
## Mesures 3D-AFM

Eau pure + HCl (pH = 4)

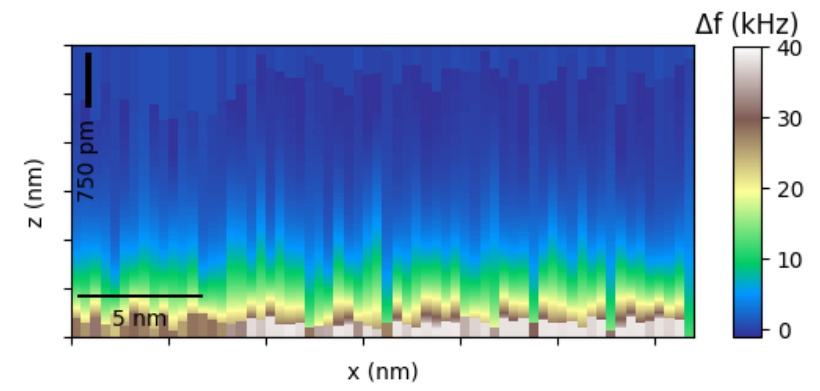
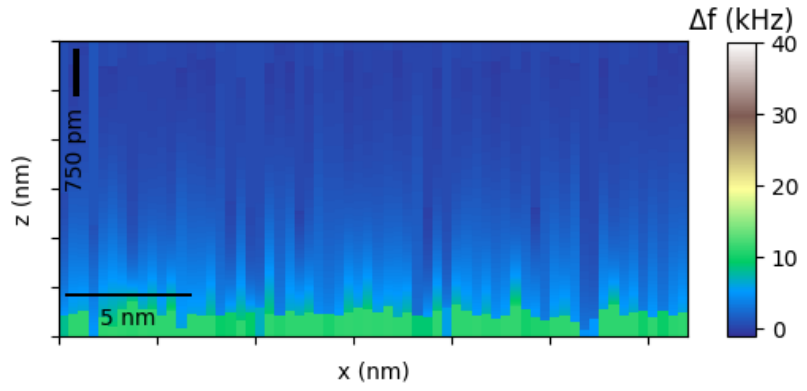
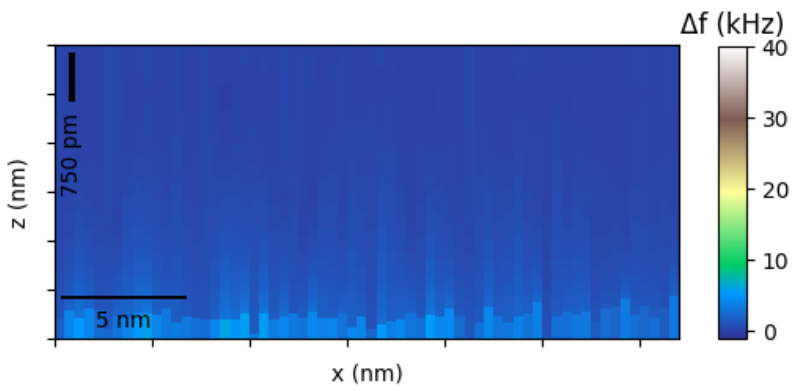
Eau pure (pH = 5,5)

PBS (pH = 7,4)

Or



PAA





# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM

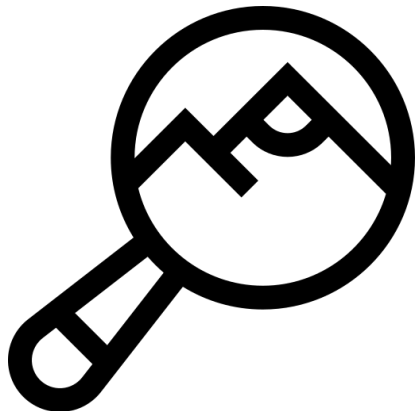


## Conclusions

1. Le pH affecte la longueur des brosses pour le PAA et les forces interactives or/silice
2. Une concentration élevée du sel conduit au repliement des brosses et la présence de forces répulsives sur l'or pur
3. L'augmentation des  $\Delta f$  dans les images en 3D-AFM représente la zone de transition du liquide vers la surface cela dépend plus de la nature de la solution que de la surface dans nos conditions



## Perspectives



1. Trouver une méthode de nettoyage efficace pour l'or
2. Faire des études avec solutions moins concentrées en sels
3. Mesurer en 3D des surfaces typiques (mica)
4. Travailler avec des pointes différentes

Merci pour  
votre  
attention!!

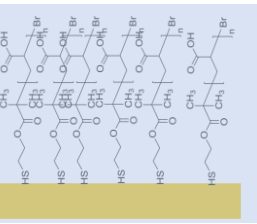
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Courbes des Forces

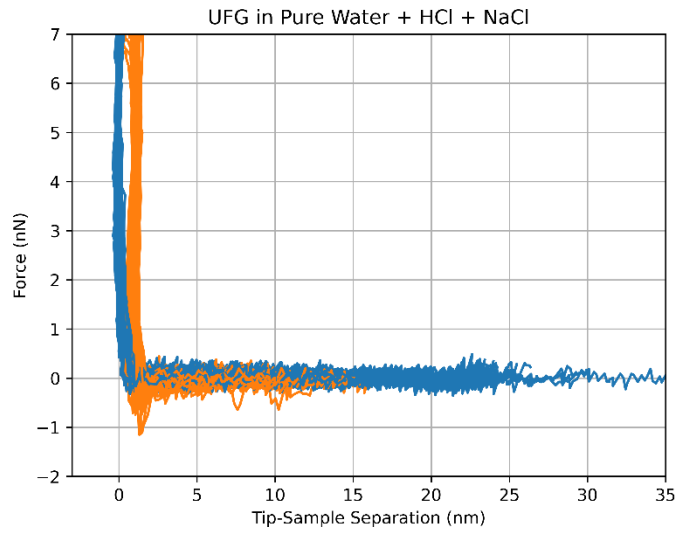


or

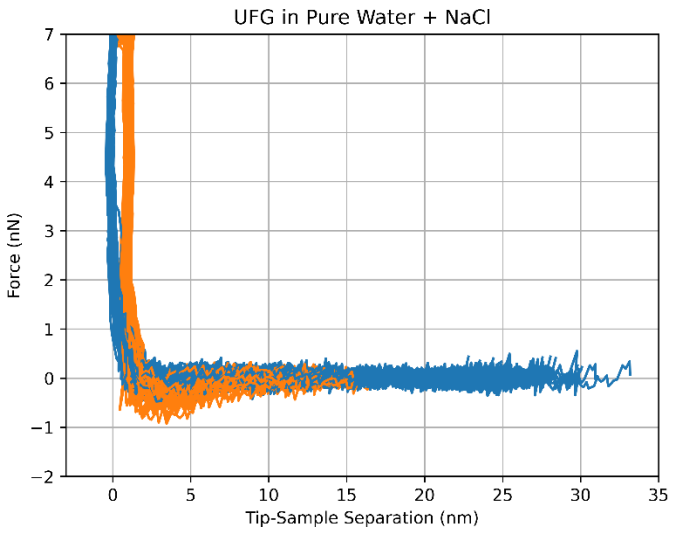


PAA

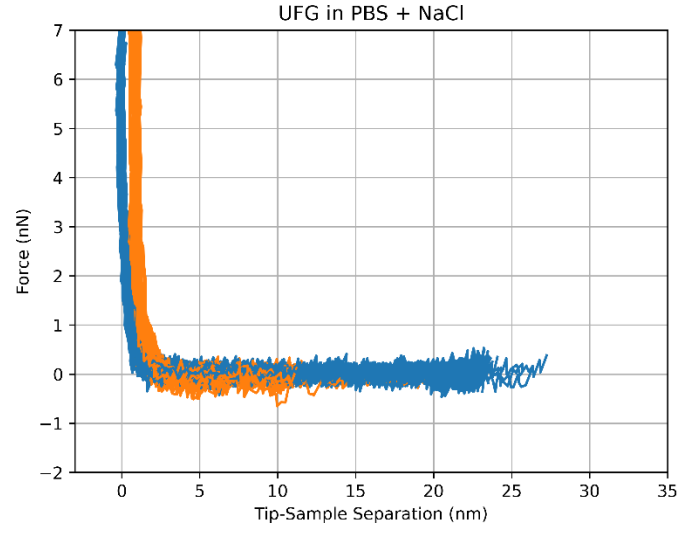
Eau pure + NaCl + HCl (pH =4,5)



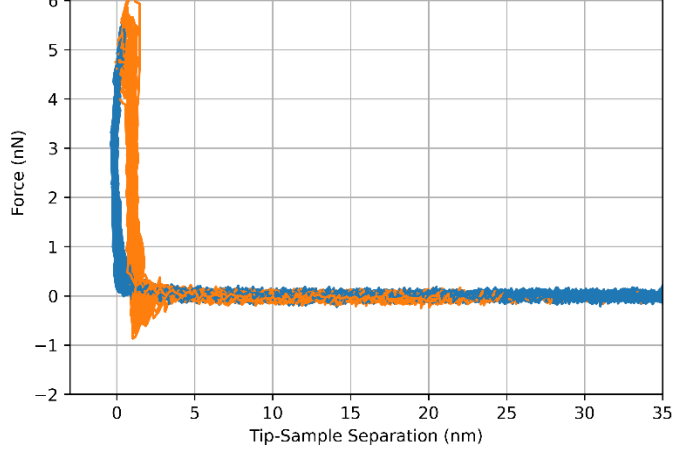
Eau pure + NaCl (pH=5)



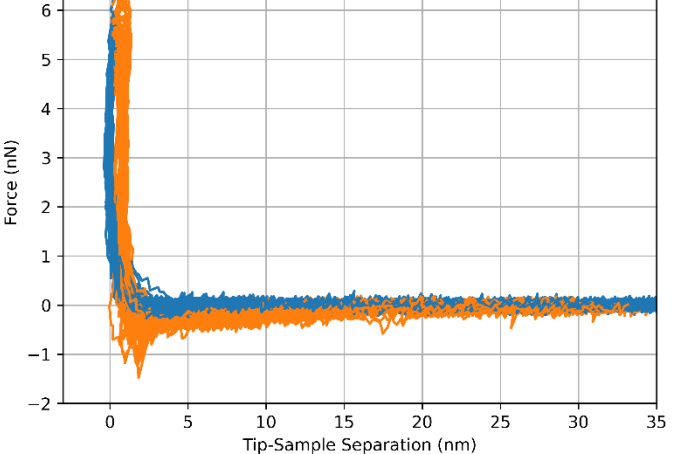
PBS + NaCl (pH = 7,4)



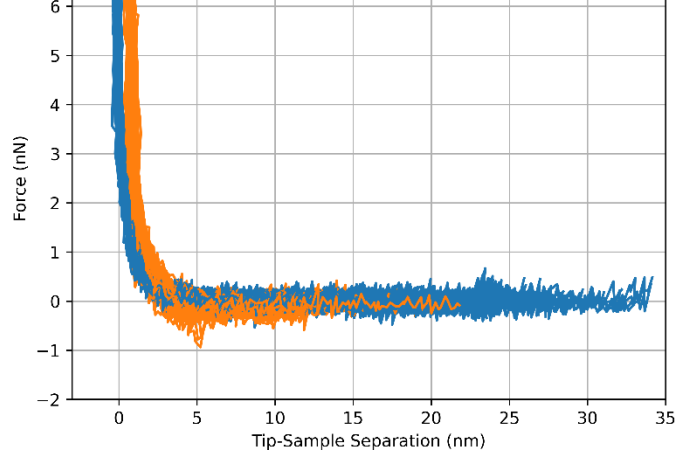
PAA in Pure Water + HCl + NaCl



PAA in Pure Water + NaCl



PAA in PBS + NaCl



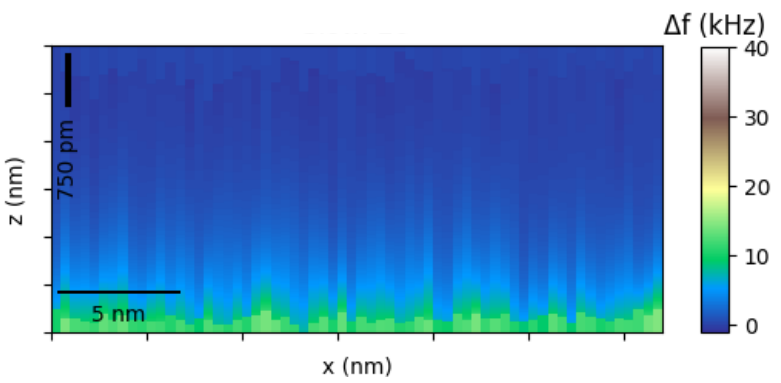
# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



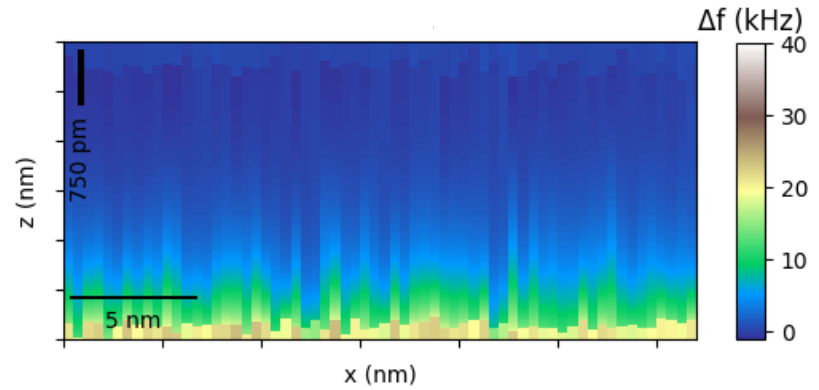
## Mesures 3D-AFM

Or

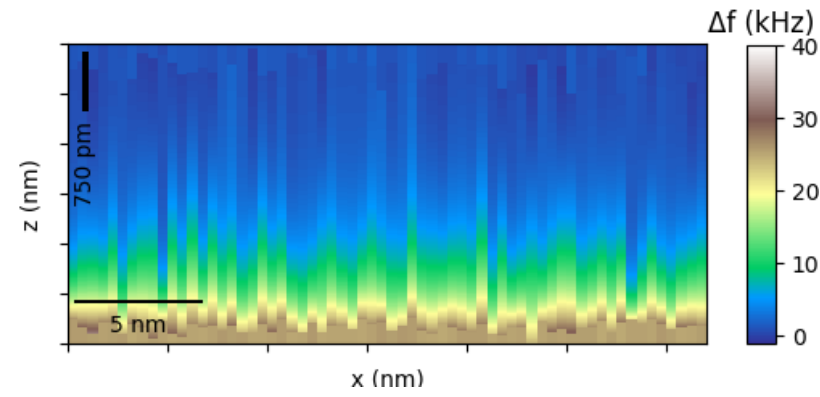
Eau pure + HCl (pH = 4)



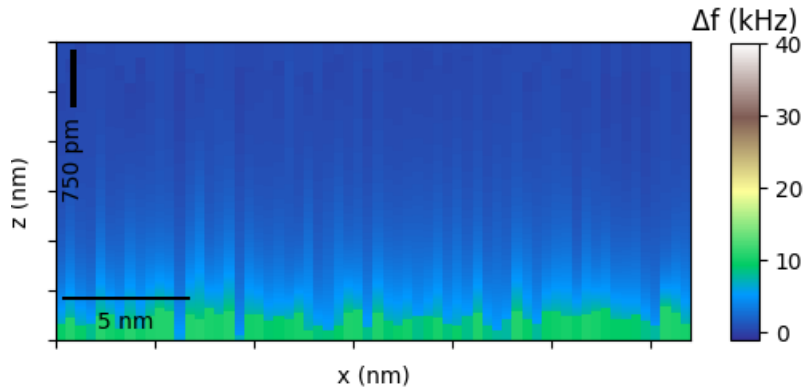
Eau pure (pH = 5,5)



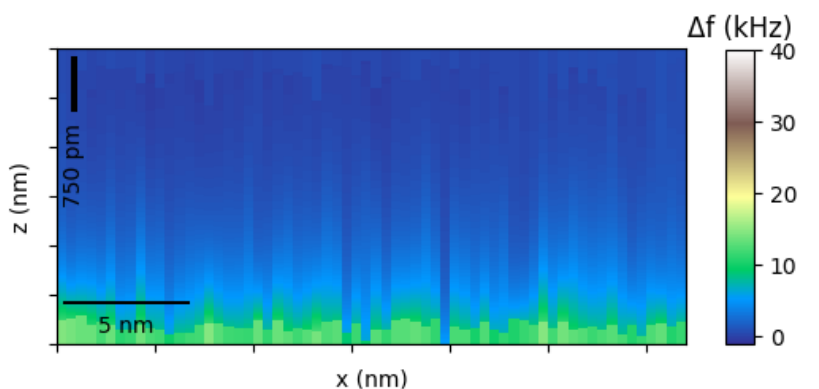
PBS (pH = 7,4)



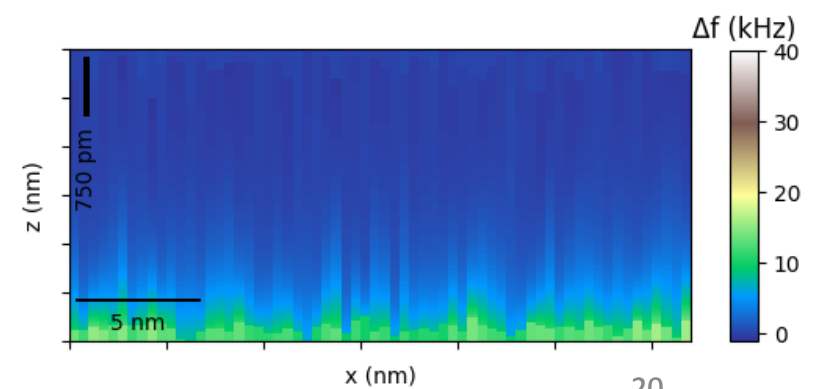
Eau pure + NaCl + HCl (pH =4,5)



Eau pure + NaCl (pH=5)

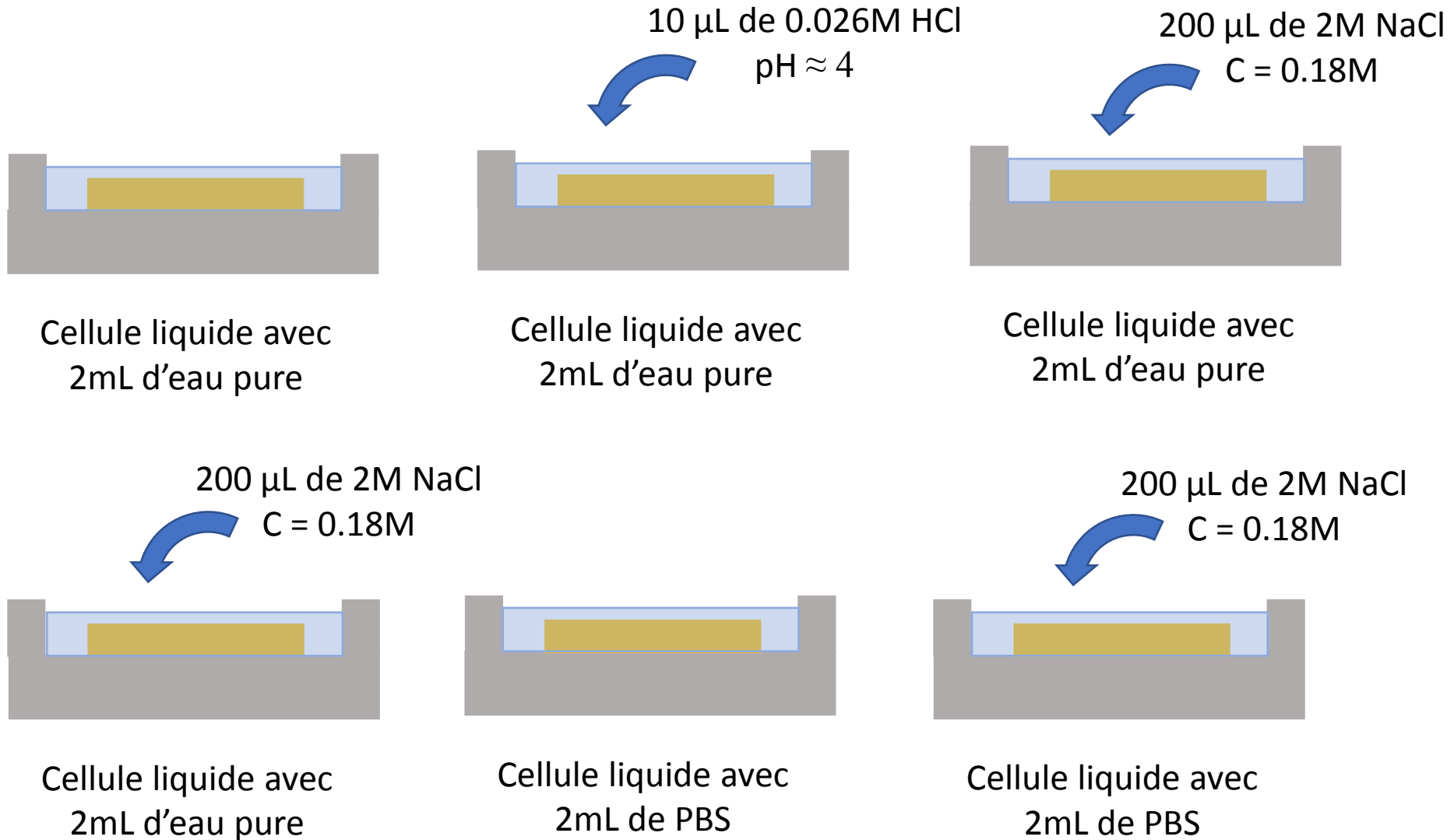


PBS + NaCl (pH = 7,4)



# Extras

## Solutions utilisées pour les mesures

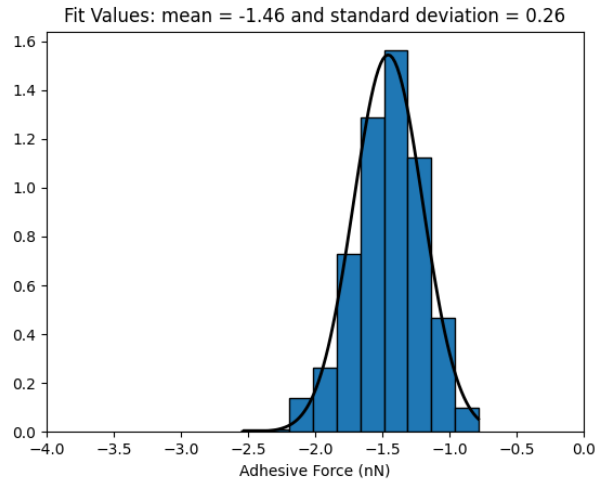


# Extras

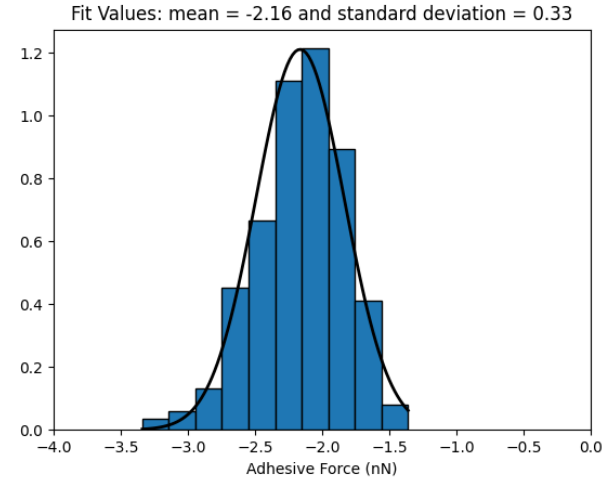
## Statistiques des courbes de forces pour l'or



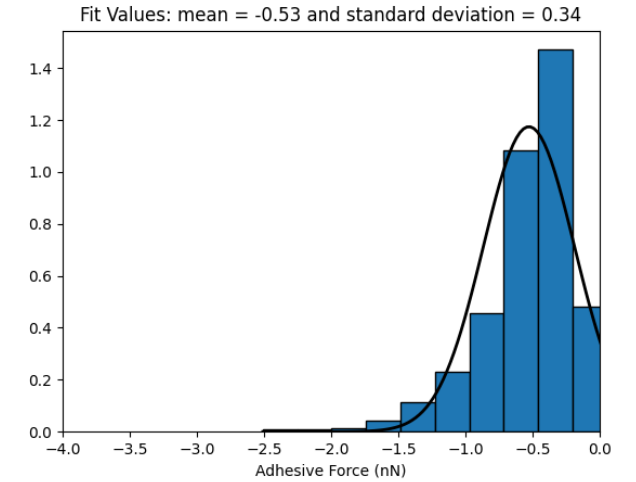
### Eau pure + HCl



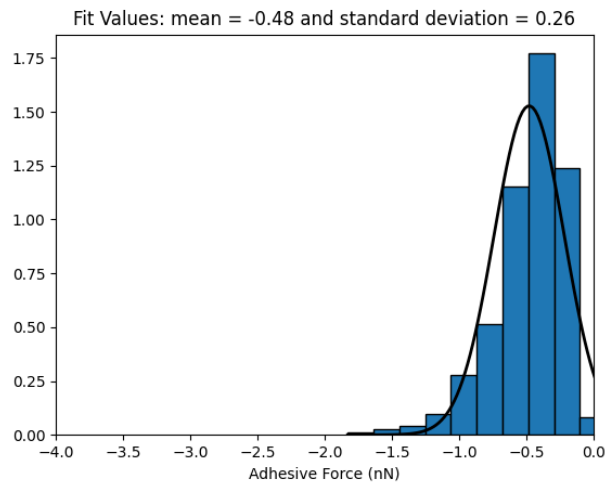
### Eau pure



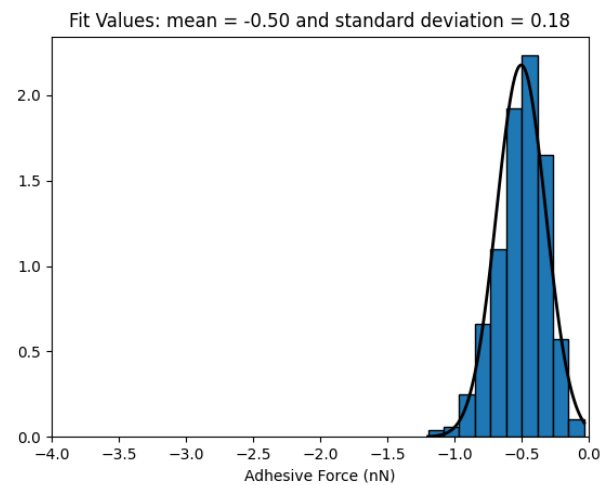
### PBS



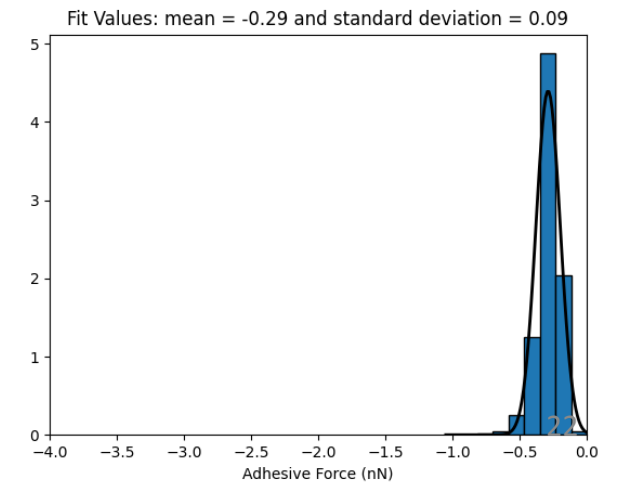
### Eau pure + NaCl + HCl



### Eau pure + NaCl

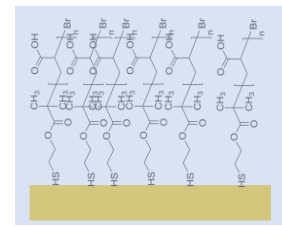


### PBS + NaCl

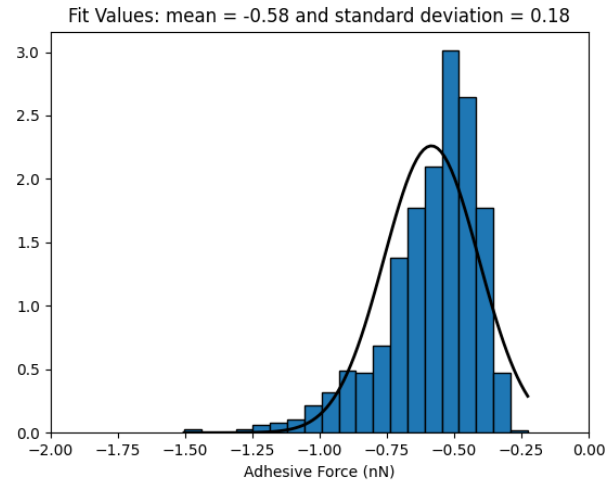


# Extras

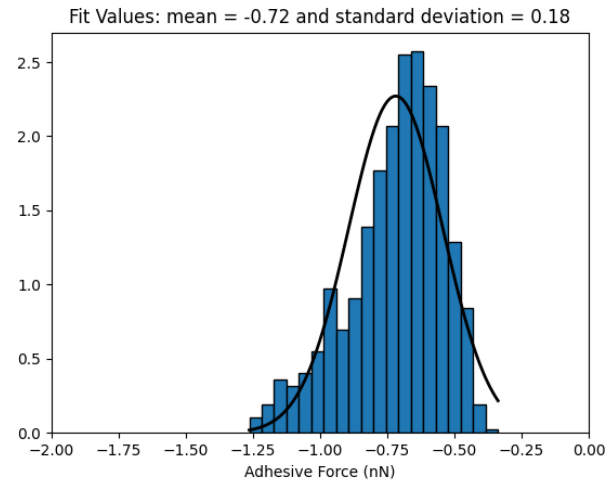
## Statistiques des courbes de forces pour le PAA



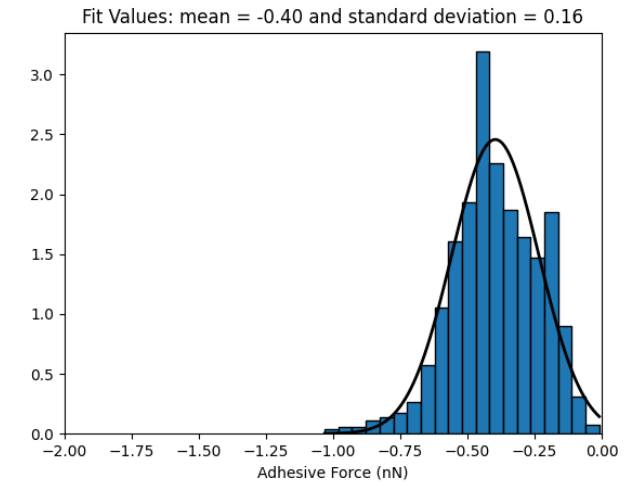
Eau pure + HCl



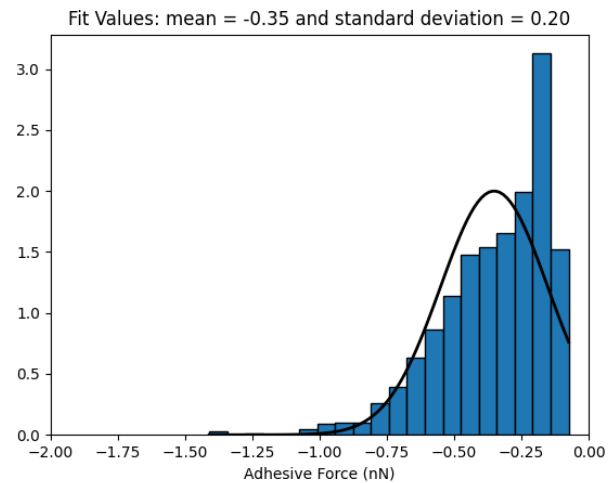
Eau pure



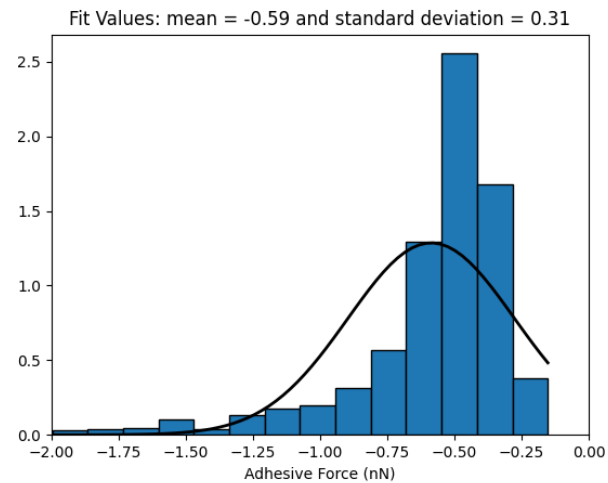
PBS



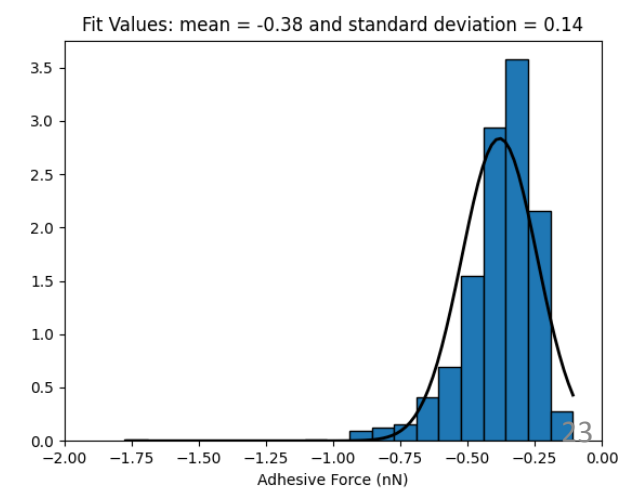
Eau pure + NaCl + HCl



Eau pure + NaCl



PBS + NaCl

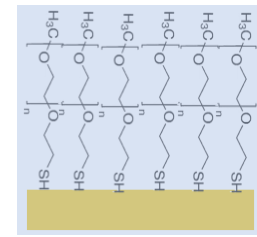




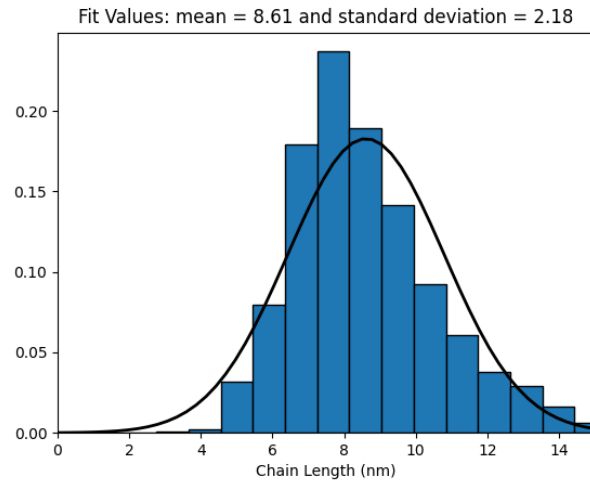


# Extras

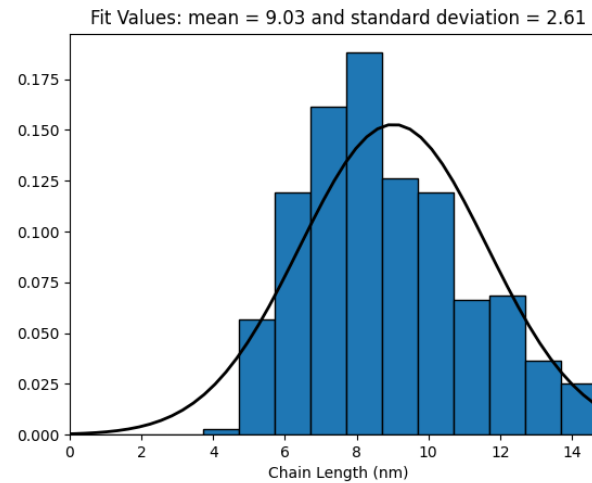
## Statistiques des longueurs de chaînes du PEO



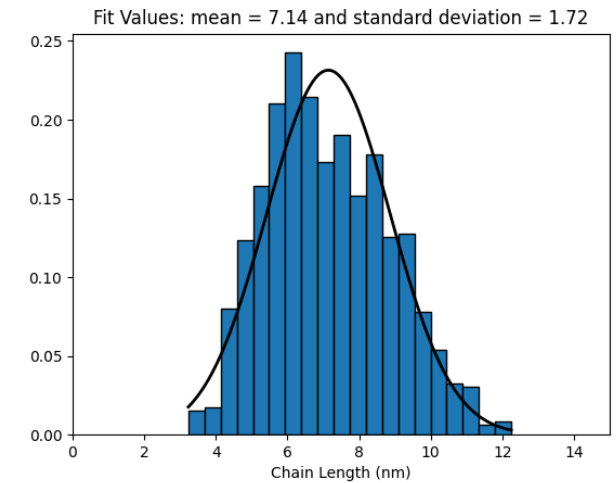
Eau pure + HCl



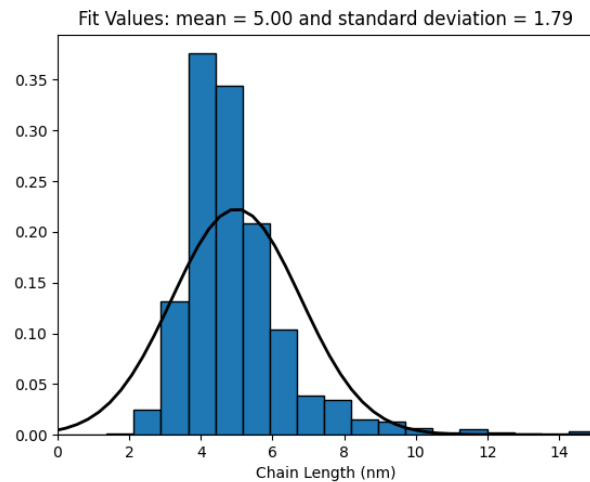
Eau pure



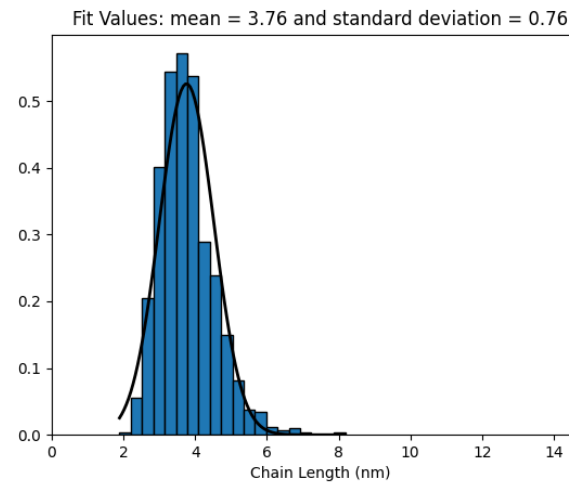
PBS



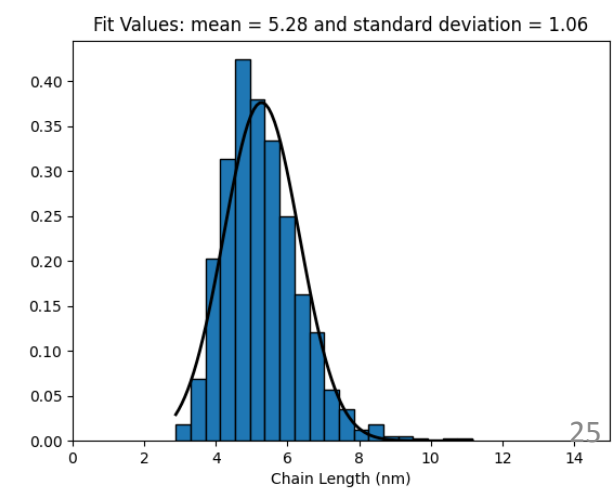
Eau pure + NaCl + HCl



Eau pure + NaCl

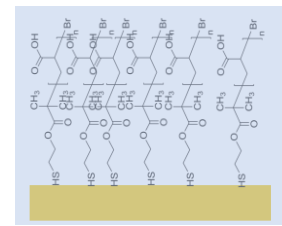


PBS + NaCl

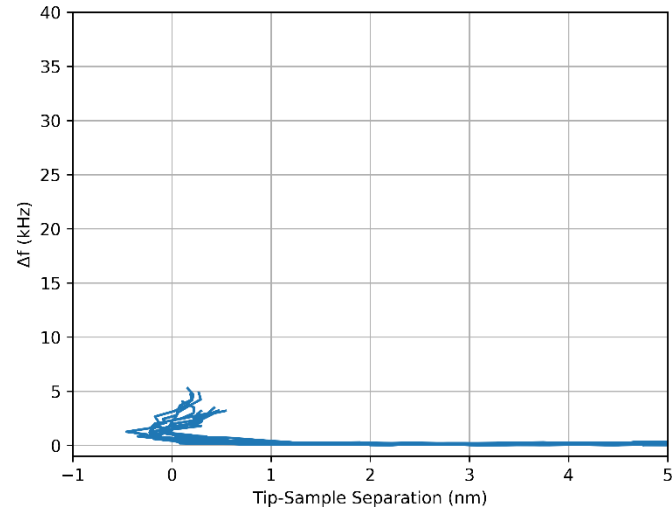


# Extras

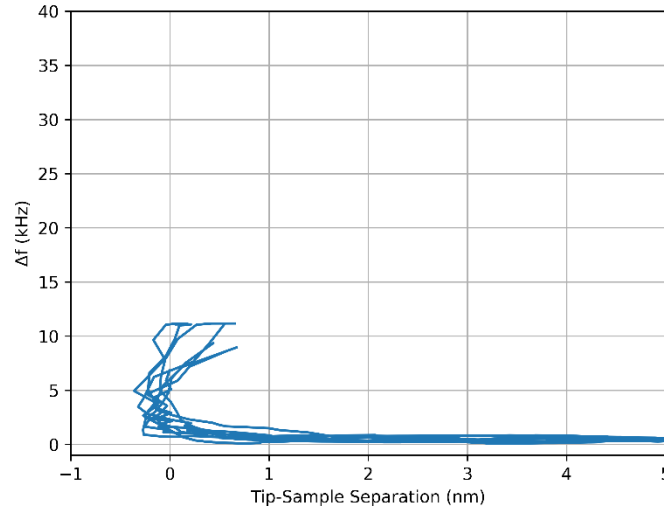
## Courbes de $\Delta f$ pour le PAA



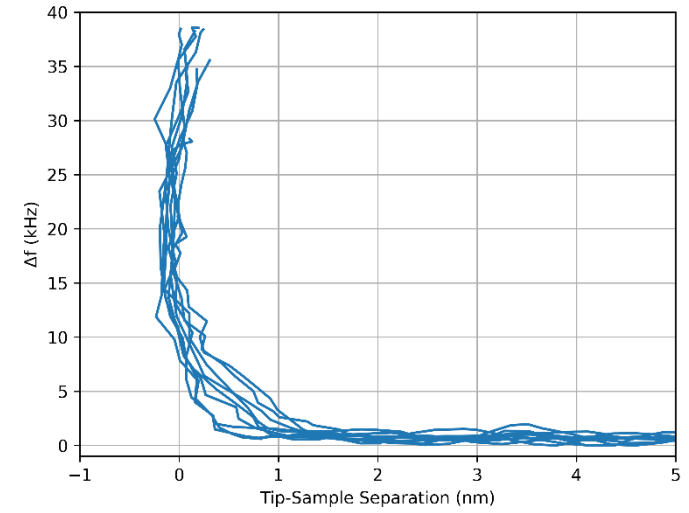
Eau pure + HCl



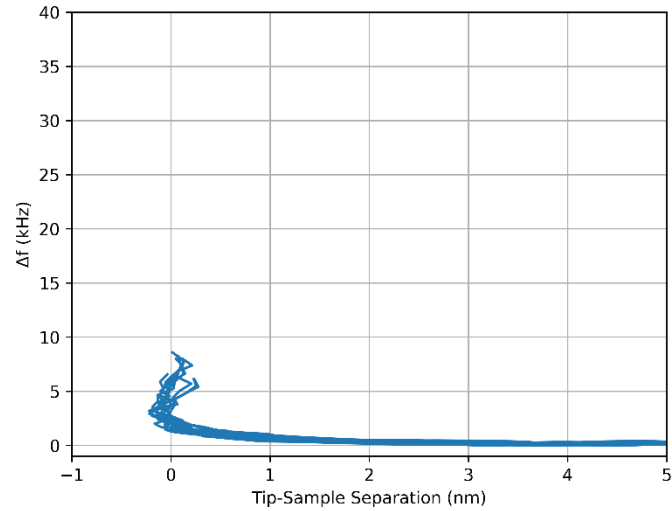
Eau pure



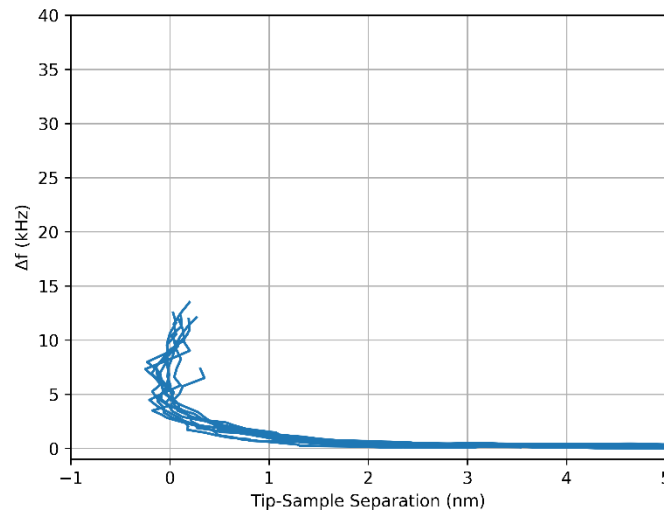
PBS



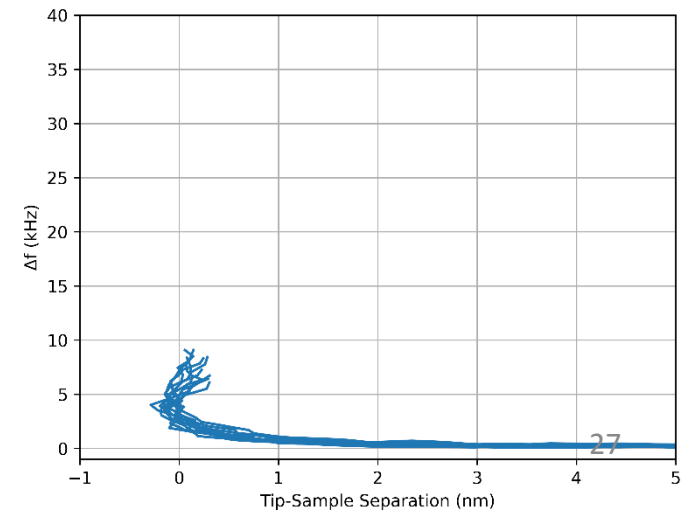
Eau pure + NaCl + HCl



Eau pure + NaCl



PBS + NaCl



# Caractérisation de l'interface liquide/ brosses de polymères déposées sur surfaces d'or par spectroscopie de force 1D-AFM et 3D-AFM



## Image 3D des Interfaces

Cartographie de volume en force

- Lente vitesse de balayage
- Résolution
- Dérive pendant le balayage

- Courbe  $\Delta f/d$  sur différents positions (xy)
- Images 2D (xy) sur différents z offsets



Interface Calcite-eau

