Mission pour les initiatives transverses et interdisciplinaires (MITI)

Journée thématique

Fonctionnalisation de sonde et analyses de données

Toulouse, 29 novembre 2023

Adhesion at the interface of nanocellulosic surfaces measured via colloidal probe force microscopy

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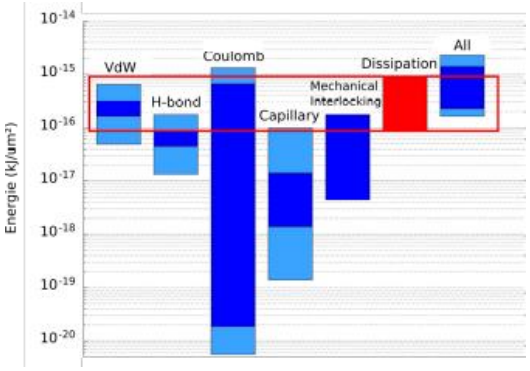
CTP Fleur ROL
FCBA Sandra TAPIN-LINGUA
DCM Hugues BONNET

Mechanisms of fiber bonding in paper

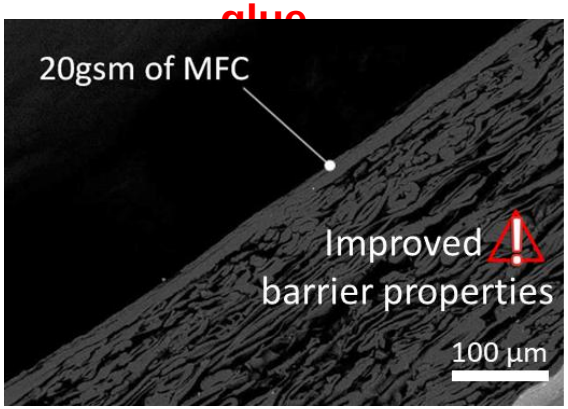


U. Hirn et al., Sci. Rep. (2015)

Cellulose fibers bonds via:

- Interdiffusion, entanglement,
- Capillary forces,
- Intermolecular interactions
  - Coulomb forces
  - Hydrogen bonds
  - VdW forces

Packaging material made of a layer of MFC film adhered to a paper without glue

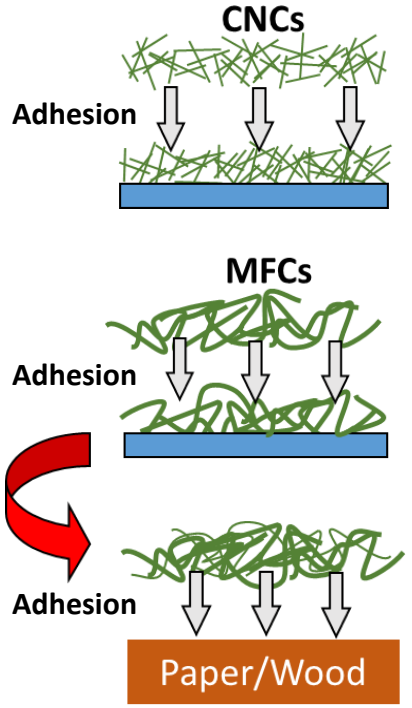


CTP : Guérin et al.

OBJECTIVE: Understanding the **parameters** and **mechanisms** contributing to the **adhesion between two nanocellulosic layers** by probing the **morphology, structure and composition** of the films via near-field microscopy:

Decouple the contributions to Adhesion → **Better control of the bonding processes**

STRATEGY:



Model Cellulose NanoCrystals (CNC) with controlled size

Model MFCs with controlled surface chemistry

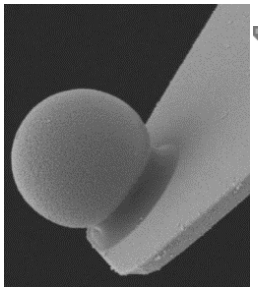
Macroscopic "real" objects

PARAMETERS

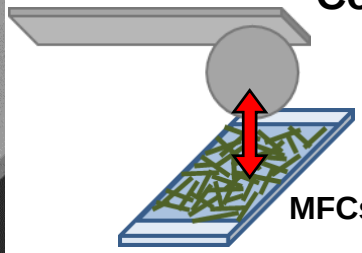
Size of the fibers	Applied pressure Surface chemistry	Relative humidity	Type of solvent
↓	↓	↓	↓
Van der Waals	Hydrogen bonding	Capillarity	Coulomb

EXPECTED PREDOMINANT ADHESION MECHANISM

Coatings characterizations:



Radius: 2.5 - 5 µm

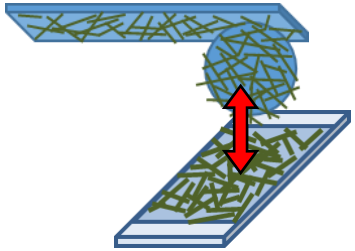


Colloidal Probe (CP)

- Adhesion
  - Force
  - Energy

Adhesion between "large" surfaces

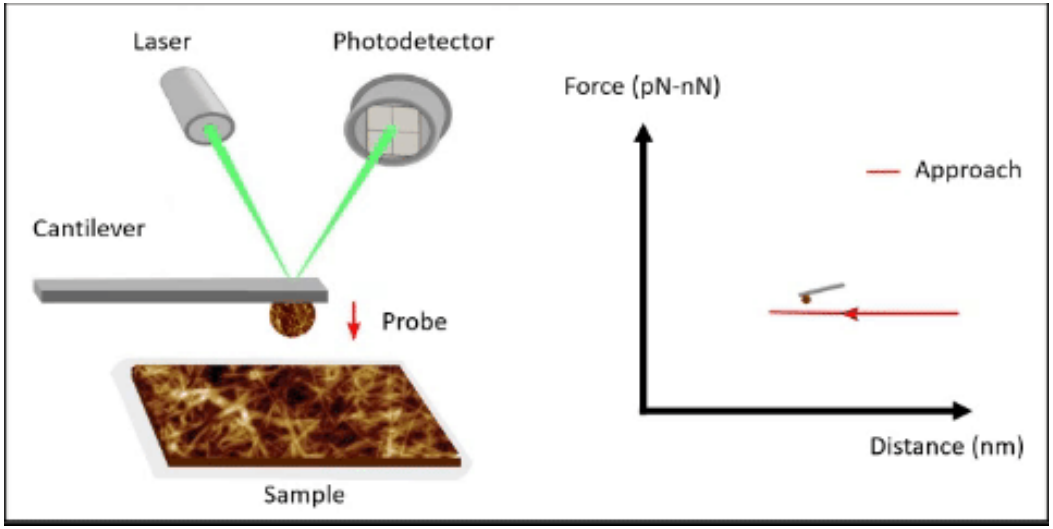
Probe functionalization



CP with MFC or CNCs

- MFCs
- T-CNC
- C-CNC
- W-CNC

Adhesion between cellulosic surfaces



Peak Force QNM

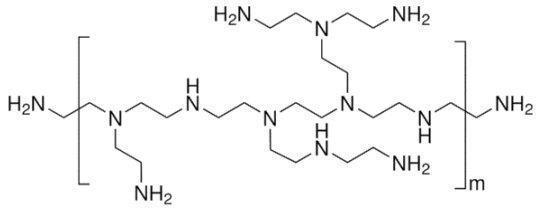
Acquisition of force-distance curves provides mechanical properties

- Indentation
- Modulus (Hertz, DMT, JKR)
- **Adhesion Force**
- **Adhesion Energy**
- ...

Sample preparation:

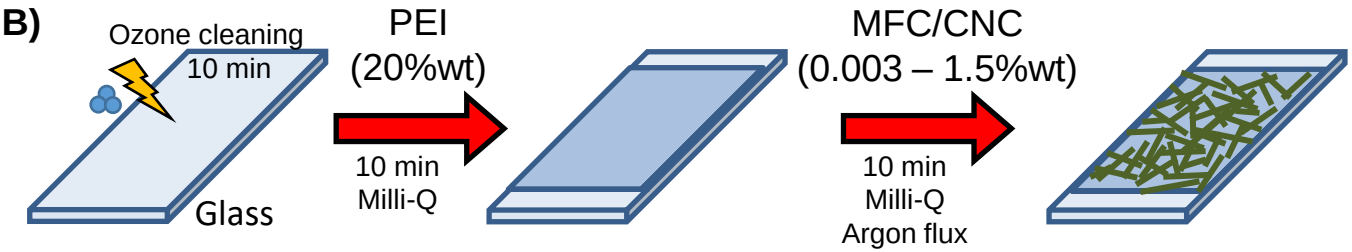
Polyethylenimine (PEI)

A)



To adhere the fibers to the substrate

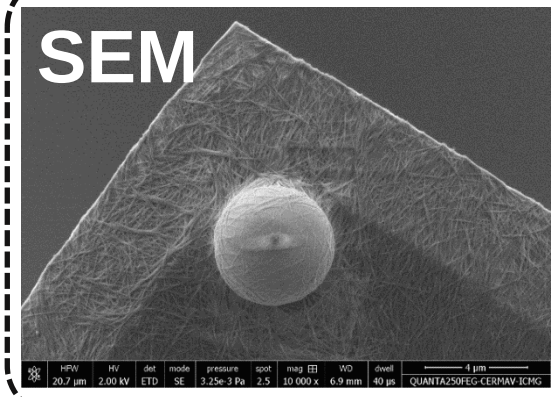
B)



R.W.N. Nugroho et al., Colloids and Surfaces B: Biointerfaces 173 (2019)

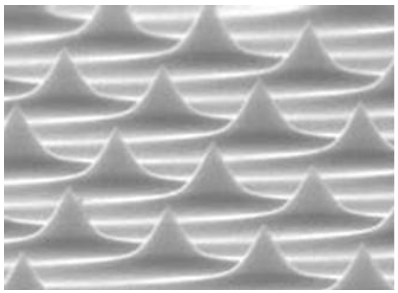
Fonctionnalisation de sonde : Microfibrille/Nanocristaux de Cellulose

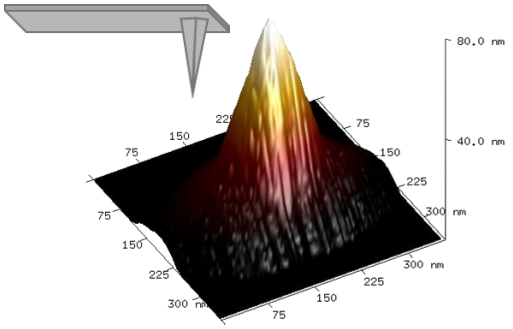
GT Fonctionnalisation



Problem:
Electron beam changes the surface

"Tip Check" sample:

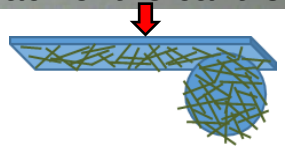




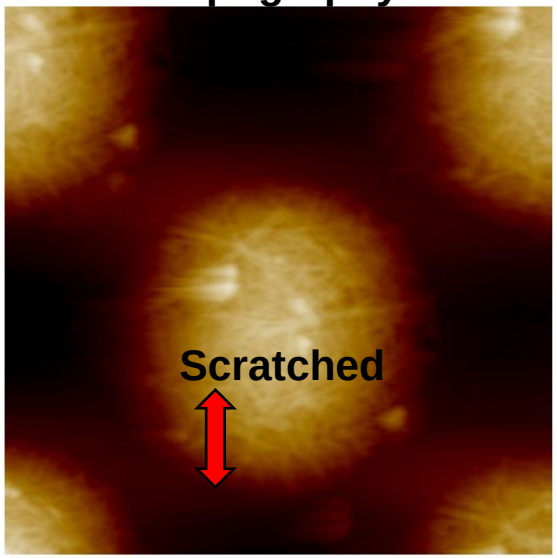
Images the tip instead of the sample

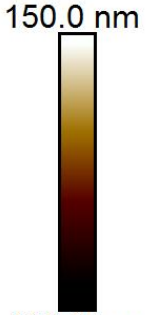
Colloidal Probe on Tip Check

Optical Microscopy

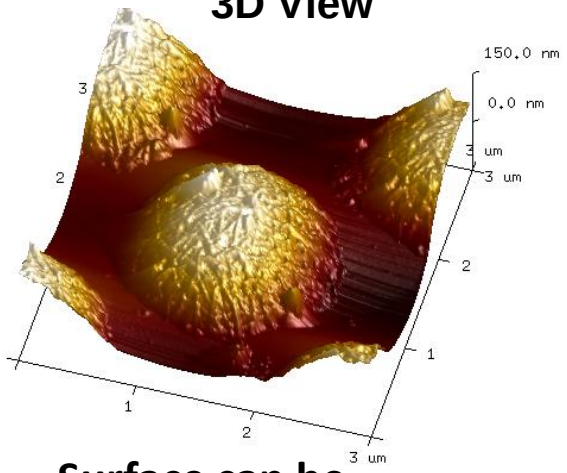


Topography





3D View

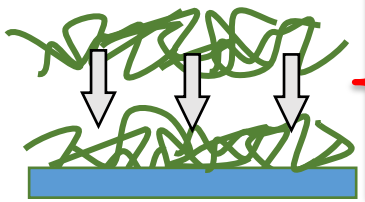


Surface can be characterized without damaging the coating prior to analyses

Fonctionnalisation de sonde : Microfibrille/Nanocristaux de Cellulose

GT Fonctionnalisation

MFCs



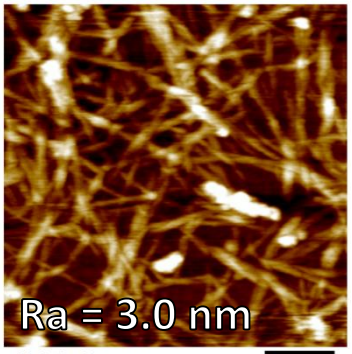
- MFC standard
- MFC – TEMPO
- MFC – Bisultite
- Kraft – Macrofibrils

Surface chemistry & Composition

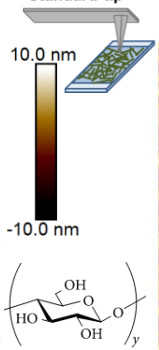
Size of the fibers → Van der Waals

Applied Pressure Surface Chemistry → Hydrogen bonding

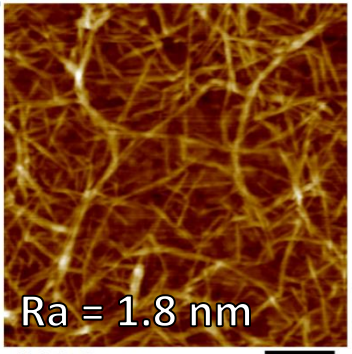
MFC 3P

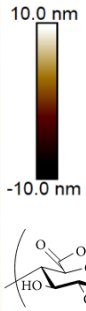


Standard tip

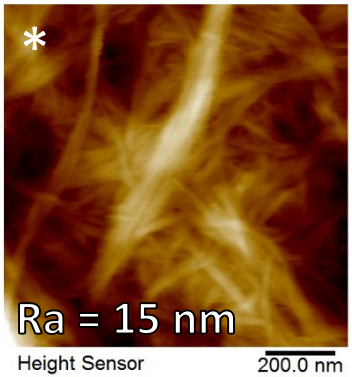


TEMPO

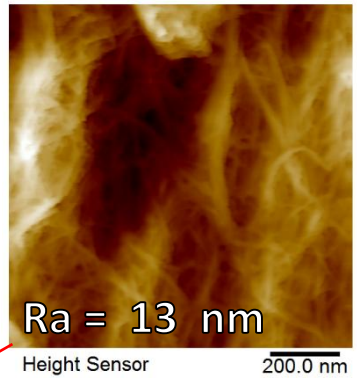




Bisulfite

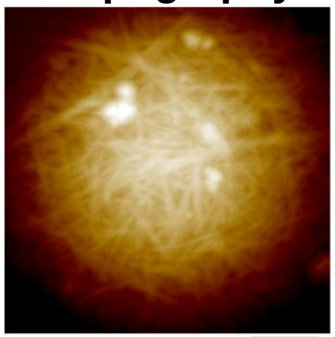


Kraft

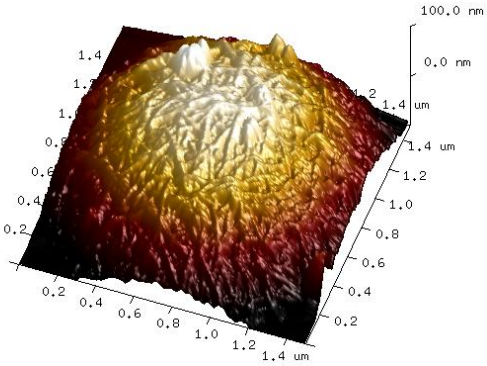


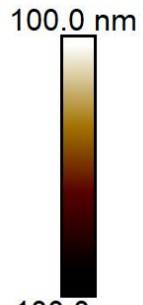
CP with Standard MFCs

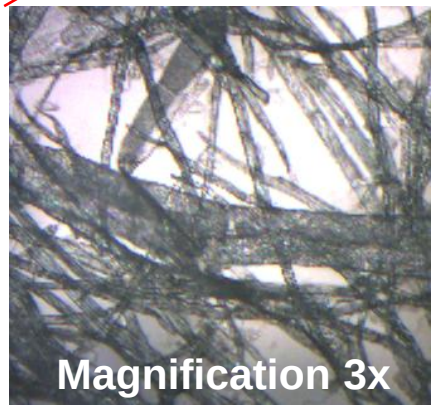
Topography



3D View







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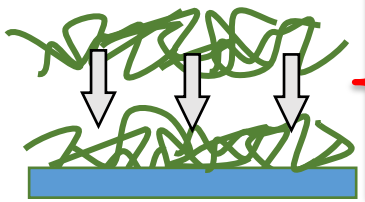

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Surface chemistry & Composition

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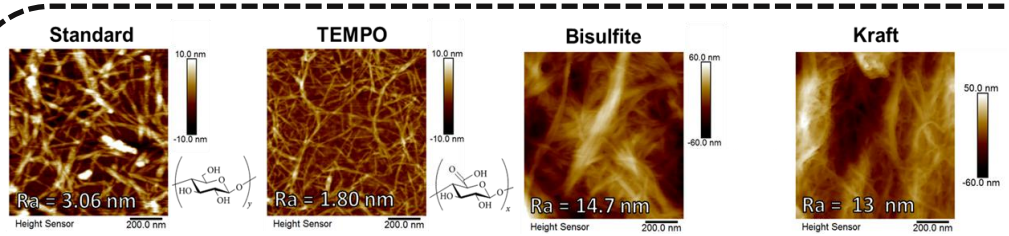
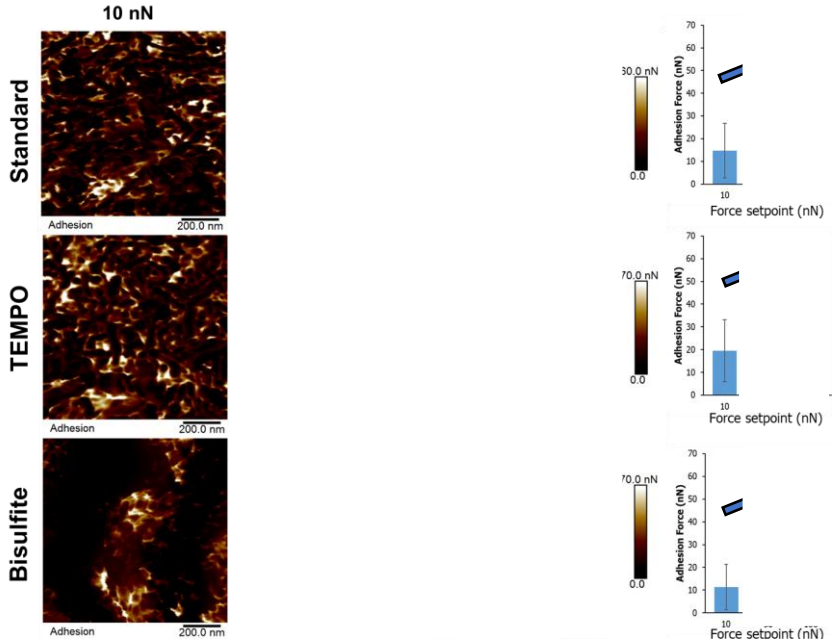
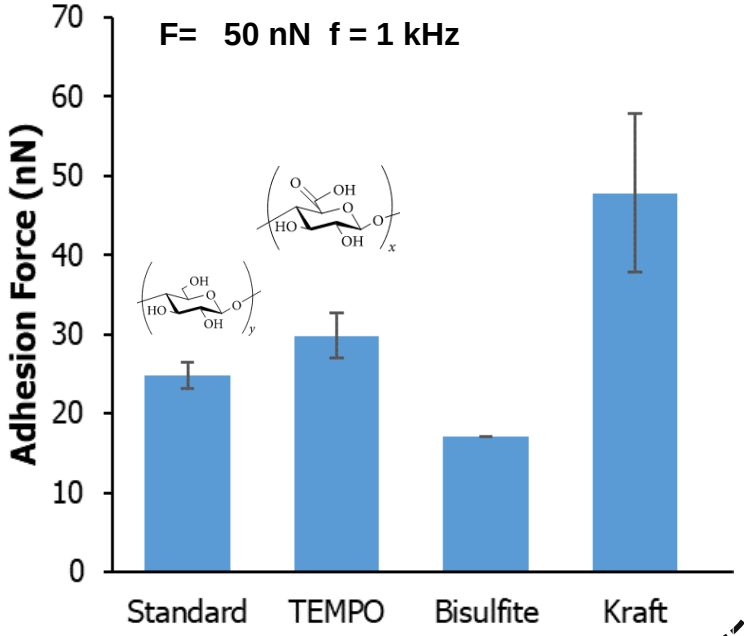


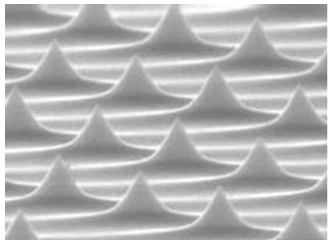
Complex interactions

- Roughness
- Surface chemistry (OH, COOH,…)
- Composition (hemicellulose %)



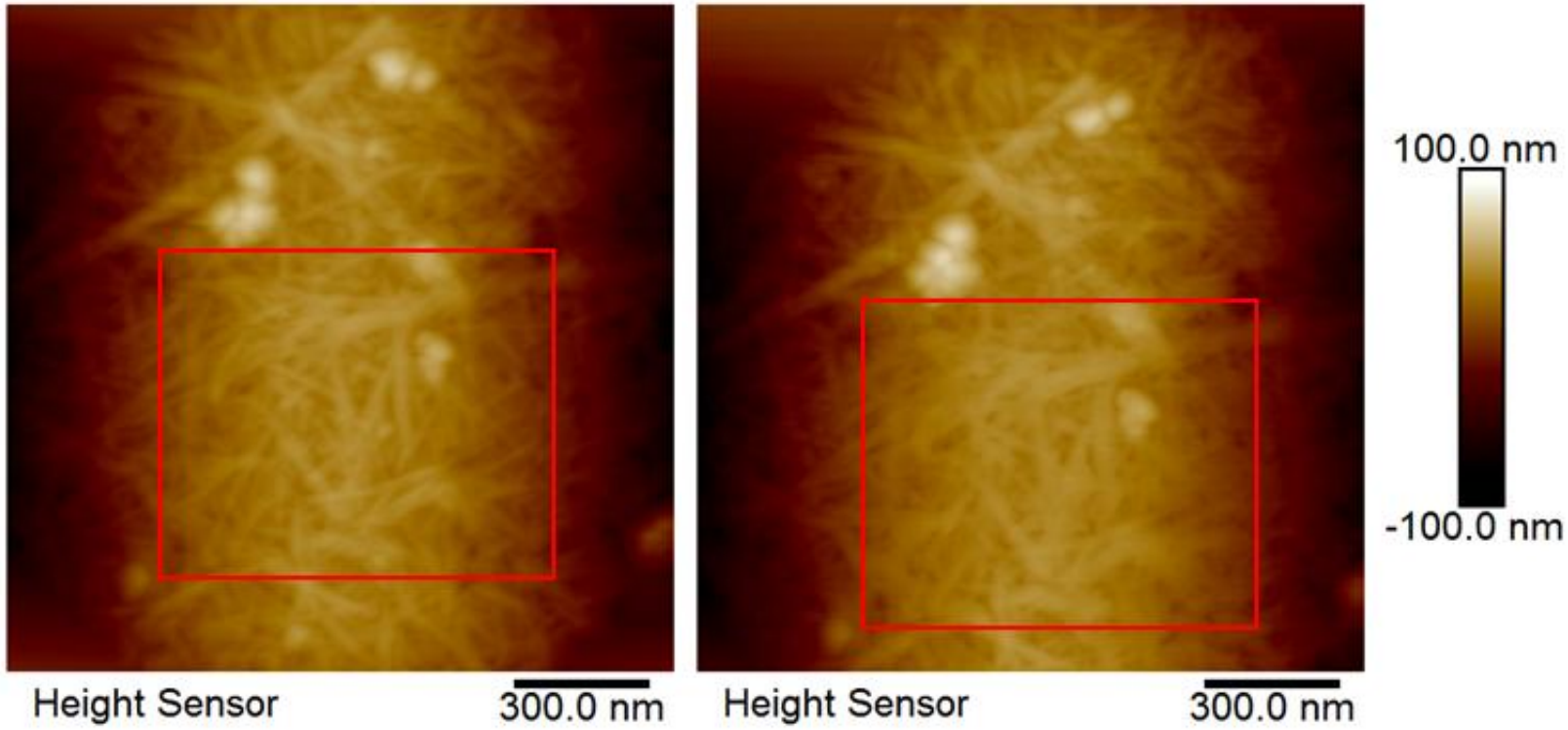


“Tip Check”



Before analyses

After analyses

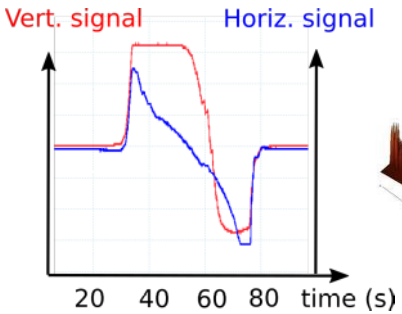


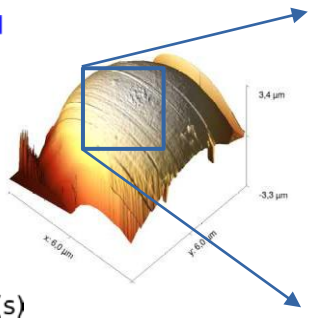
Further developments

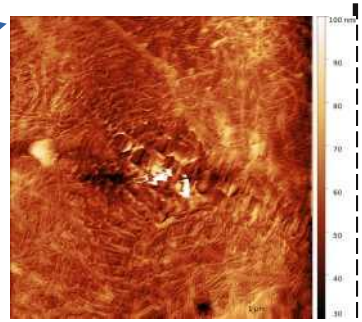
Testing 3 approaches for dipping the probe in PEI solution

- Drop of the PEI solution directly onto the cantilever-tip
  → influence on the cantilever sensitivity ?

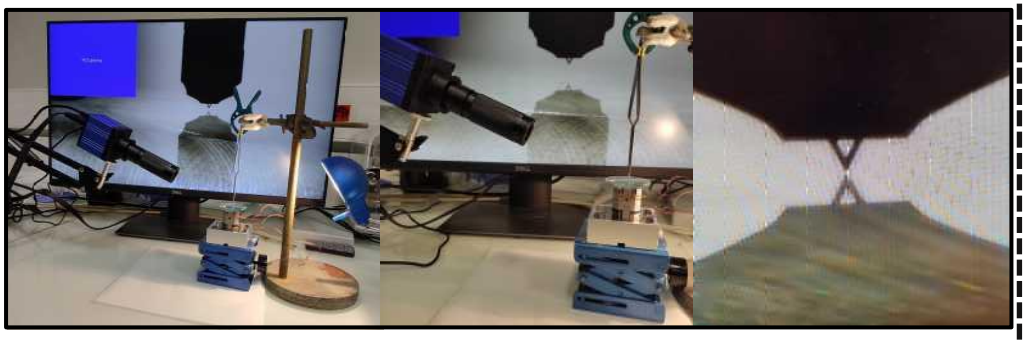
- AFM coarse movement and its optical microscope used to dip the CP into PEI. The oscilloscope records the force exerted in real time.
  → suction due to capillarity
  → 'neck' effect



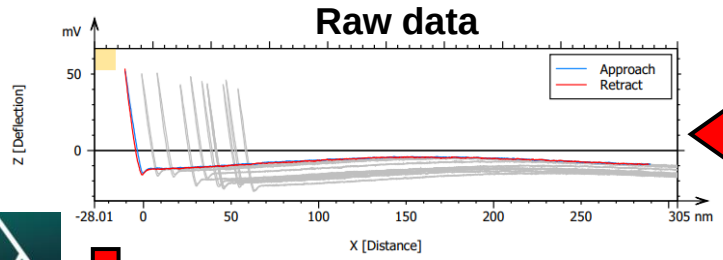


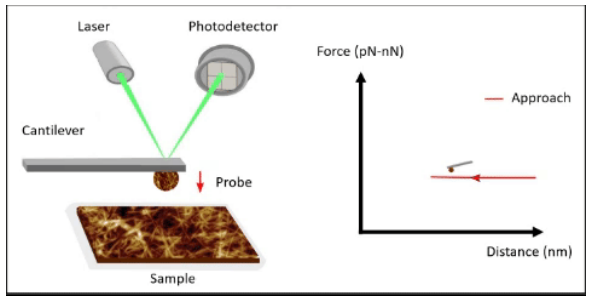


- Fine control of the gap between the CP and the solution using piezotables and USB-microscope in order to dip only the probe.



Developed by Franck DAHLEM





Acquisition of Force Curves by AFM

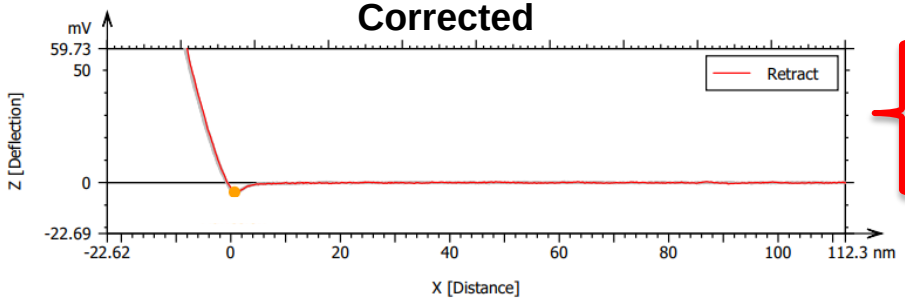
Mountains 9

Force curve analysis

Correct the base-line

Calibrate constants

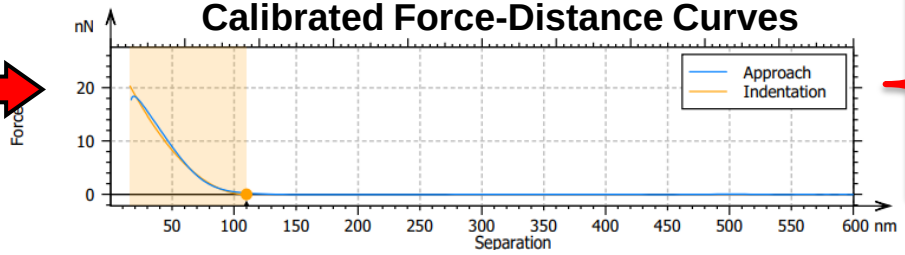
Calibrated force curve



- Baseline correction
- Contact point
- Noise

- Cantilever spring constant (k)
- Deflection sensitivity
- Tip radius

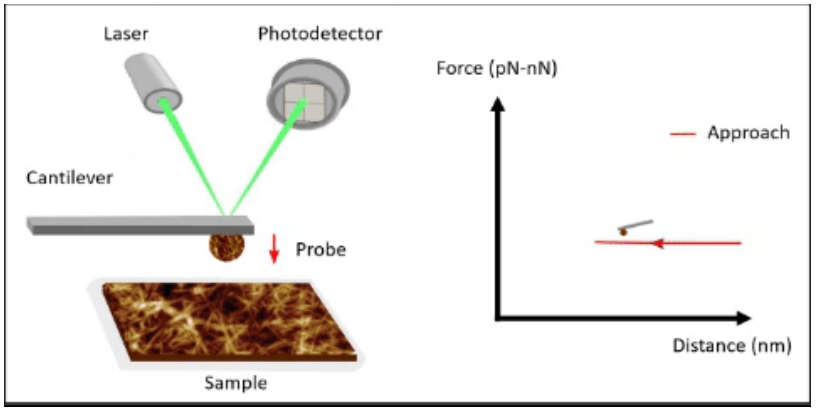
Used for nanomechanical analysis



- Indentation
- Modulus (Hertz, DMT, JKR)
- Adhesion Force
- **Adhesion Energy**
- ...

MountainsSPIP allows for automatic calibration of hundreds of curves and images

Adhesion at the interface of nanocellulosic surfaces measured via colloidal probe force microscopy - CLAC -



MERCI !

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