Mesures quantitatives des propriétés mécaniques à la nanoéchelle ? Restons en contact !

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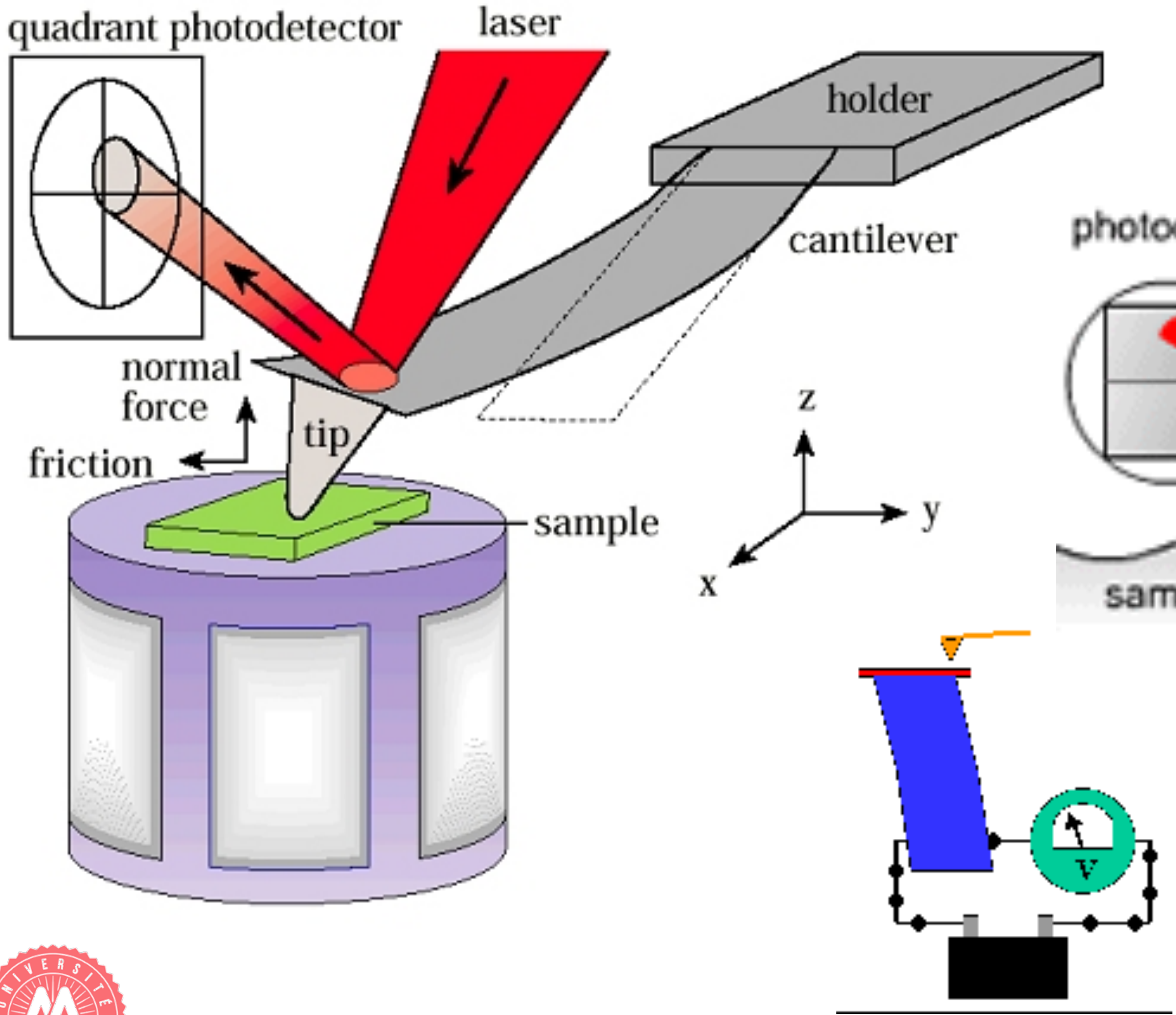
www.sondeslocales.fr/forum2017

Forum des Microscopies à Sonde Locale

20 – 24 mars 2017
Juvignac (France)

Principle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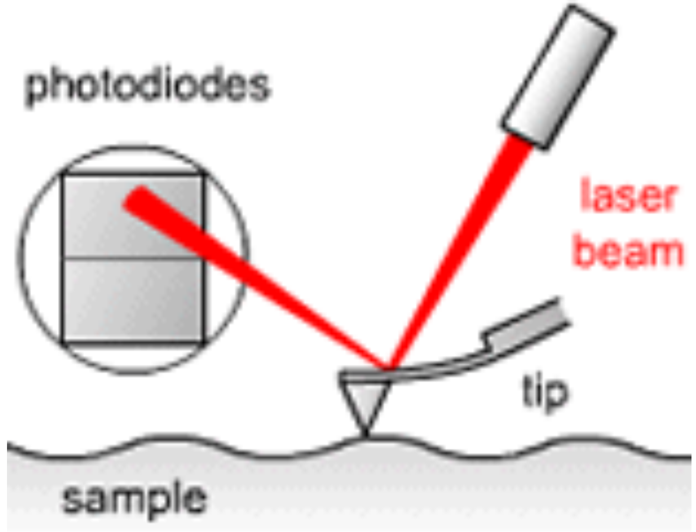
photodiodes
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tip
sample

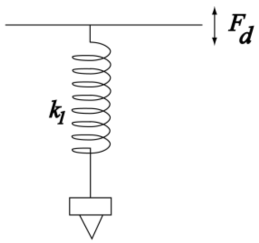
AFM Measurements

Short range
"contact"

Long range
"non-contact"

Distance

$f < f_0$



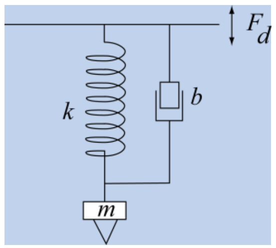
Contact
Indentation
Force Curves

Static
deflection

Pulsed Force, Peak Force, QI, Hybrid , Pinpoint, Jump Mode, Ringing Mode…

Force
Modulation

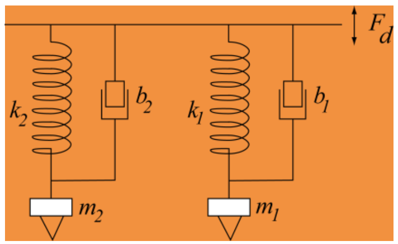
$f \approx f_0$



FM, Noncontact

AM, Tapping

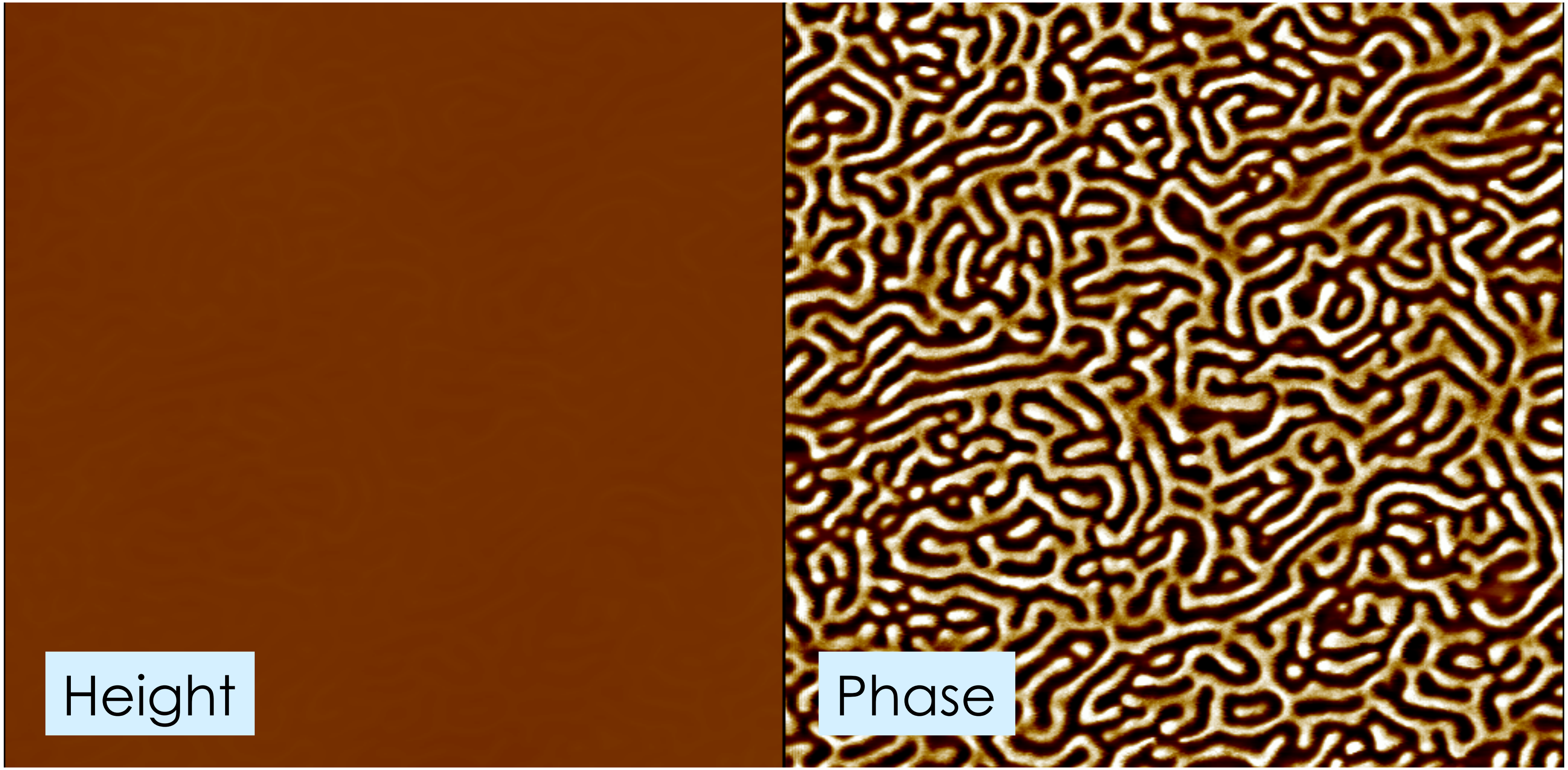
$f > f_0$



Ultrasonic and
Acoustic Force
Microscopy, CR

Bimodal, Dual AC, Intermodulation AFM, HarmoniX,
Band Excitation, G Mode SPM …

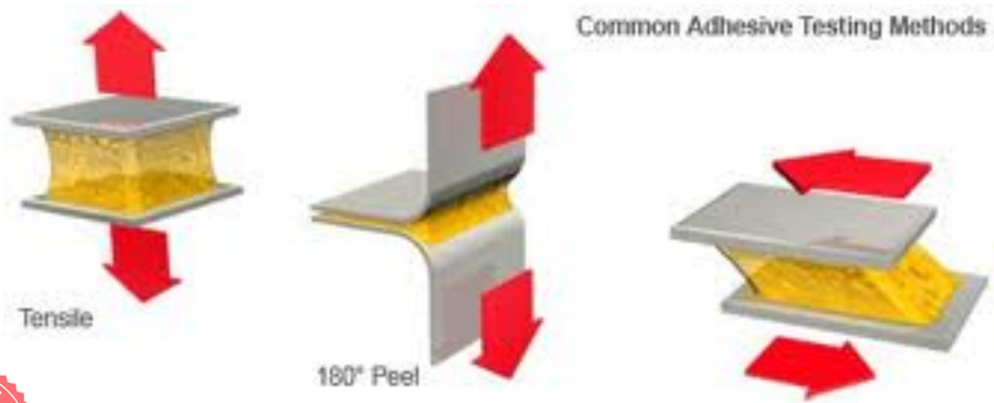
Thermoplastic Elastomers



Scan Size : 2.0 μm

Ph. Leclère *et al.*, Langmuir 12 (1996), 4317-4320.

Mechanical Properties



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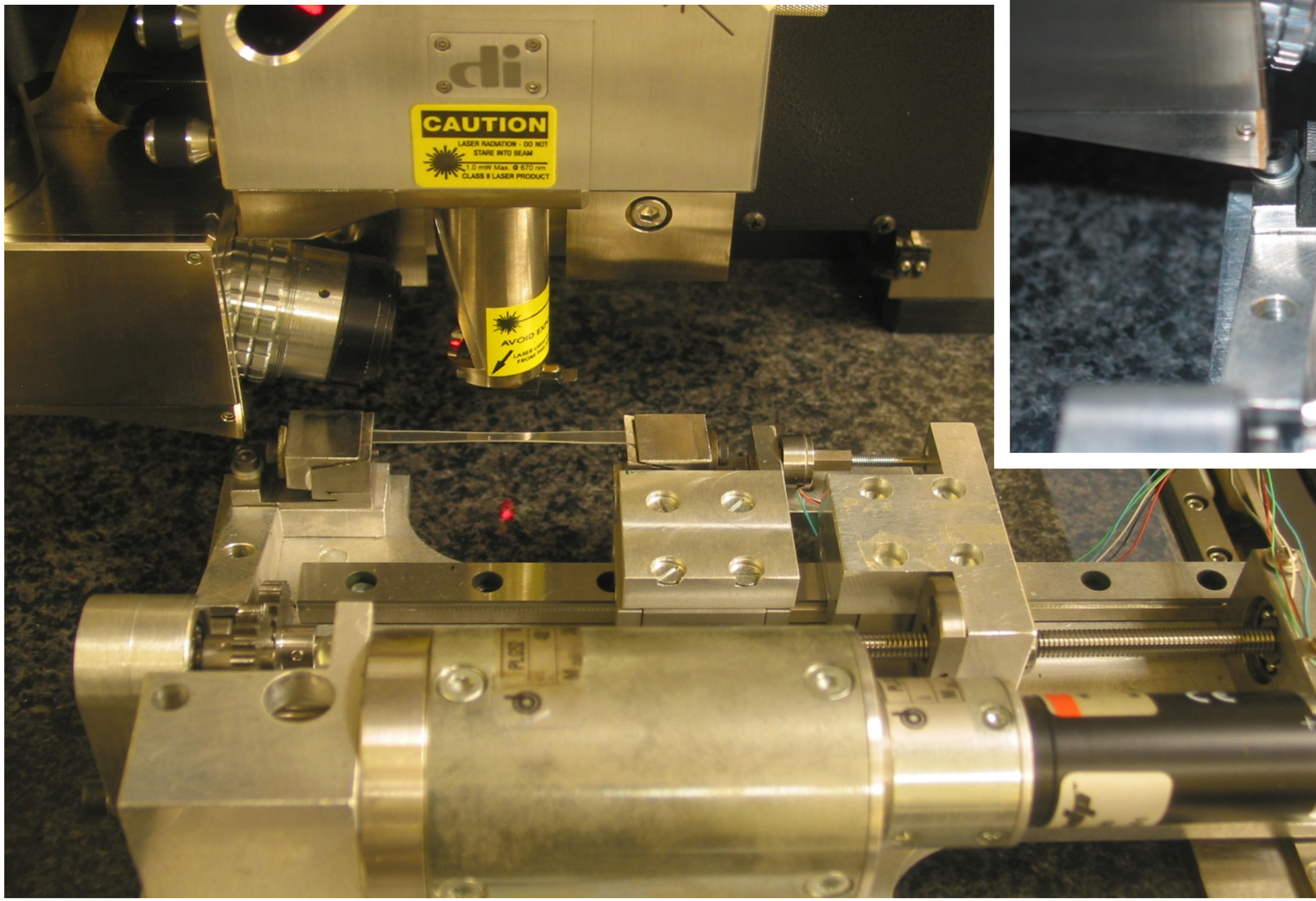
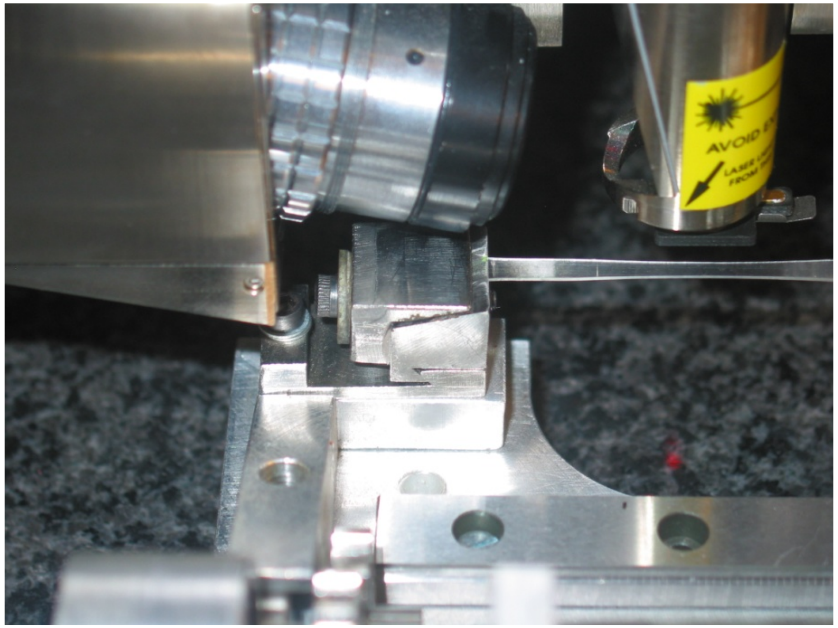
TPE upon tensile loading …

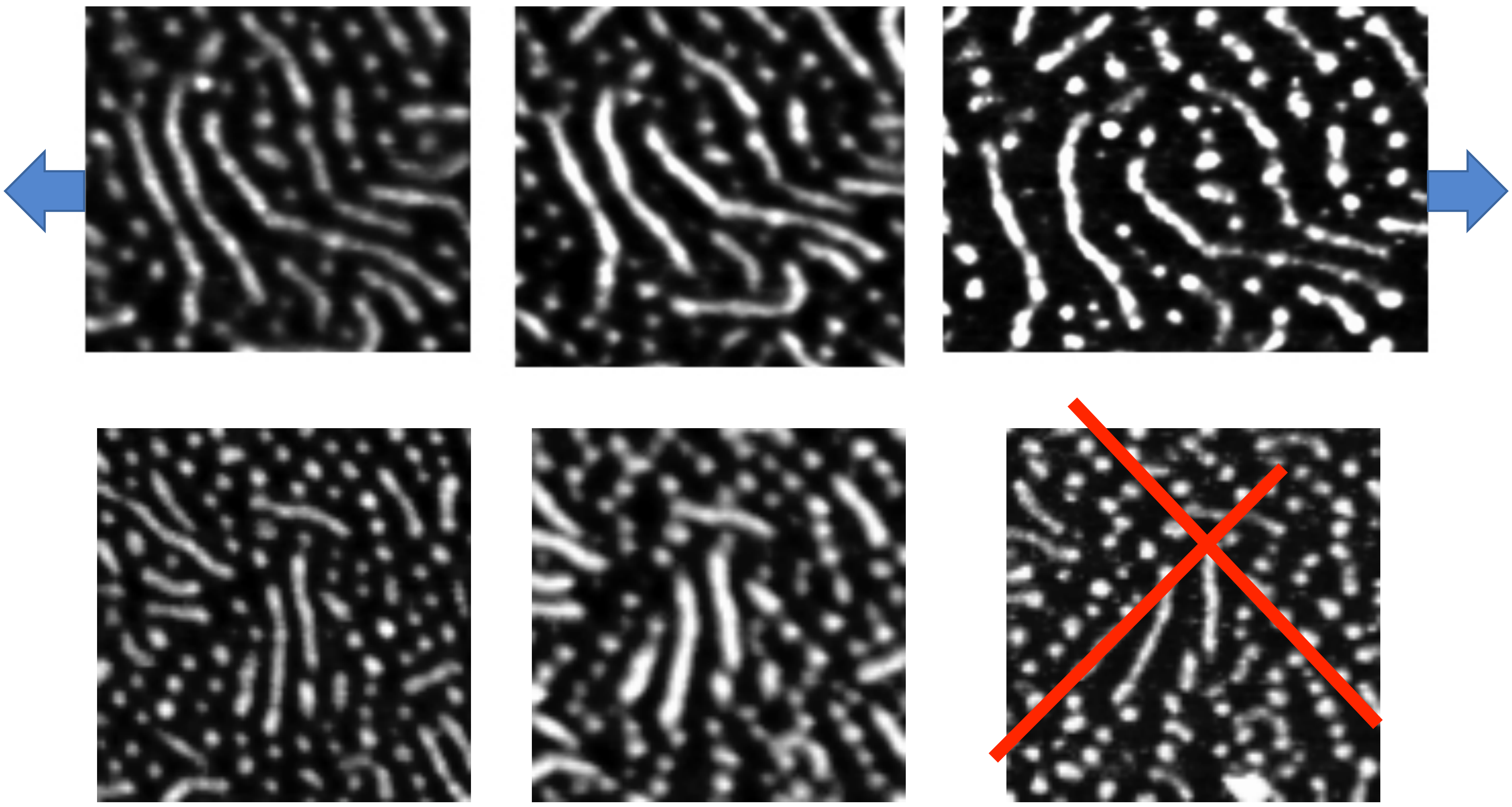
USTL, Lille (France)





TPE upon tensile loading …

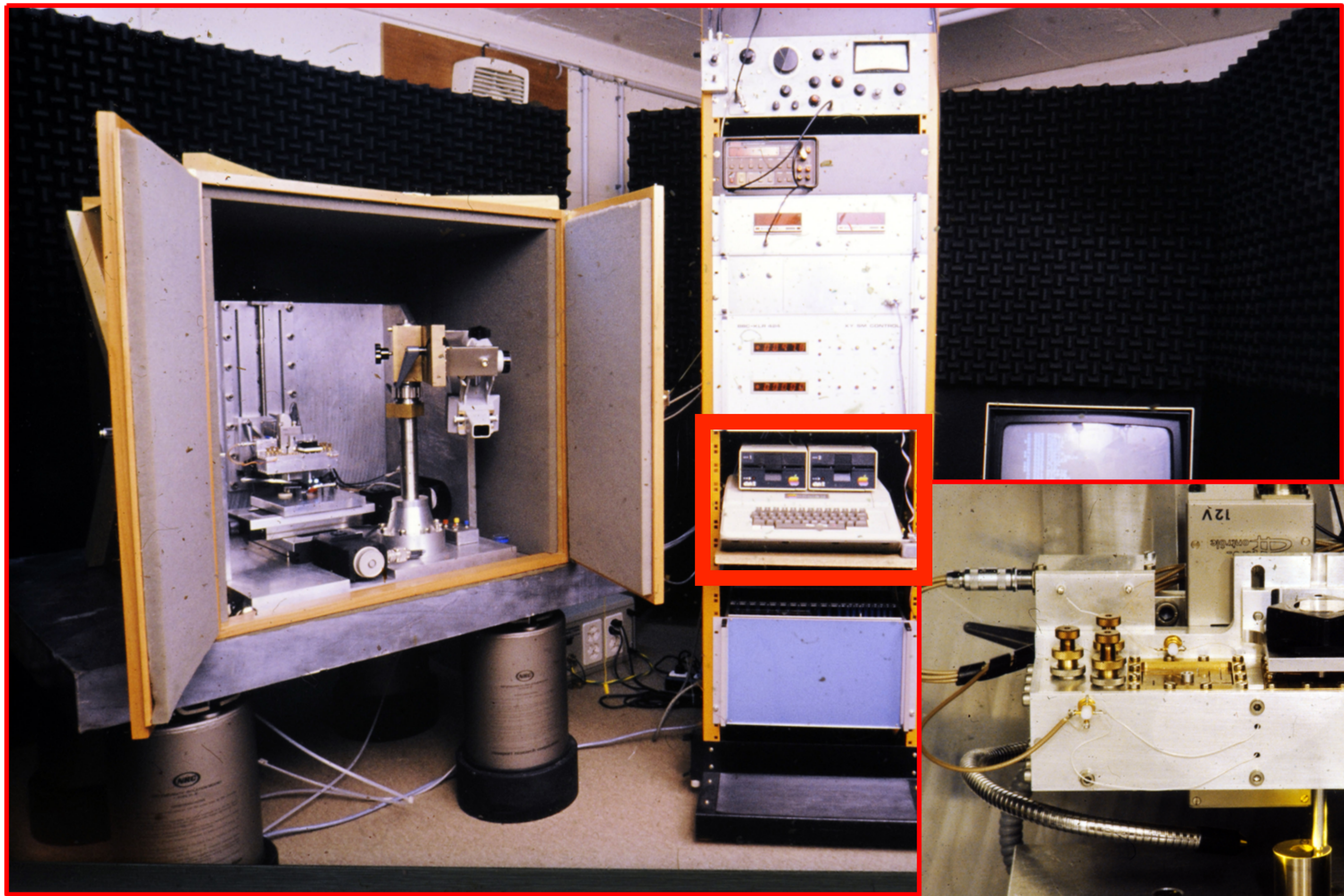
0 % 30 % 50 %

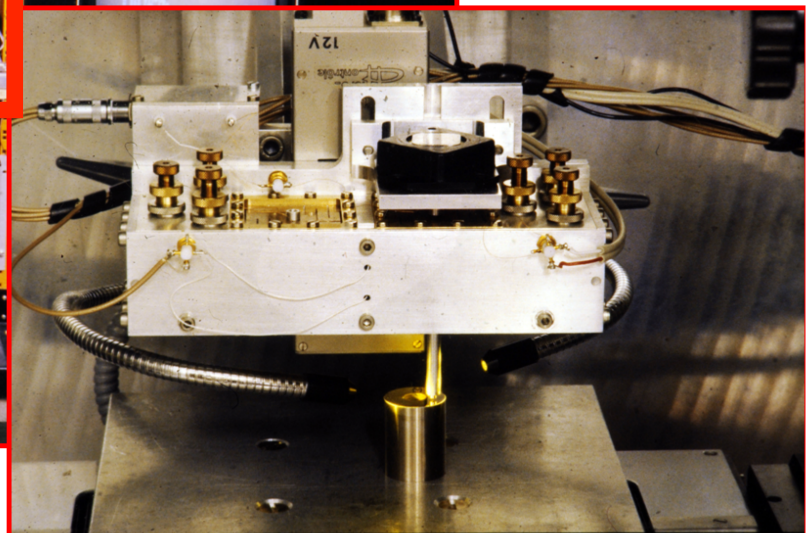


Shear (maximum stress directions at an inclination of 45 °)

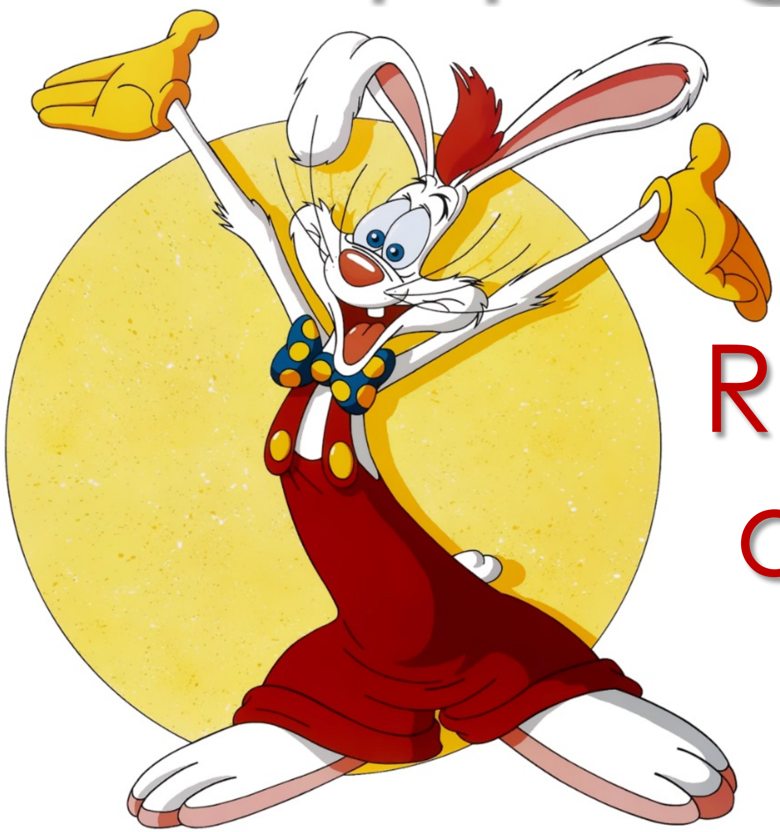
THE ORIGINAL NANOINDENTER

- Pethica, Hutchings, and Oliver, *Phil Mag A***48**, 593(1983)





Quantitative Nanomechanical Mapping



Real, Dream or … Fake ?

What do we need ?

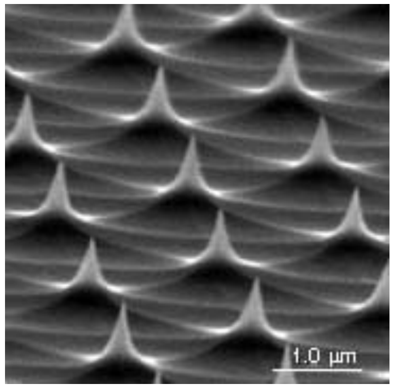
A proper calibration of the AFM and the probe

- **scanner, photodetector sensitivities** : approach-retract curve on stiff sample (silicon, sapphire, ...)
- **probe**: spring constant, resonance frequency, quality factor, tip geometry and dimension (electron microscopy or tip shape reconstruction).

A suitable contact mechanics model

- DMT model, JKR model, Sneddon model, ...

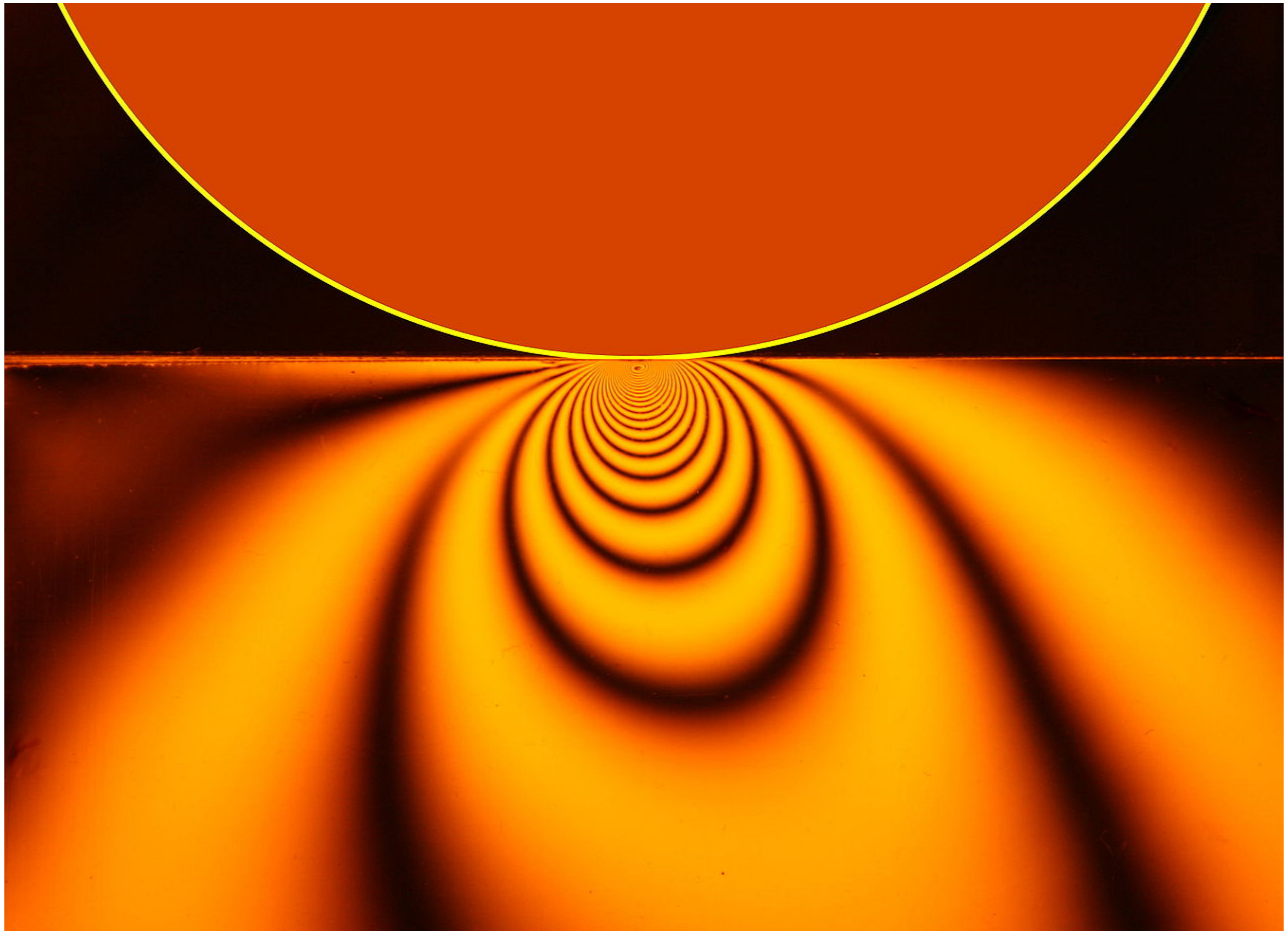
A signal giving access to the tip-surface contact stiffness



- "slope" of force-curve in the contact region,
- modulated cantilever vibration,
- phase-shift in AM-AFM,
- contact resonance frequency,
- higher harmonics vibration amplitude,
- In phase and quadrature signals, ...

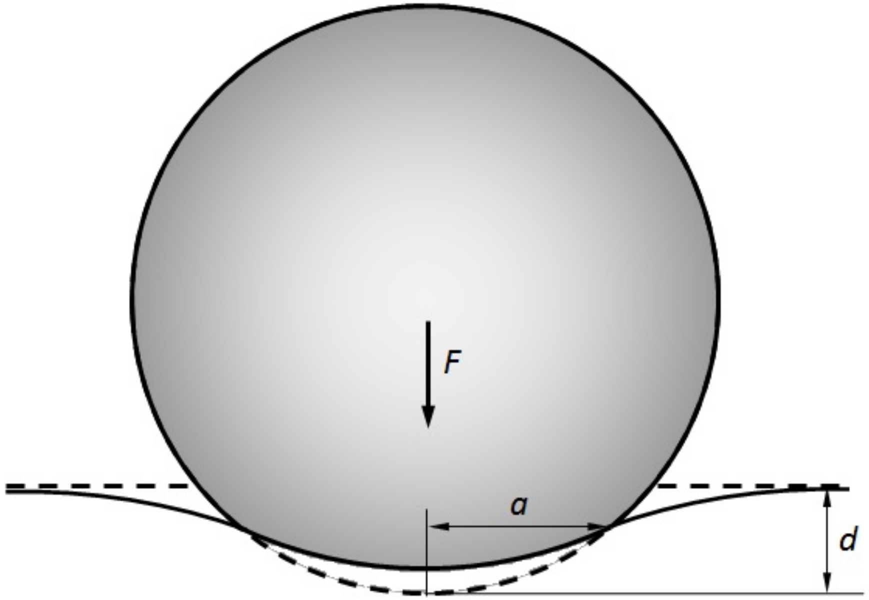
Contact Mechanics Forces

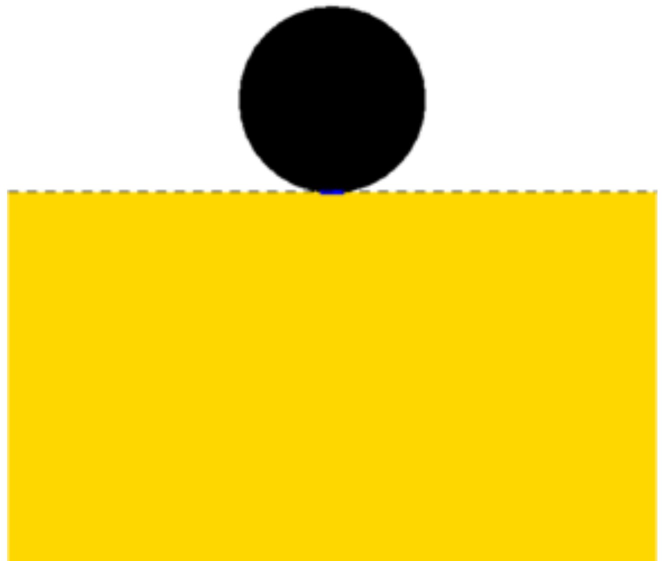
Basic Hertz elastic solution (1881)



Contact Mechanics Forces

Basic Hertz elastic solution (1881)





Contact Mechanics Forces

To determine the deformation of two elastic objects in contact, we have to establish and resolve the relationship between the stress and strain tensors. This functional relationship is called the **constitutive equation**.

$$\Gamma_{ij} = \lambda \varepsilon_{ll} \delta_{ij} + G \varepsilon_{ij}$$

λ is the Lamé coefficient

The **shear modulus** G is given by :

$$G = \frac{E}{2(1+\nu)}$$

At equilibrium, the **elasticity parameter**

$$\lambda_e = \Gamma_0 \left(\frac{9R}{2\pi W_{ad} E_{eff}} \right)^{1/3}$$

W_{ad} is the work per unit of area required to fully separate the surfac

$$\frac{1}{E_{eff}} = \left(\frac{1-\nu_t^2}{E_t} + \frac{1-\nu_s^2}{E_s} \right)$$

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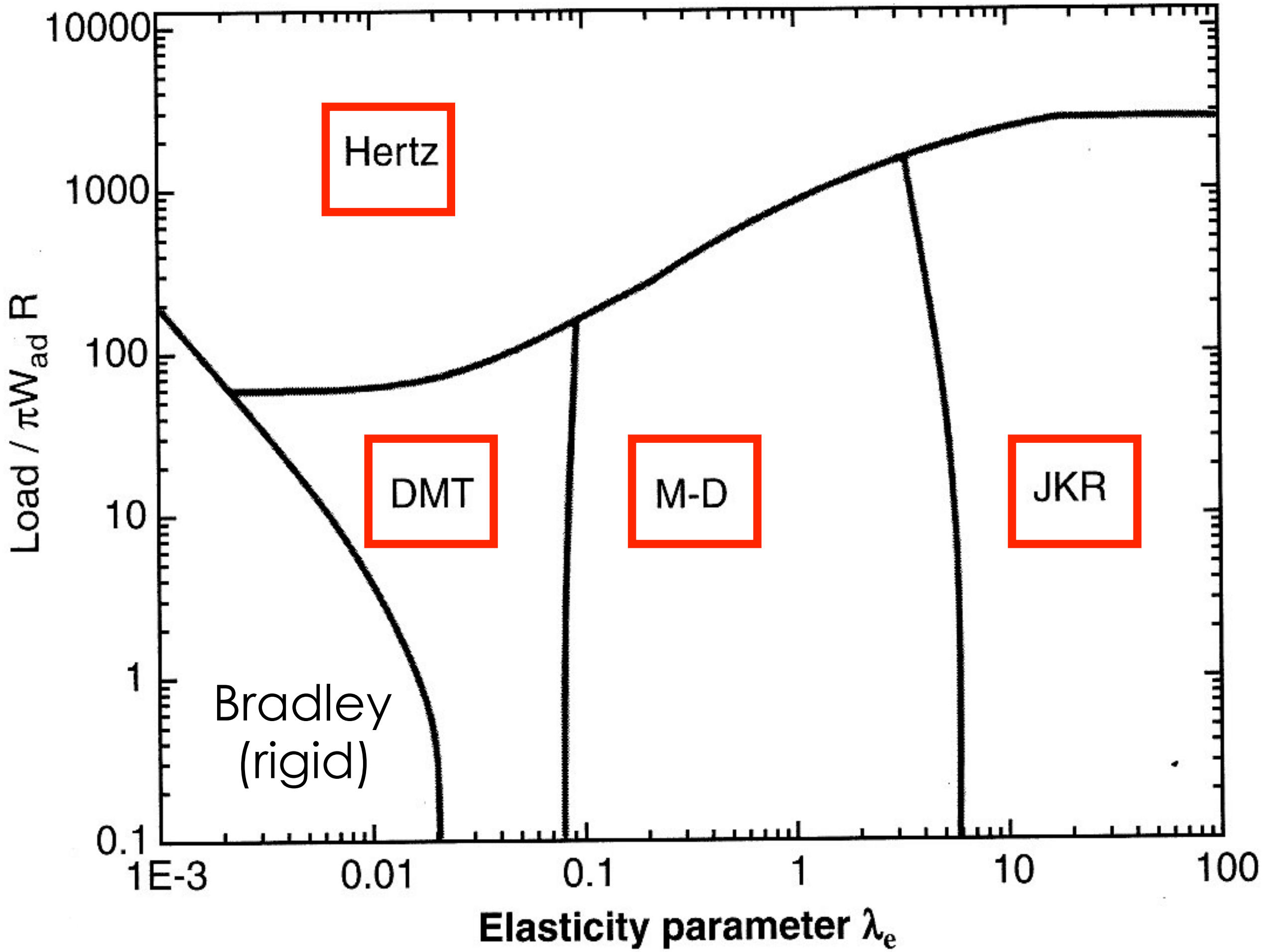
Contact Mechanics Forces

DMT = Dejarguin – Muller – Toporov *(stiff contacts, low adhesion)*

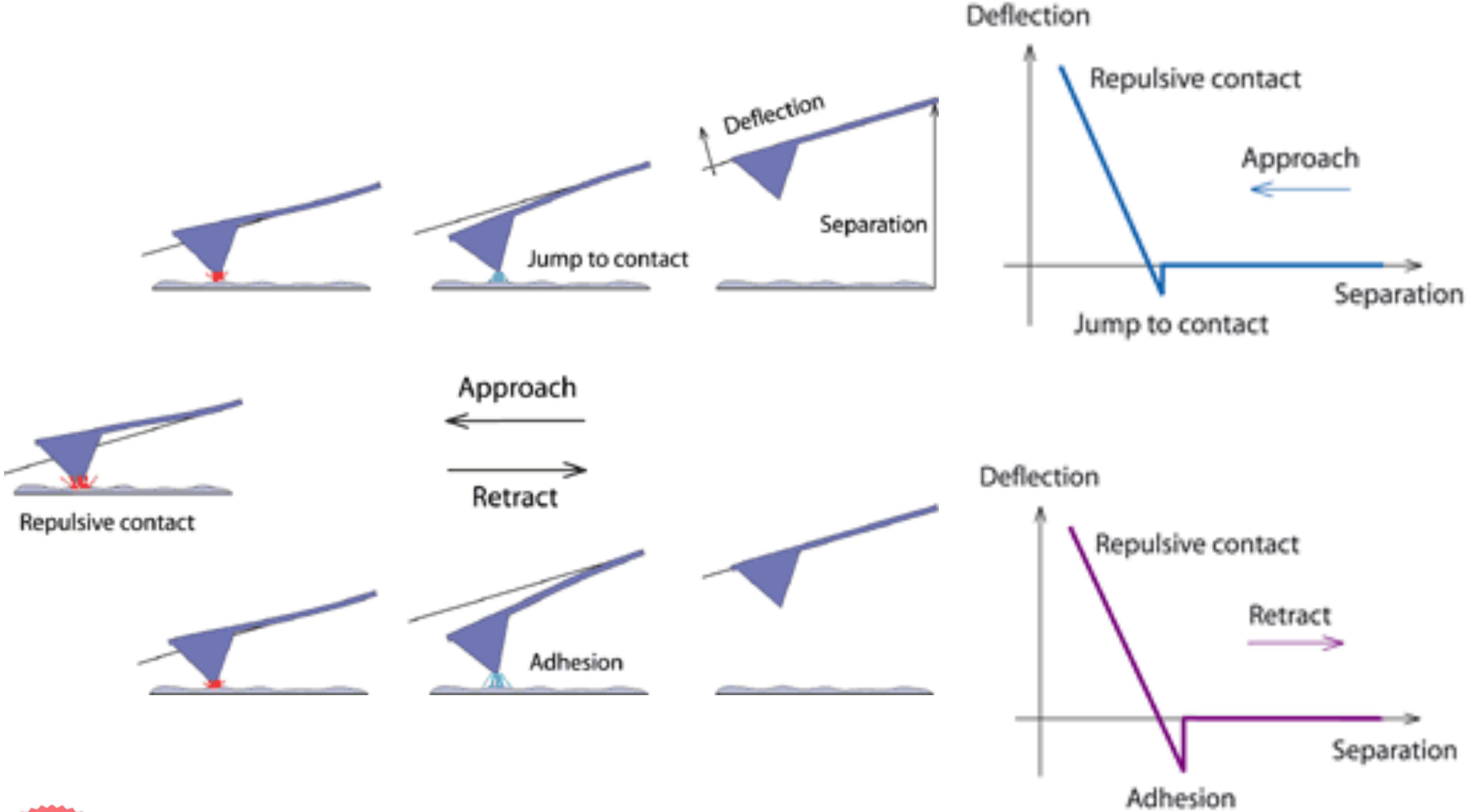
M-D = Maugis - Dugdale

JKR
Johnson – Kendall – Roberts
(low stiffness, high adhesion, large tip)



Johnson, Greewood, J. Colloid Interface Sci., 1997, 192, 326.

Force curves



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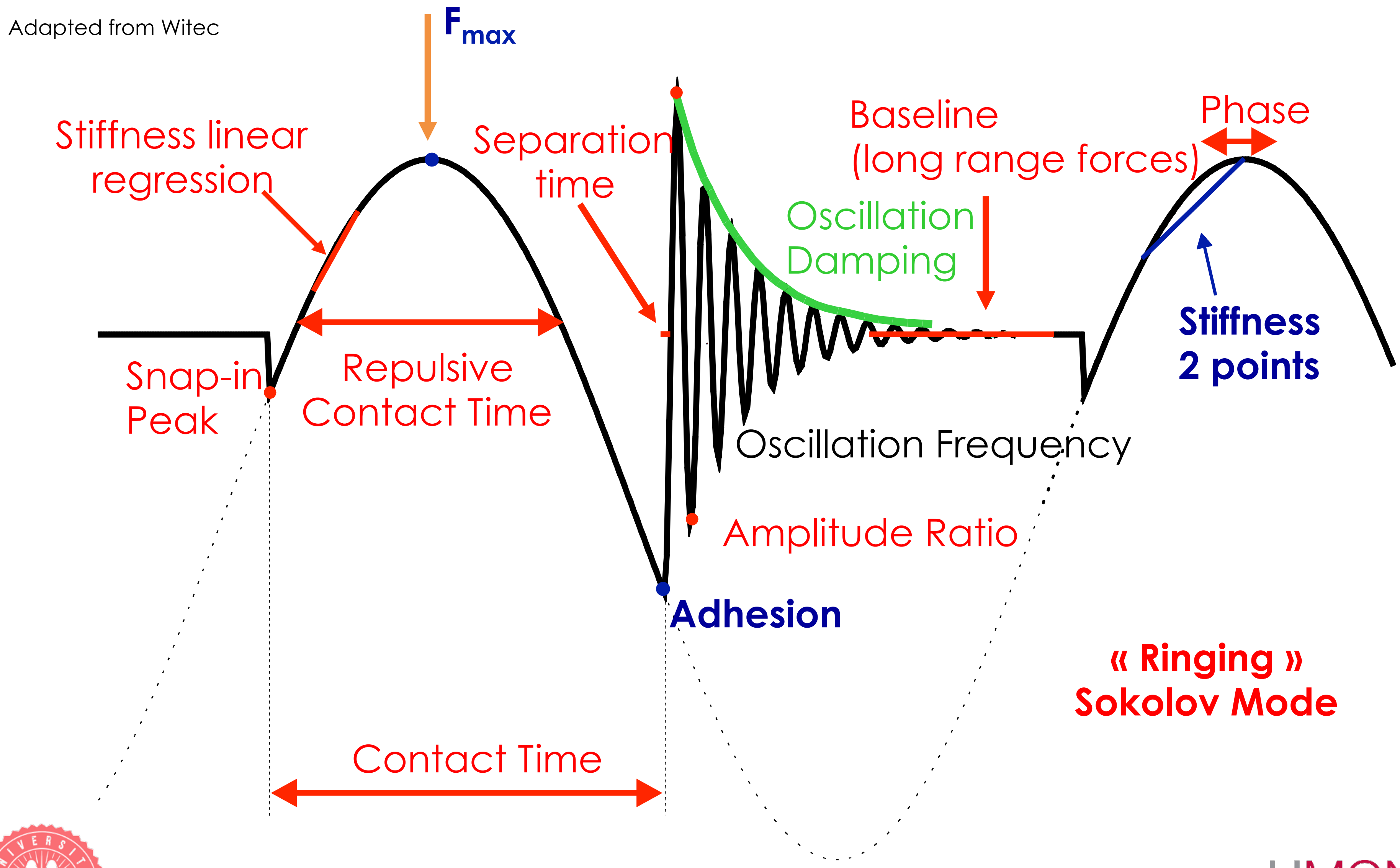
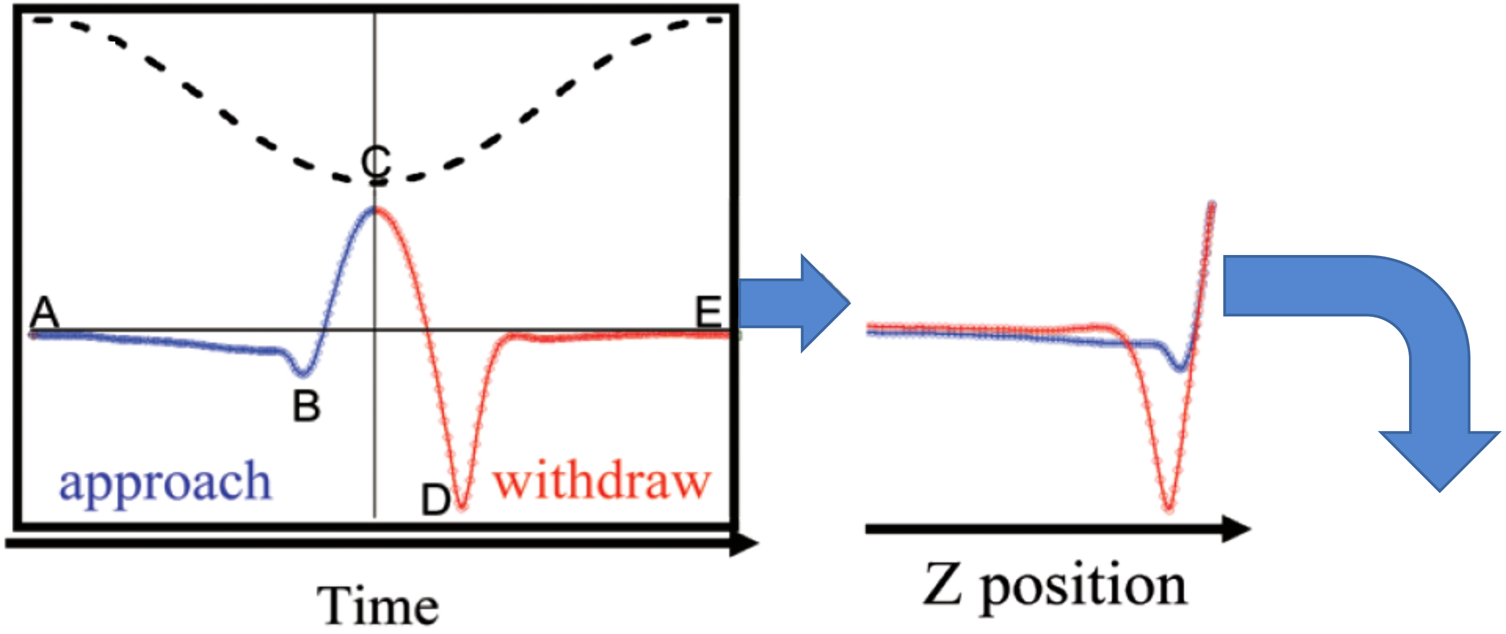
Peak Force Tapping

aka Jump Mode, Hybrid™, Pinpoint™, QI™, « Ringing » Mode AFM, …

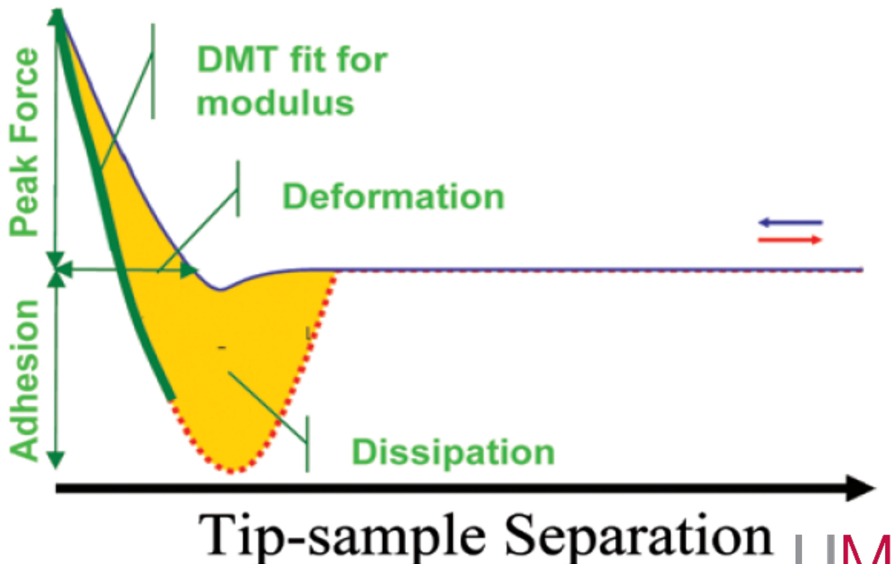
Information contained in a PFM Curve



Peak Force Tapping (QNM)

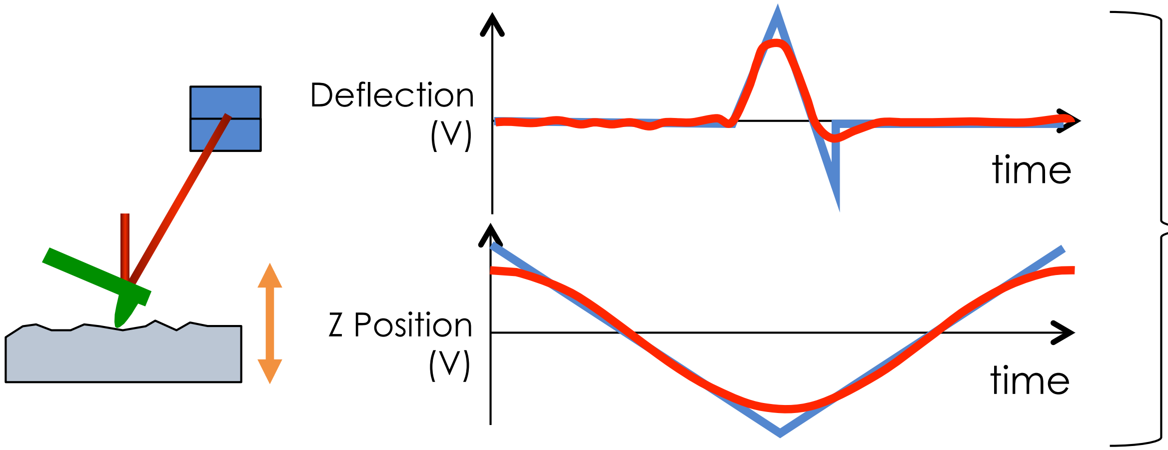


Modulus: 0.6 MPa-60 GPa
Energy Dissipation:1eV-tens keV
Adhesion: 10s pNs ~ mN
Deformation: 10s pm ~ 10s nm

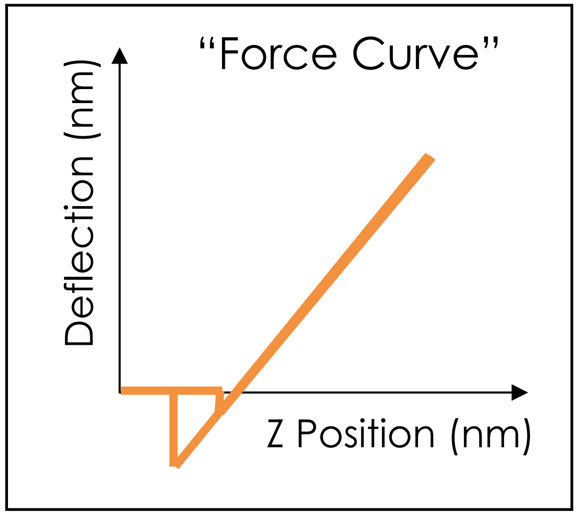


Analyzing Force Curves

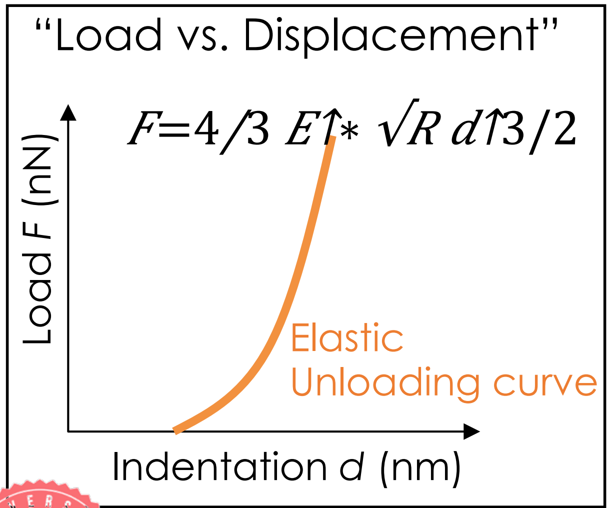
From Deflection and Z to modulus



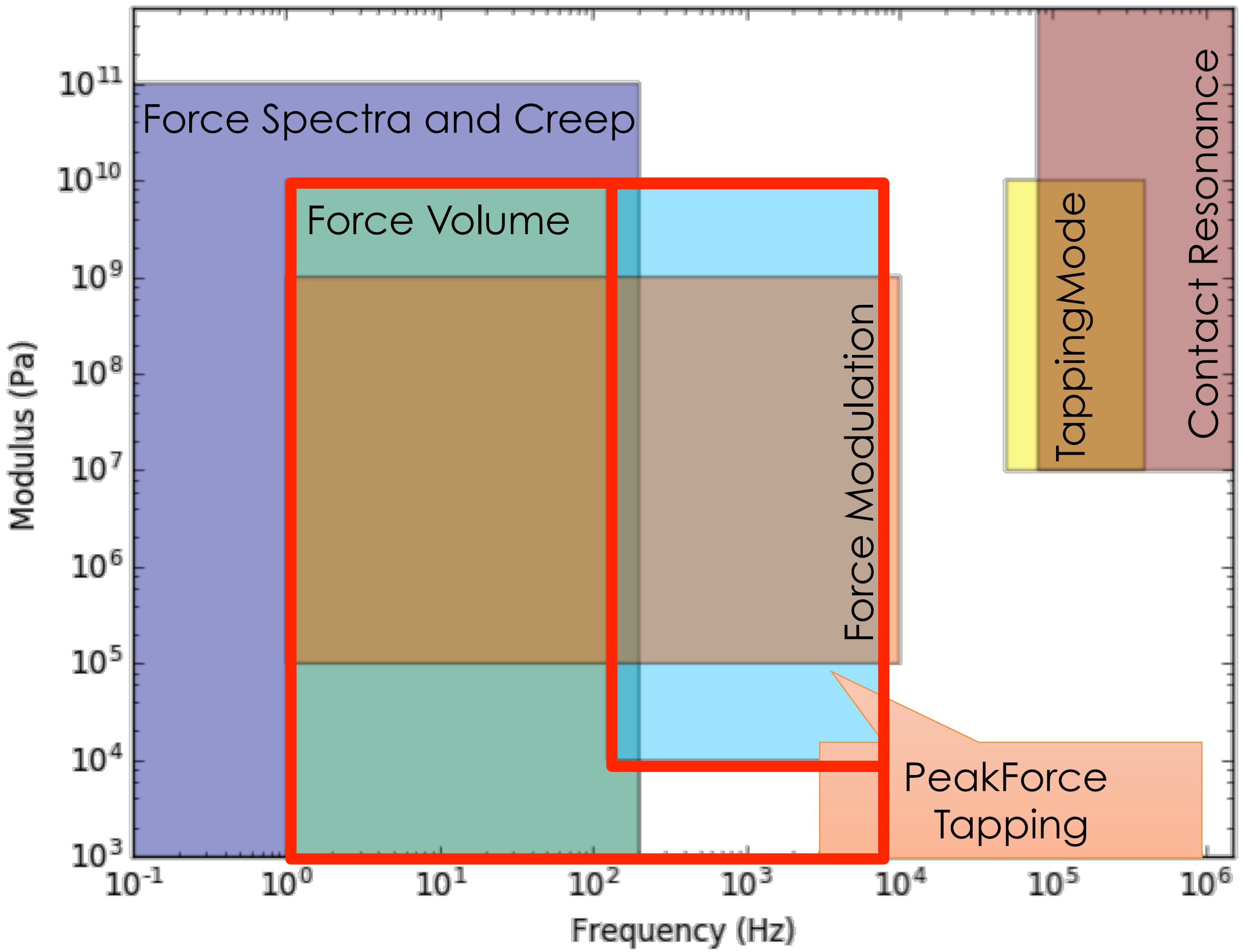
1. Eliminate time
2. Apply ‘Deflection sensitivity’
3. Apply ‘Z sensitivity’



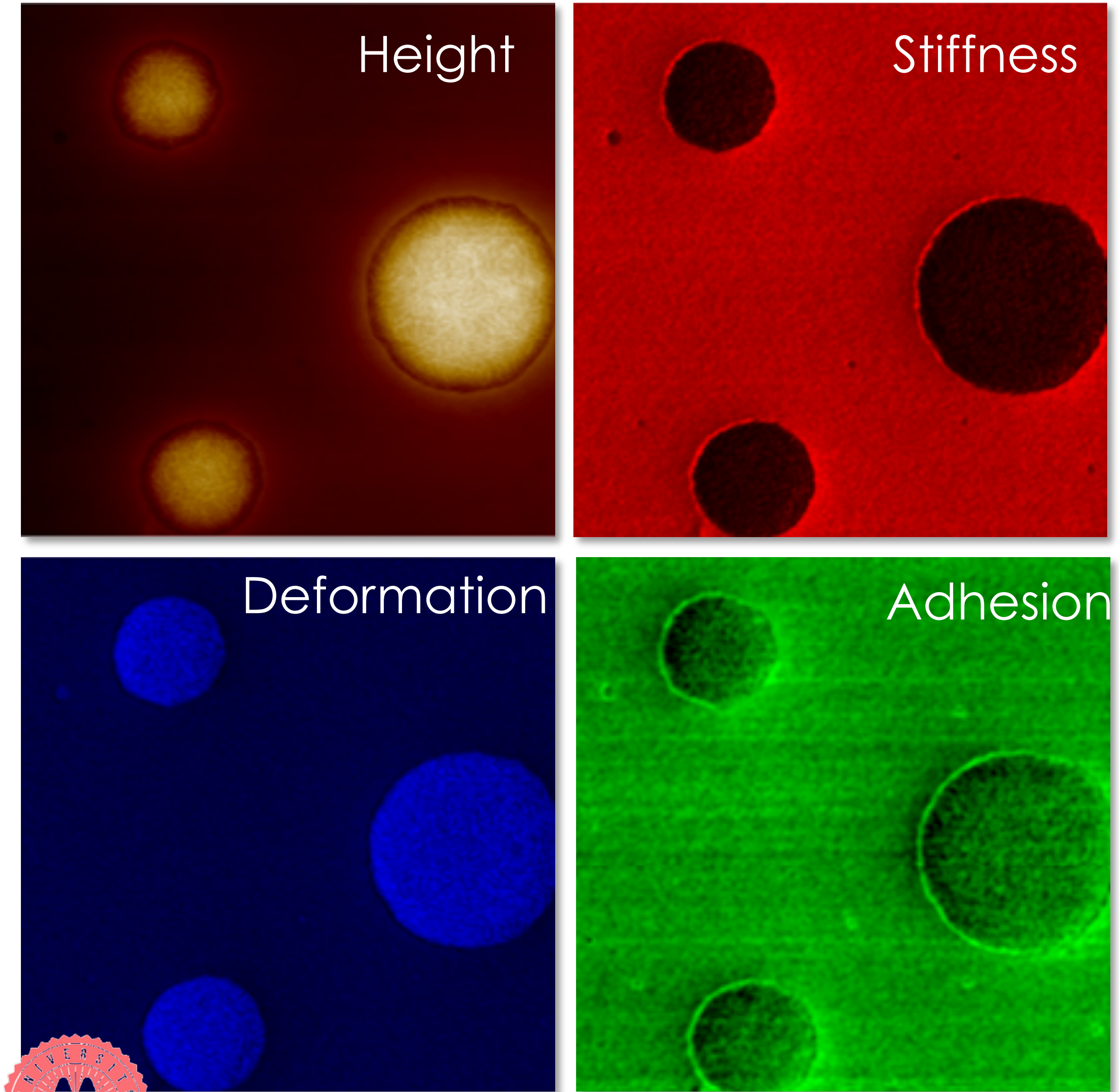
4. Calculate indentation
5. Apply ‘Spring constant’
6. Fit data with contact mechanics model



AFM frequency and modulus ranges Force Volume and PeakForce Tapping



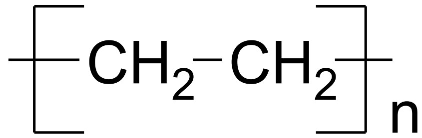
Blend of PS/LDPE



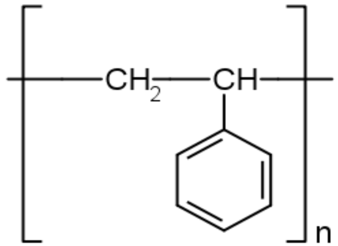
Macrophase separation

Information about mechanical properties at the nanoscale

LDPE

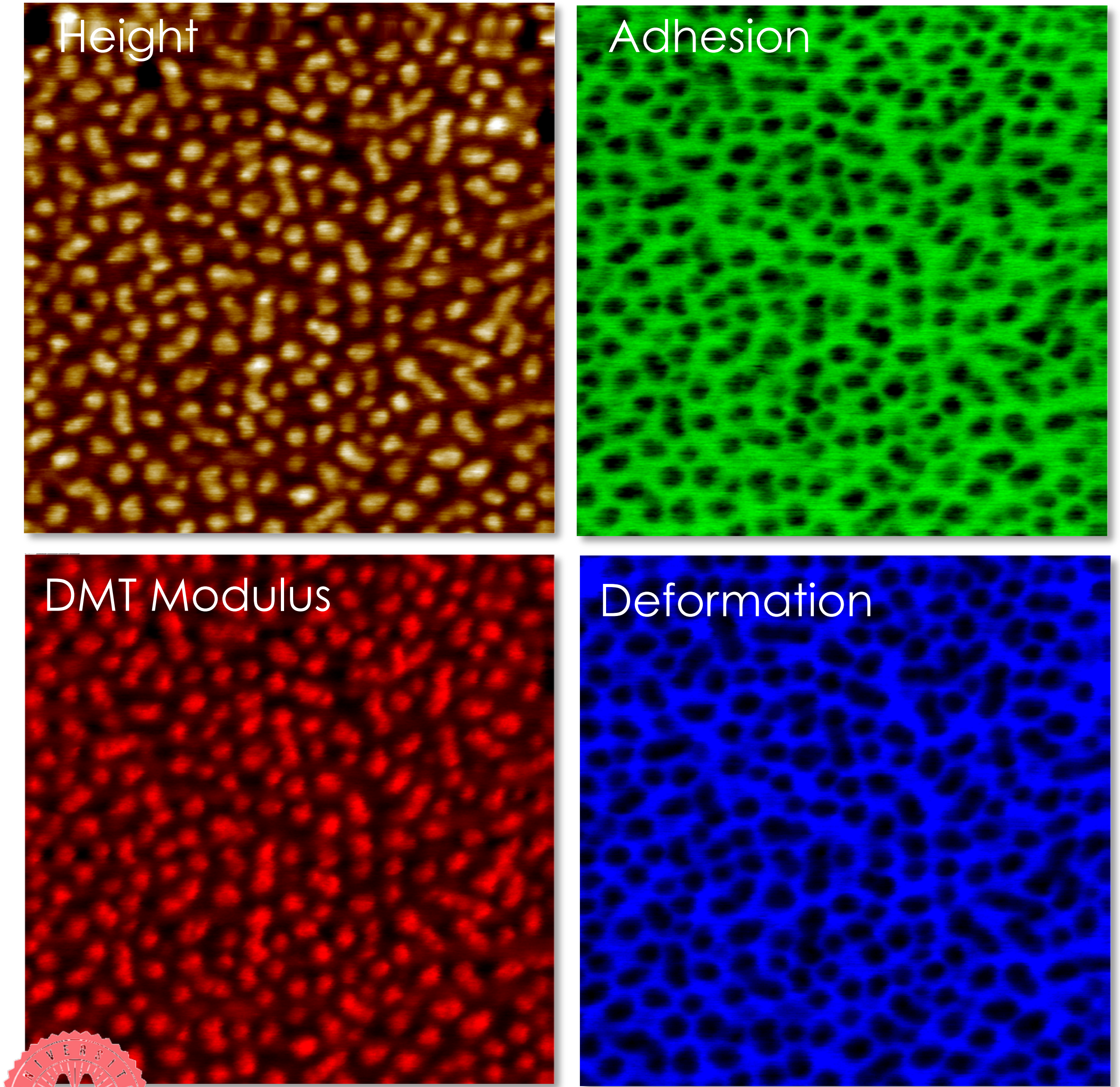


PS



Scan Size : 3.0 µm

Pressure Sensitive Adhesive



Microphase separation

PSA

Scan size 1.0 µm

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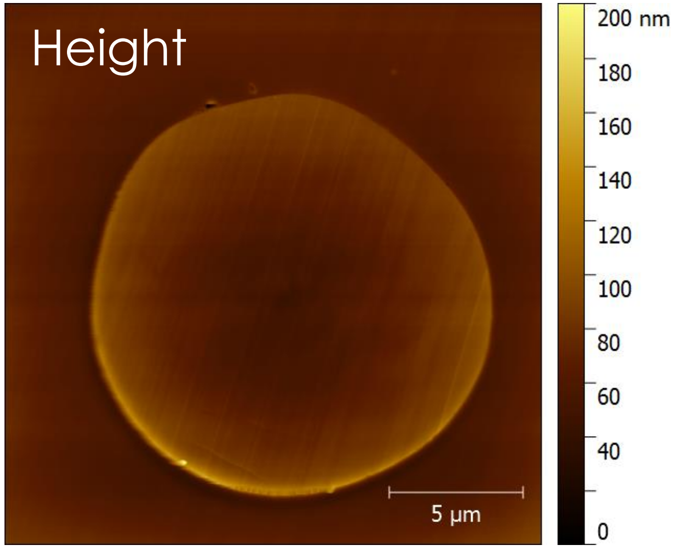
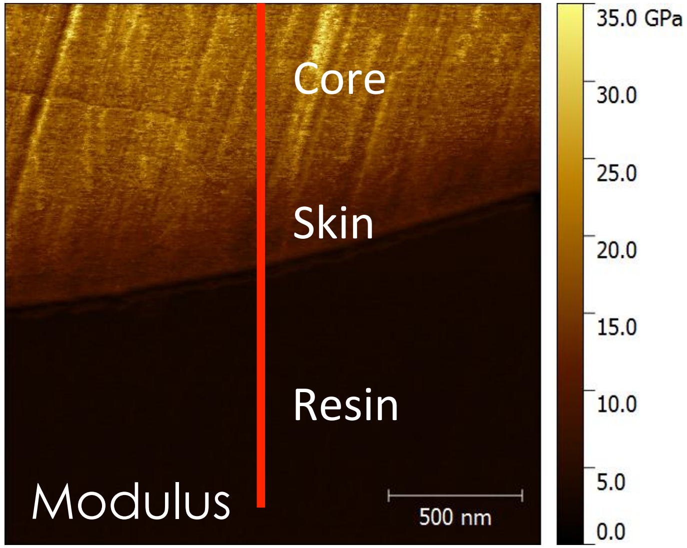
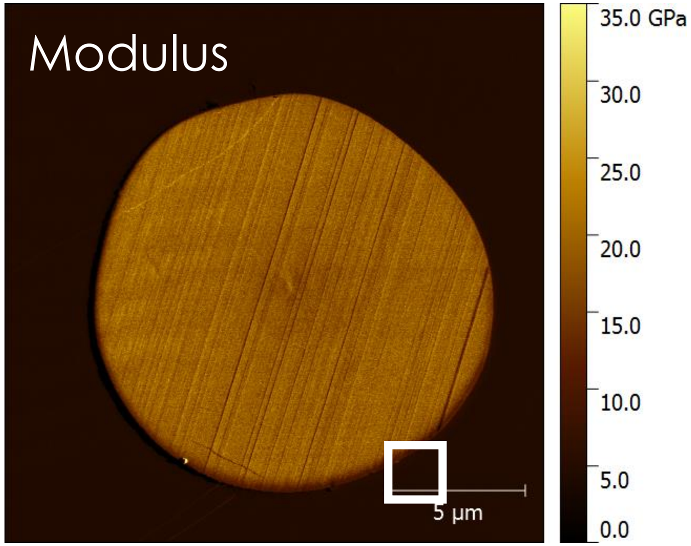
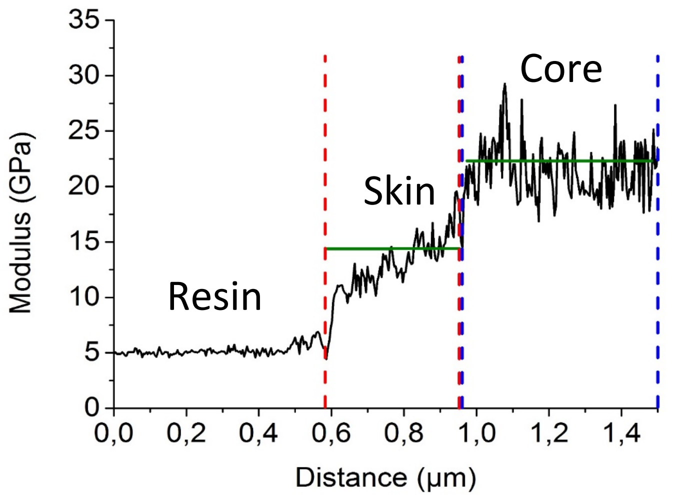
Fibre de Kevlar – résine époxy









$M_{core\ NI} = 22.8 \pm 1.7$ GPa

$M_{core\ calc} \approx 21$ GPa

$M_{skin\ calc} \approx 17$ GPa

O. Arnould *et al.*, Ind. Crops Prod 97 (2017), 224-228.

Paroi cellulaire de fibres de lin

Image d'une section de tige

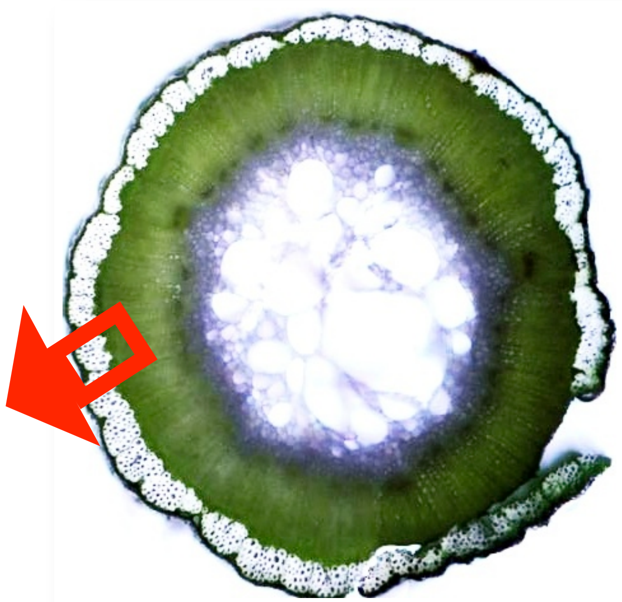
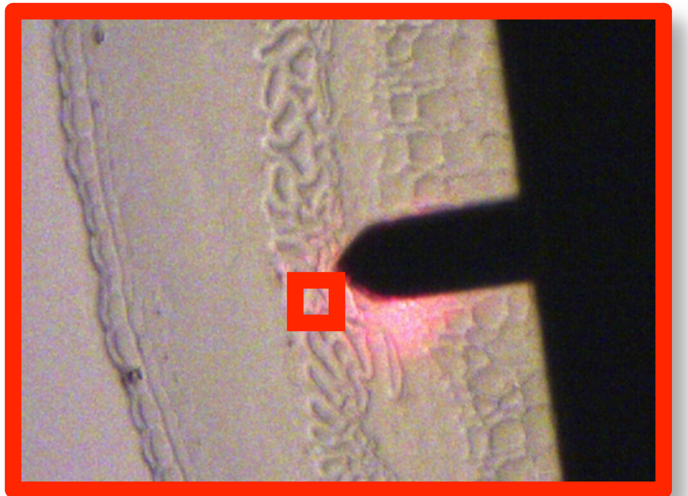


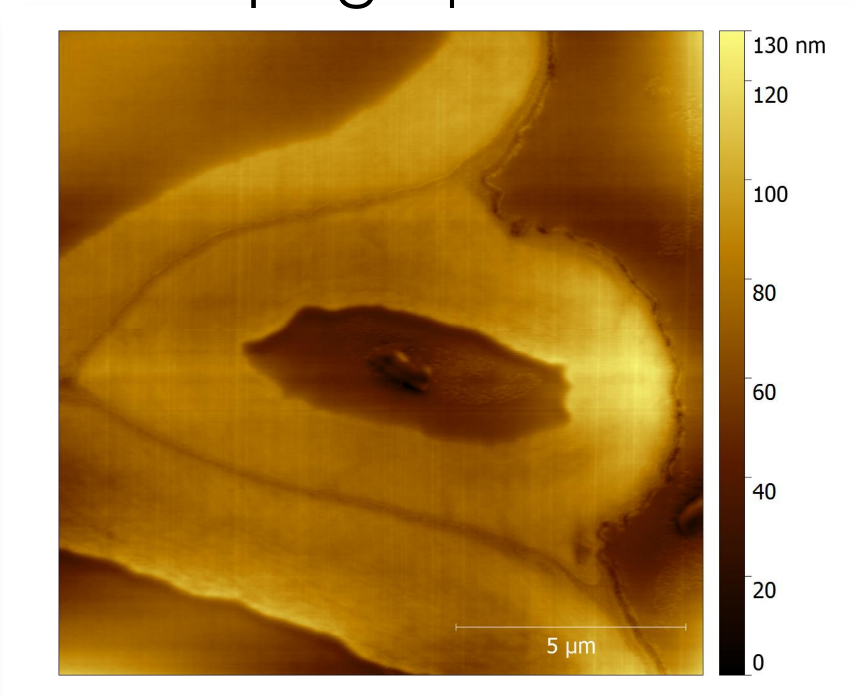
Image optique dans l'AFM



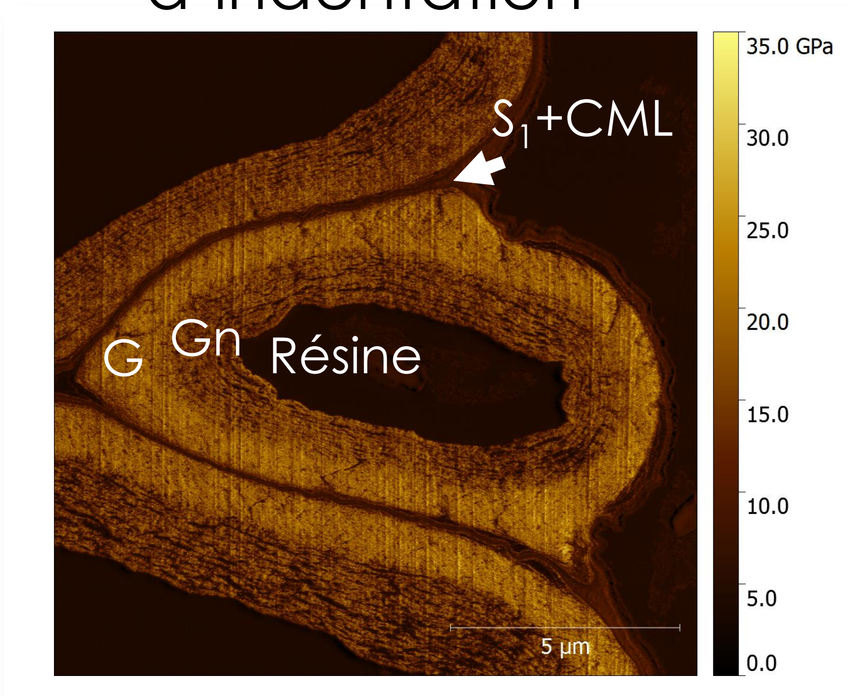
IRDL, Université Européenne de Bretagne, CNRS FRE 3744, Lorient

Paroi cellulaire de fibres de lin en développement

Topographie

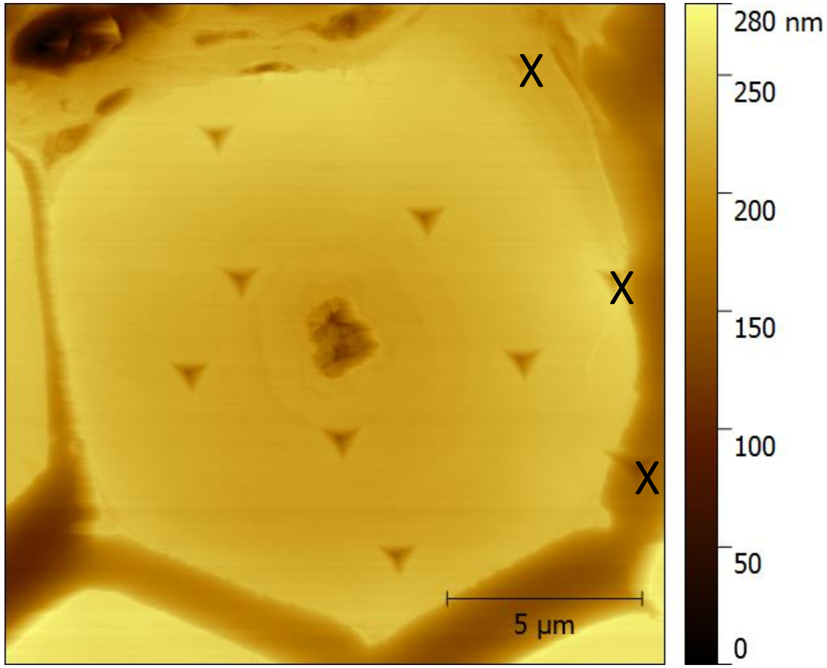


Module d'indentation



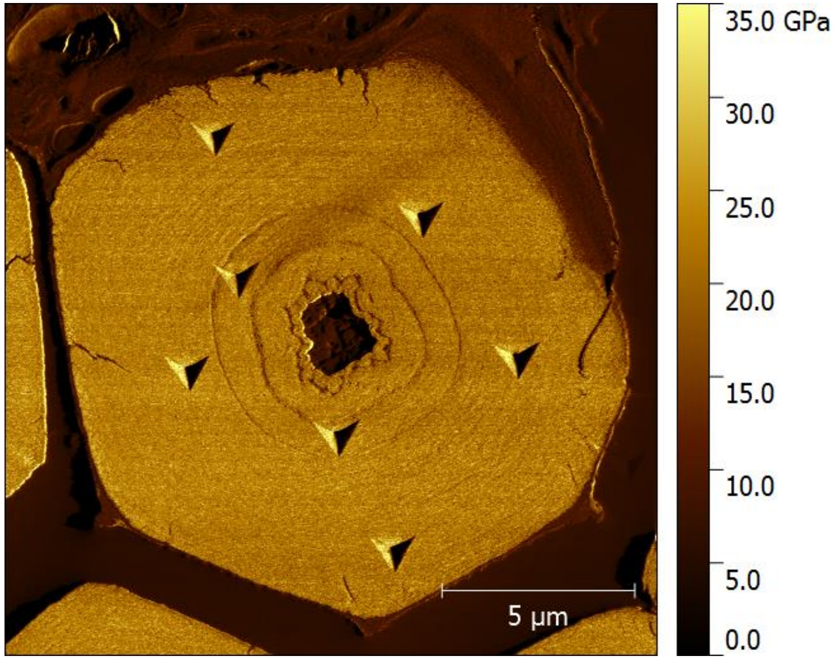
O. Arnould *et al.*, Ind. Crops Prod 97 (2017), 224-228.

Paroi cellulaire de fibres de lin matures



Topographie

Module d'indentation

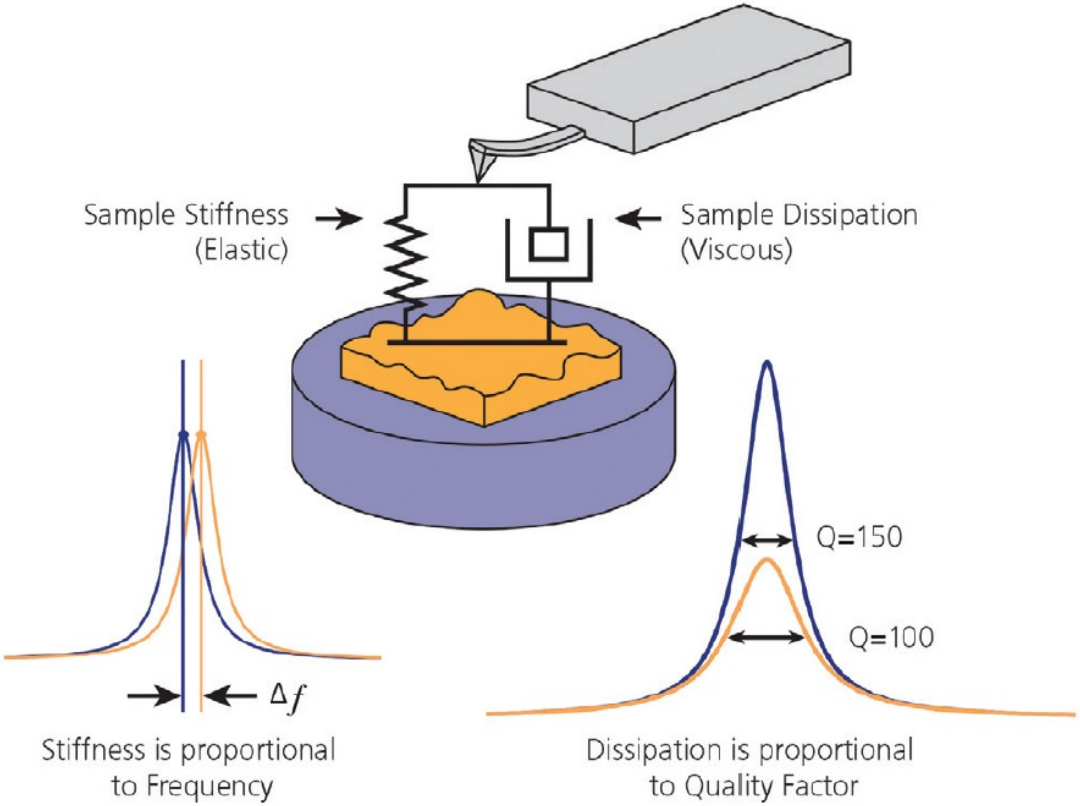


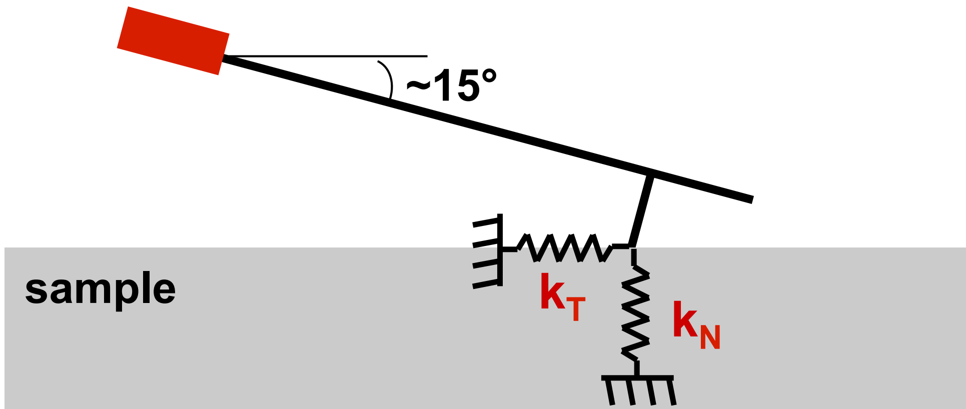
$M_{NI\ fibre} = 21.3 \pm 2.2$ GPa

O. Arnould *et al.*, Ind. Crops Prod 97 (2017), 224-228.

Contact Resonance

Contact Resonance





Introduction

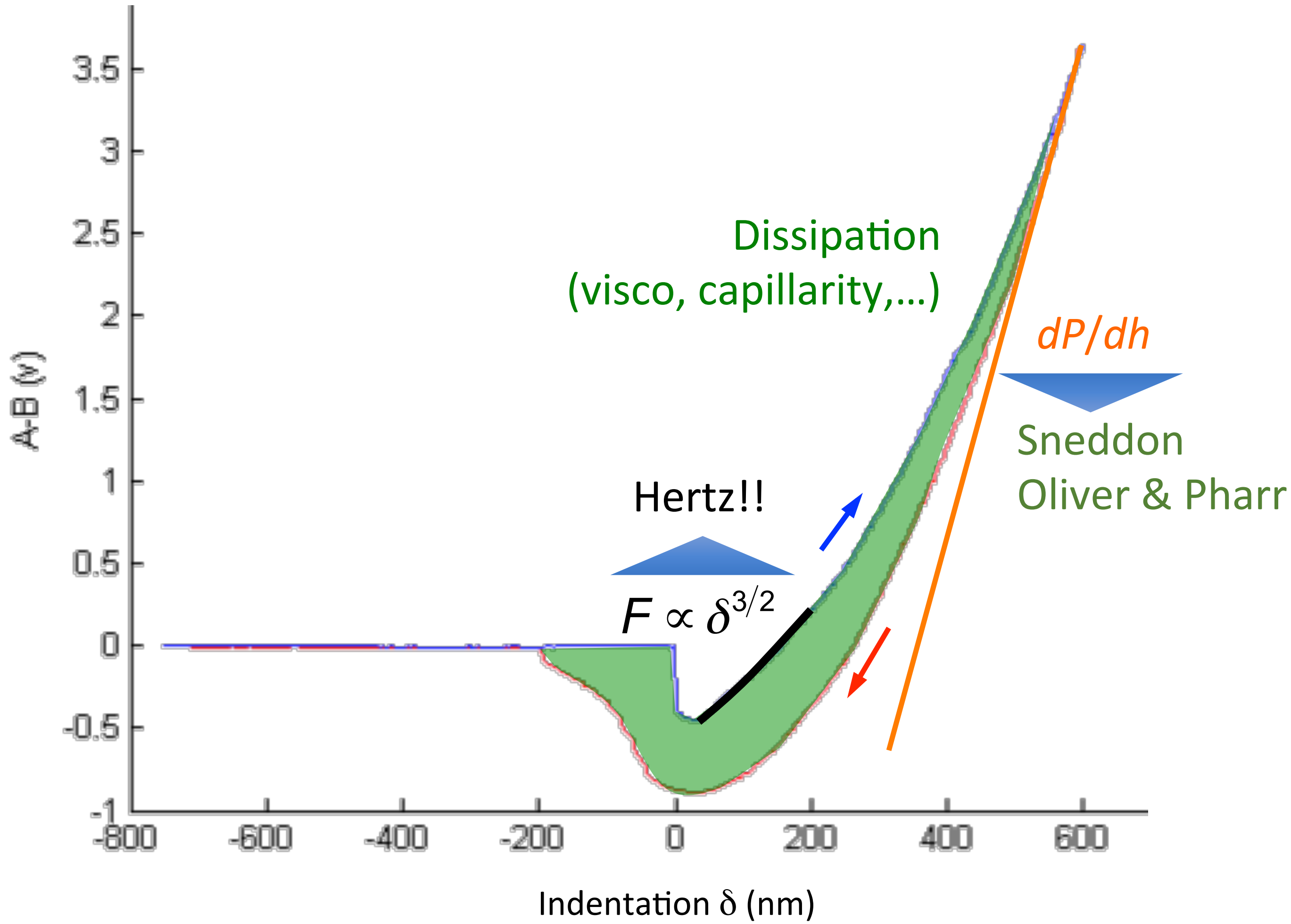
PU (3420)

$R \approx 130$ nm

$k_C \approx 2.8$ N/m

$f = 1$ Hz

$P_{Cap} \approx 110$ nN



Contact mechanics

Objectives: Find the relationship between k_N and E

Existing models:
- **Paraboloïd/plane models for homogeneous and isotropic samples**
- **Indentation depth δ << R (!!)**
- **+ non conforming surfaces (!!)**

✓ **Hertz (1885):**
- **The oldest**
- **Without adhesion**

$$k_{N_{Hertz}} = 2Ma_c = \left(6M^2 R_{eq} F\right)^{1/3}$$

→ Not frequently used in AFM, used for high applied loads (> DMT – JKR)

M: Reduced/contact/indentation modulus

(linear) **ISOTROPIC**:
$$\frac{1}{M} = \frac{1-\nu_{Tip}^2}{E_{Tip}} + \frac{1-\nu_{Sample}^2}{E_{Sample}}$$

Orthotropic material in the main axes:
[Delafargue and Ulm, 2004; Vlassak et al, 2003]

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

S_2 wood cell wall: $M_{//} \approx 20$ / $E_{//} \approx 50$ GPa
[Jäger *et al*, 2011; Arnould *et al*, 2015]
Kevlar fibre: $M_{//} \approx 15\text{-}20$ / $E_{//} \approx 80$ GPa
[Arnould *et al*, 2017]

Contact mechanics - conclusion

Nanoindentation-like approach:

- Cantilever stiffness requirement

$$\frac{d}{z} = \frac{1}{1+\frac{k_C}{k_N}} \quad \Bigg| \quad \begin{array}{l} k_N >> k_C \rightarrow d = z \\ k_N << k_C \rightarrow d = 0 \end{array}$$

$$k_N \sim k_C$$

$$k_{N_{DMT}} = \left(6M^2R\left(F+F_{ad_{DMT}}\right)\right)^{1/3}$$

with

$$F = k_c d = k_c \chi V_{A-B}$$

- Calibration of the laser/photodetector
- Calibration of the cantilever stiffness
- Measurements of the real tip apex shape + *suitable* contact model…
- Non-normal load (shear) due to cantilever tilt + tip sliding?
- Limited resolution (>100 nm on polymer) due to large tip surface contact area

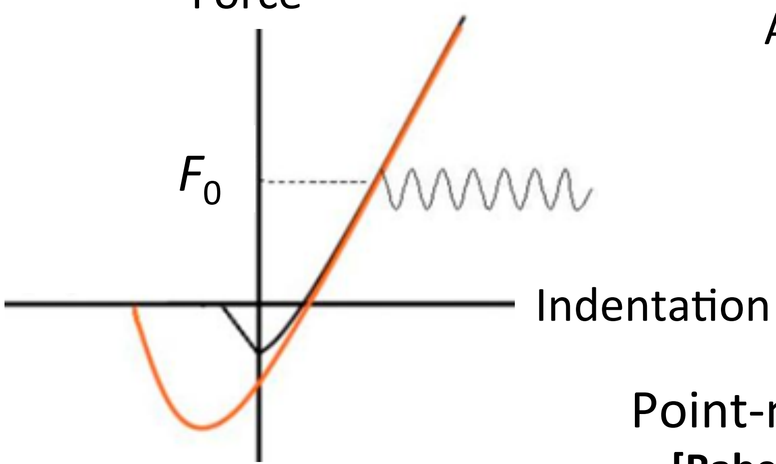
---

- Mapping (Force-Volume mode) of the elastic properties is very time consuming (256 x 256 points = 18h)

→ Force Modulation Mode [Maivald, 1991]:
the ancestor of CR-AFM at low frequencies!

CR-AFM principle

IDEA: To probe the local elastic stiffness of the tip-sample system by means of cantilever's resonance frequency in contact mode at reduce applied force



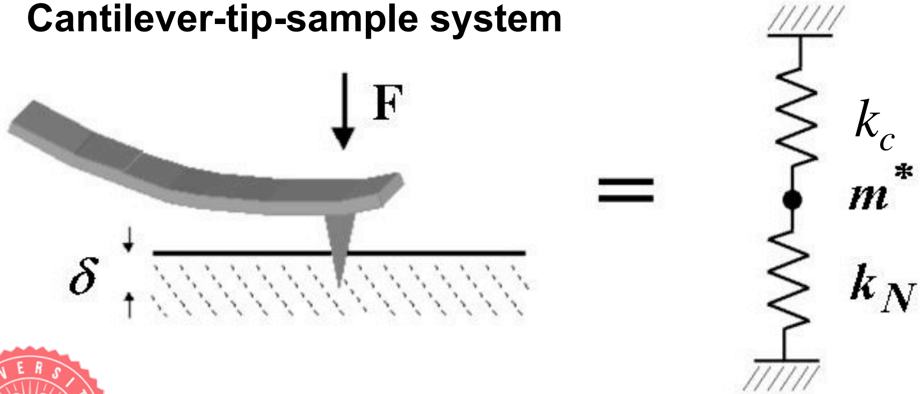
Applied force is modulated $F = F_0 + F_{excitation} \times \sin \omega t$

if $F_{excitation}$ is small → ≈LINEAR contact stiffness

if F_0 is small → Good spatial resolution + Hertz theory validity

Point-mass model [Rabe et al, 1996] $f_0 = \frac{1}{2\pi}\sqrt{\frac{k_c + k_N}{m^*}}$ with $m^* = \frac{1}{4}m + m_{tip}$

Cantilever-tip-sample system

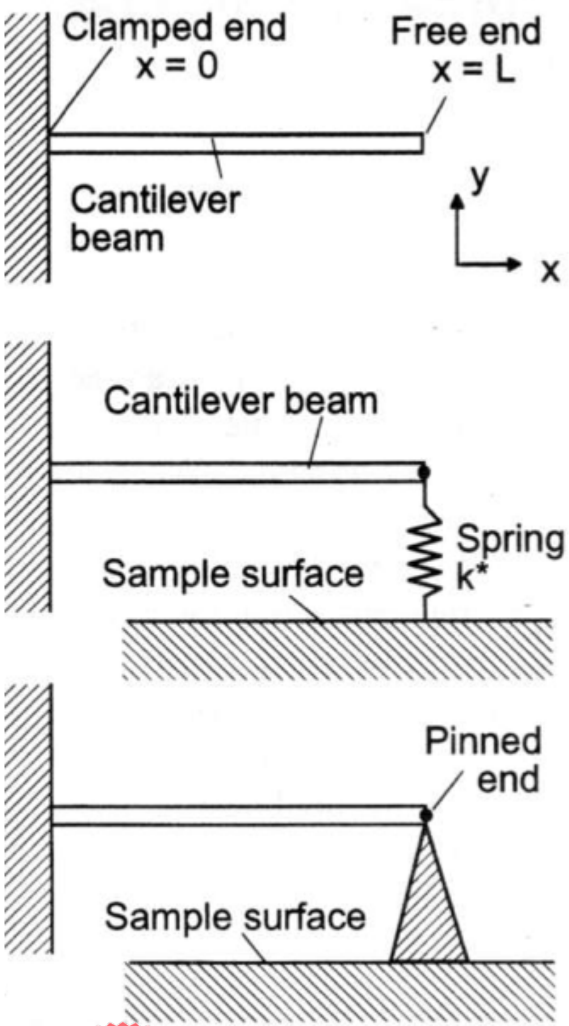


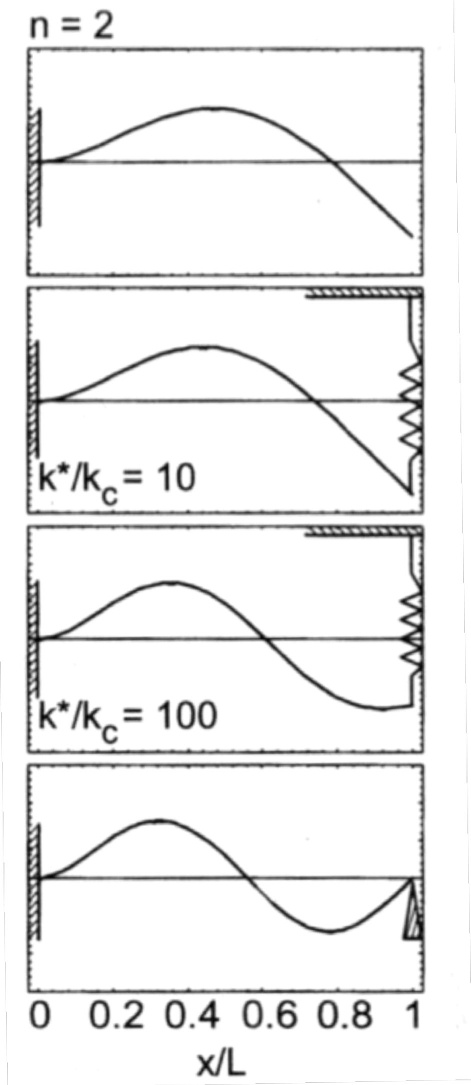
Amplitude of vibration and resonance frequency depend on the contact stiffness k_N… but how?

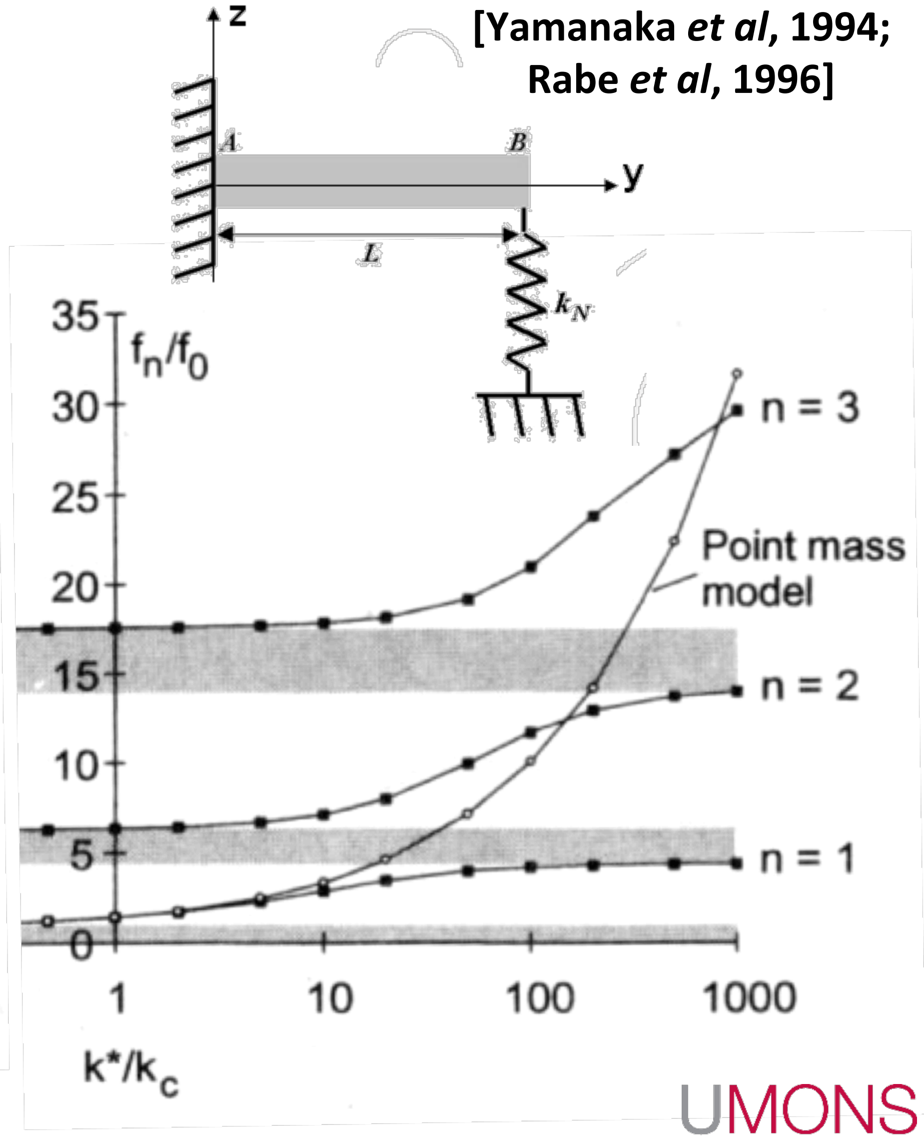
Cantilever dynamic: analytical models

Clamped beam coupled with a normal spring

[Yamanaka *et al*, 1994; Rabe *et al*, 1996]







Cantilever dynamic: analytical models

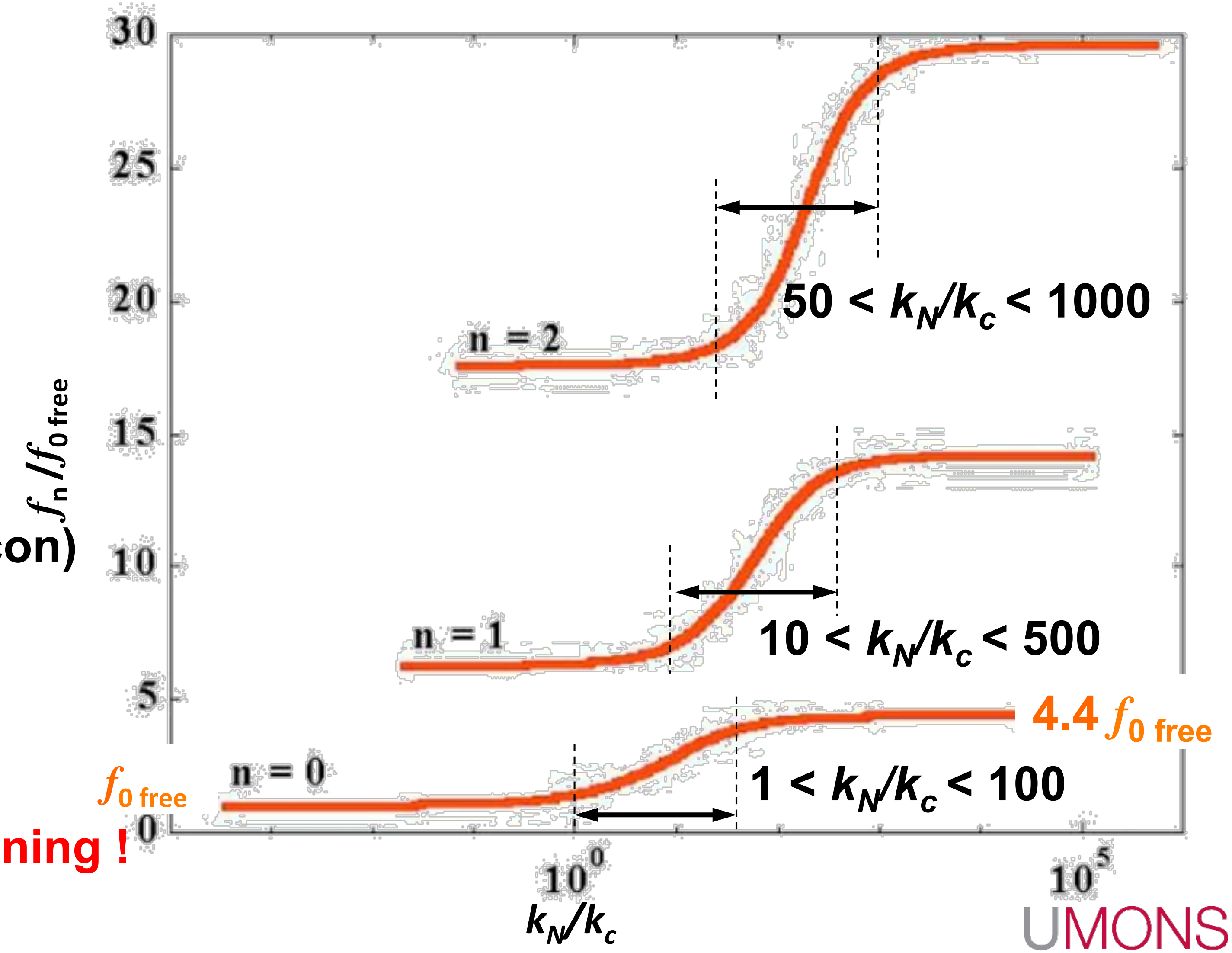
Sensitivity of the cantilever
contact stiffness and considered mode

Example:

Probe: $k_c \approx 3$ N/m,
$R \approx 50$ nm
$F_0 \approx 200$ nN

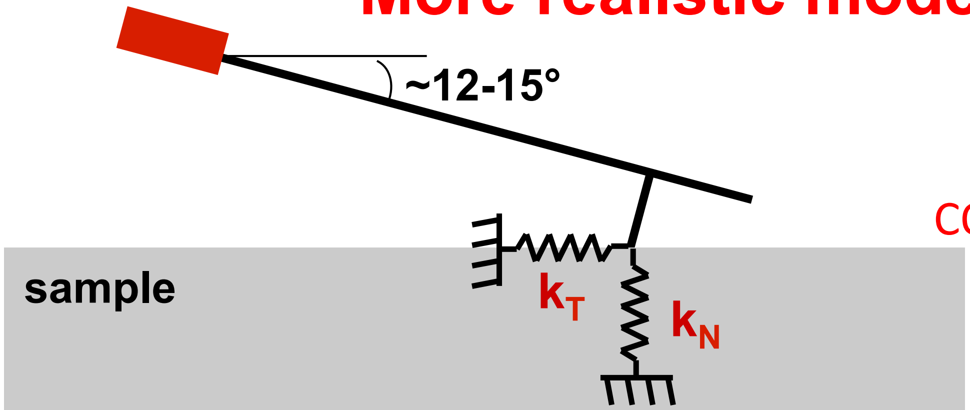
"Soft" sample
(Low T_g polymer)
$k_N \approx 10$ N/m
OK using n = 0

"Hard" sample (Silicon)
$k_N \approx 1000$ N/m
Not OK using n = 0
OK using n > 0
with low applied
static force for scanning !



Cantilever dynamic: analytical models

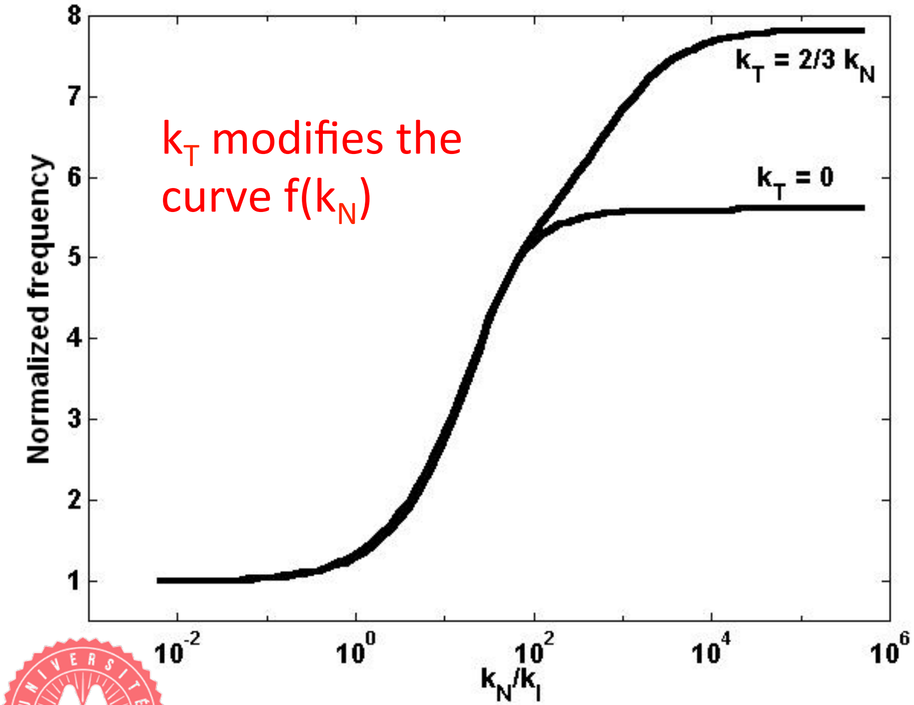
More realistic modelling: cantilever tilt



Normal and tangential components
of the tip displacement

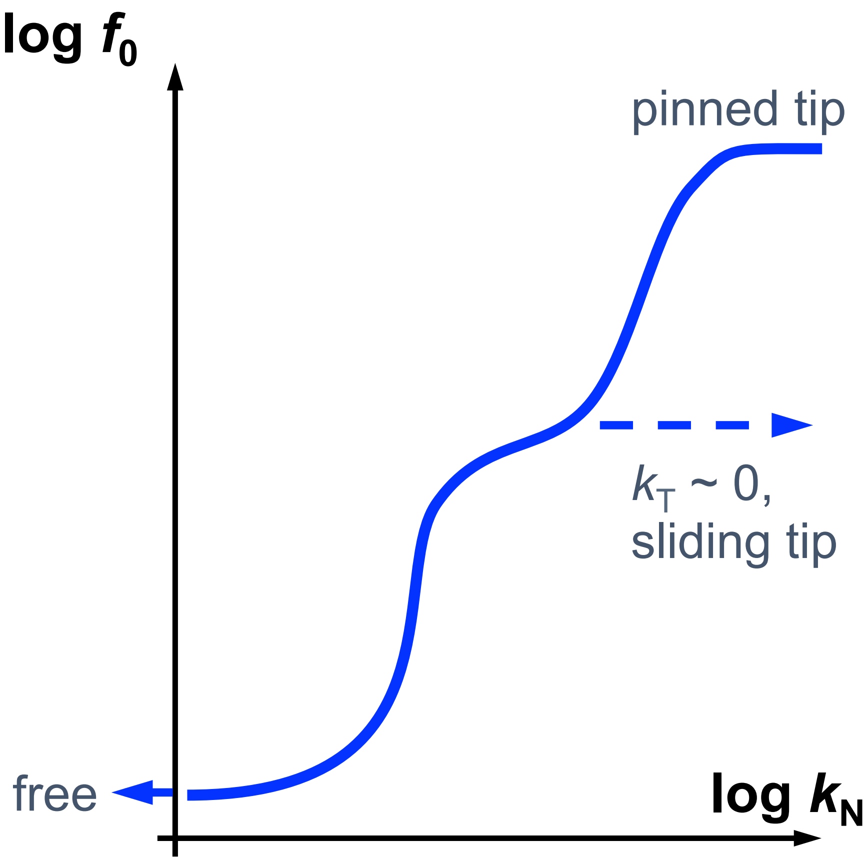
CONTACT = normal spring k_N + tangential spring k_T

2 cases:
- $k_T \neq 0$ + adhesion ⟶ Pinned contact
- $k_T = 0$ or no adh. ⟶ Sliding contact

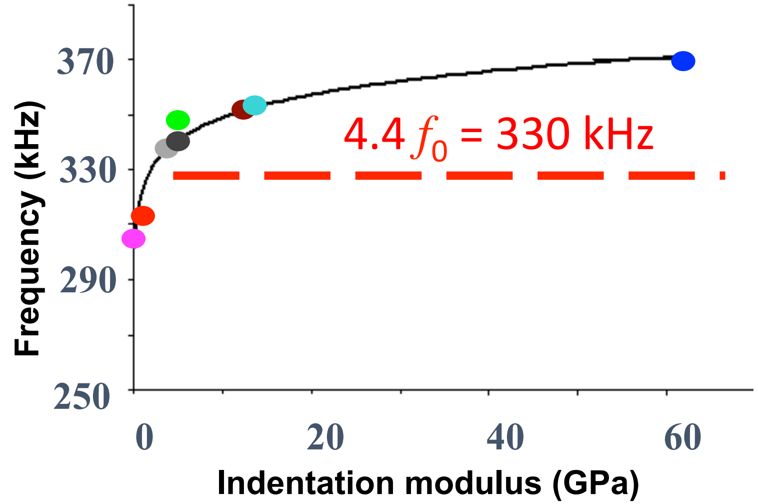


Problem: Analytical model do not allow to take into account the exact geometry of the cantilever (defaults, V-shaped…) and the specificities of the real excitation

Cantilever and tip calibration / reference samples



Nanoworld ARROW FMR:
$k_C \approx 2.8$ N/m, $f_0 = 75$ kHz, $R \approx 55$ nm
Veeco Enviroscope: $F_0 \approx 180$ nN



Material	M_N (GPa)	f_0 (kHz)
PU	0,14	305
PE	1,2	313
PMMA	4,9	350
glass	62	370
LR-White	5	338
S1/LM	5,5	341
S2	13	352
G	15	354

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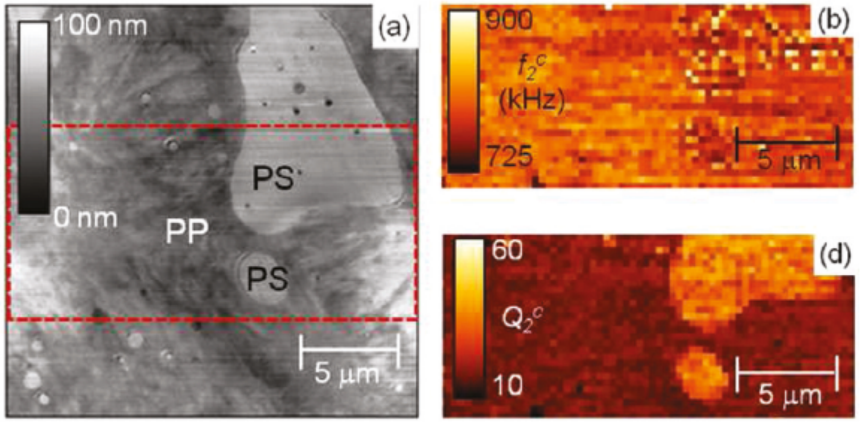
Cantilever dynamic: effect of scanning velocity

Polystyrene polypropylene blend

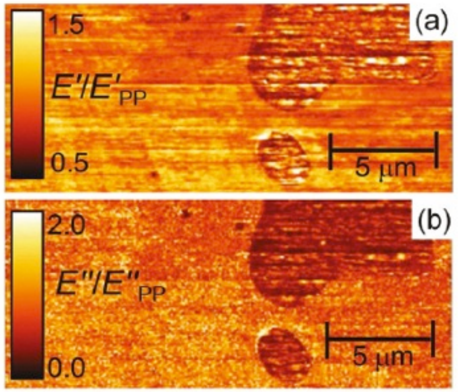
[Killgore et al, langmuir, 27, 13983, 2011]

PS regions: f_2=792.1 ±31.7 kHz, Q_2=37.3 ±5

PP regions: f_2=801.7 ±17.4 kHz, Q_2=18.4 ±2.7

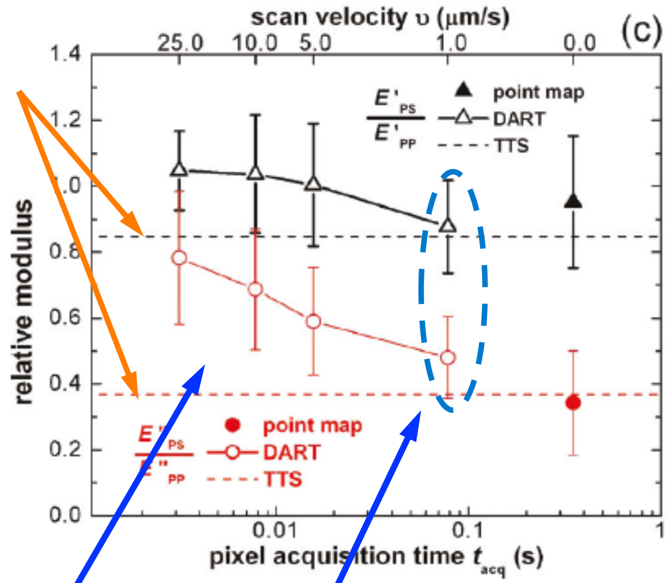


Tracking images



Cantilever modelling
+contact mechanics model

Expected at 1MHz (DMA low freq and low T + time temp superposition)



Higher scan speeds NO ! (contact mechanics or instruments effects)

V = 1 µm/s OK !

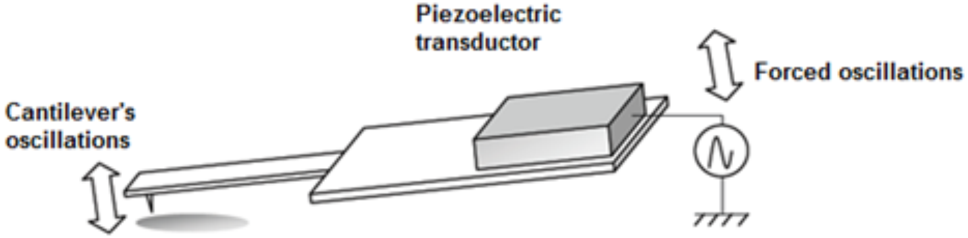
Image duration ~1h
15 µm*15 µm
256*256 pixels

Indirect vs. direct modulation techniques

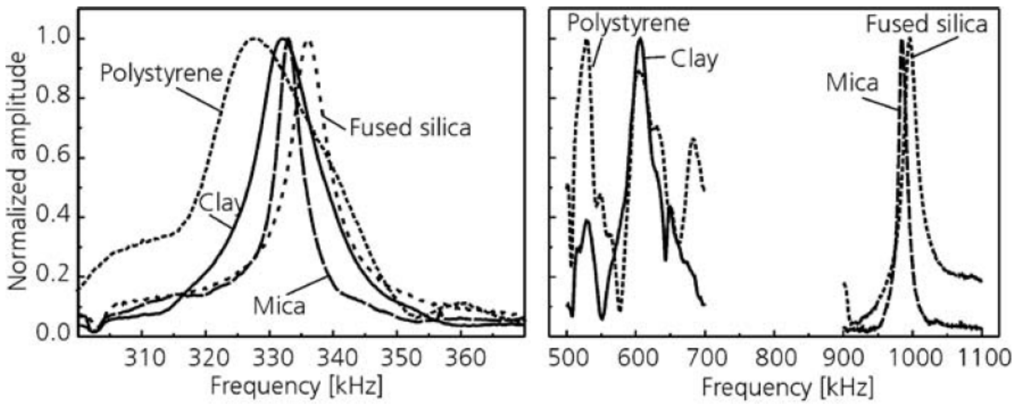
Modulation via the cantilever holder

The cantilever is
<u>not directly</u> excited

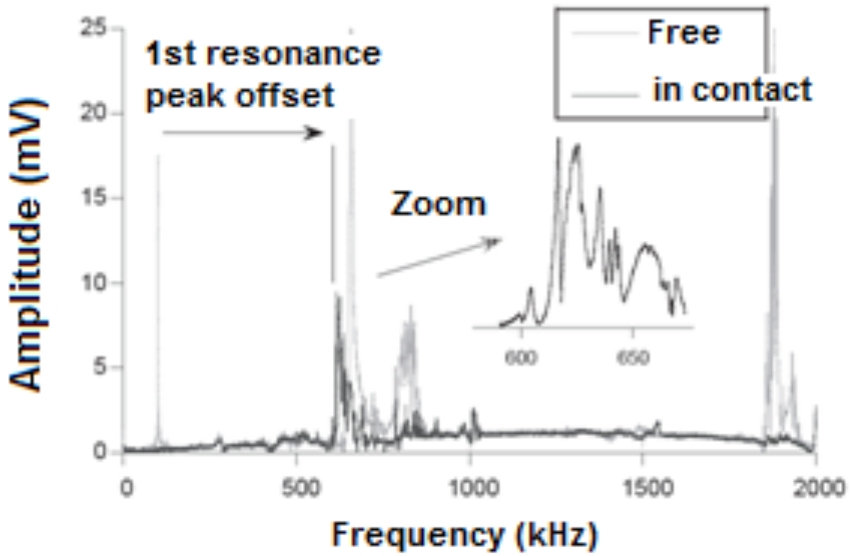
U. Rabe et al *Surf. Interf. Anal.*, 27, 1999
K. Yamanaka et al, *Jpn. J. Appl. Phys.*, 35,1996



CR-AFM excited by means of piezoelectric actuation of the cantilever's holder



Contact-resonance spectra on polystyrene, clay, mica and fused silica . The spectra of the first and the second contact-resonance frequency of a cantilever with a spring constant of 1.5 N/m are shown



Silicon sample

F. Mege, PhD thesis 2011

The sensitivity to "hard" samples is better using higher harmonics

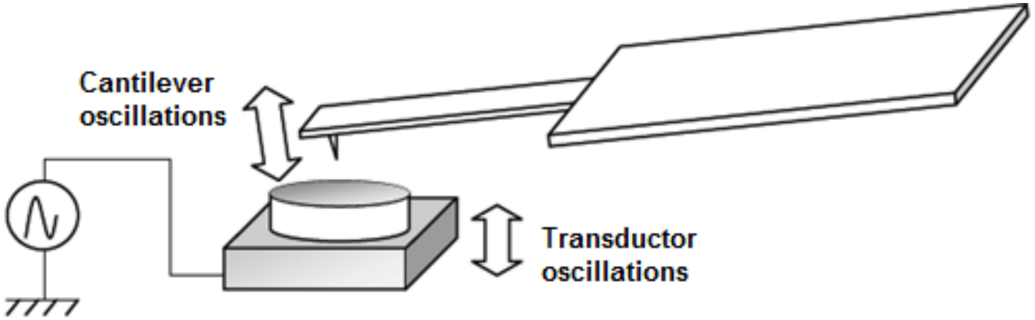
Prasad et al (2002) Geophys Research Lett 29:13-1

Indirect vs. direct modulation techniques

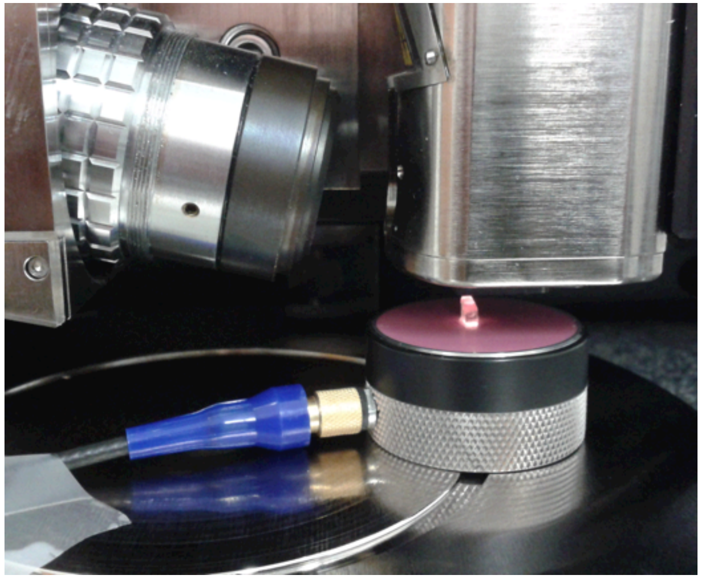
The cantilever is <u>not directly</u> excited

Modulation via the sample holder

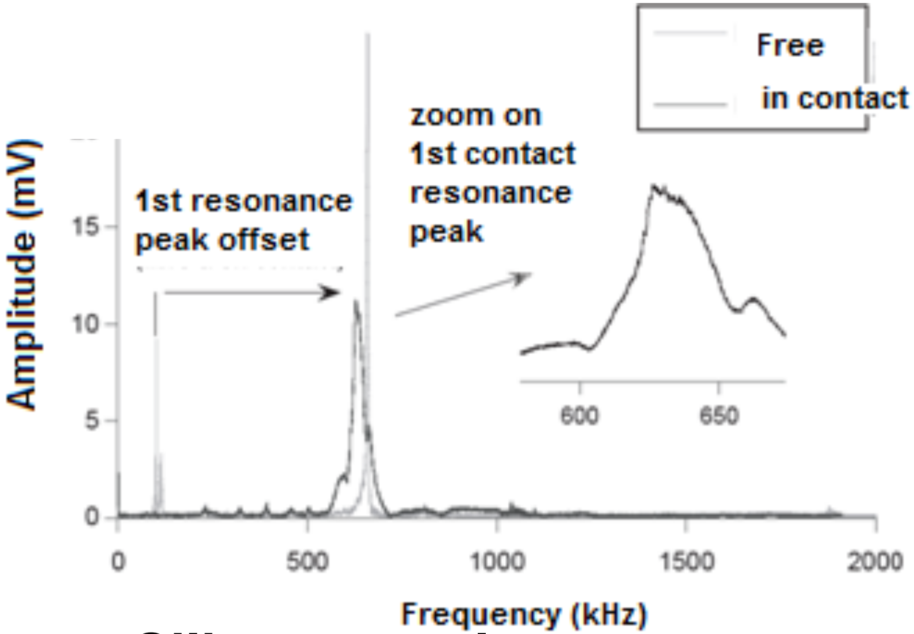
U. Rabe and W. Arnold., *Applied Physics Letters*, 64, 1994
U. Rabe et al, *Review of Scientific Instruments*, 67, 1996



CR-AFM excited via a piezo transductor located under the sample



AFAM (Atomic Force Acoustic Microscopy)



Silicon sample

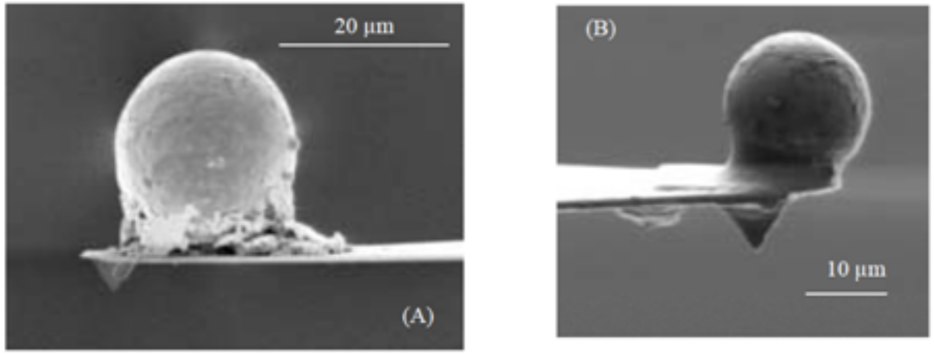
F. Mege, PhD thesis 2011

Indirect vs. direct modulation techniques

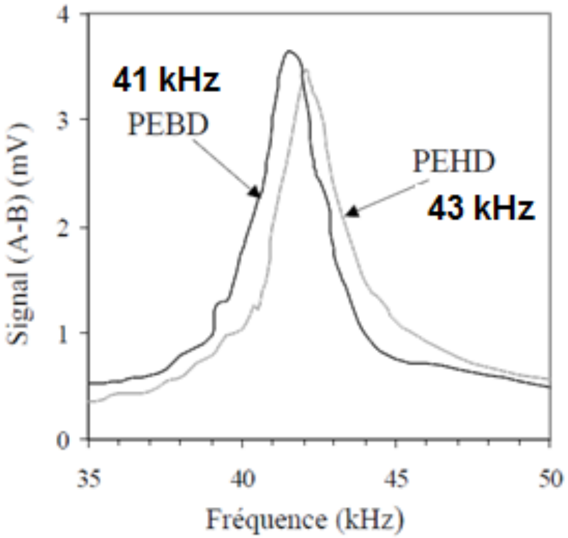
The cantilever is <u>directly</u> excited

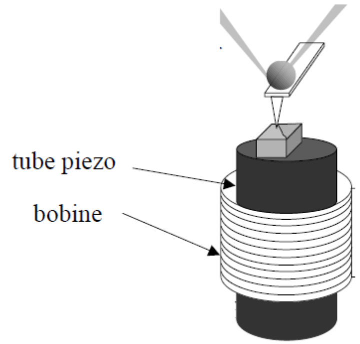
Magnetic excitation

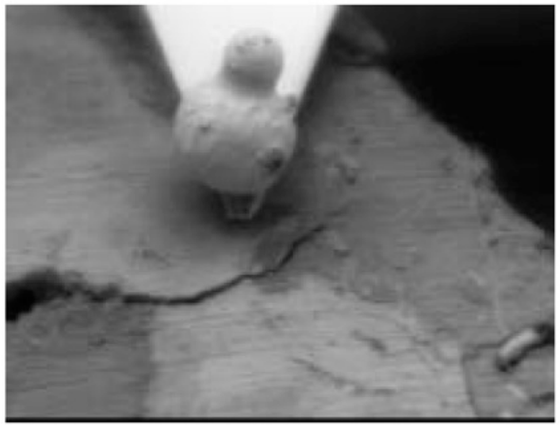
O. Piètrement, PhD Thesis (2000)



Cantilevers with magnetic particles glued at their extremity







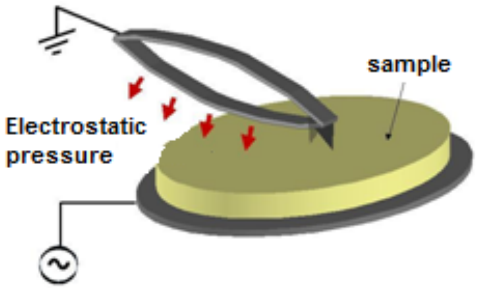
Indirect vs. direct modulation techniques

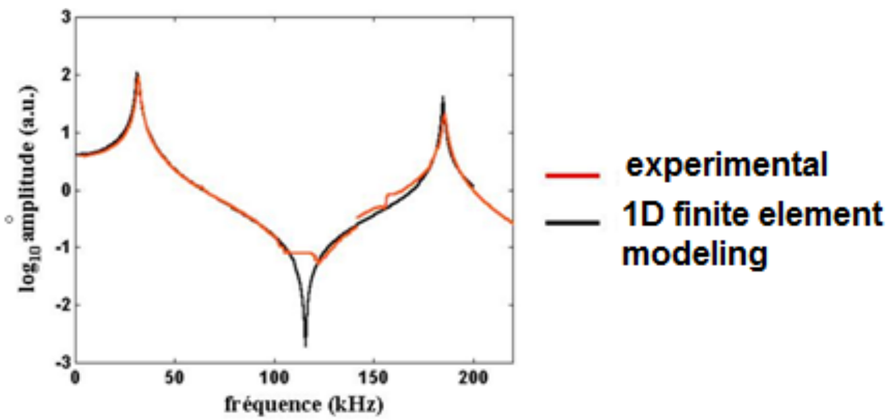
The cantilever is <u>directly</u> excited

Electrostatic excitation

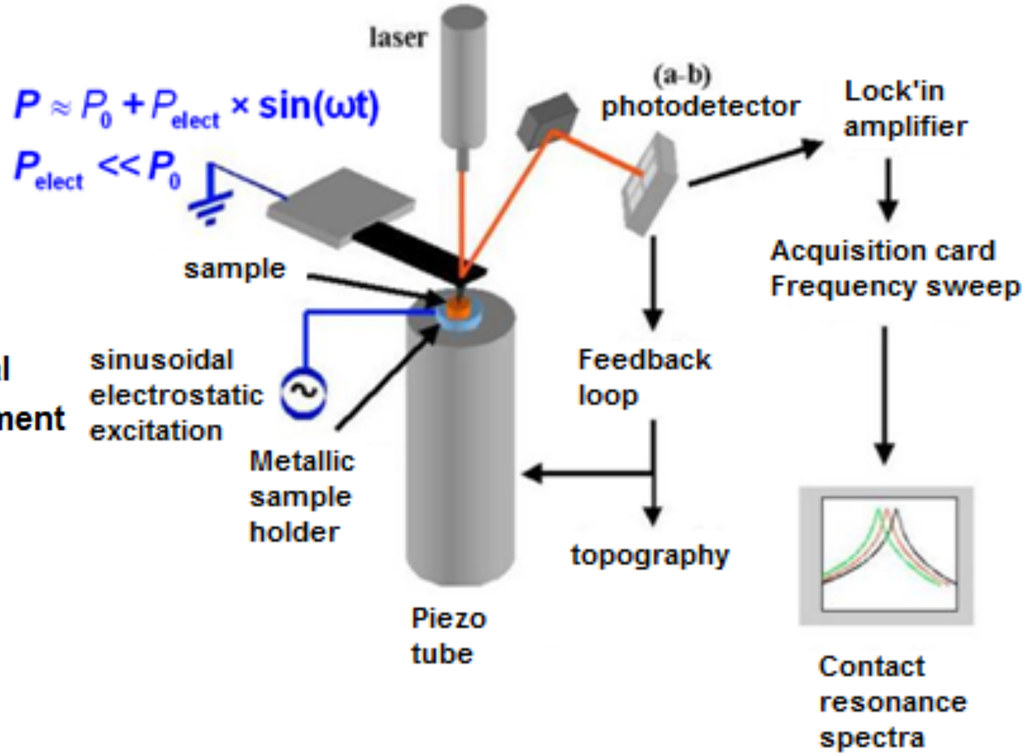
$$F_{élec} = \frac{1}{2} V^2 \frac{\partial C}{\partial z} = F_0 + F_\omega + F_{2\omega}$$

S. Cuenot, PhD thesis 2002
R. Arinero, PhD Thesis 2003



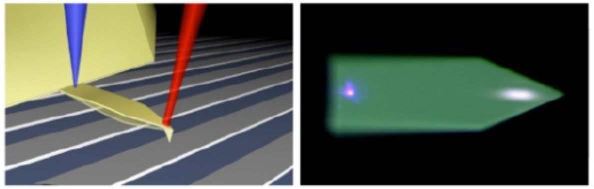


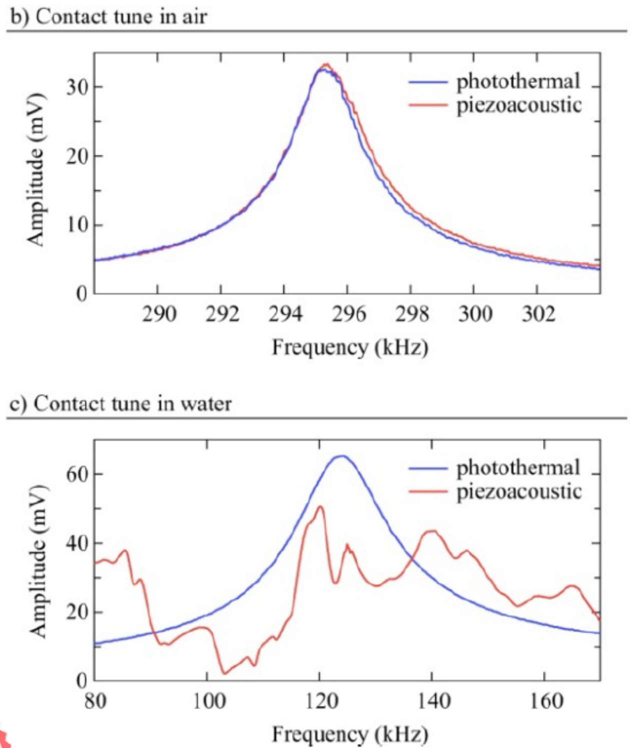
Example of free cantilever vibrating in the air



Indirect vs. direct modulation techniques

The cantilever is <u>directly</u> excited





Photothermal excitation

Imaging in Air and Water

Amplitude cantilever oscillation is induced by modulating the blue laser power that is focused at the base of the cantilever

Advantage of using photothermal actuation becomes clear when the contact resonance tunes are performed in water

[Kocun *et al*, 2015] - Asylum

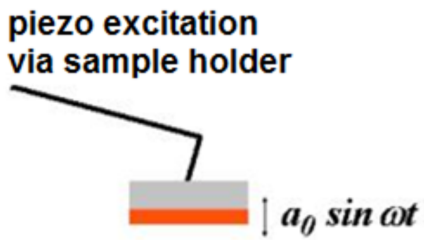
Indirect vs. direct modulation techniques

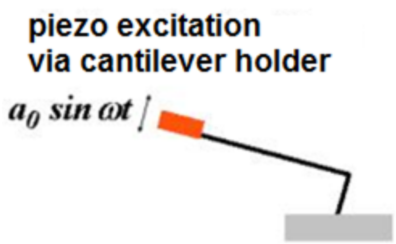
SUMMARY

Indirect modulation

Possible mechanical coupling effects

Wide bandwidth

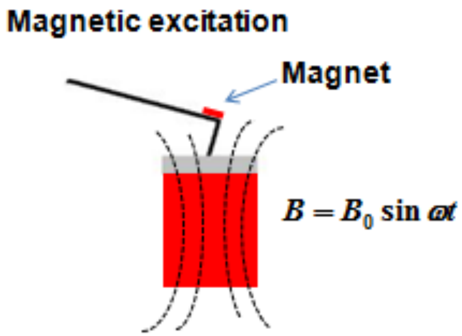


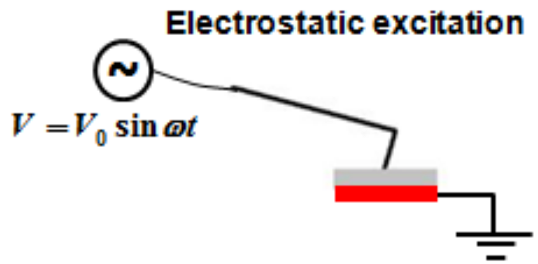


Direct modulation

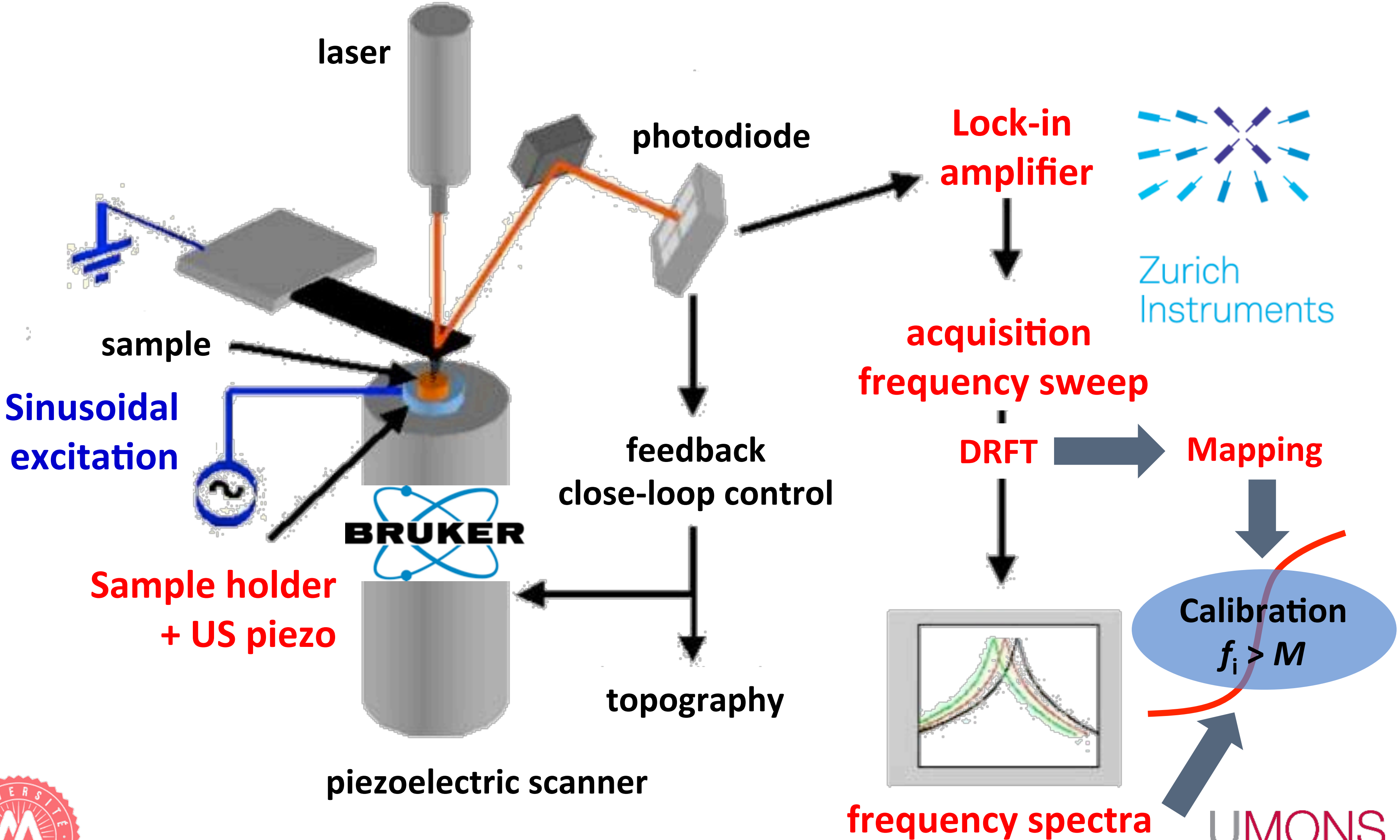
No mechanical coupling effects

Limited to low frequencies (< 1 MHz)





Contact Resonance-AFM principle [Arinero and Lévêque, Rev. Phys. Instr., 2003] with Dual Resonance Frequency Tracking [Gannepalli et al., Nanotechnol. 2011]



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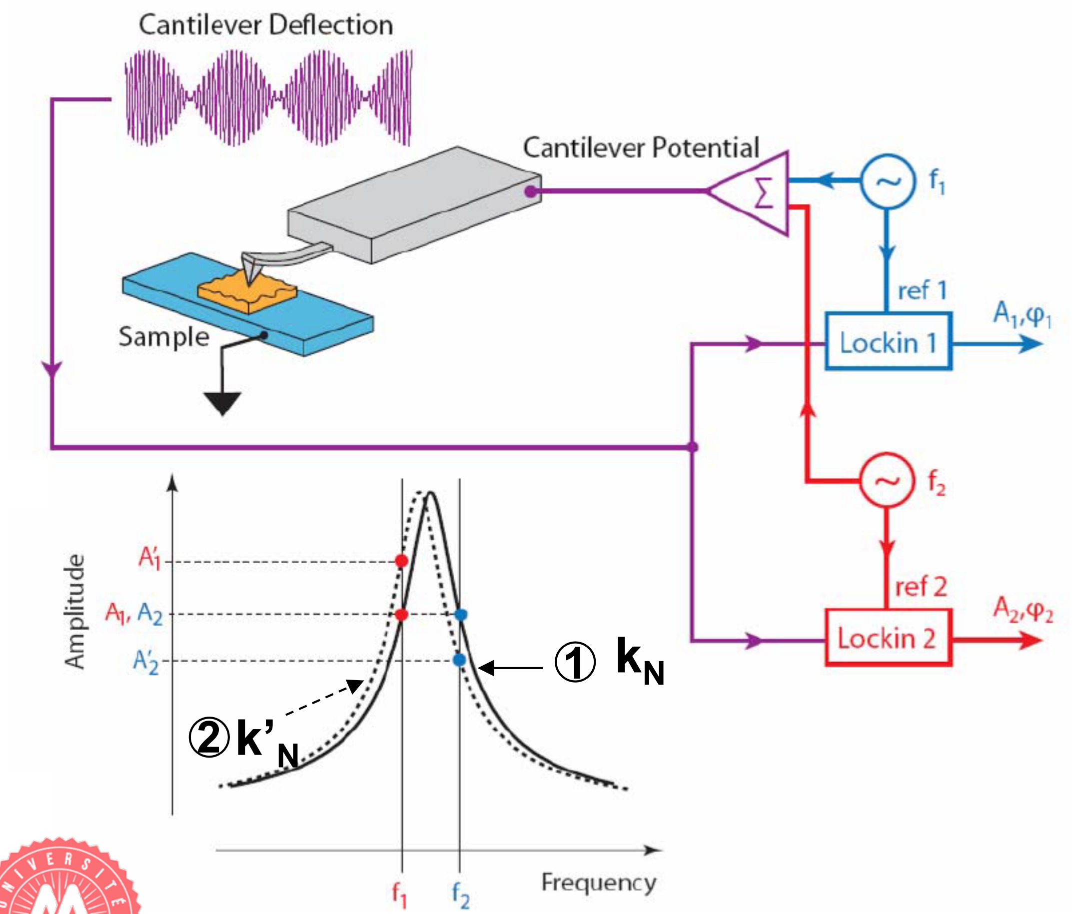
Measuring the resonance frequency

Dual Resonance Frequency Tracking (DRFT)

B J Rodriguez *et al* 2007 *Nanotechnology* 18



Use of 2 lock-in amplifiers

Modulation = sum of two frequencies f_1 and f_2 near to resonance

① Stiffness k_N

$$A_1 = A_2 \qquad f_c = \frac{f_1 + f_2}{2}$$

② Stiffness k'_N

$A'_1 > A'_2 : k'_N < k_N$

$A'_1 < A'_2 : k'_N > k_N$

Resonance tracking:

$\Delta f = f_1 - f_2 = \text{constant}$

+ feedback loop to maintain $A'_1 = A'_2$

$$f'_c = \frac{f'_1 + f'_2}{2}$$

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Measuring the resonance frequency

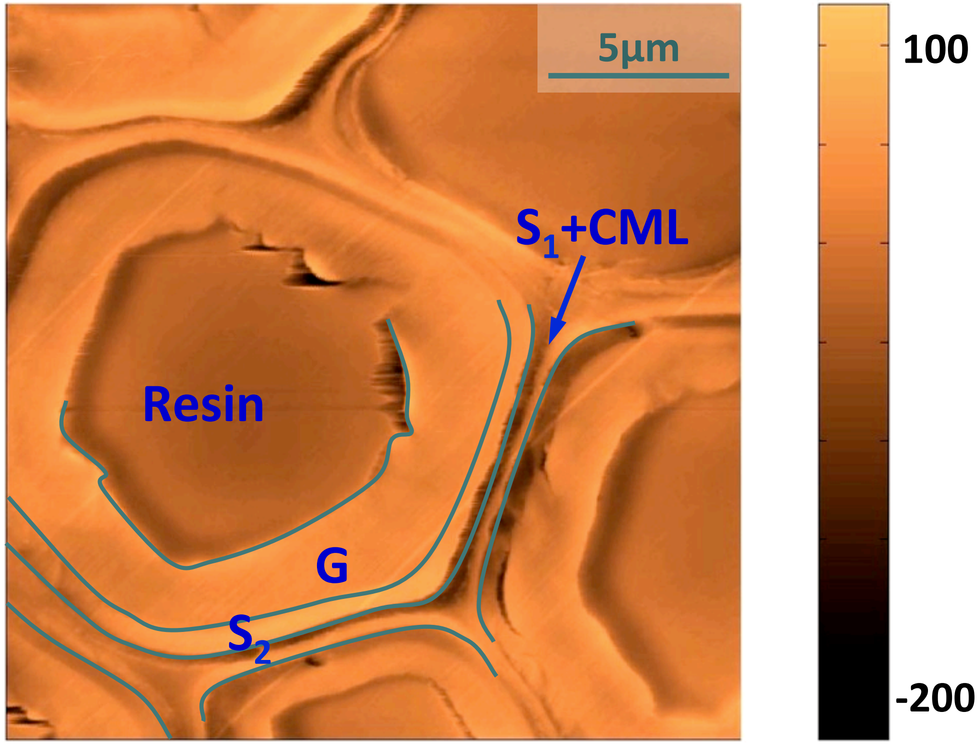
Methods	What it does	Benefits	Disadvantages
Fixed frequency[2]	The cantilever response is measured at a fixed frequency, which varies as the contact resonance frequency shifts.	Simple to implement and produces elastic contrast images.	Produces only qualitative results since the frequency shift itself is not measured. Contrast is lost if the peak shifts too far from the selected frequency.
PLL frequency tracking[1]	A phase-locked loop (PLL) uses the phase of the cantilever response to track the contact resonance frequency.	The actual contact resonance frequency is tracked.	Difficult to tune the PLL to achieve stable frequency tracking due to spurious phase shifts in the response. Does not measure the Q of the resonance.
Frequency sweep (chirp)[3,4,5]	A frequency sweep (chirp) is done at each point. The cantilever response is Fourier analyzed to recover the full frequency response.	Measures the entire frequency response, so both the frequency and Q are obtained. Additional analysis is possible based on more complex models.	Mapping is quite slow when collecting large numbers of pixels. Each sweep must be done slowly enough for the cantilever to respond (rate limited by Q).
DART[6,7,8] (DRFT)	The amplitude and phase response at two frequencies (bracketing the contact resonance) is measured, which enables the contact resonance to be tracked.	Provides both the contact resonance frequency and Q. The tracking is extremely fast, so DART imaging can be done at normal imaging rates.	The full response is not measured, so analysis is more limited than frequency sweep or band excitation methods.
Band Excitation[8,9]	A continuous band of frequencies is excited. The cantilever response is Fourier analyzed to recover the full frequency response.	The entire frequency response is measured. By exciting the entire band at once, it is much faster than other full spectrum techniques (e.g. sweep).	Data transfer bandwidth limitations make the current implementation significantly slower than DART. Future speed improvements are possible.

From Asylum (CR-AFM application note)

Some practical examples

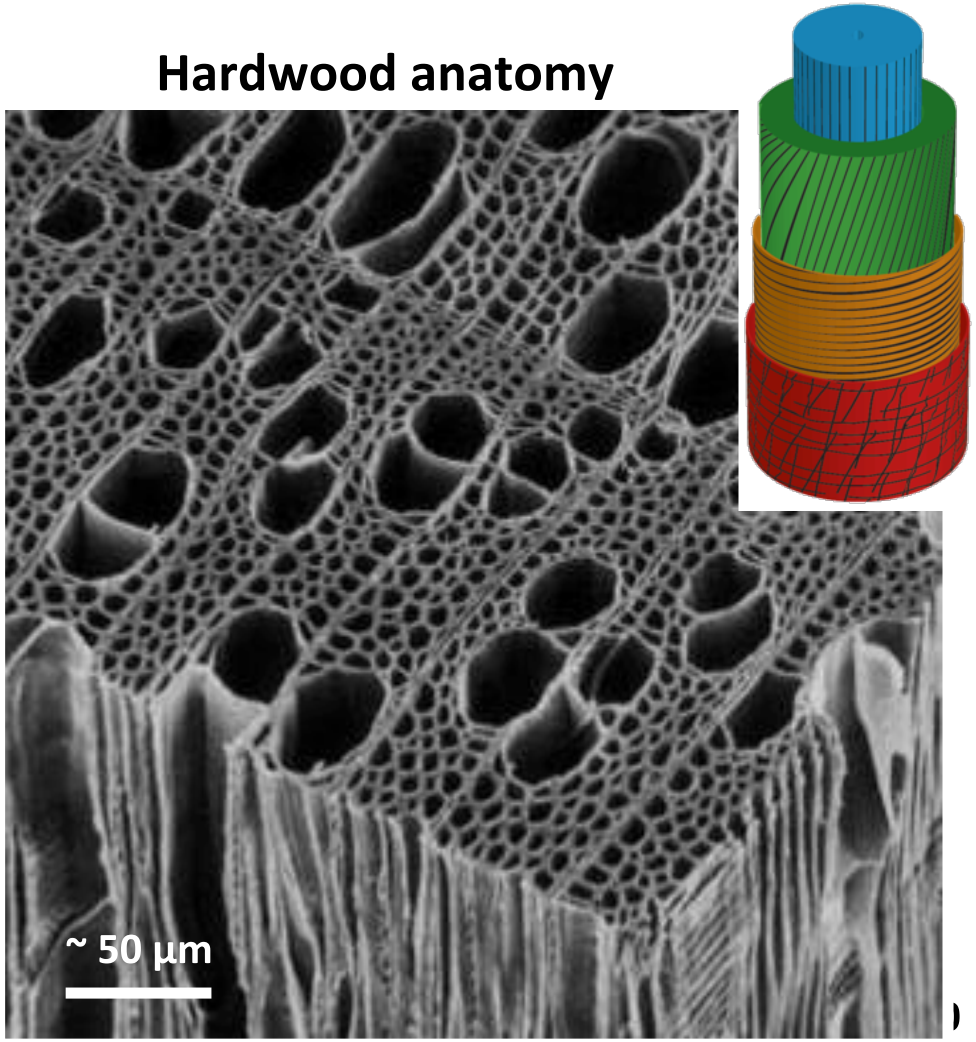
Chestnut tension wood

Arnould and Arinéro, Composites A 74 (2015) 69-76



Topography (nm)

Hardwood anatomy



Frequency spectra (kHz)

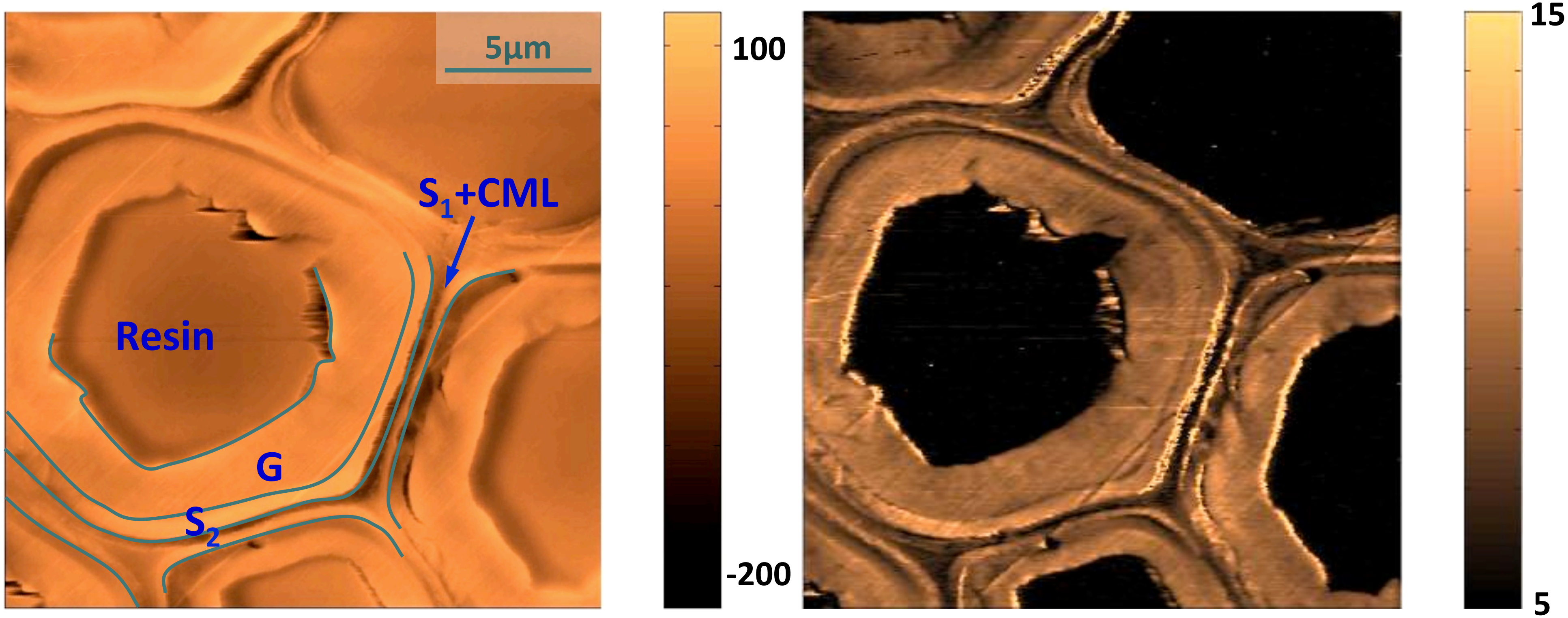
Nanoworld ARROW FMR, $k_C \approx 2.8$N/m, f_0 = 75kHz, $R \approx 55$nm

Veeco Enviroscope, $F_0 \approx 180$nN

Some practical examples

Chestnut tension wood

Arnould and Arinéro, Composites A 74 (2015) 69-76



Topography (nm) **Contact modulus (GPa)**

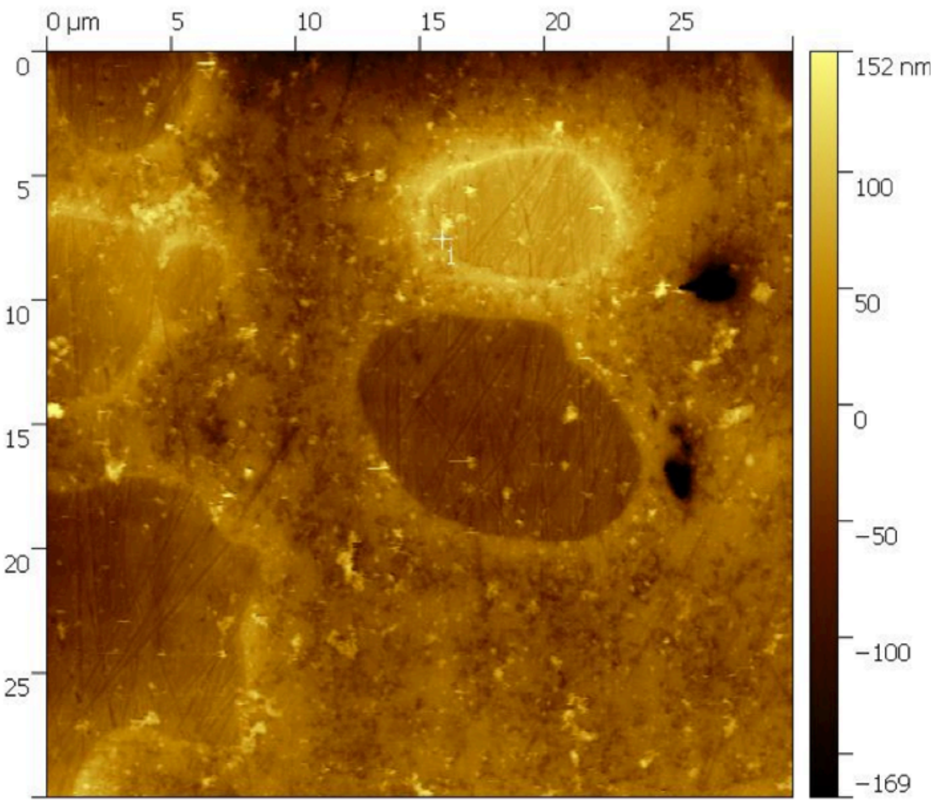
Nanoworld ARROW FMR, $k_c \approx 2.8$N/m, f_0 = 75kHz, $R \approx 55$nm

Veeco Enviroscope, $F_0 \approx 180$nN

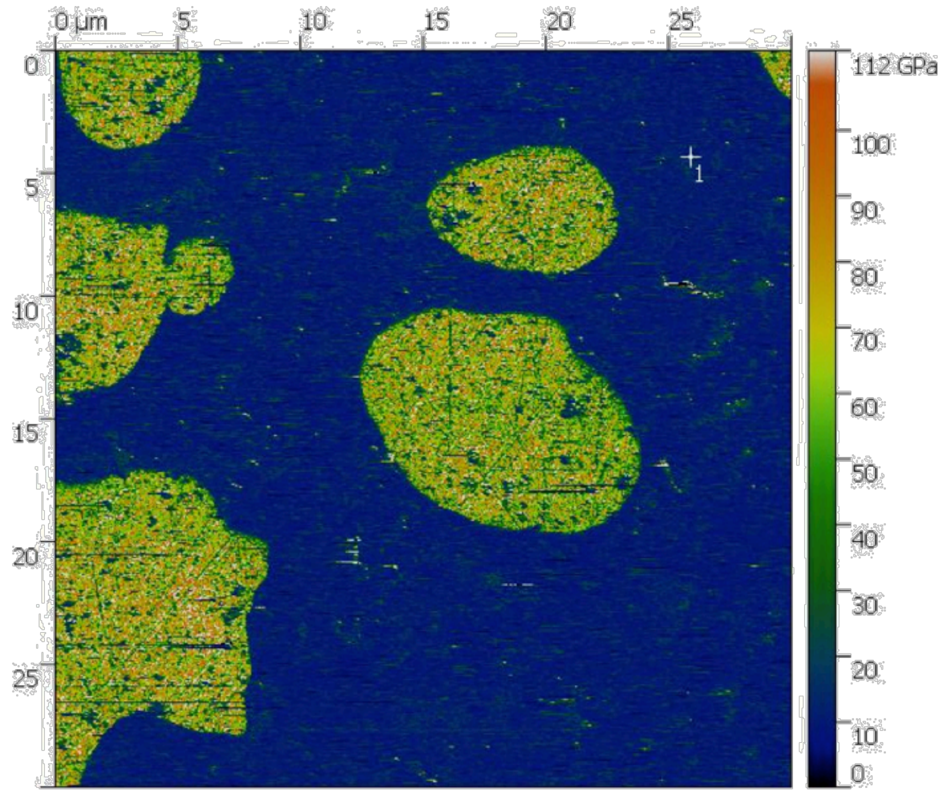
Some practical examples

Hysol EA9394 epoxy adhesive/Al particles (using DFRT)

Jumel et al, 5th Int Symp Adv Sci Technol Exp Mech 2010; M. Ramonda, atelier RéMiSoL DFRT nanoméca



Topography (nm)



Contact modulus (GPa)

Partial conclusions

- Versatility (air/liquid, bending/torsion, tomography, ...)
- Ease of implementation + cheap
- "High" range of material stiffness with the same cantilever and reduce applied force

But :

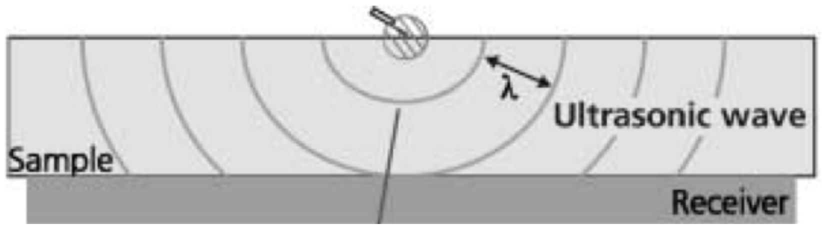
- Calibration vs. analytical model
- No measurement of F_{adh}!! (tip coating to avoid it...)
- Interpretation and use of Q??
- Tip wear (hard coating or high R)
- Acquisition time
- High order eigen-modes not so easy to measure...
- High frequencies / viscoelastic material

[Marinello *et al*, 2010]

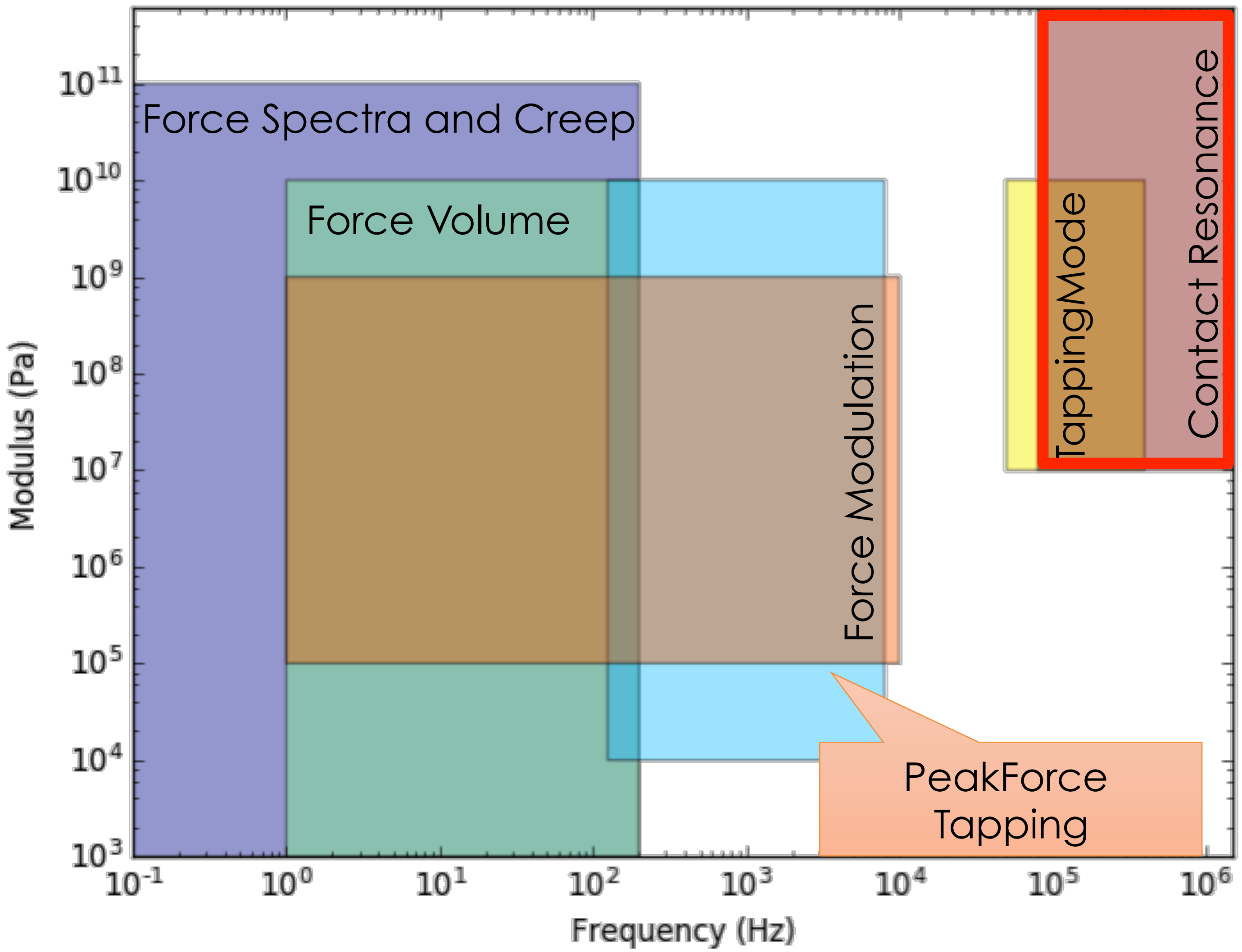
Variability of different parameters for different measurements with the same probe and for different probes (– negligible, + medium, ++ high).

	Variability	
	For a given probe	Between probes
Length L_1	–	++
Tip height h	+	+
Incidence angle α_0	+	+
Tip radius	++	++
Resonance frequency	–	++
Cantilever stiffness	–	++

[Hirsekorn *et al*, 2001]

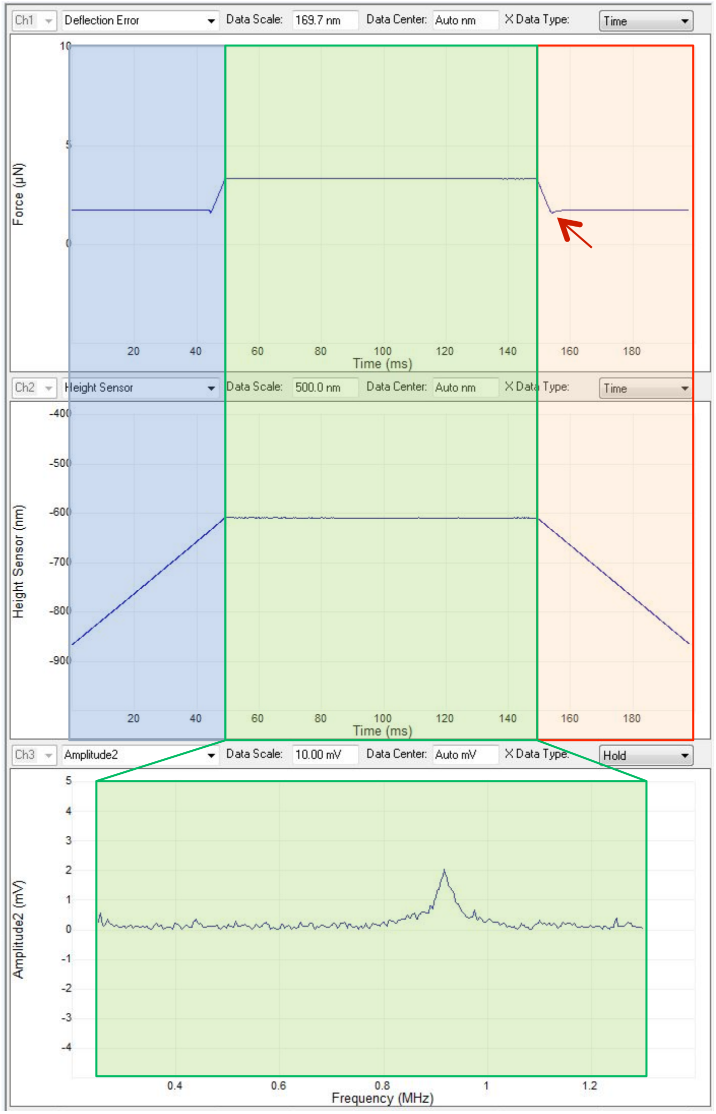


AFM frequency and modulus ranges
Contact Resonance



Peak Force Tapping - Contact Resonance

- CR is based on *FAST*Force Volume
  - Provides standard force curve for comparison for each pixel in map
    - Approach
    - Hold Force and sweep frequency
    - Retract
  - **More repeatable**: lateral force on tip is minimized, reducing tip wear
  - **More information**: allows measurement of Adhesion force for each pixel better contact mechanics modeling
  - **Real-time maps** of both raw data and mech props (E', E'', loss tan)
  - **Whole sweep is saved**, allowing detection of artifact peaks, etc. (unlike freq tracking methods like DART)



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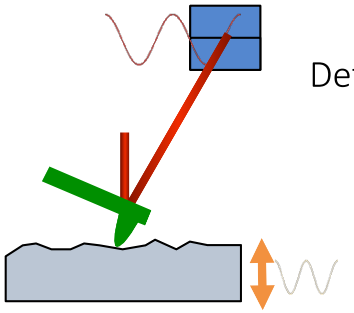
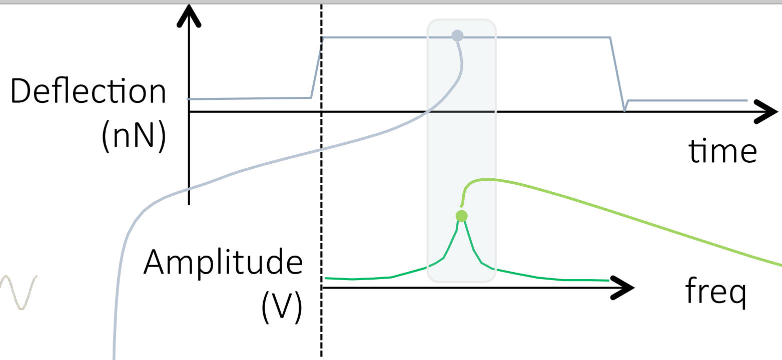
Contact Resonance

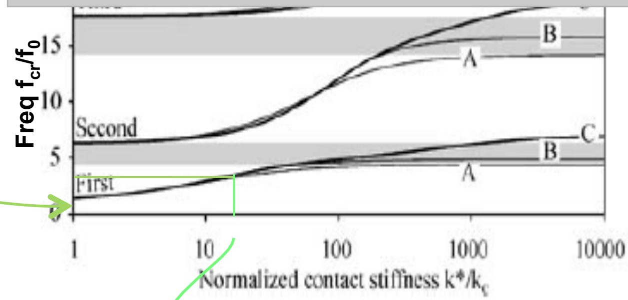
From Frequency and Deflection to modulus

1. Measure frequency **(fcr)** & Deflection





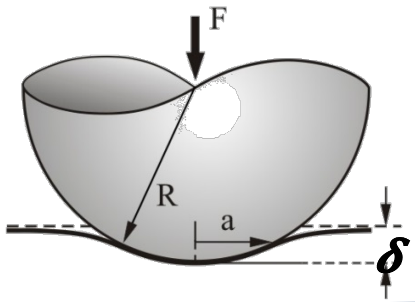
2. Apply cantilever dynamics to calculate k*/kc from fcr/f0



3. Convert Deflection to Force using deflection sensitivity & spring constant (kc)

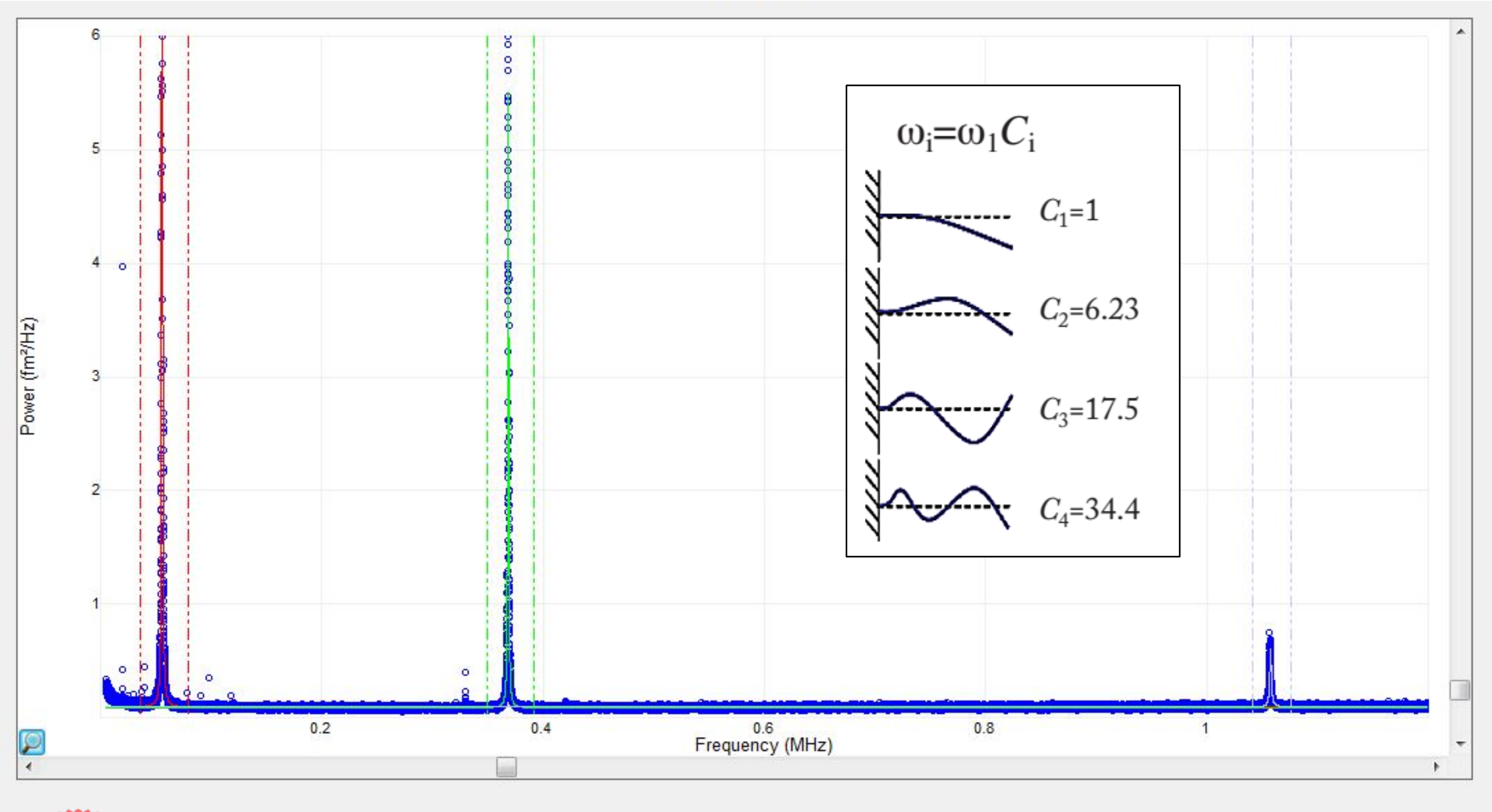
4. Apply Contact Mechanics to calculate E* from Radius (R), Force (F) and contact stiffness (k*)

Hertzian Contact

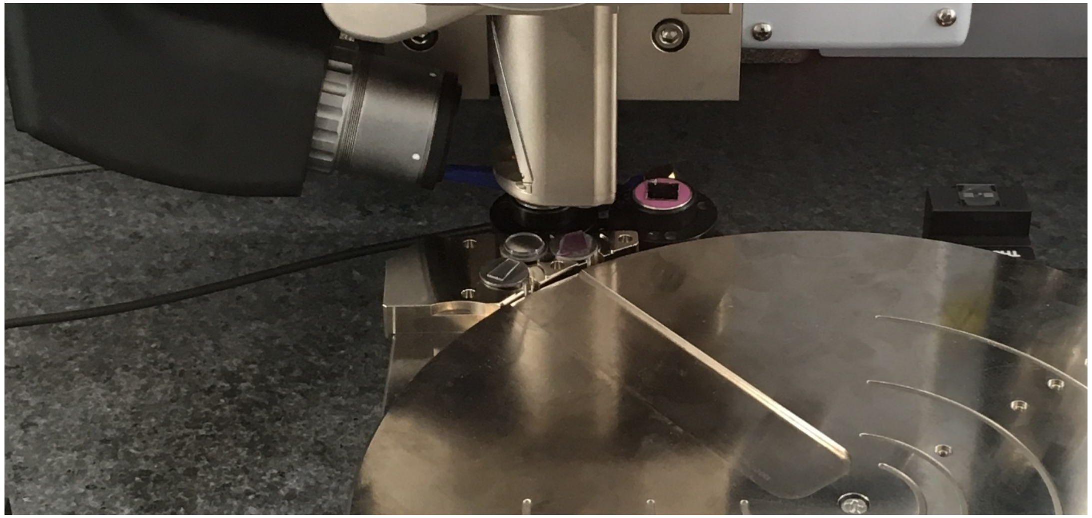


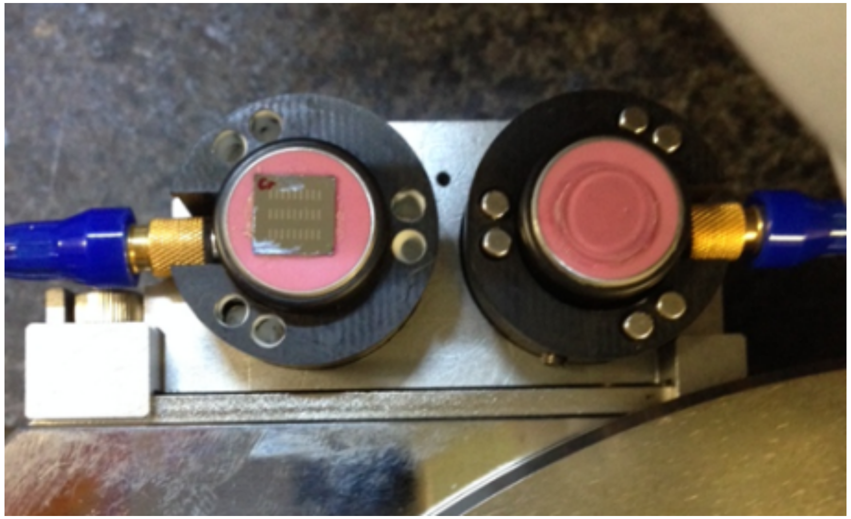
$$E^* = \sqrt{k^{*3}/6RF}$$

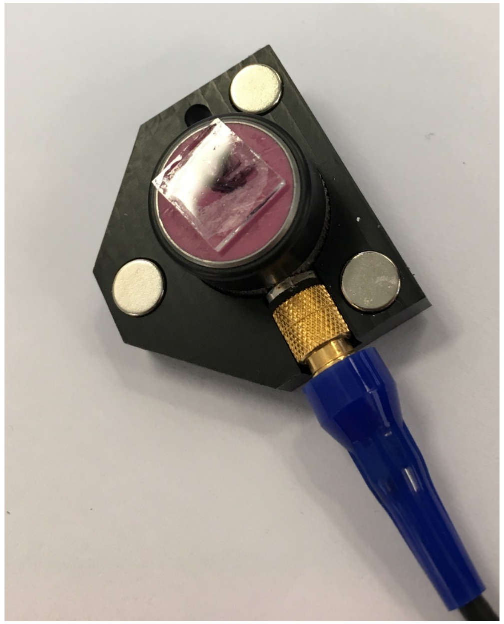
Peak Force Tapping - Contact Resonance

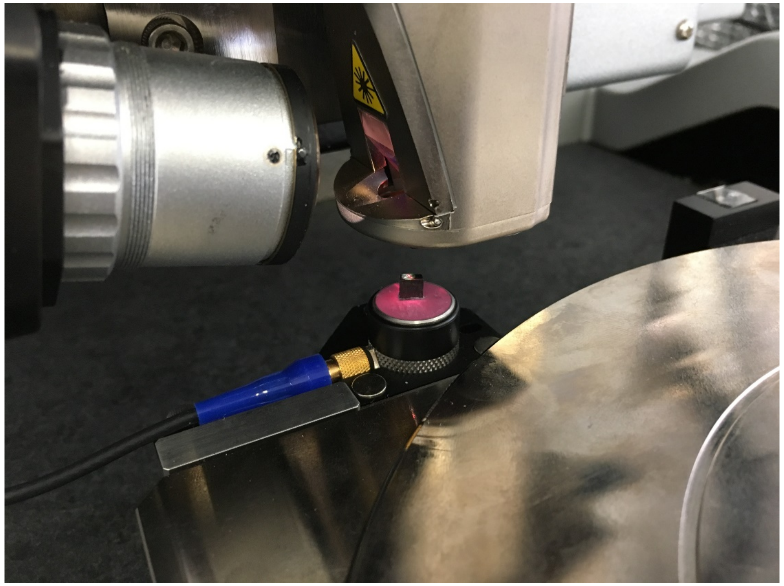


Peak Force Tapping Contact Resonance









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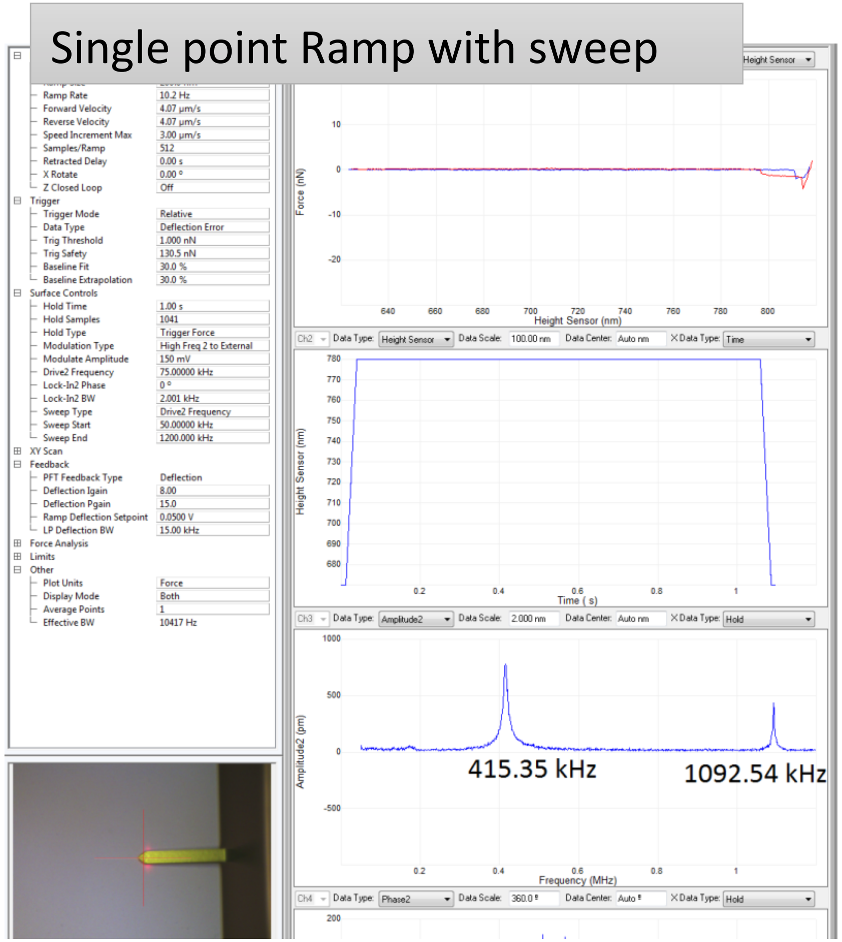
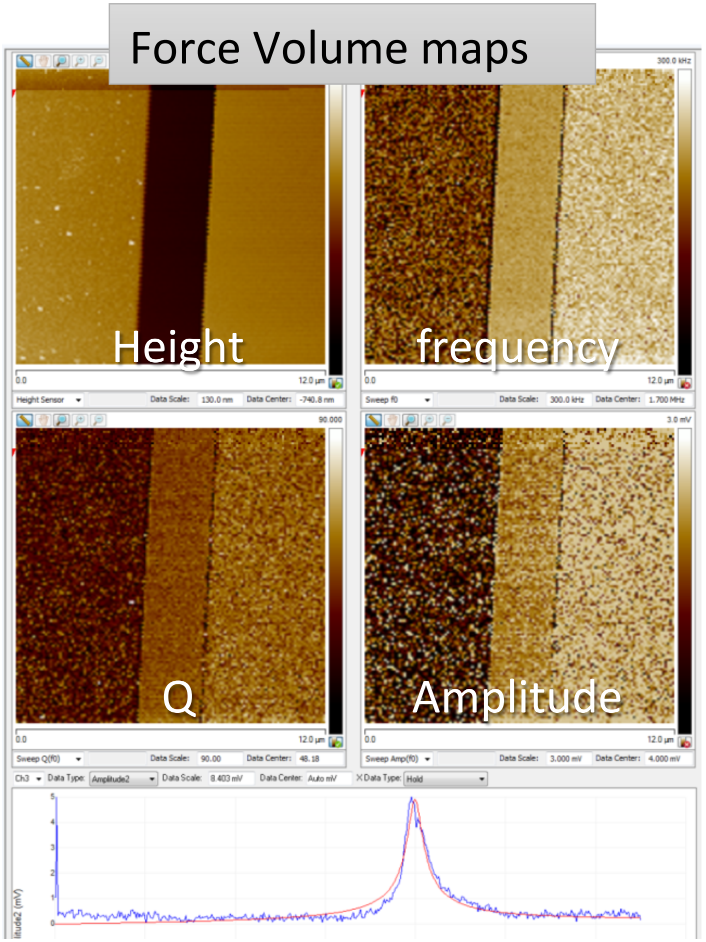
Real-time Contact Resonance Sweeping

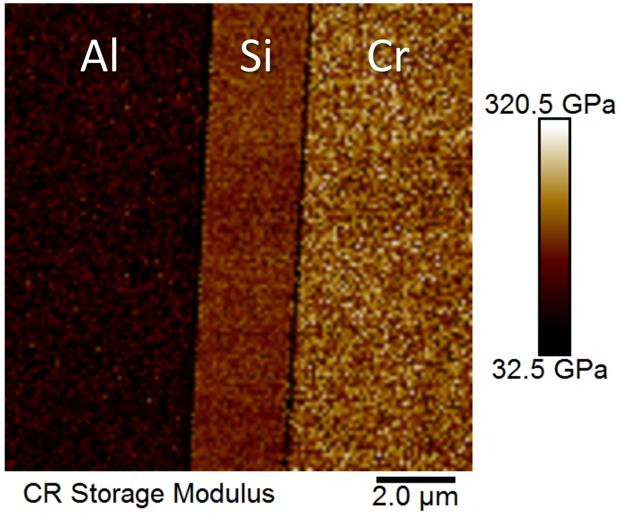
Force Volume for mapping, Ramp for single points



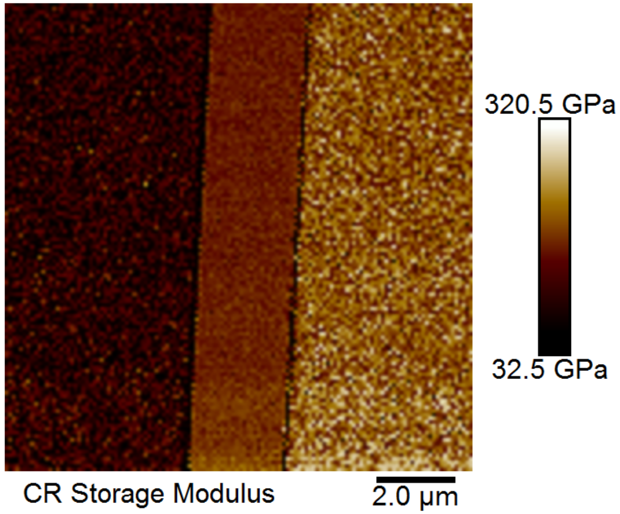


In Force Volume: Ramp and hold trigger force, then sweep at each pixel.

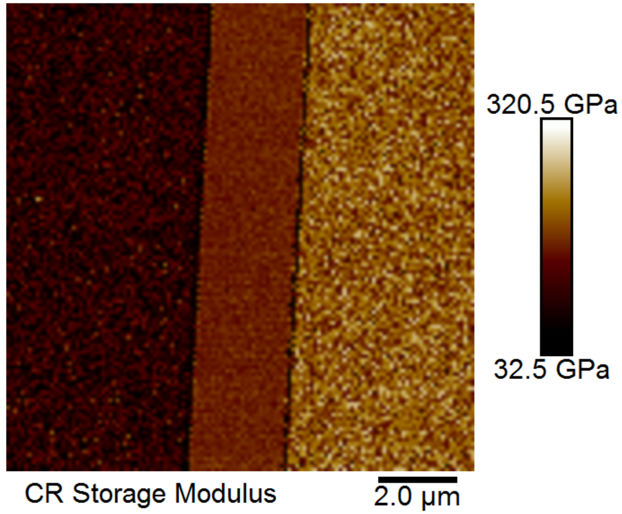
Contact Resonance



Load=200nN
Si: 165±15 GPa
Al: 85±24 GPa
Cr: 192±31 GPa

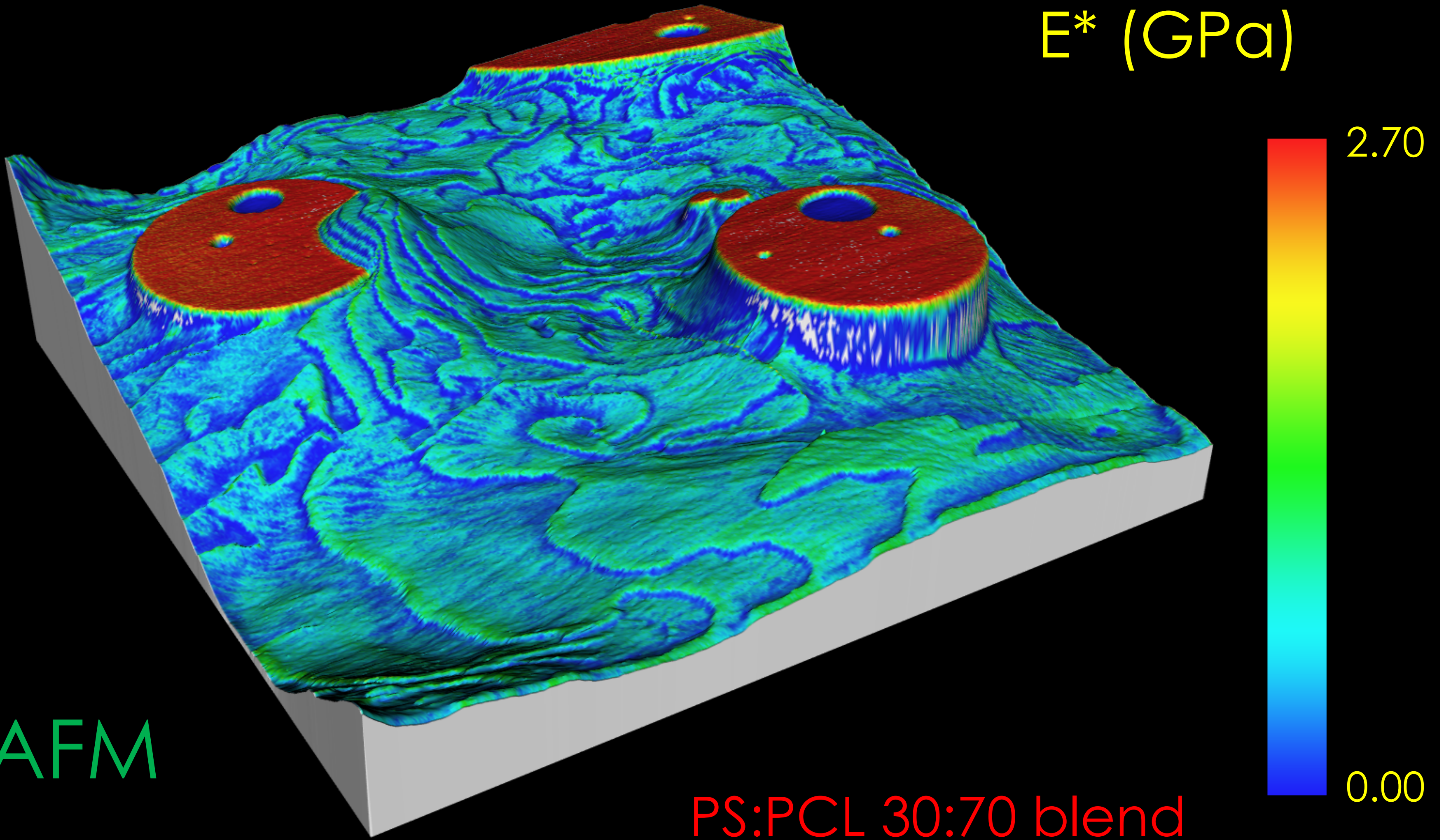


Load=500nN
Si: 165±10 GPa
Al: 101±29 GPa
Cr: 201±30 GPa



Load=1000nN
Si: 165±7 GPa
Al: 103±25 GPa
Cr: 202±26 GPa

Water on Mars ...

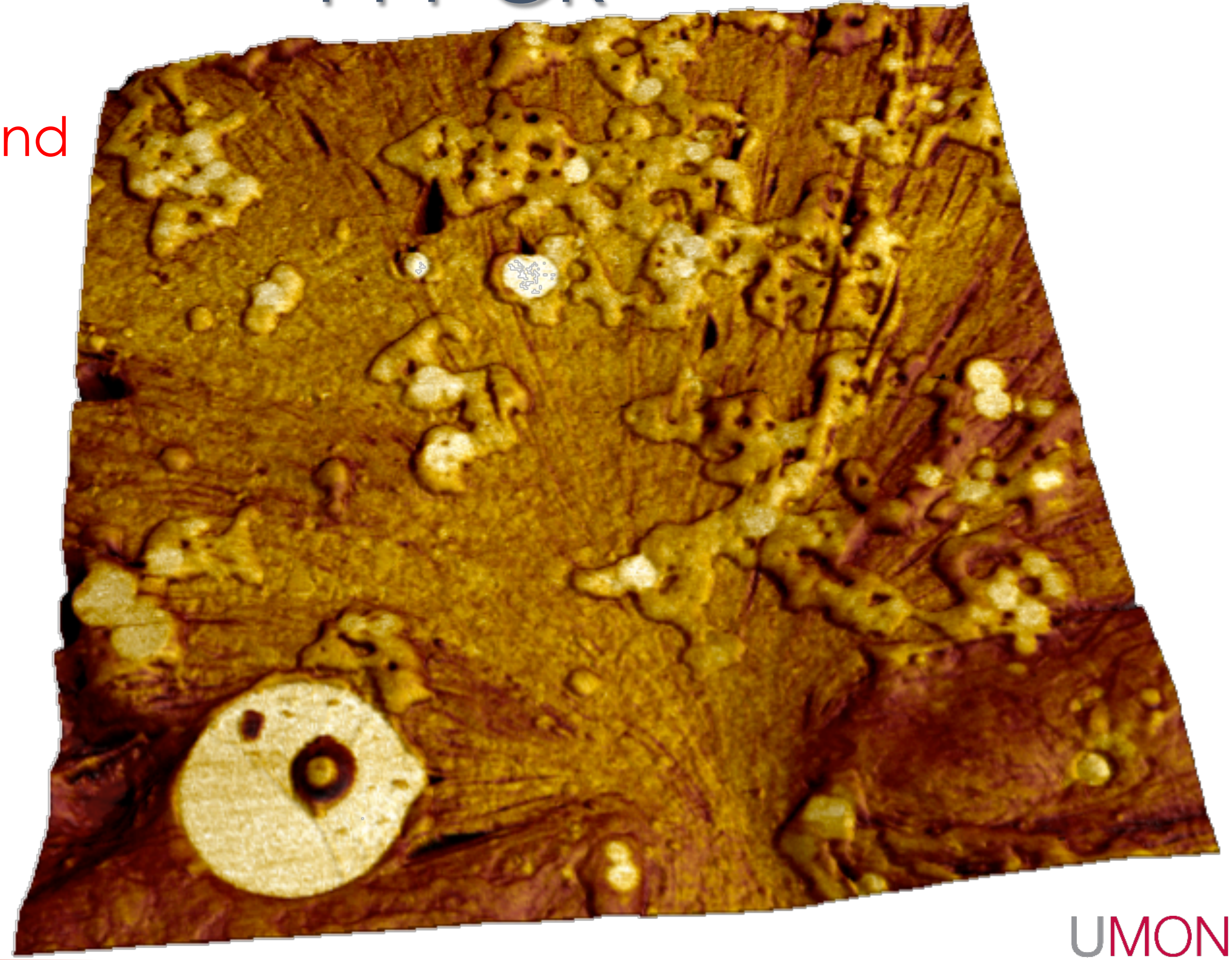


ImAFM

Soft Matter (2016), 12, 619.

Peak Force Tapping Contact Resonance PFT-CR

PCL-PS
Polymer blend



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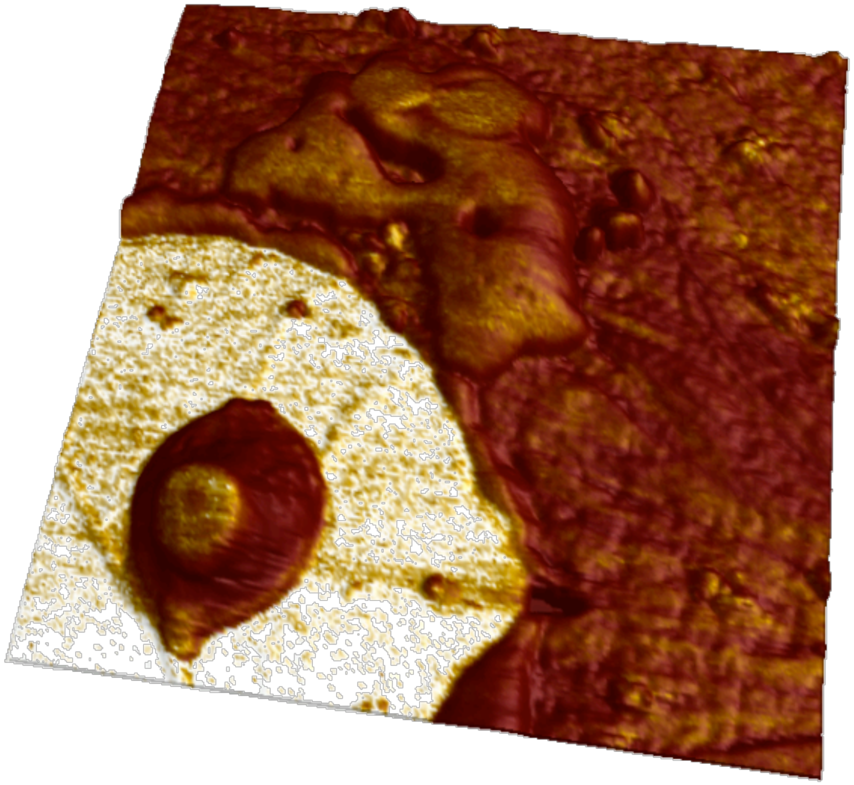
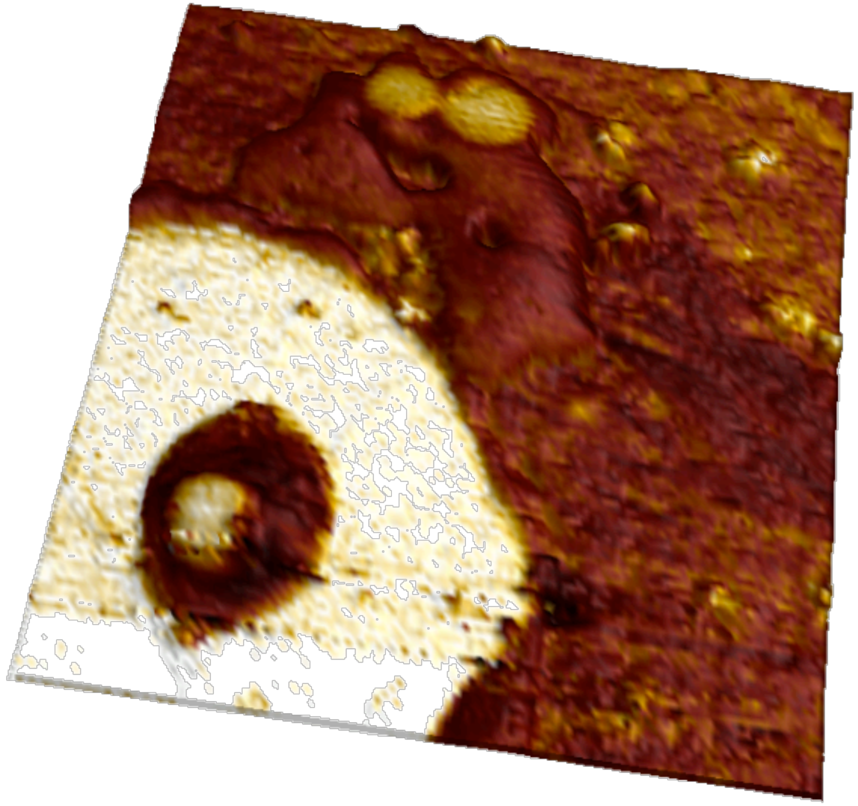
Results
Comparing PFTQNM and CR

- PFTQNM

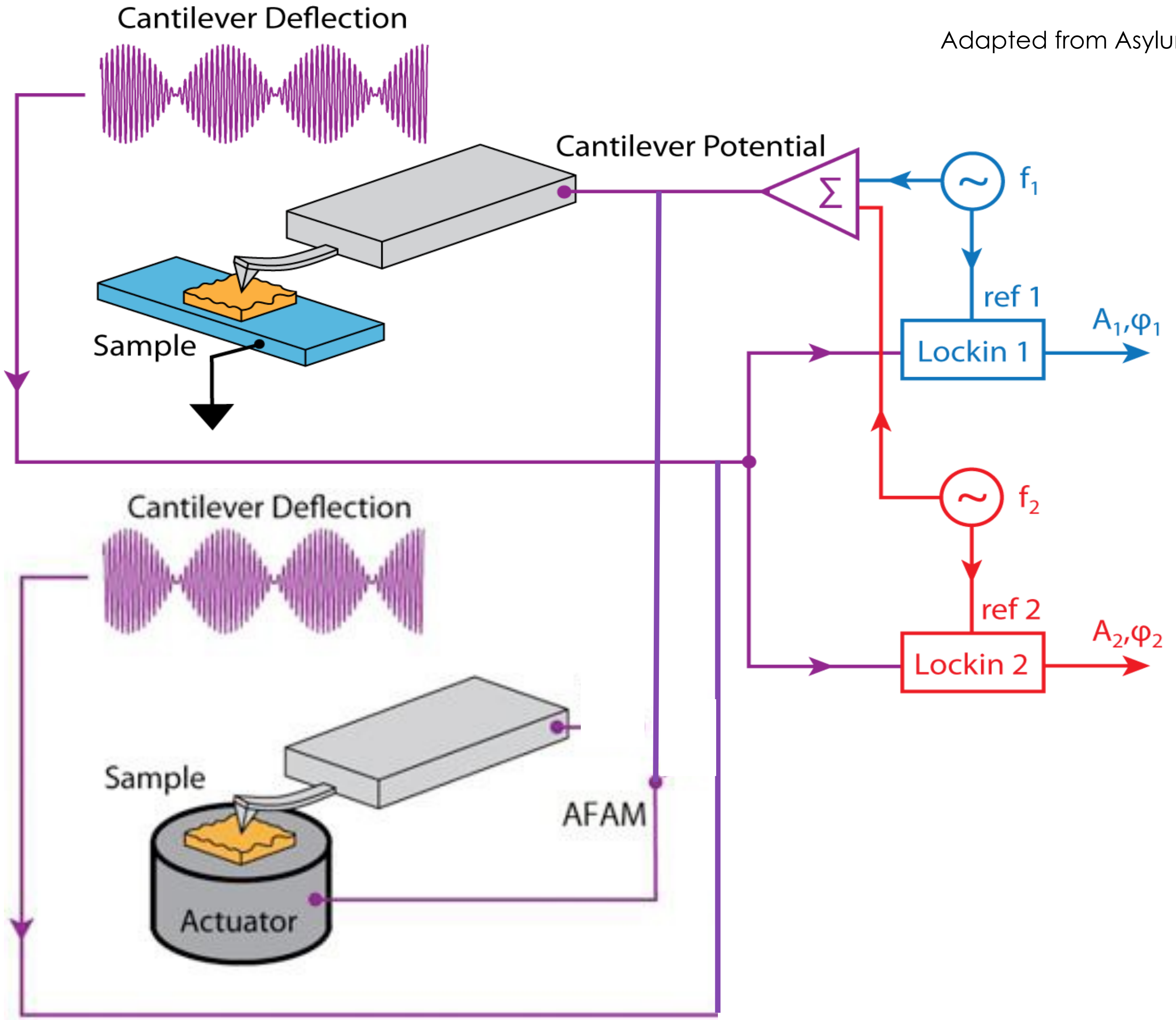


- CR 128x128



Contact Resonance : Tip or Sample ?

Adapted from Asylum Research



Conclusions

- **Combined, AFM measurements with non-resonant modes and resonant modes can provide**
  - Huge range of properties covered
  - FV based Contact Resonance for stiff samples at higher frequencies
  - FV force curves for soft samples at low frequencies
  - FV and PFT cover wide range of ramp rates for time-temperature studies

- **Understanding the relative contribution of the various error sources allows us to prioritize improvements to address them**
  - Spring constant and tip shape are key parameters for all of the methods
  - Force Volume can have fairly high accuracy if k and R are well known, PFT is not quite as accurate, but is often worth using for resolution and speed
  - Contact resonance has a lot of parameters that need to be calibrated, making ‘relative’ measurements more practical than ‘absolute’
  - Appropriate modeling is required to quantify the modulus depending on the sample and measurement conditions