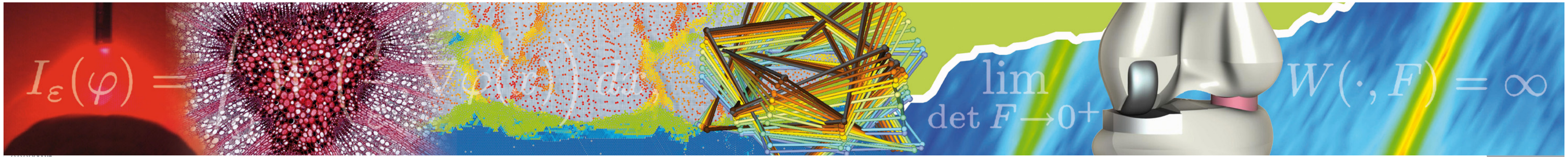

Mesure de champs cinématiques et de propriétés (visco)élastiques par Microscopie à Force Atomique (AFM)

Olivier ARNOULD

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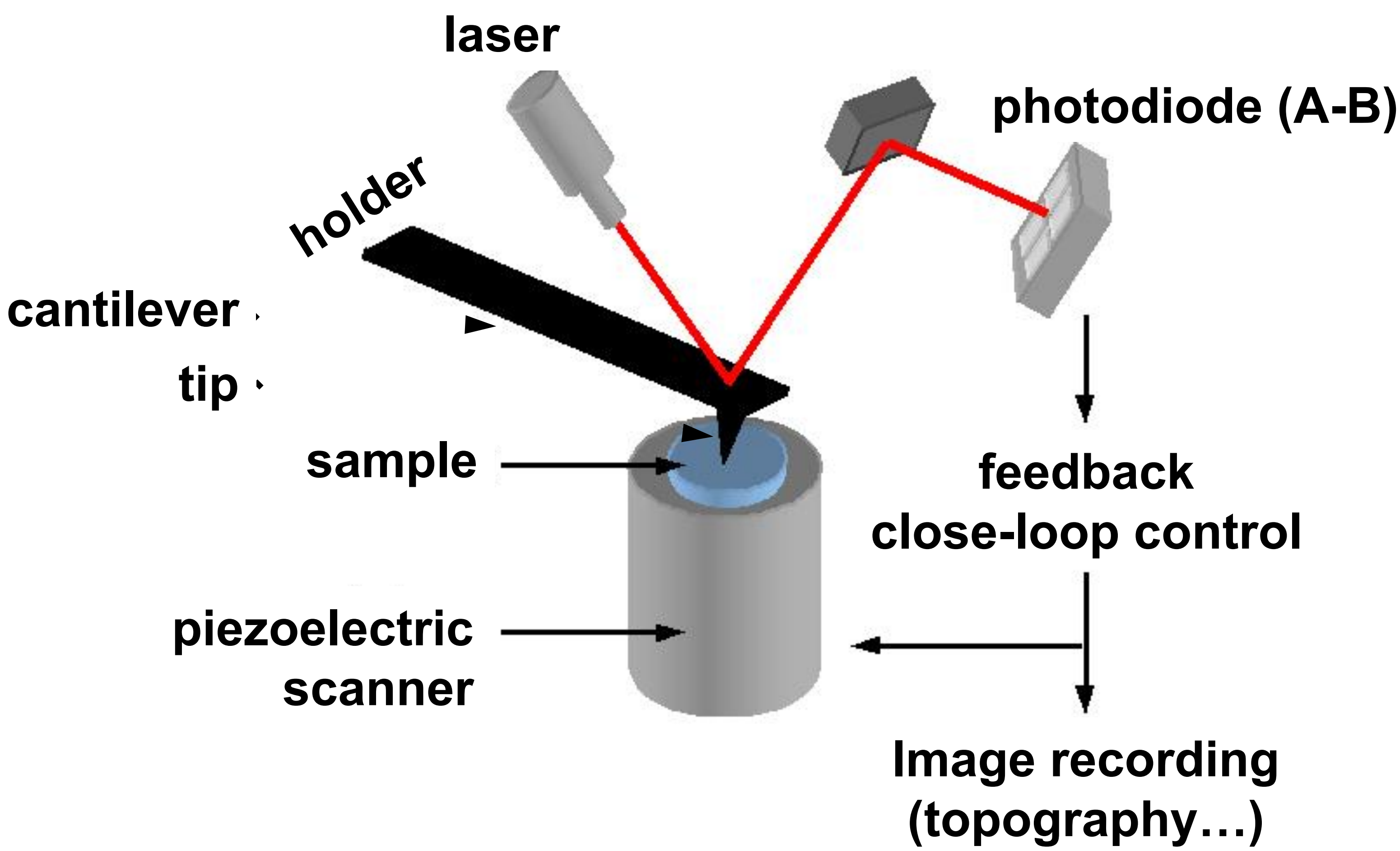
olivier.arnould@umontpellier.fr

Equipe bois

LABORATOIRE DE MÉCANIQUE ET GÉNIE CIVIL - UM/CNRS

Atomic Force Microscopy Principles

- Typical AFM setup



Atomic Force Microscopy Principles

- Typical AFM setup
  - ➲ Cantilever

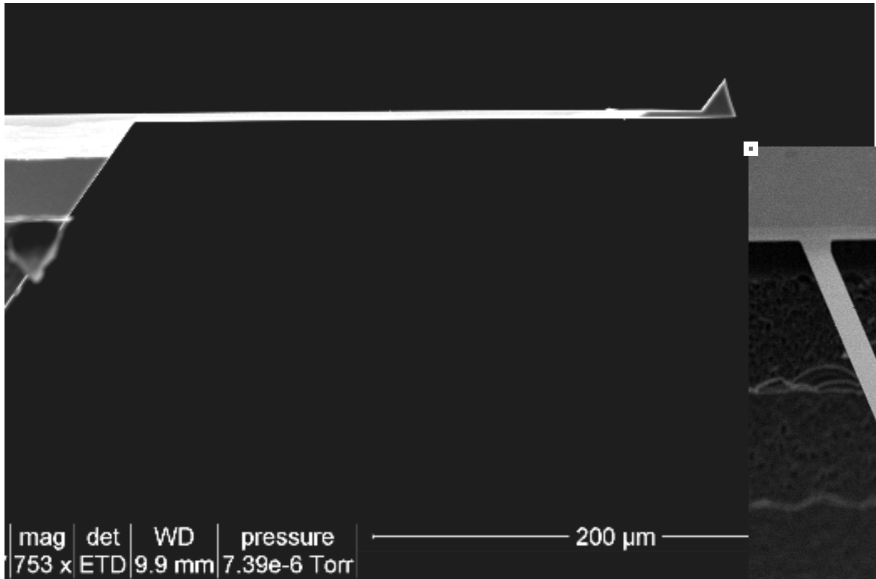
Stiffness k_C: 0.01 - 100N/m

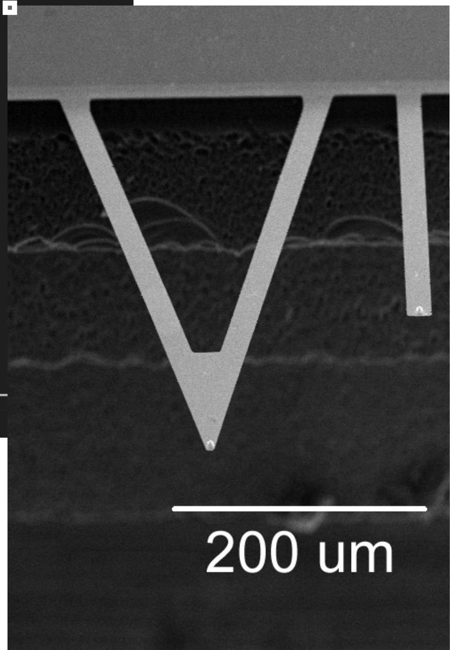
Length L: 100-300µm

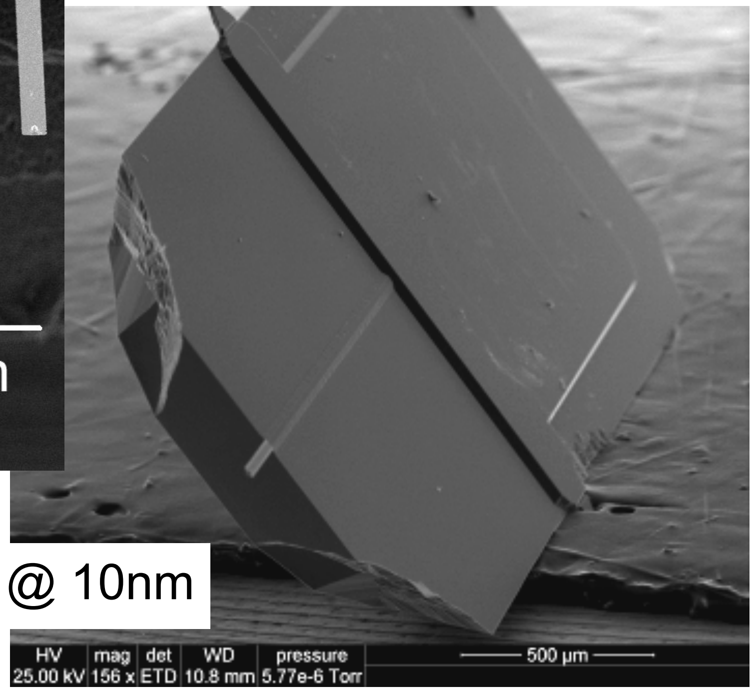
Witdth w: 10-50µm

Thickness e: 0.3-4µm

Coating







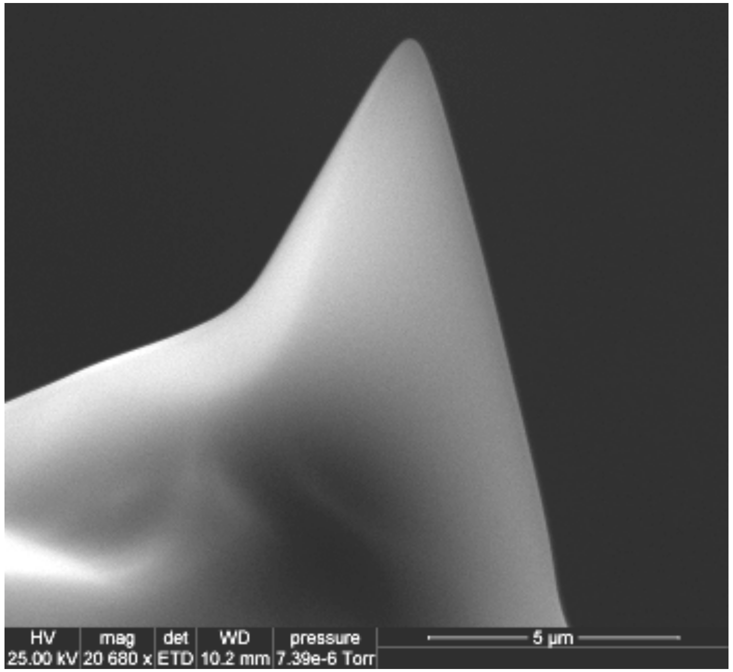
[NanoAndMore, NT-MDT, BudgetSensor, …]

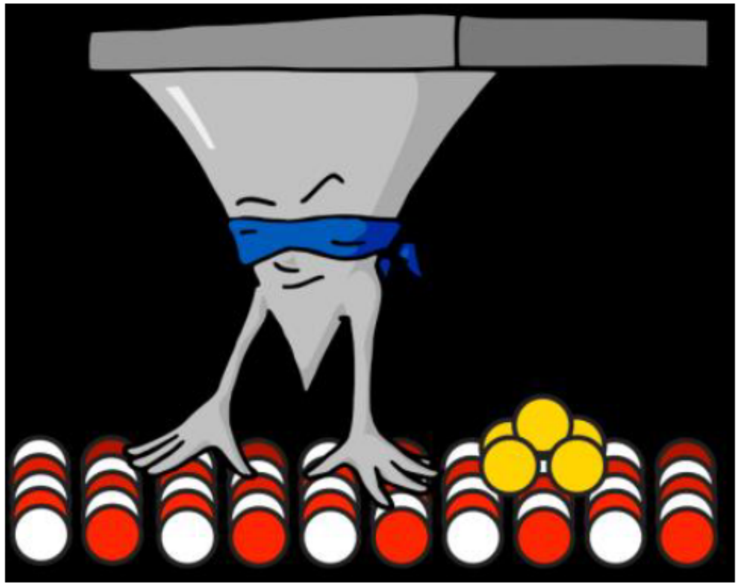
Minimum measurable force:
$k_C \cdot d \approx$ 1pN! (→ 20µN)
(thermal noise $k_B T$ → ~ 8pN)

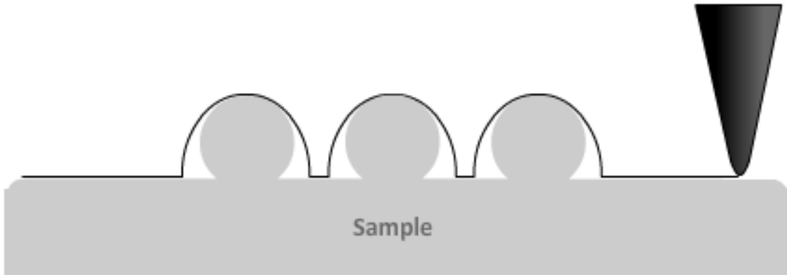
Ionic bond ~10nN - covalent bond ~1nN
van der Waals ~50pN @ nm - electrostatic ~0.1nN @ 10nm
capillarity ~10nN…

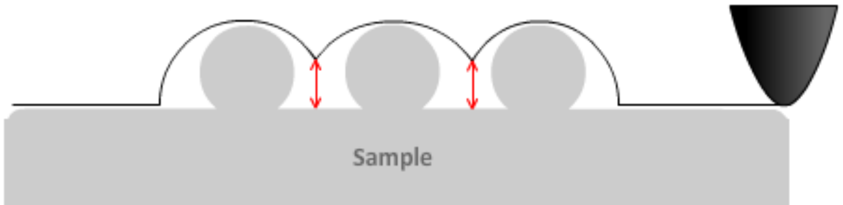
Atomic Force Microscopy Principles

- Typical AFM setup
  - ➲ Tip... feels the surface!









Apex radius *R* ≈ 2-200nm

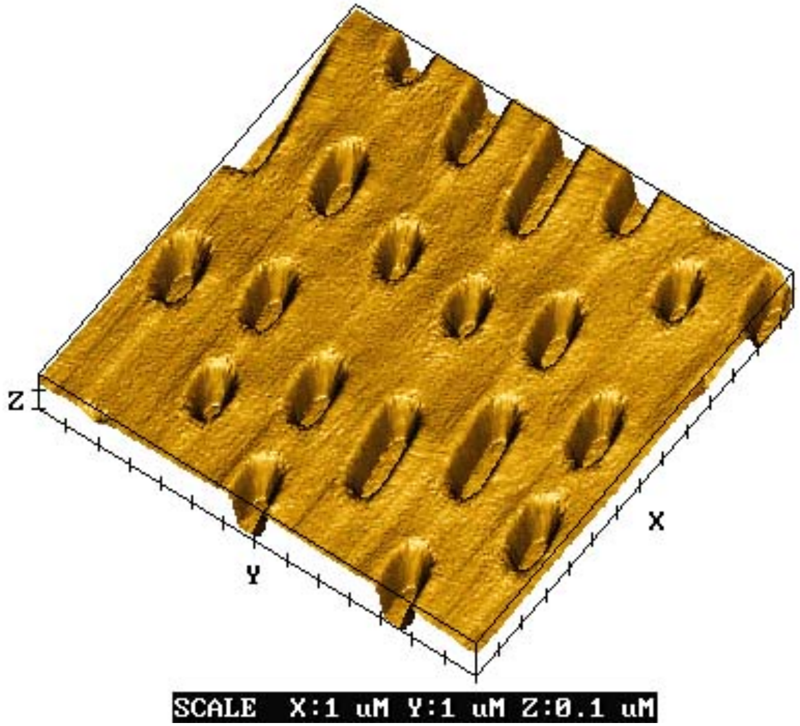
Height *H* ≈ 10µm

Coating, functionalization, …

[NanoAndMore, NT-MDT, BudgetSensor, …]

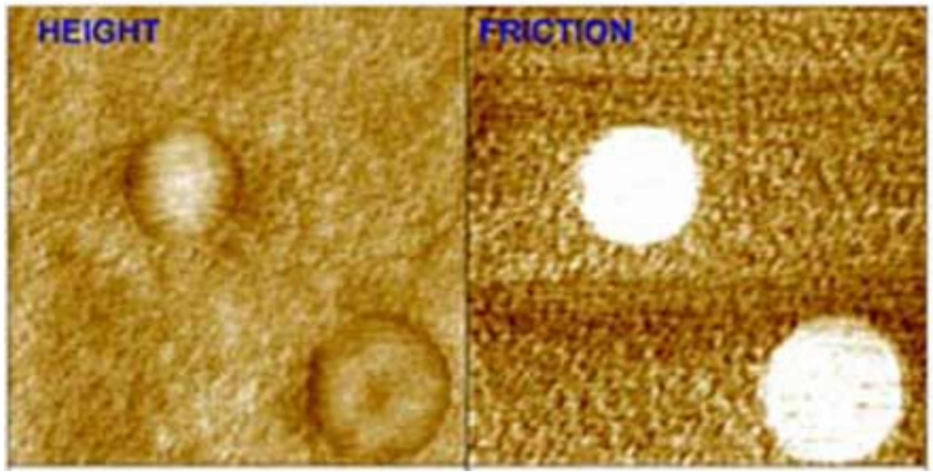
Atomic Force Microscopy Principles

- Contact mode: constant height/force and friction



CD disk surface
[www.ntmdt.com]

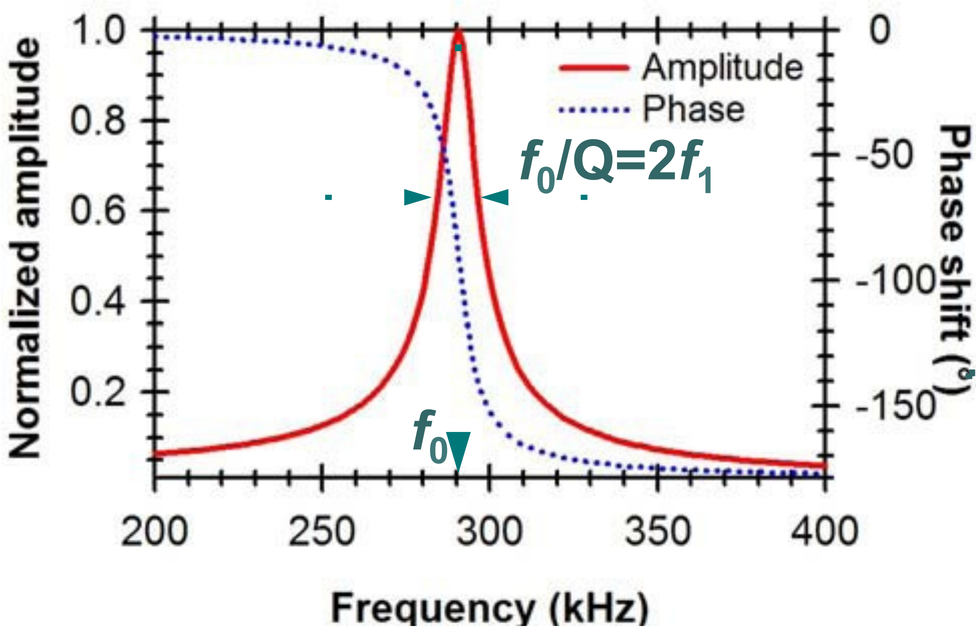
±Fast scan speed in constant force mode (topography/closed-loop feedback)
Limited topography in height force mode
Tip wear
~Poor resolution (surface deformation, large tip surface contact area)

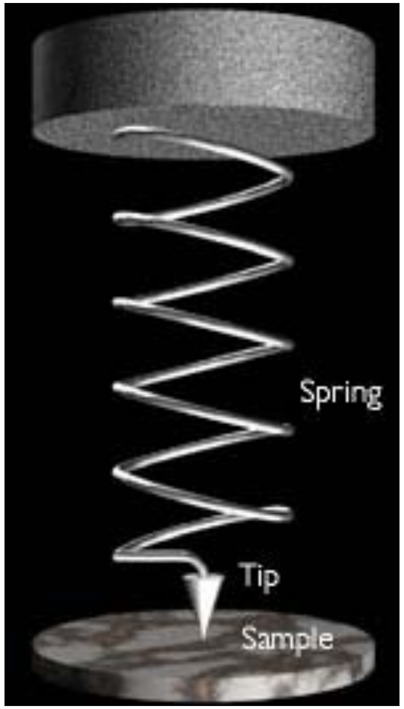


PS-PMMA polymer blend
[Feldman et al., *Langmuir*, 1998]

Atomic Force Microscopy Principles

- Intermittent contact/tapping™/amplitude modulated… mode: knocking on the surface!
  - ➲ Linear harmonic oscillator approximation (free)





$$\omega_0 = \sqrt{\frac{k_C}{m_{eff}}}$$

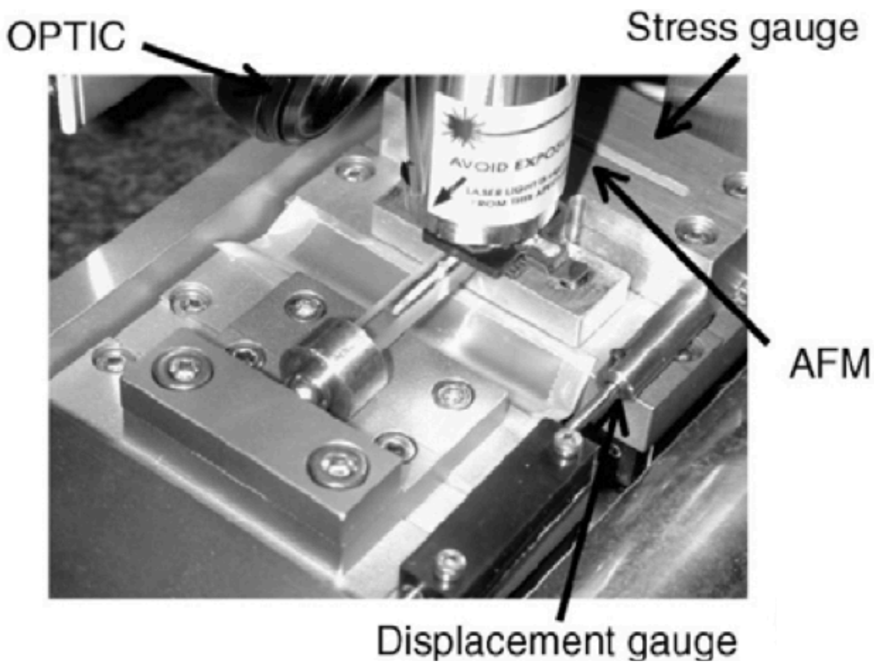
k_C > 10N/m

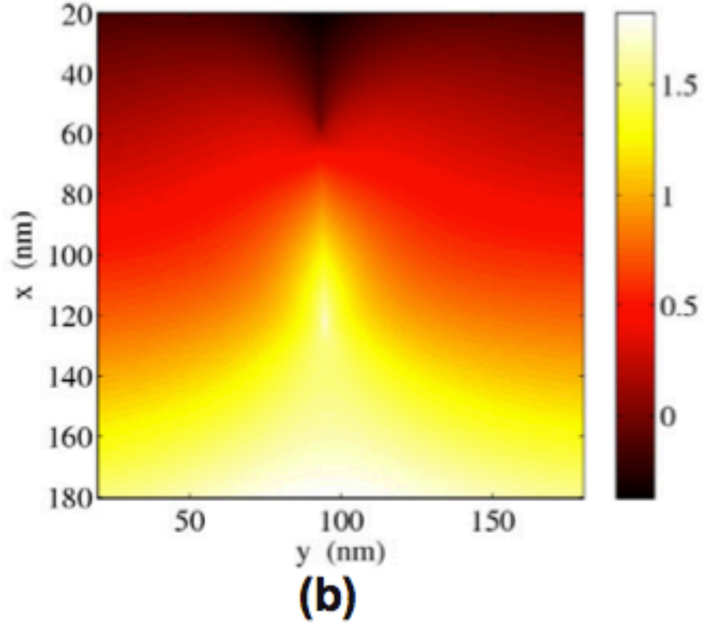
f_0 > 100kHz

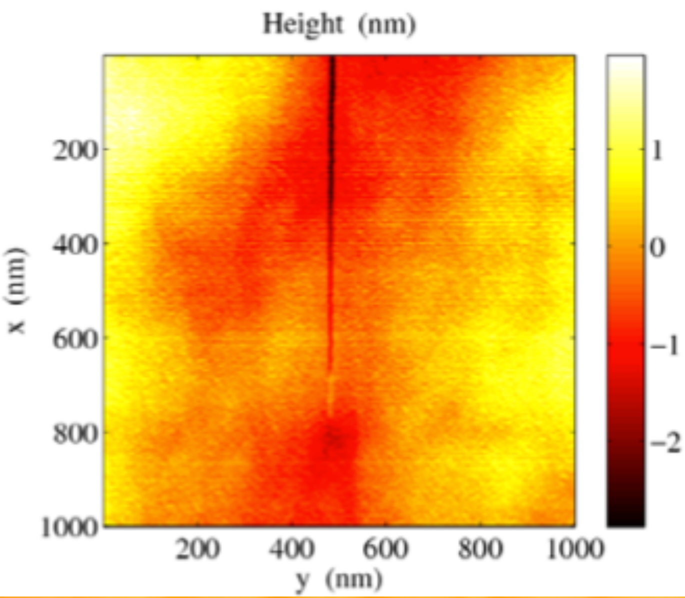
Media	Liquid	Air	High vacuum
Q	10	400	10^4

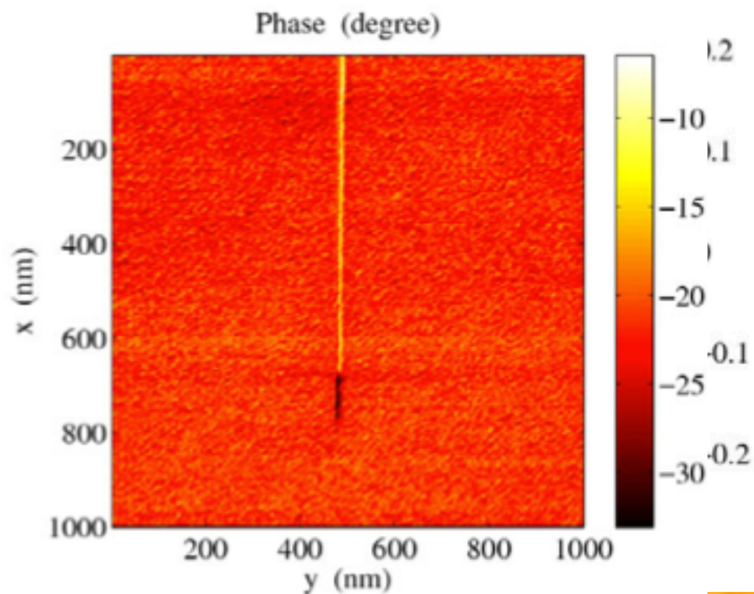
Mesure de champs cinématiques

K. Han, M. Ciccotti and S. Roux
EPL, 89 (2010) 66003



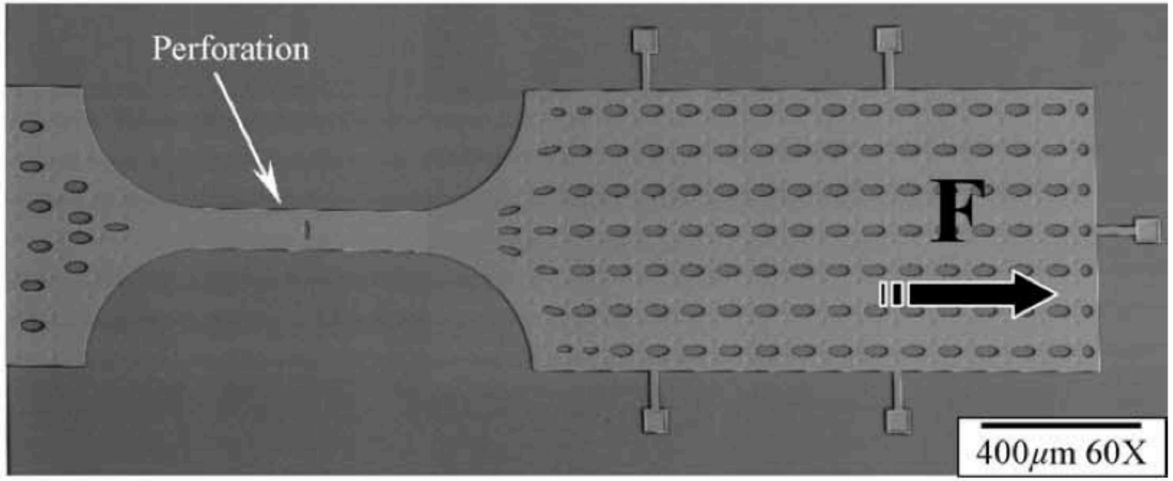


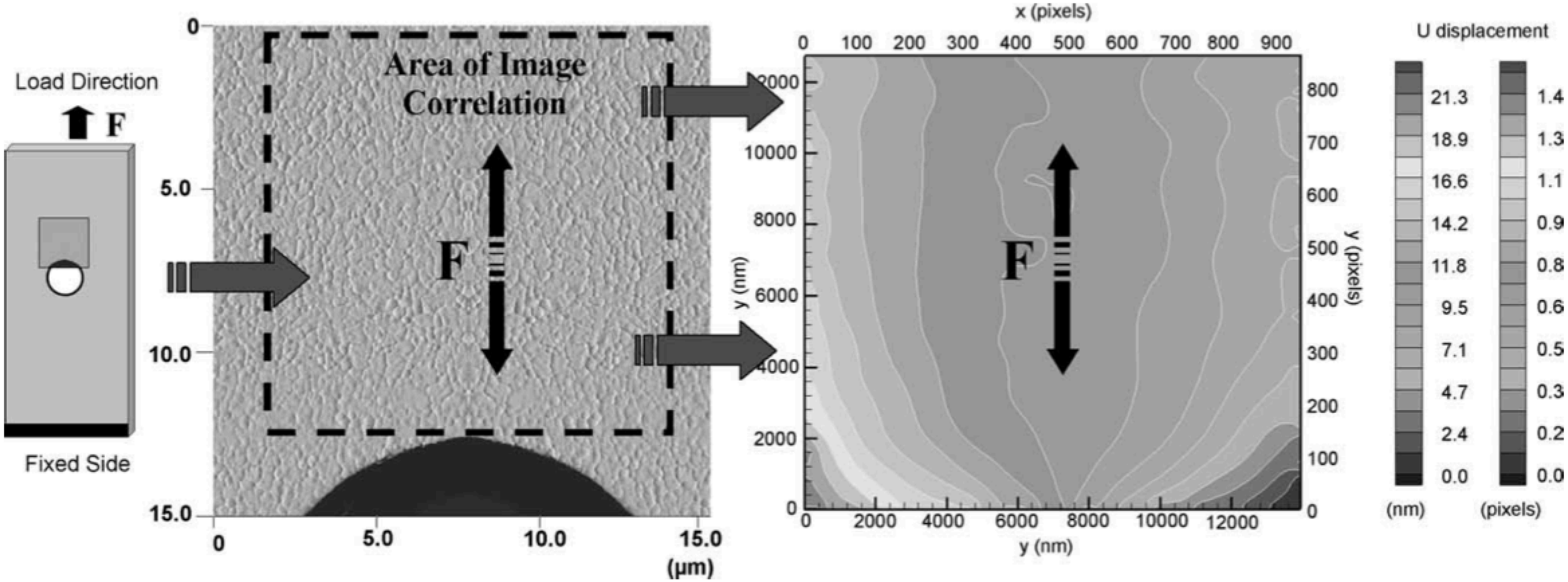




Mesure de champs cinématiques

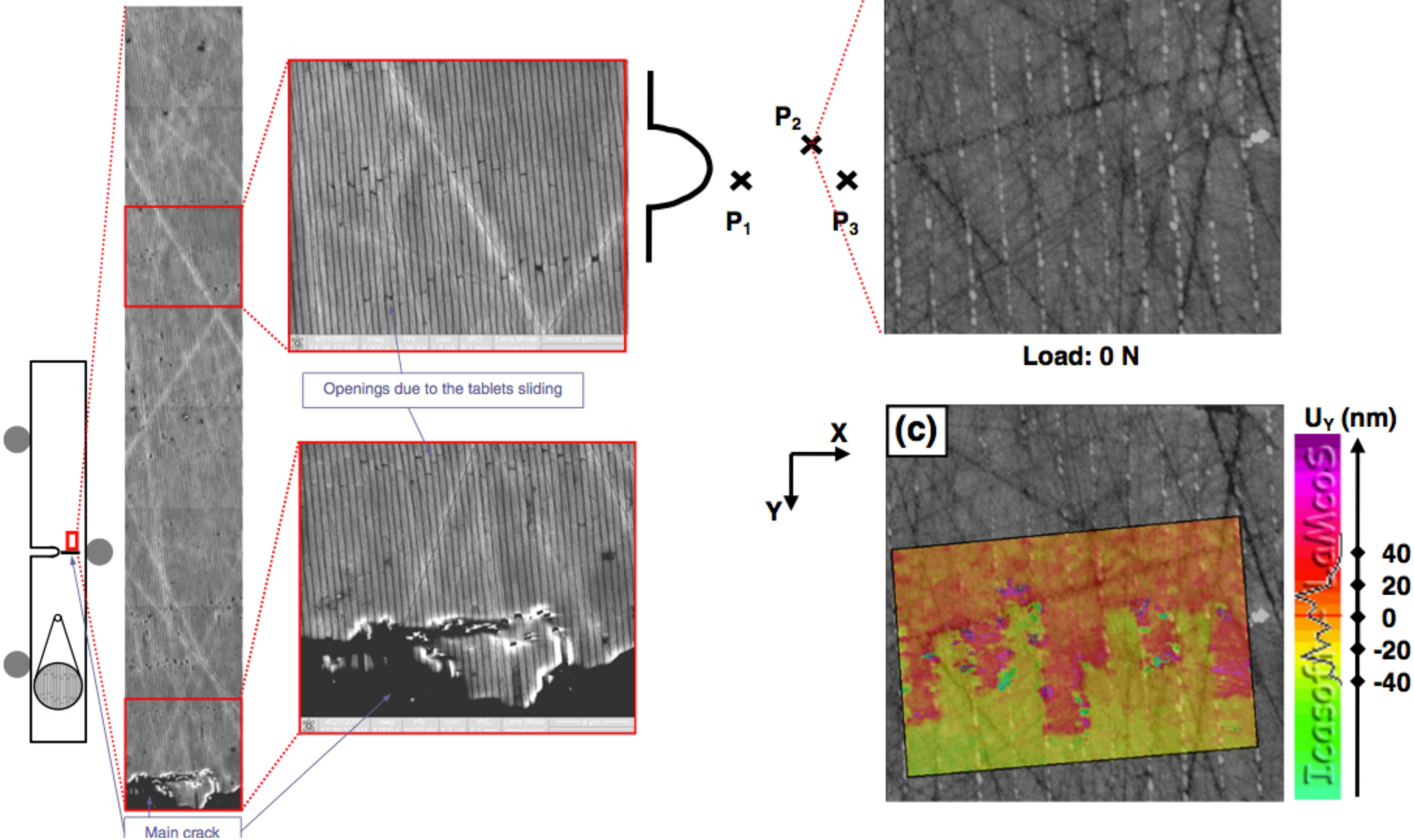
S. Choa, J.F. Cardenas-Garciab, I. Chasiotis
Sensors and Actuators A 120 (2005) 163–171





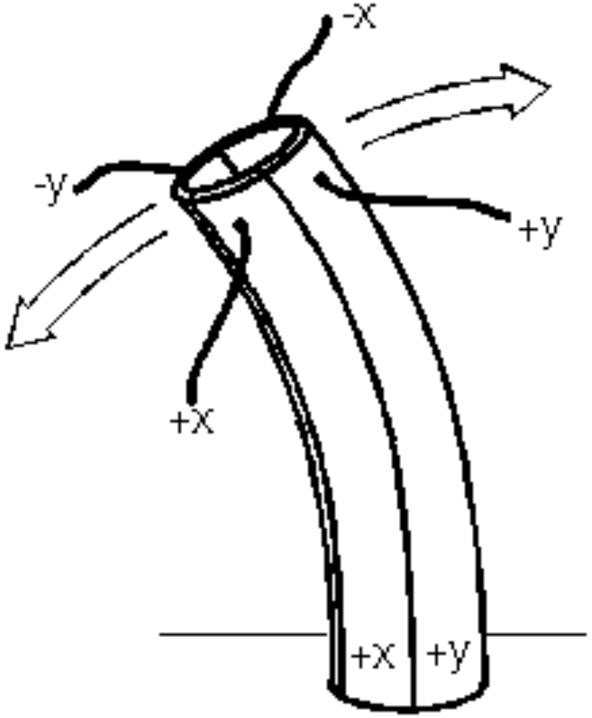
Mesure de champs cinématiques

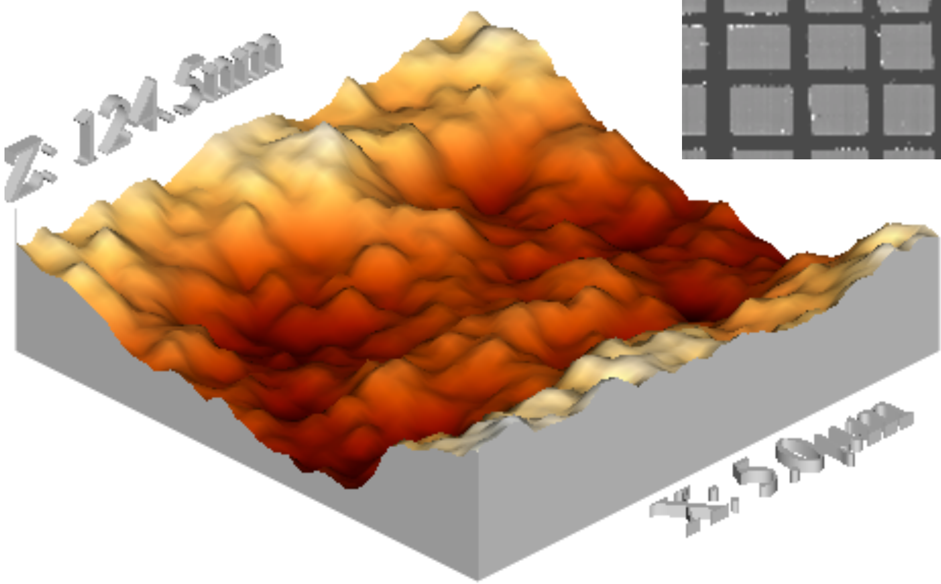
D. Grégoire, O. Loh, A. Juster, H.D. Espinosa
Experimental Mechanics (2011) 51:591–607

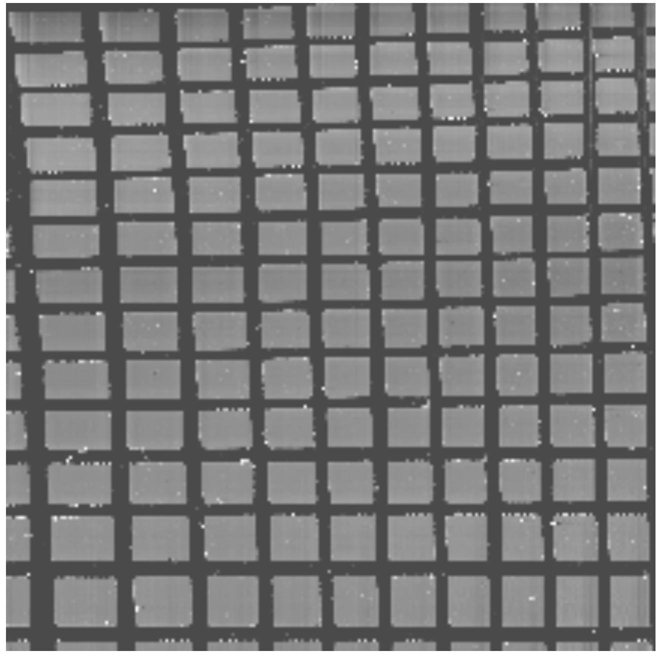


(une) Limite : distorsion des images

- Non-linear piezo-scanner response + ageing/creep + thermal drift
- Background bow/tilt

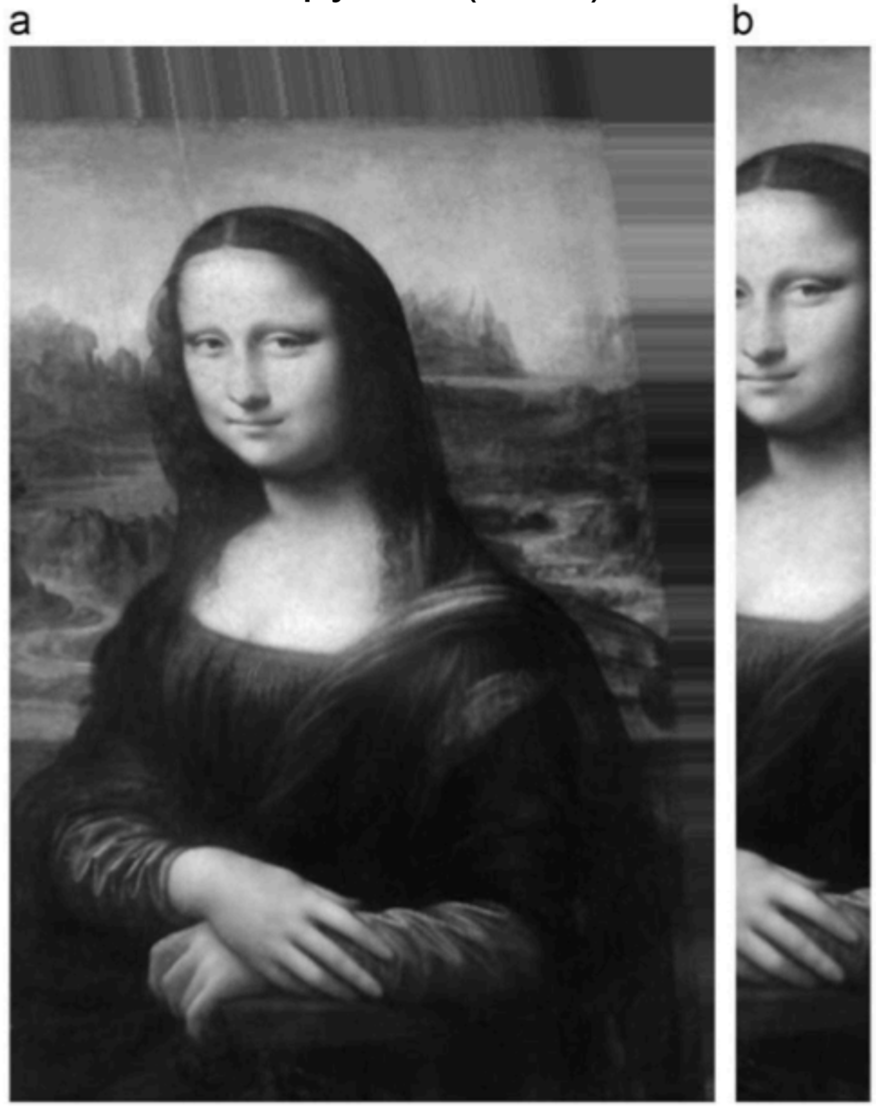






(une) limite : distorsion des images

B.S. Salmons, D.R. Katz, M.L. Trawick
Ultramicroscopy 110 (2010) 339–349



Y. Sun, J.H.L. Pang
Nanotechnology 17 (2006) 933–939

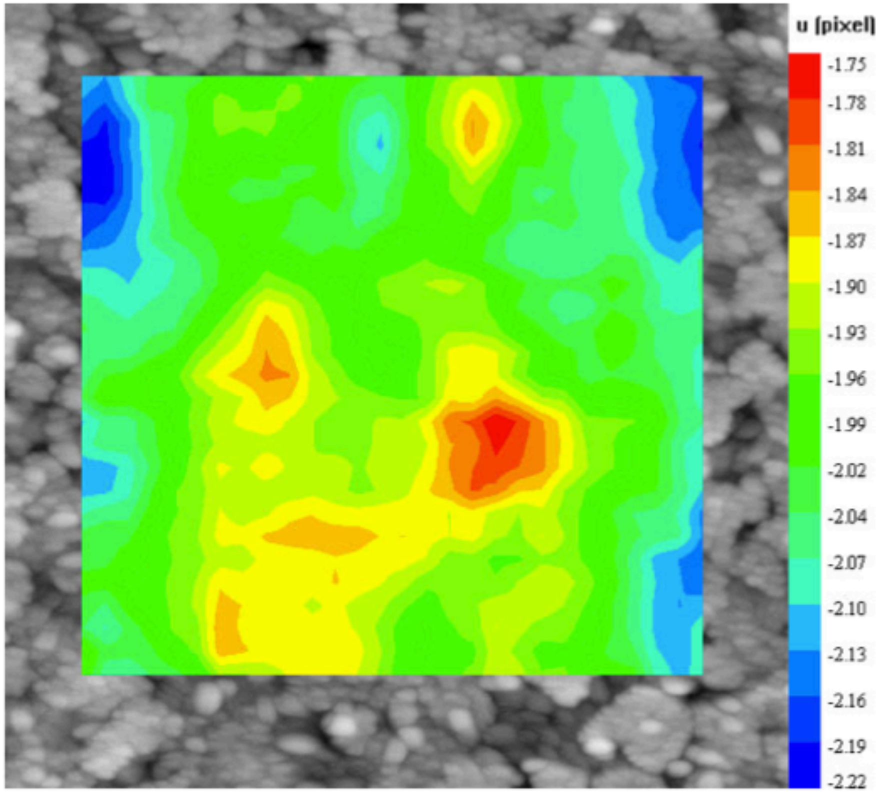
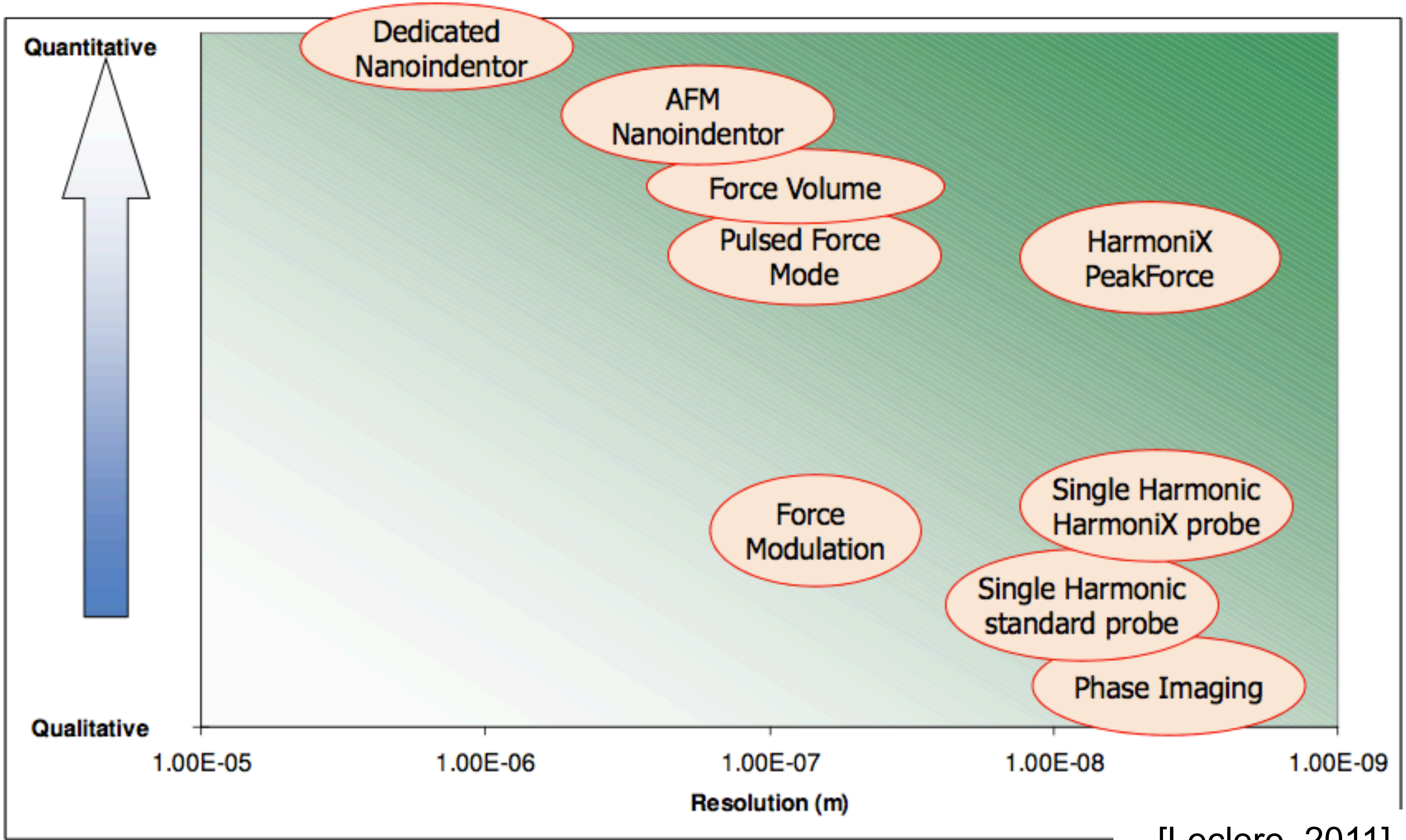


Figure 3. *u*-displacement in the horizontal/fast-scan direction between a 'trace' image and its 'retrace' image with size 512 × 512 pixels.

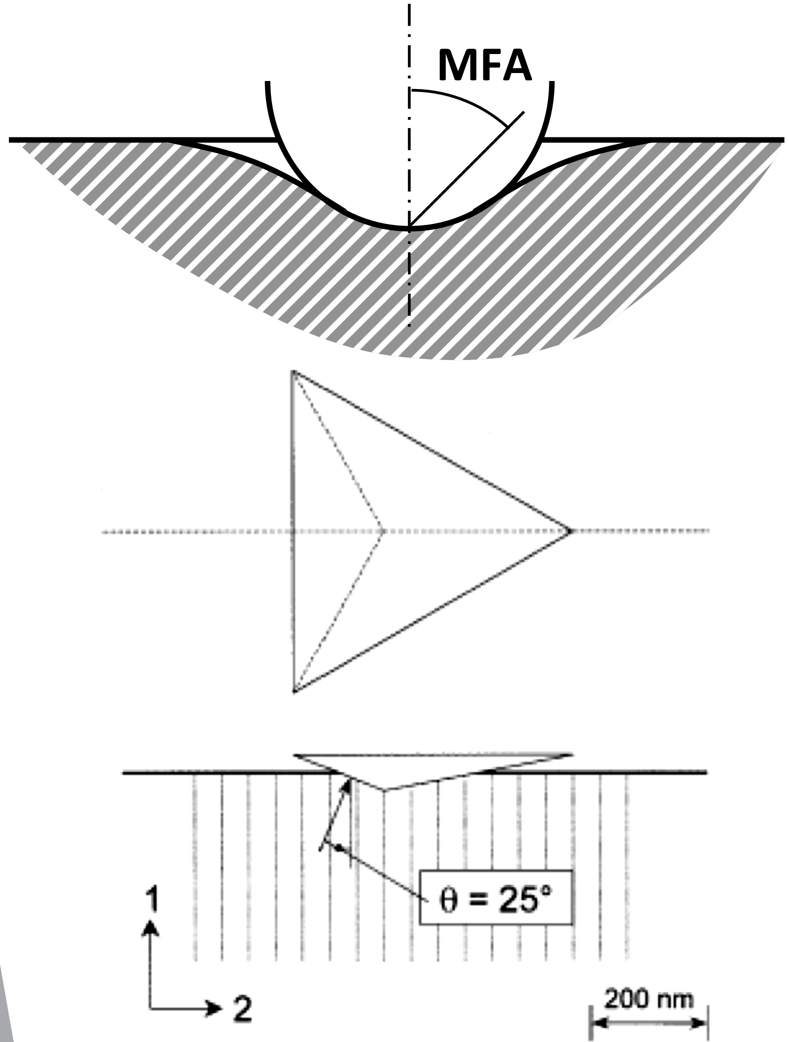
Mesure de champs de propriétés



[Leclere, 2011]

Nano-Indentation

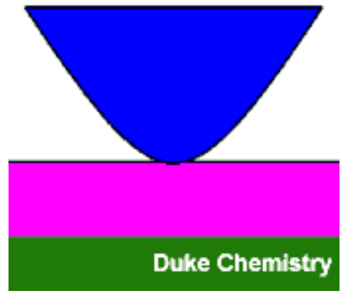
Effet du comportement anisotrope de la paroi



[Gindl et Schöberl, Comp. A, 2004]

Théorie de Hertz
pour un solide isotrope

$$\frac{1}{E^*} \approx \frac{1-\nu_e^2}{E_e} = \frac{1}{M_N}$$



Pour un solide orthotrope dans les axes principaux
[Delafargue et Ulm, Int. J. Sol. Struct., 2004]

$$M_3^2 = 4\sqrt{\frac{\frac{C_{11}C_{33}-C_{13}^2}{C_{11}} \cdot \frac{C_{22}C_{33}-C_{23}^2}{C_{22}}}{\left(\frac{1}{C_{44}}+\frac{2}{\sqrt{C_{11}C_{33}}+C_{13}}\right)\cdot\left(\frac{1}{C_{55}}+\frac{2}{\sqrt{C_{22}C_{33}}+C_{23}}\right)}}$$

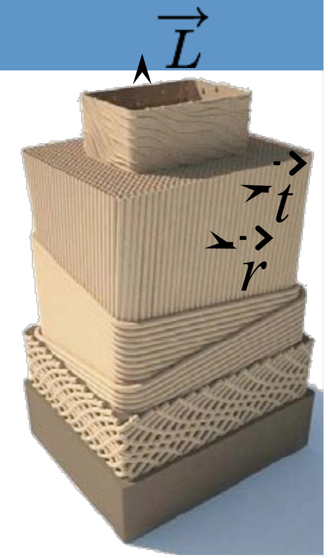
Nano-Indentation

[Delafargue et Ulm, Int. J. Sol. Struct., 2004]

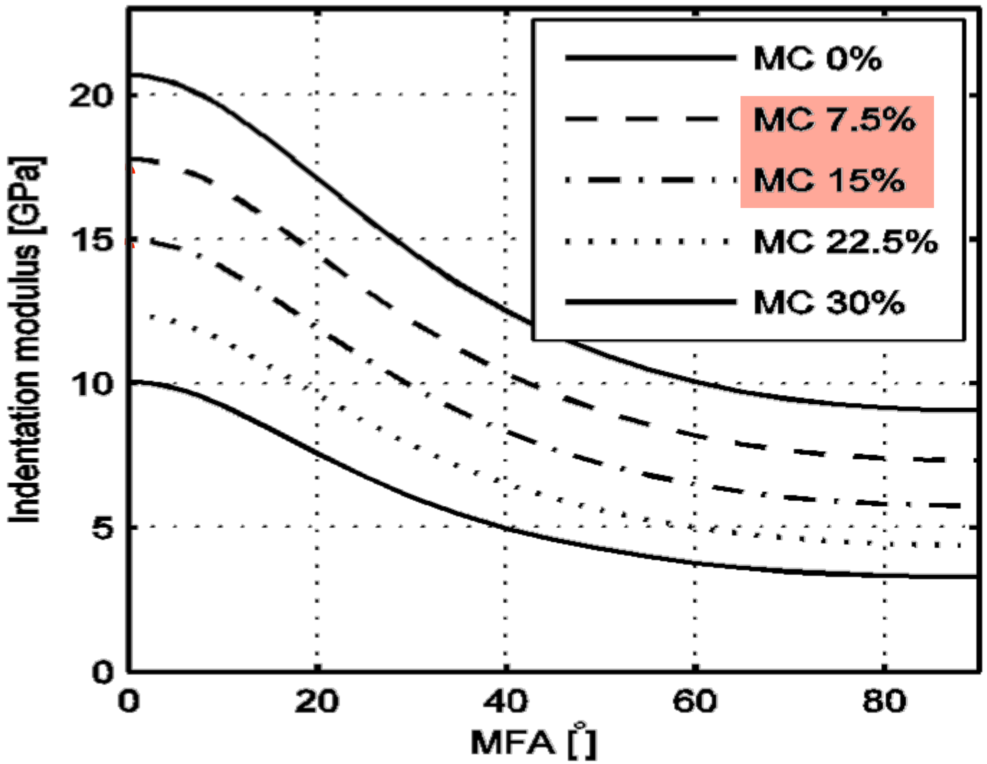
Couche S2 typique de peuplier
(30% cellulose cristalline + 70% matrice, AMF~0°)

$E_L \approx 45$ GPa, $E_t \approx E_r \approx 12$ GPa, $\nu_{tL} \approx \nu_{rL} \approx 0{,}028$, $\nu_{rt} \approx 0{,}28$
$G_{tL} \approx G_{rL} \approx 2{,}5$ GPa, $G_{rt} \approx 2$ GPa

$\rightarrow M_L \approx 19$ GPa et $M_{r\ ou\ t} \approx 9{,}5$ GPa



[Eder, thèse, 2007]



Pour un solide anisotrope hors axes…
[Vlassak *et al.*, J. Mech. Phys. Sol., 2003]

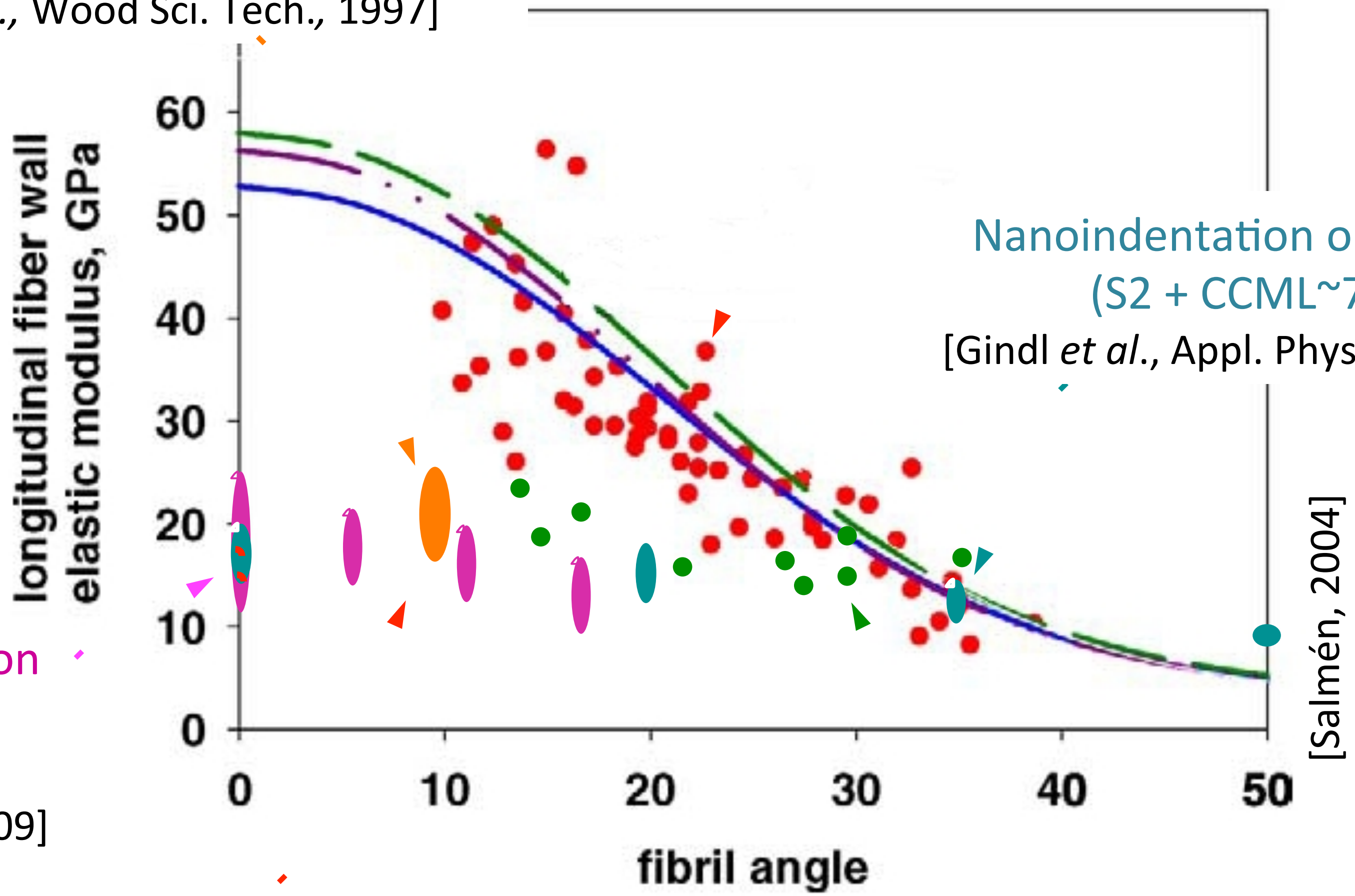
Appliqué dans le cas d'une couche S2 (typique de pin)
[Jäger *et al.*, Comp. A, 2011]

Nano-Indentation

Nanoindentation on Spruce
(S2-AMF? + CCML ~ 5-10GPa)
[Wimmer *et al.,* Wood Sci. Tech., 1997]

Tensile test on Pine stick
[Cave et Hutt, Wood Sci. Tech., 1969]

Nanoindentation on Spruce
(S2 + CCML~7-12GPa)
[Gindl *et al.*, Appl. Phys. A, 2004]



Nanoindentation on Spruce
[Konnerth *et al.*,
J. Mater. Sci., 2009]

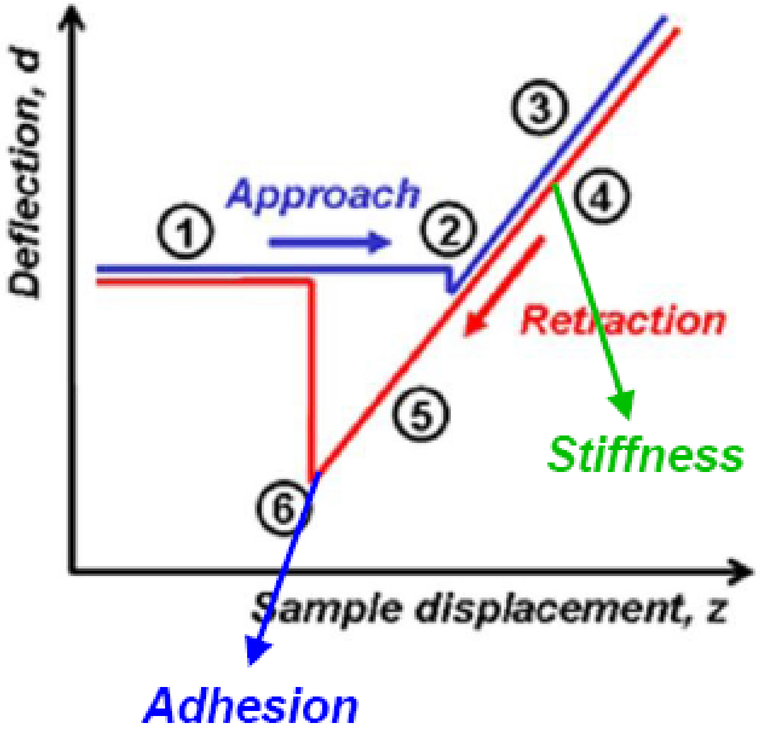
Anisotropic indentation model (7,5-15%)
[Vlassak *et al.*, J. Mech. Phys. Sol., 2003]
[Jäger *et al.*, Comp. A, 2011]

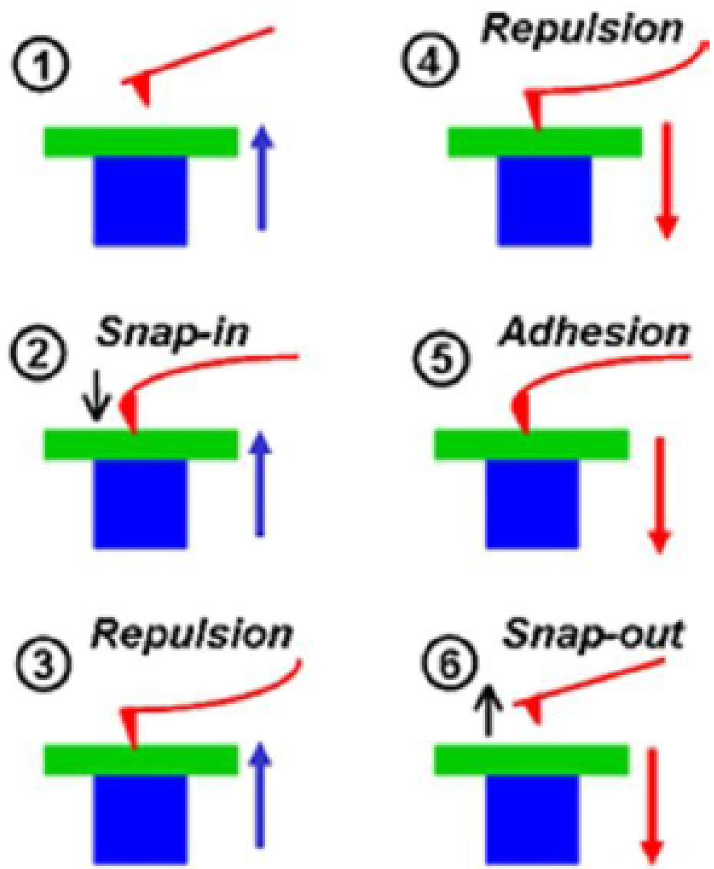
Nanoindentation on Pine (S2)
[Tze *et al.*, Comp. A, 2007]

Eder, Arnould et al, Wood Sci Technol (2013) 47:163–182

Contact mode

- Force-distance curves (spectroscopy)
  - ➲ Contact stiffness
  - ➲ Adhesion force

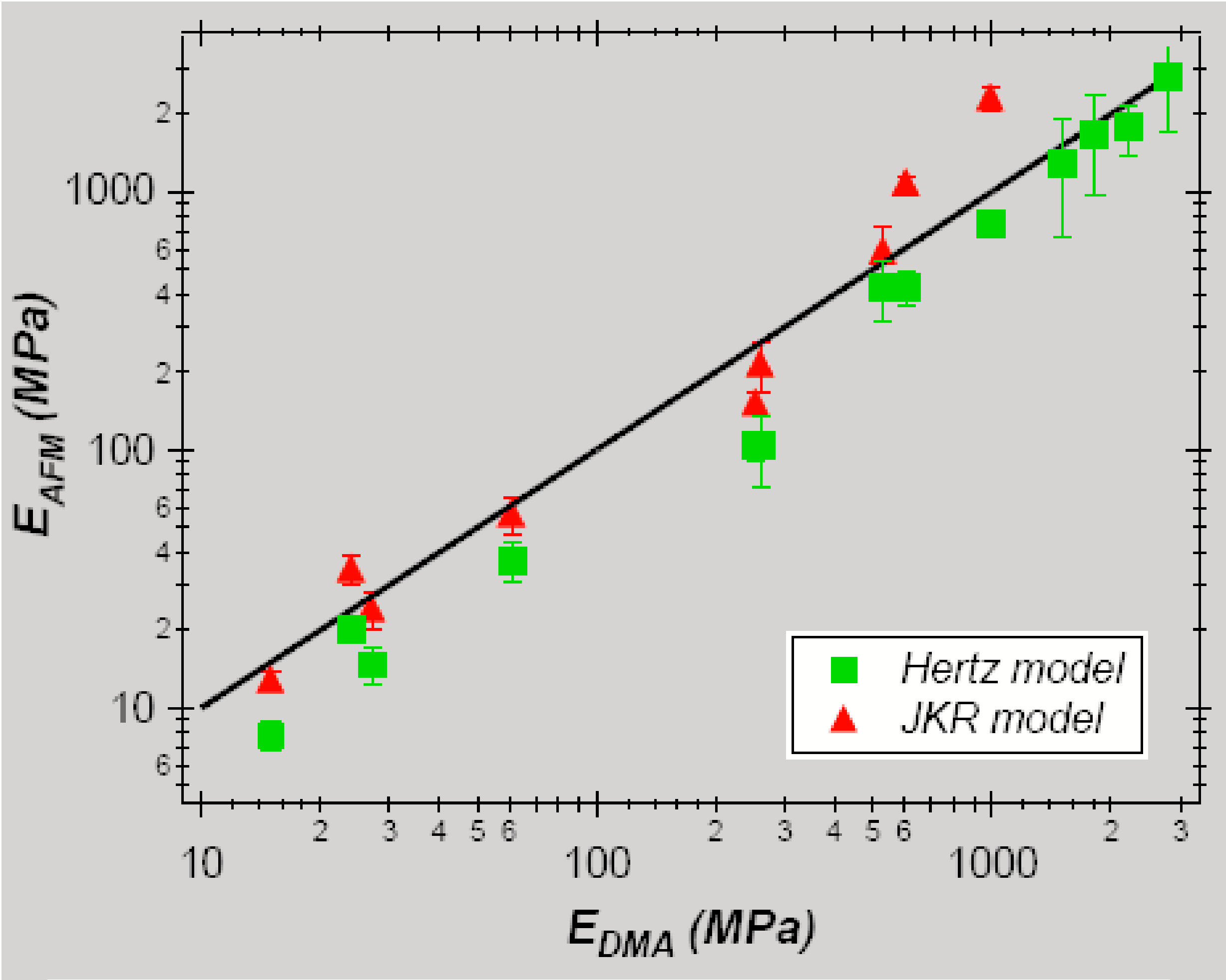




[B. Nysten, 2007]

Contact mode

- Force-distance curves

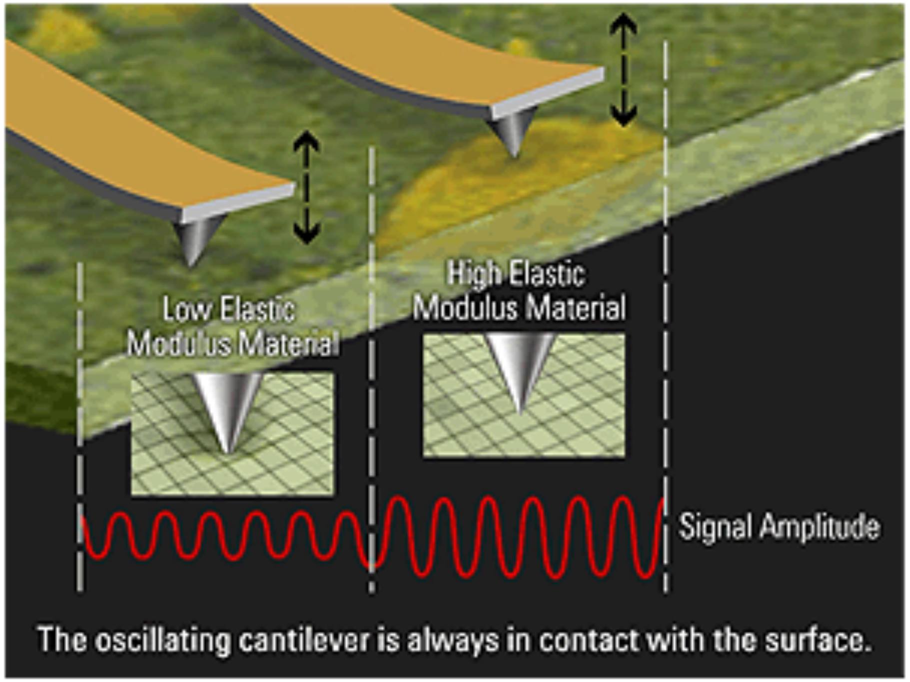


[E. Tomasetti et al., *Nanotechnology*, 1998]

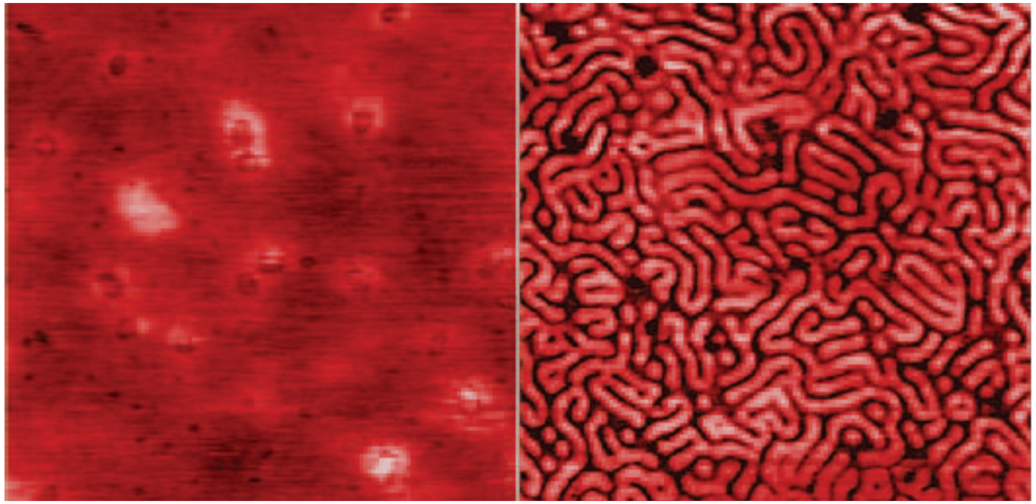
Comparative study on different polymers

Contact mode

- Force Modulation ~ DMA
  - Few nm oscillations @ few kHz, longitudinal or transversal!
  - Cantilever vibration amplitude and phase-shift related to surface elastic and viscoelastic properties
  - Same limitations as F-d curves but better resolution (≈100nm on polymer) and lower imaging time (scan rate <0.5 line/s)



[www.afmuniversity.org]

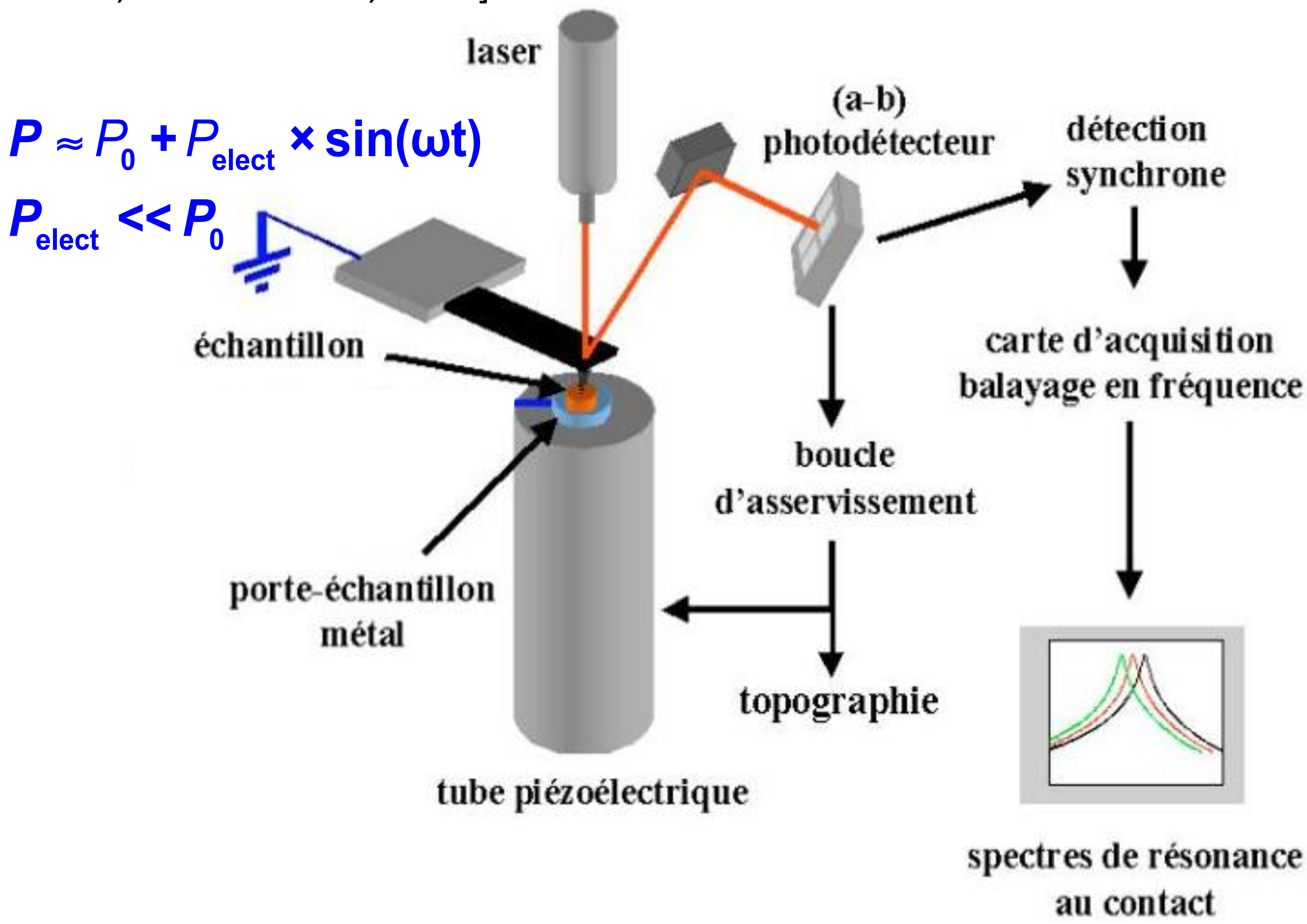


Topography and force modulation images (900nm scans) of a two-phase block copolymer (softer = black)
[www.veeco.com]

Caractérisation par CR-AFM

Principe

[Arinéro et al., Rev. Sci. Inst., 2007]

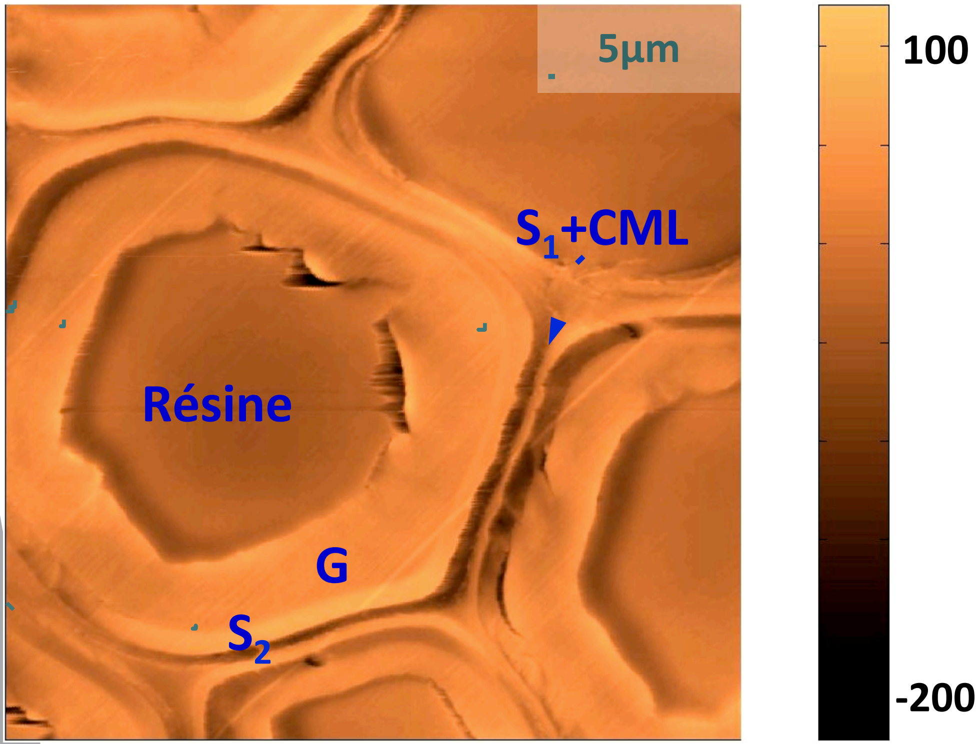


Caractérisation par CR-AFM

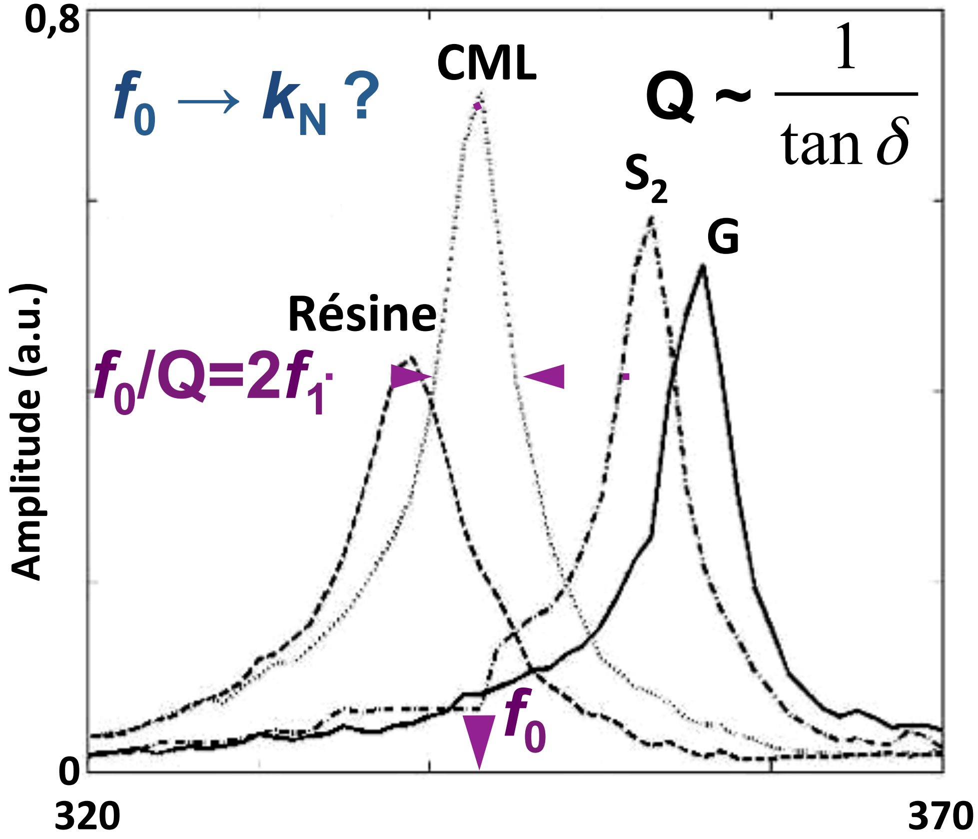
Principe

[Arnould et Arinéro, Comp. Part A, 74 (2015) 69–76]

Bois de tension de châtaignier



Topographie (nm)



Spectres en fréquence (kHz)

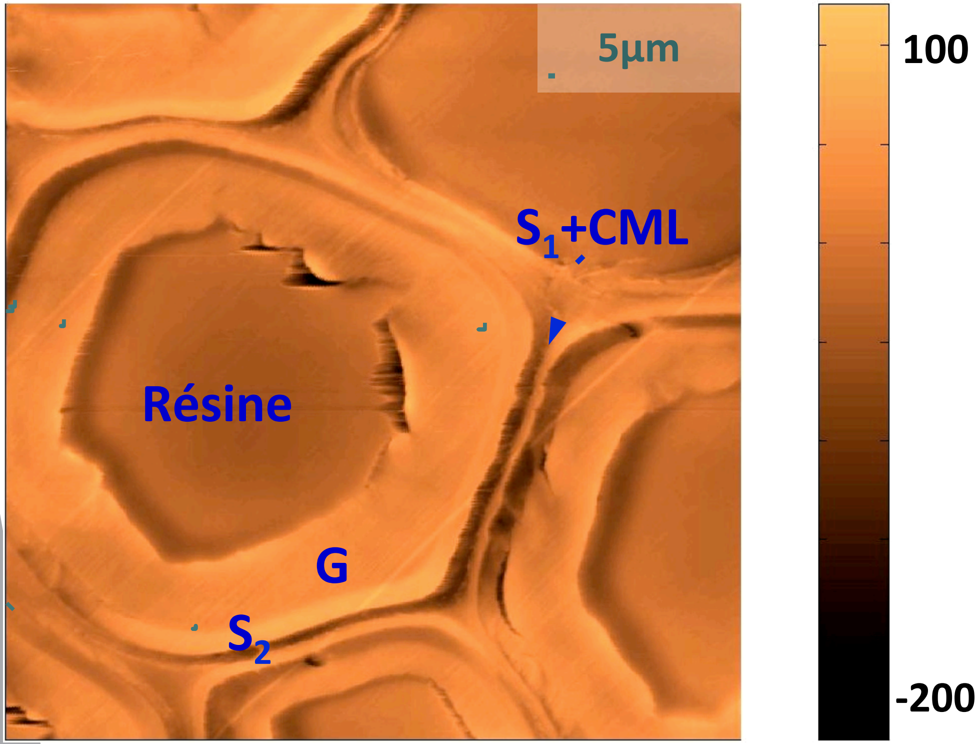
Pointe : Nanoworld ARROW FMR, $k_L \approx 2{,}8$ N/m, f_0 = 75 kHz, $R \approx 55$ nm

AFM : Veeco Enviroscope, $F_0 \approx 180$ nN

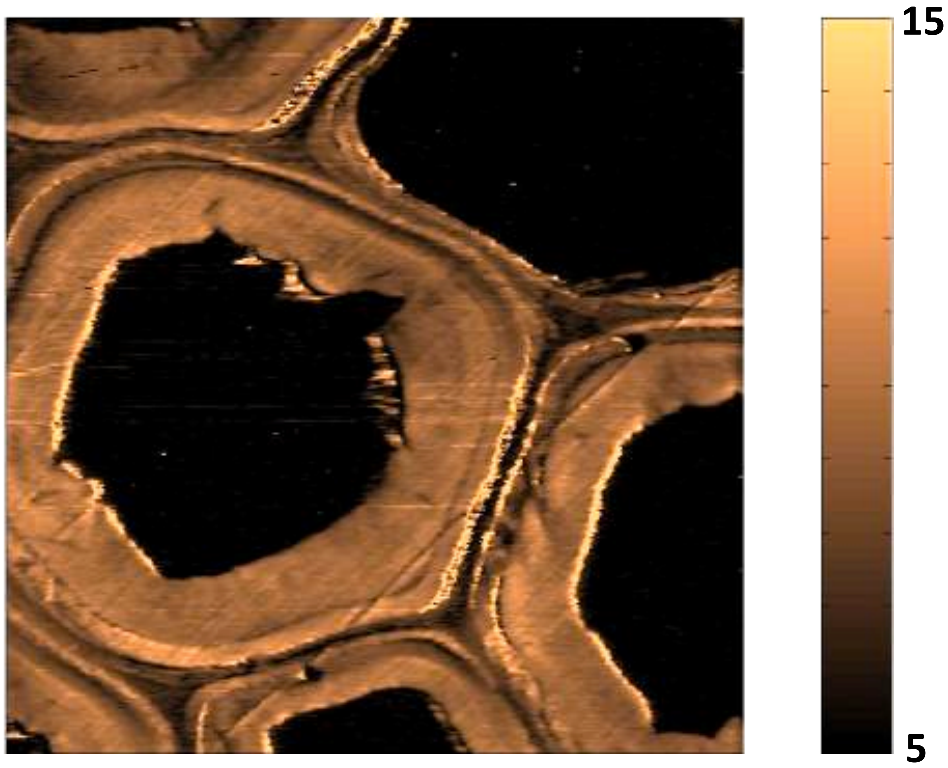
Imagerie

[Arnould et Arinéro, Comp. Part A, 74 (2015) 69–76]

Bois de tension de châtaignier



Topographie (nm)



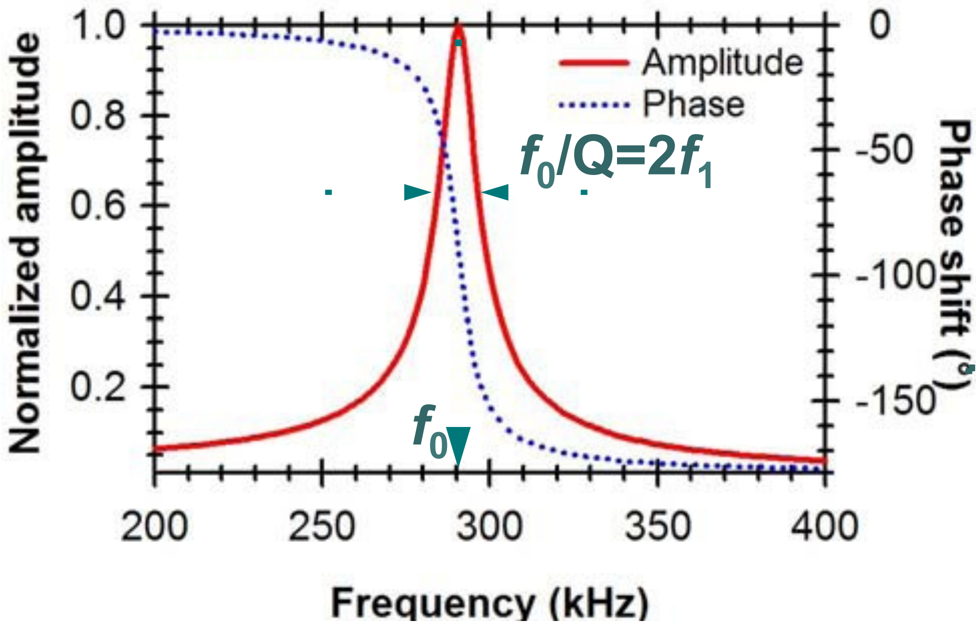
Module de contact (GPa)

Pointe : Nanoworld ARROW FMR, $k_L \approx 2{,}8$ N/m, $f_0 = 75$ kHz, $R \approx 55$ nm

AFM : Veeco Enviroscope, $F_0 \approx 180$ nN

Contact intermitent

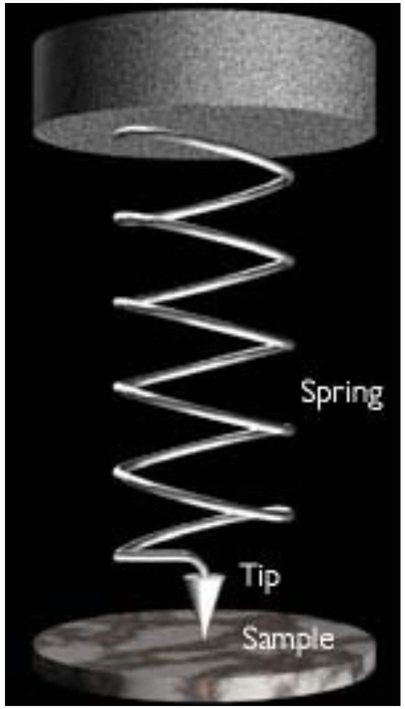
- Intermittent contact/tapping^{TM}/amplitude modulated… mode: knocking on the surface!
  - ➲ Linear harmonic oscillator approximation (free)



$$\omega_0 = \sqrt{\frac{k_C}{m_{eff}}}$$

$k_C > 10\text{N/m}$

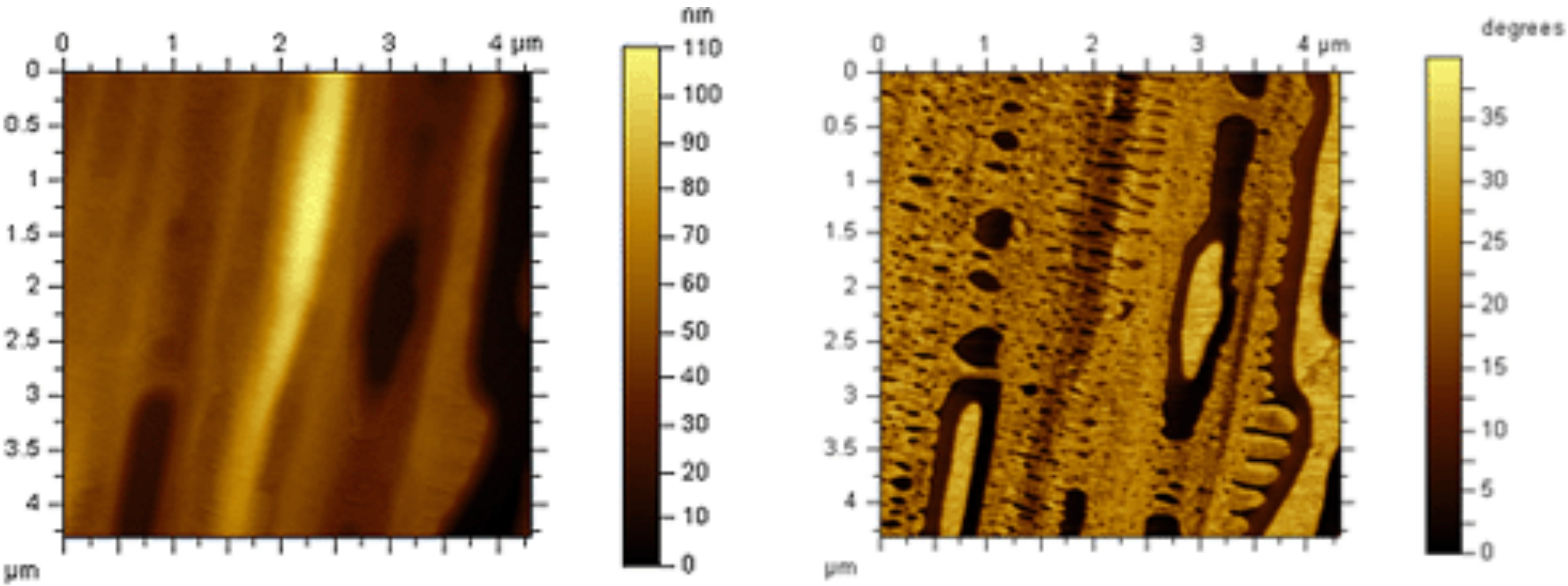
$f_0 > 100\text{kHz}$



Media	Liquid	Air	High vacuum
Q	10	400	10^4

Contact intermitent

- Intermittent contact/tapping^{TM}/amplitude modulated mode:

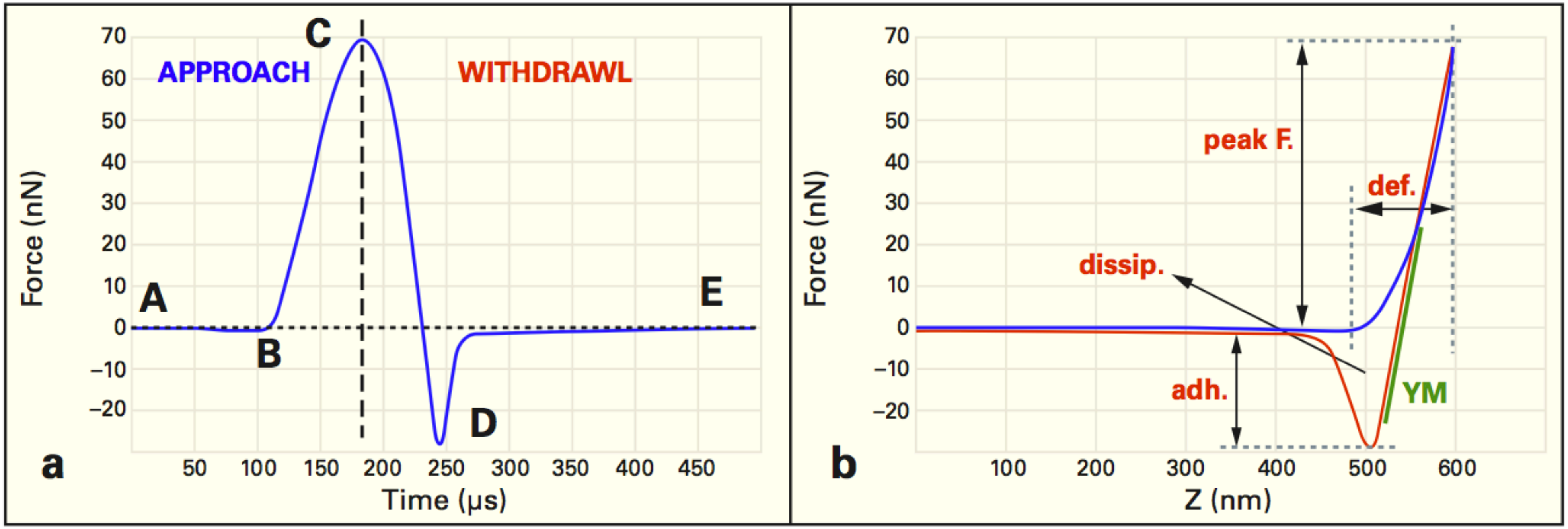


(Figure 6a & b) Topographic (Left) and phase image (Right) of polydiethysiloxane polymer

[www.afmuniversity.com]

Contact intermitent

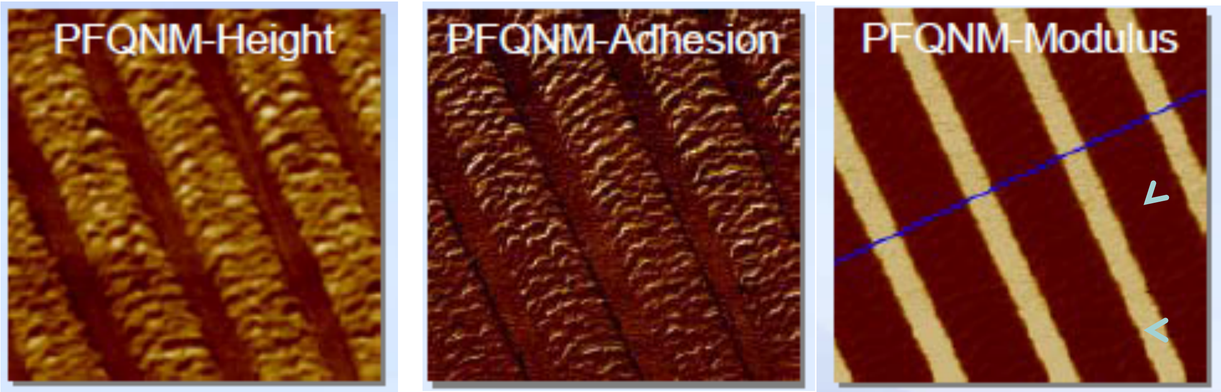
- Peak Force Quantitative NanoMechanical (QNM) [www.bruker-axs.com]
  - ➲ Tapping at some kHz (far bellow the resonance frequency) and force curve recording



Quantitative nanomechanics QNM

Multilayered polymer film

10 µm scans



100 MPa

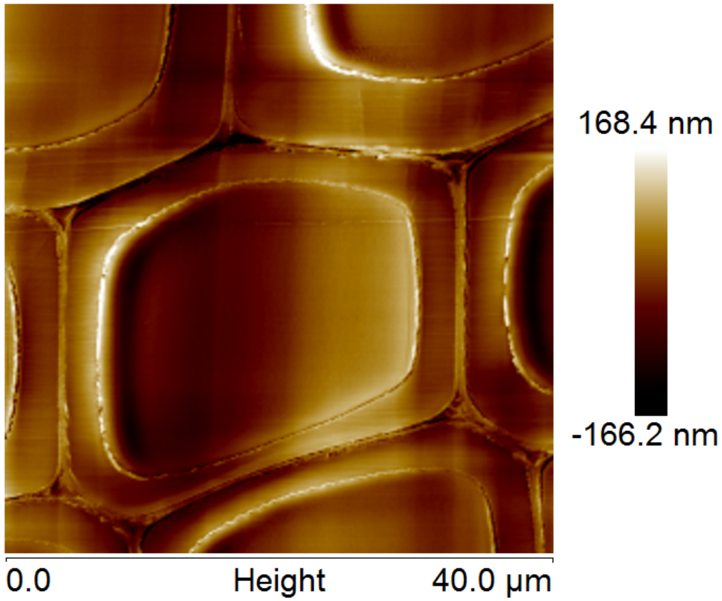
300 MPa

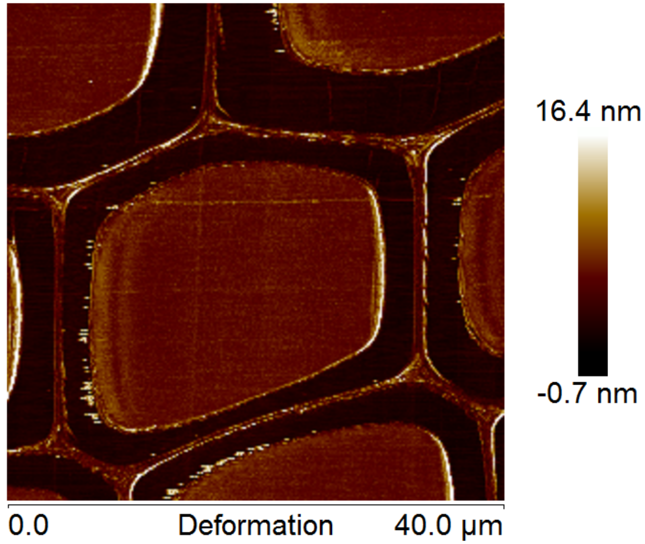
PMMA with Ag nanoparticles on glass

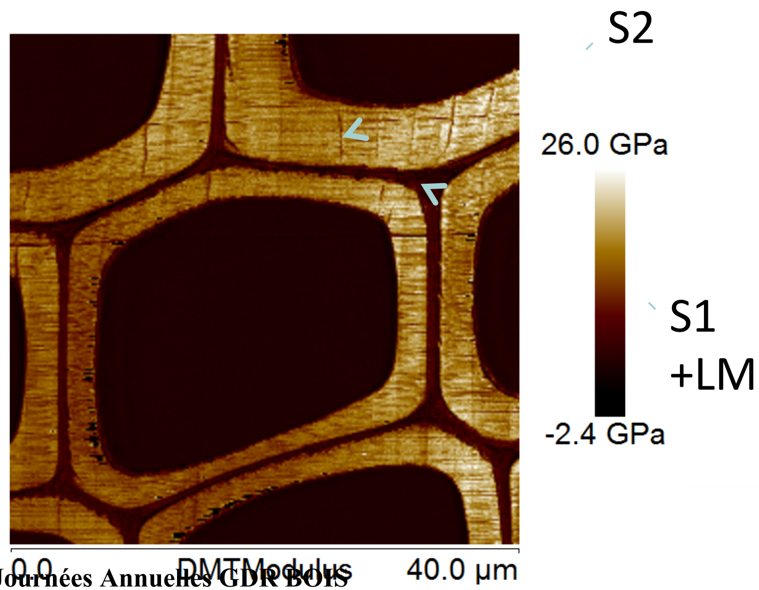
The Adhesion image clearly differentiates the PMMA from the substrate and
from the Ag particles.

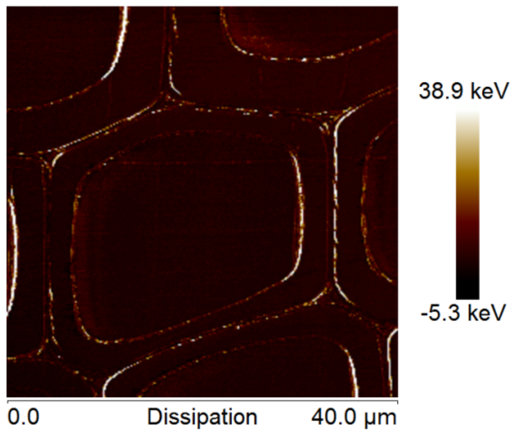
PeakForce QNM application to wood

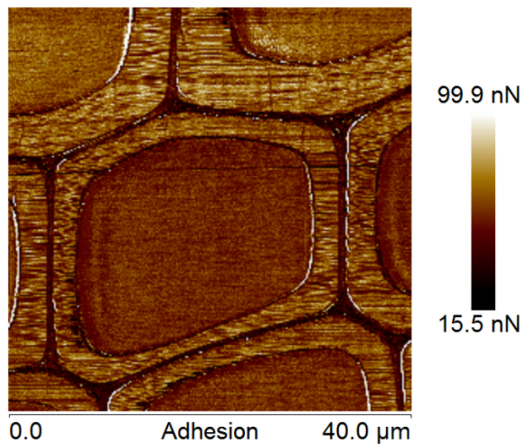
- Spruce wood [TU Zvolen]





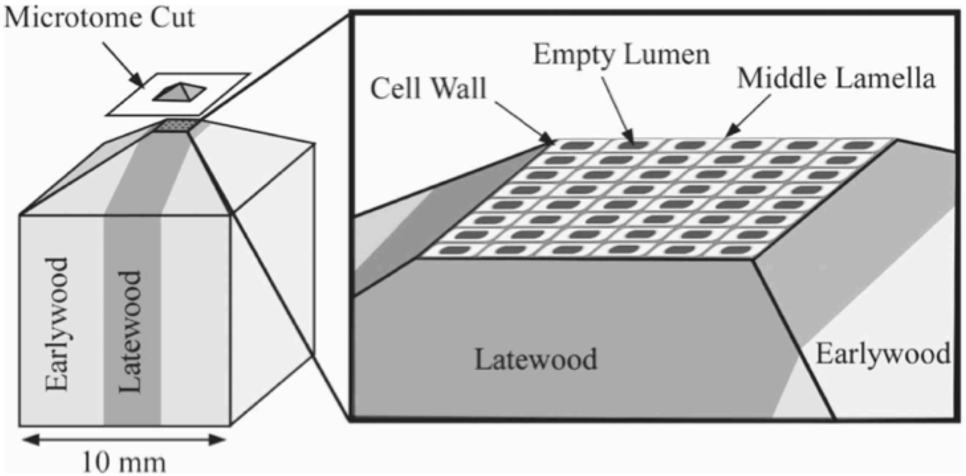






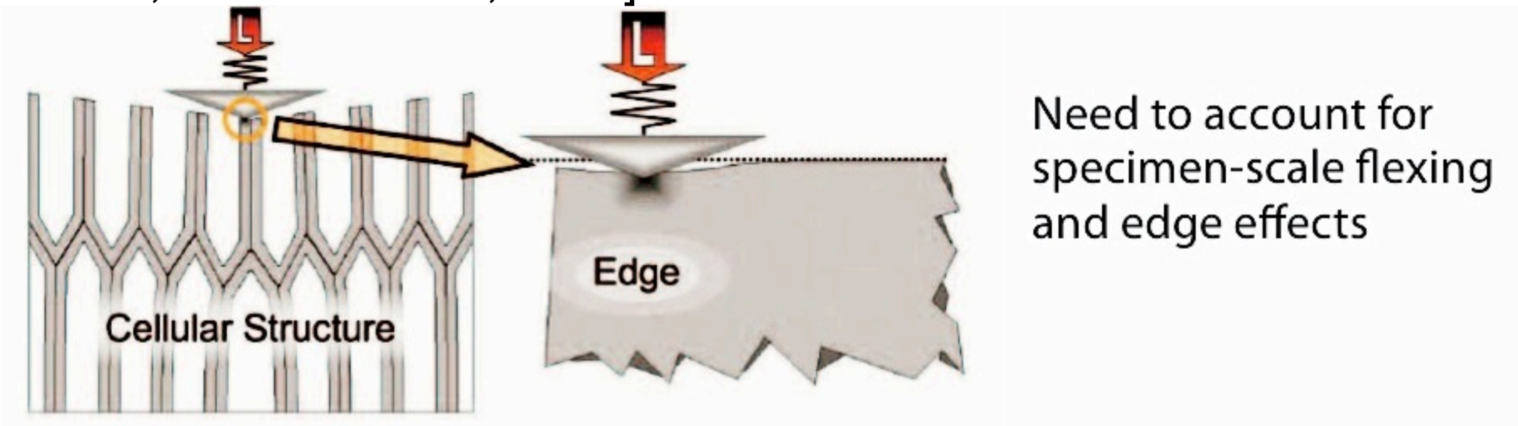
Sample preparation: no embedding?

- Advantages: no modification, no resin penetration



- Structural compliance/border effect

  [Jakes *et al*., J. Mater. Res., 2008]

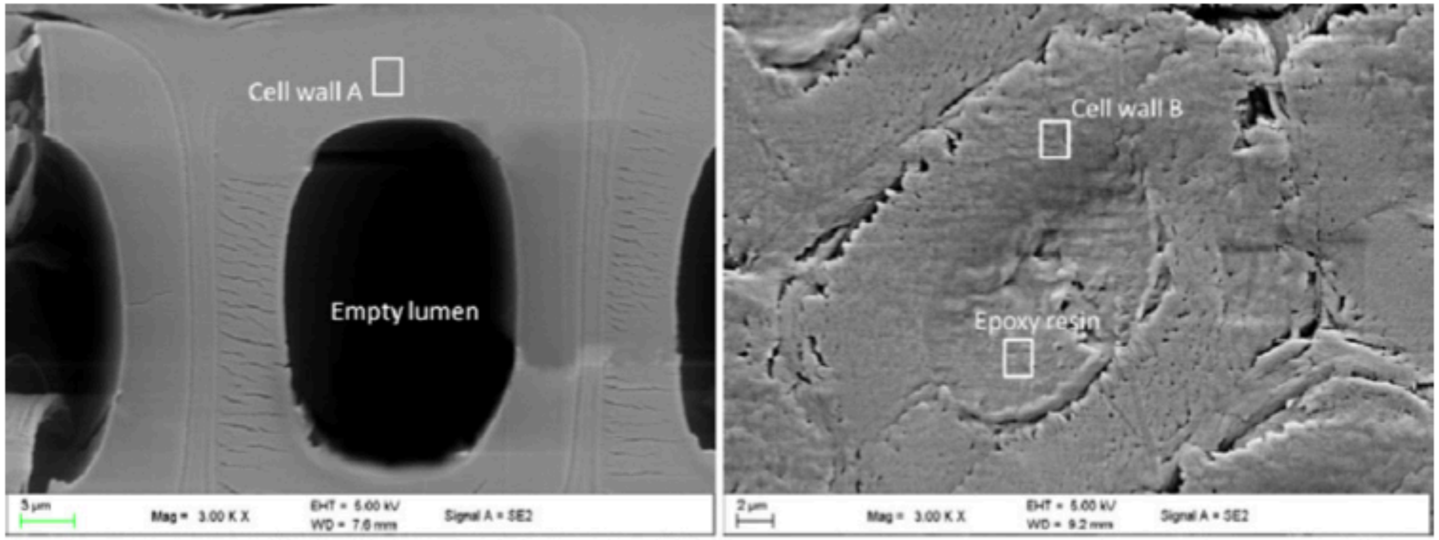


Sample preparation: embedding?

- Resin penetration… embedding vs no embedding

[Meng *et al*., Appl Phys A, 2013]

Fig. 4 (**a**) SEM image of Loblolly pine cell wall, (**b**) SEM image of Loblolly pine cell wall embedded in Spurr's resin



a b

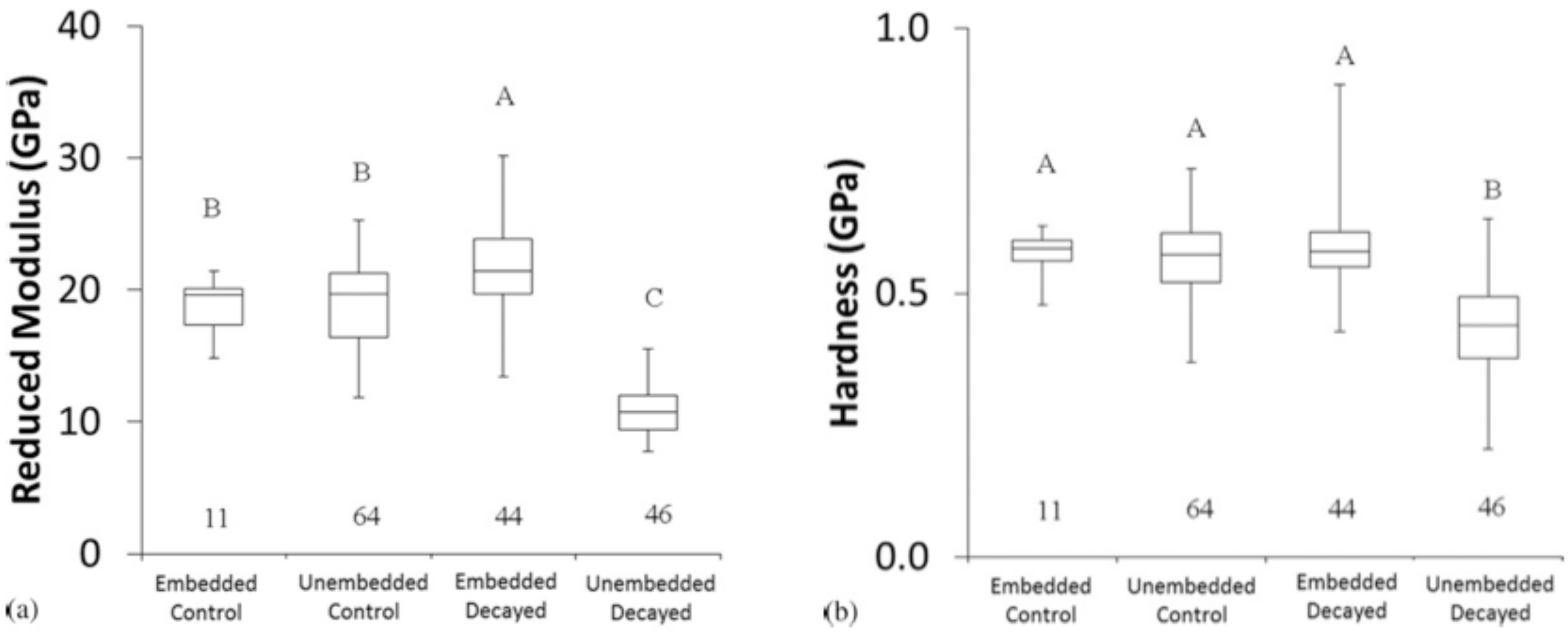
Table 2 Comparison of carbon/oxygen content between pure Spurr's resin, resin-embedded Loblolly pine cell wall and reference Loblolly pine cell wall

	Carbon content (%)	Oxygen content (%)
Epoxy resin	81.7 ± 1.8	18.3 ± 1.8
Reference cell wall A	72.2 ± 1.4	27.8 ± 1.4
Epoxy-resin-treated cell wall B	75.2 ± 1.7	24.8 ± 1.7

Sample preparation: embedding?

- Resin penetration… embedding vs no embedding

[Kim *et al.*, Wood Fib Sci, 2012]



Spurr epoxy

Sample preparation: embedding?

- Resin penetration… bonding glue
  [Gindl *et al.*, Int. J. Adh. Adh., 2004]

PF, pMDI Resin (glue)
Spruce

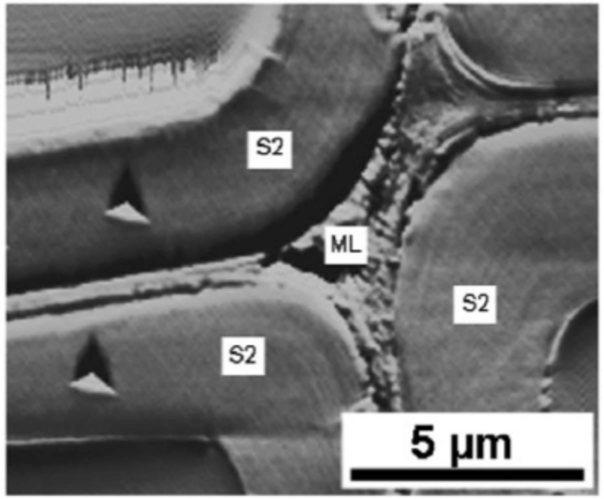
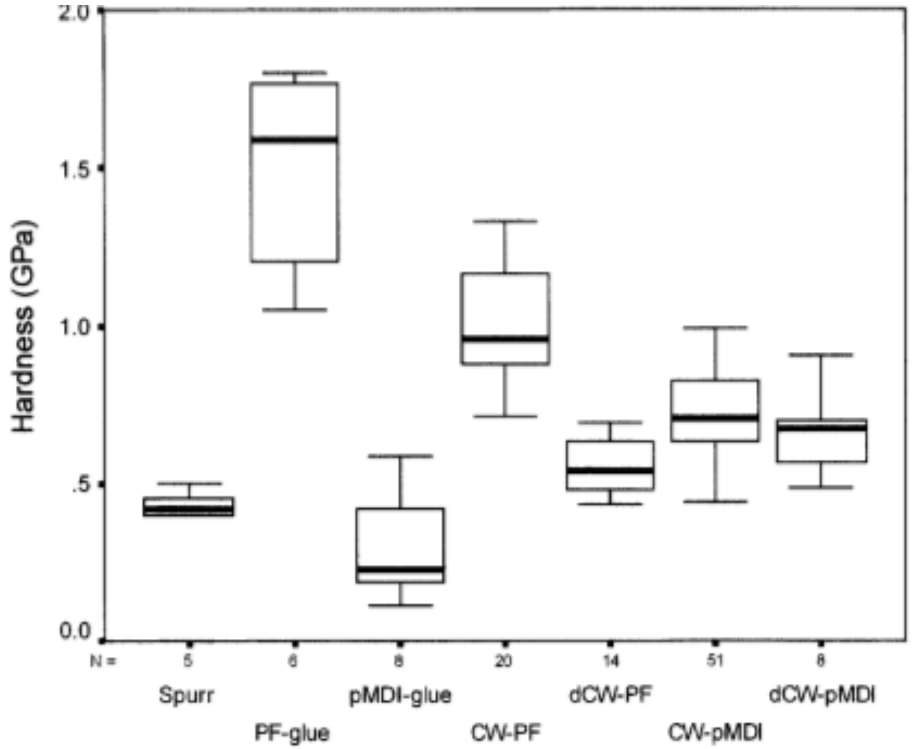
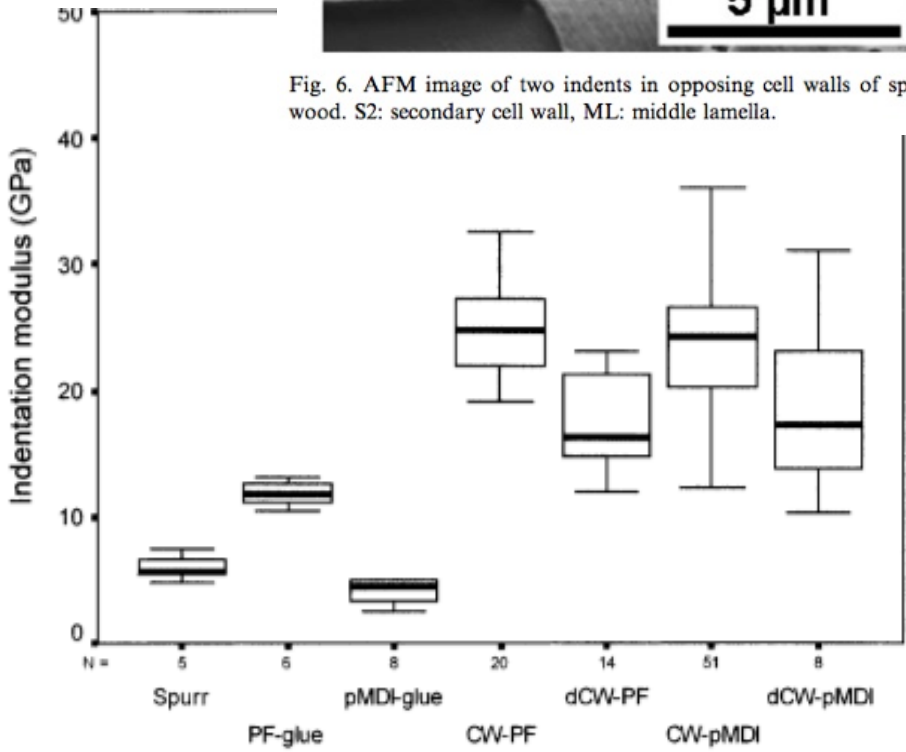


Fig. 6. AFM image of two indents in opposing cell walls of spruce wood. S2: secondary cell wall, ML: middle lamella.





Sample preparation: embedding?

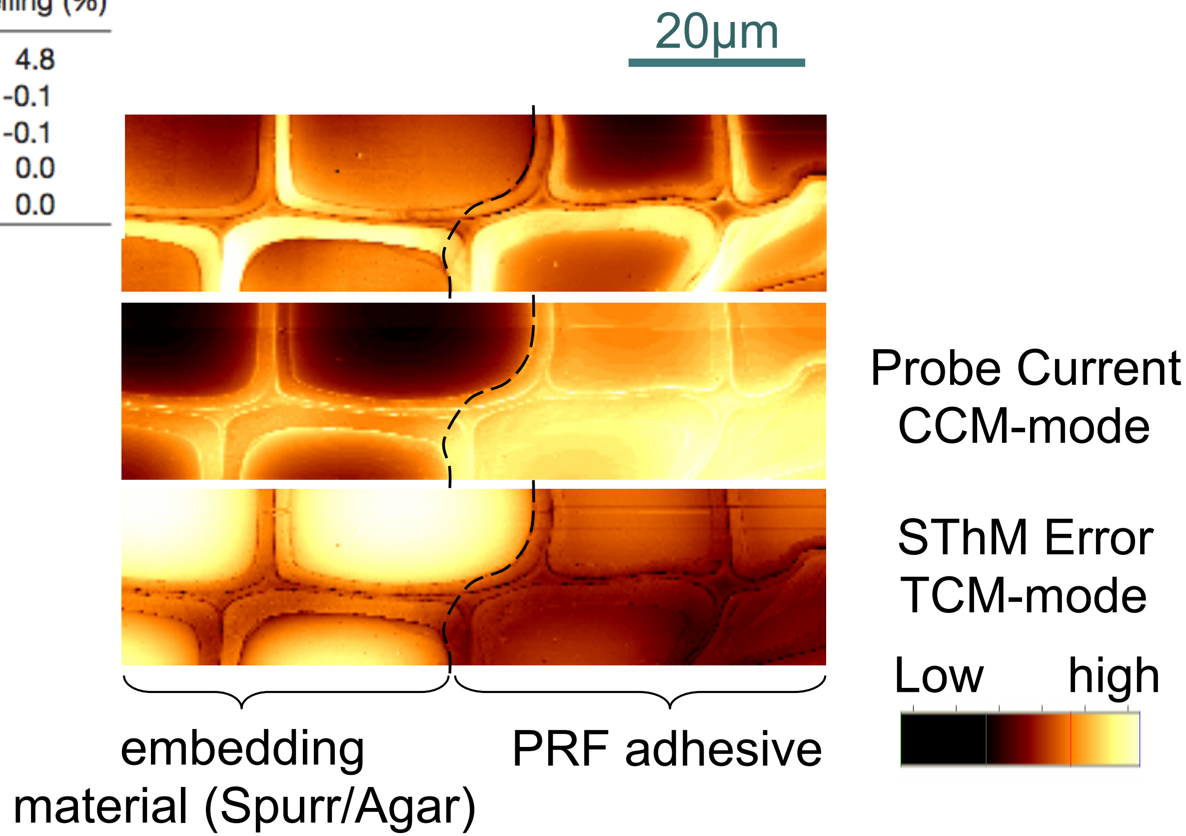
- Resin penetration… embedding epoxy vs glue

[Konnerth *et al*., Holzforschung, 2008]

Table 1 Swelling of spruce wood samples in liquid phenol-resorcinol-formaldehyde (PRF), one-component polyurethane (PUR), SPURR epoxy and AGAR epoxy.

Swelling medium	Swelling (%)
PRF	4.8
PUR	-0.1
SPURR epoxy	-0.1
AGAR epoxy	0.0
Control	0.0

SThM-AFM on spruce wood
$R \approx 100$nm
Scan rate 0.1-0.5Hz



Sample preparation: embedding?

The results of sequential treatments on each of five individual fibres are shown in Table 1. Water can swell flax fibres, increasing their perimeter by 24%. Ethyl alcohol did not significantly swell fibres beyond their original dry dimensions, however it did restore the dry dimensions of fibres that had been through a recent wetting and drying cycle. Swelling with water increased if the fibres had been pre-soaked in 6 M urea for 1 or 12 h. This extra swelling was always restored, even after two subsequent drying and wetting cycles (Table 1). After pre-treatment of the fibres with urea for 12 h and replacement of the water with ethyl alcohol (which caused a small amount of shrinkage from the water-swollen dimensions), resin could penetrate into the cells (restoring the maximum swelling dimensions). This was demonstrated by the fact that water containing a dye, which normally swells and stains the cell walls of the fibres, could no longer do so in the cured, polished composite (Table 1, last treatment of the first set). Without this treatment the resin did not penetrate into the fibres and consequently untreated fibres in cured composites could still absorb water and dye (second set of treatments in Table 1

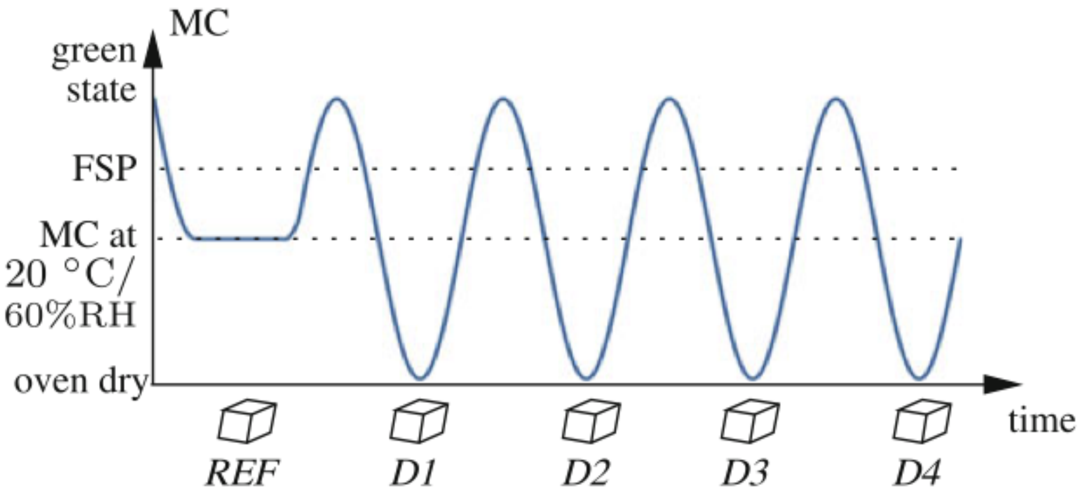
[Hepworth *et al*, Composites A, 2000]

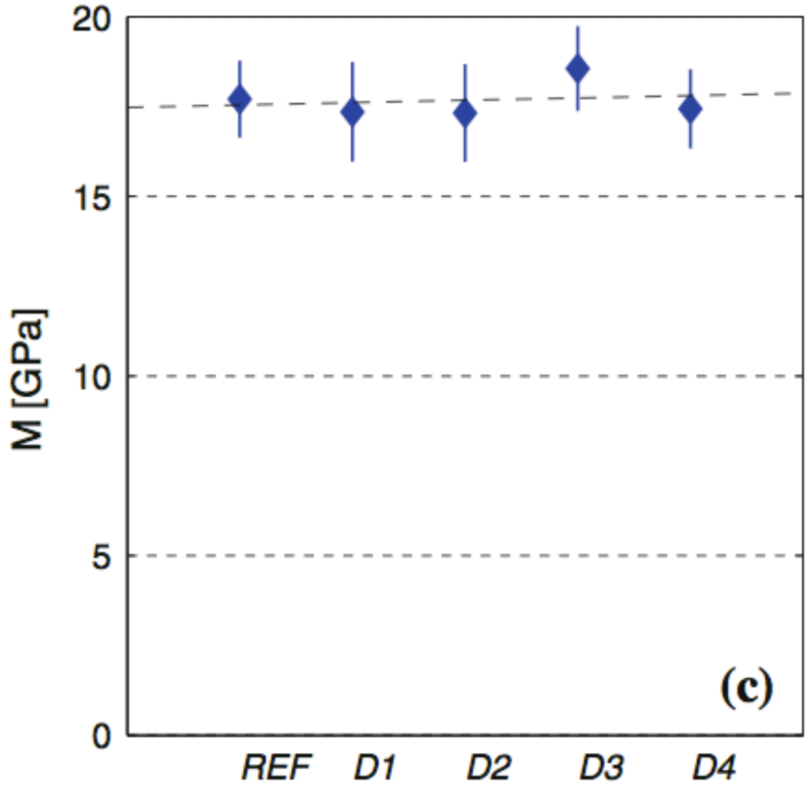
Optical microscopy observation of dimensional change (lumen and outer perimeter) of flax fibre embedded with low viscosity epoxy resin, water replacement by ethyl alcohool and urea treatment

Sample preparation: embedding?

- Resin penetration and drying cycle

[Wagner *et al*., J Mater Sci, 2014]

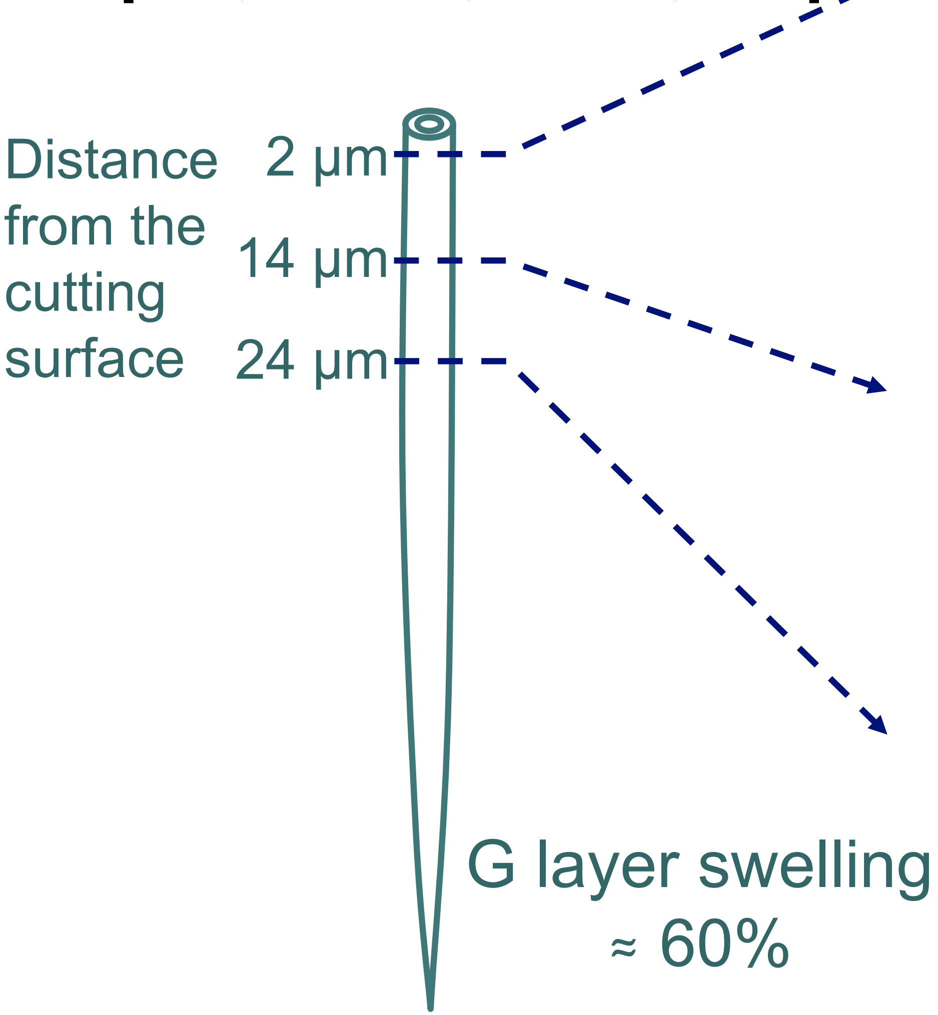


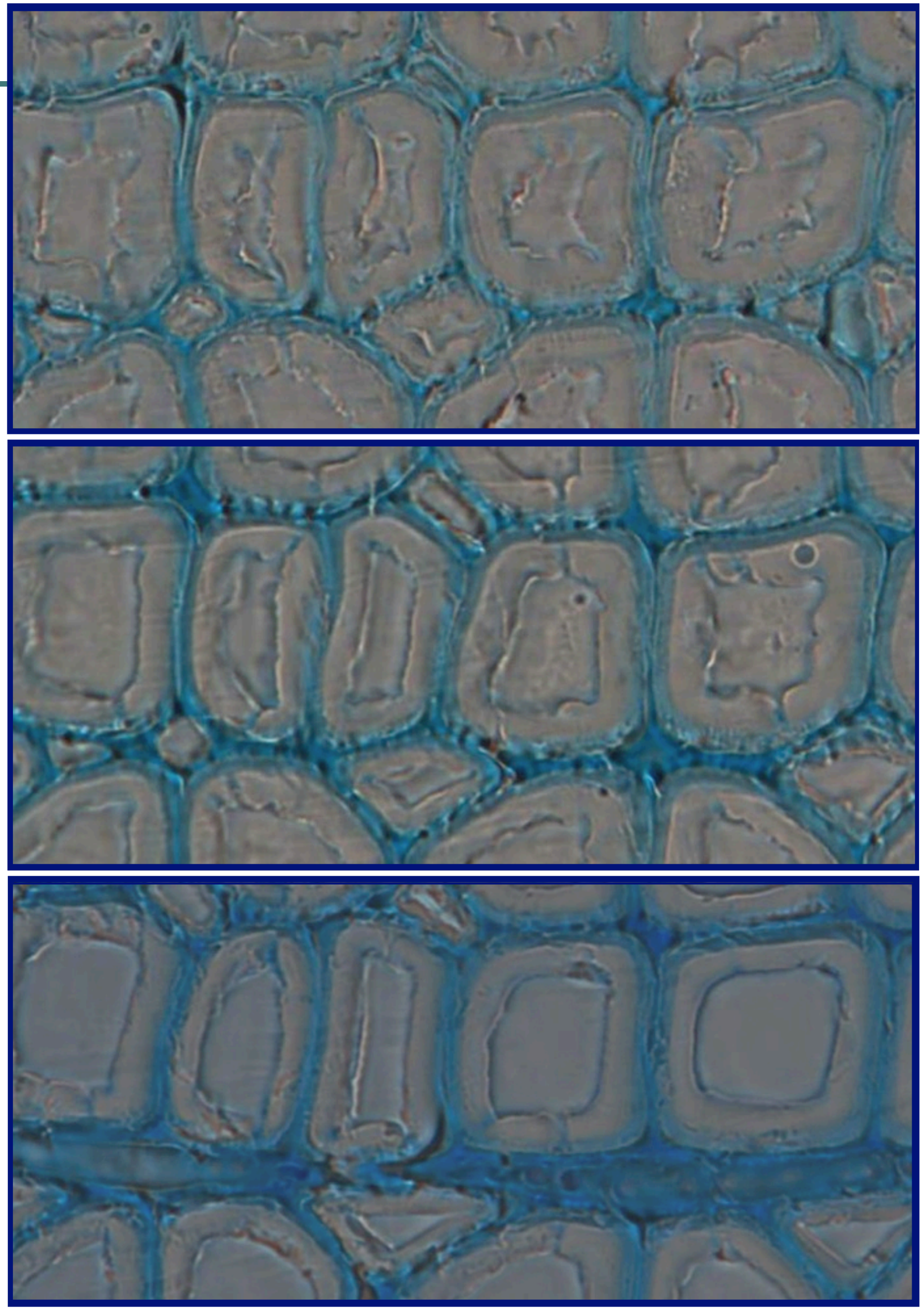


Sample	*REF* (Agar LV Kit)	*E1* (no vacuum, Agar LV Kit)	*E2* (Struers epofix)
M (GPa)	17.71 ± 1.07	17.67 ± 3.06	18.23 ± 1.36
H (GPa)	0.33 ± 0.03	0.36 ± 0.06	0.35 ± 0.03

No embedding?

- Cutting border effect
  [Clair, Gril *et al.*, IAWA J., 2003]

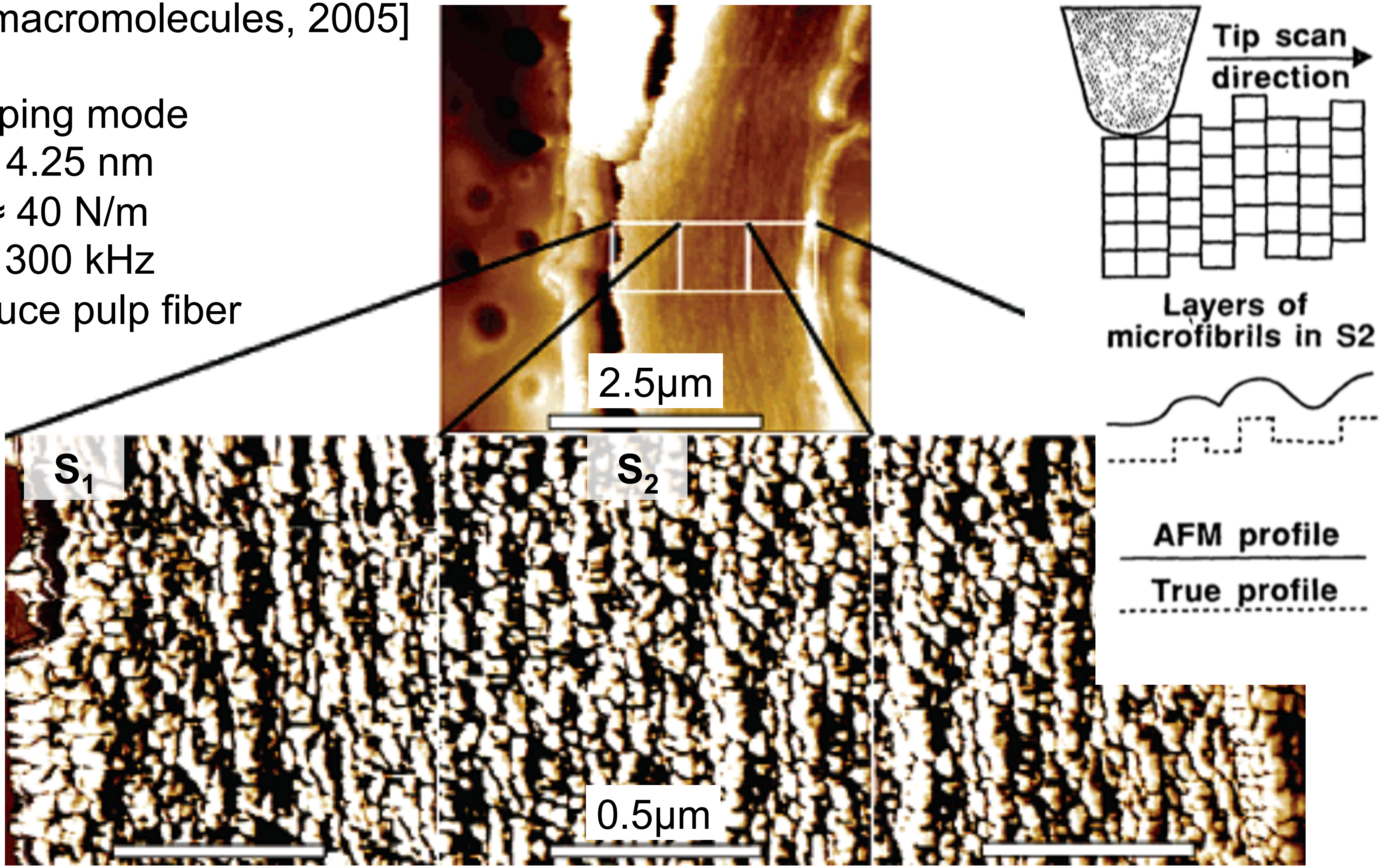




Sample preparation: microtoming, polishing, …?

- Surface topography and texture by microtoming
  [Shaune *et al*, Holzforschung, 1994; Fahlén and Salmén, Biomacromolecules, 2005]

Tapping mode
$R \approx 4.25$ nm
$k_C \approx 40$ N/m
$f_0 = 300$ kHz
Spruce pulp fiber



Sample preparation: microtoming, polishing, …?

- Comparison on spruce
[Zimmermann *et al*, J. Struct. Bio., 2006]

AFM tapping mode - phase image