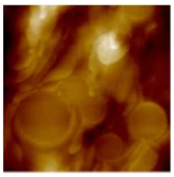
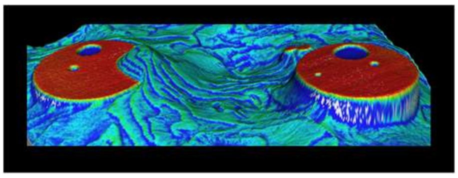
Propriétés mécaniques des matériaux à la nanoéchelle : des observables à la cartographie quantitative !

Philippe LECLERE





Journée Nanomécanique en Champ Proche
Grenoble (France)

Outline

What do we need ?

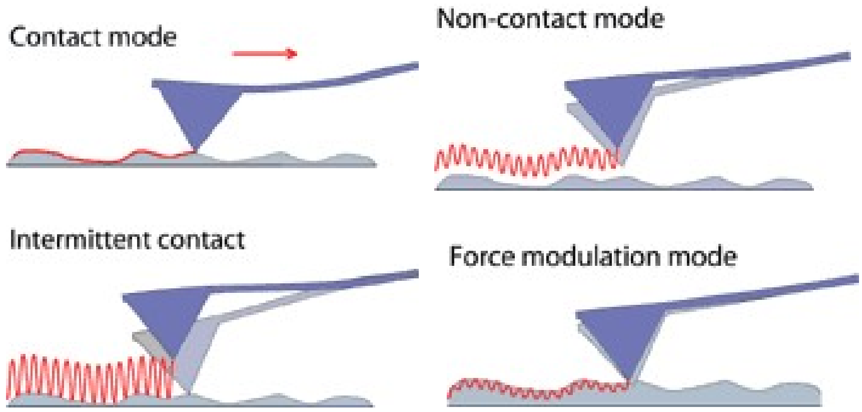
How to proceed ?

From observables to mapping …

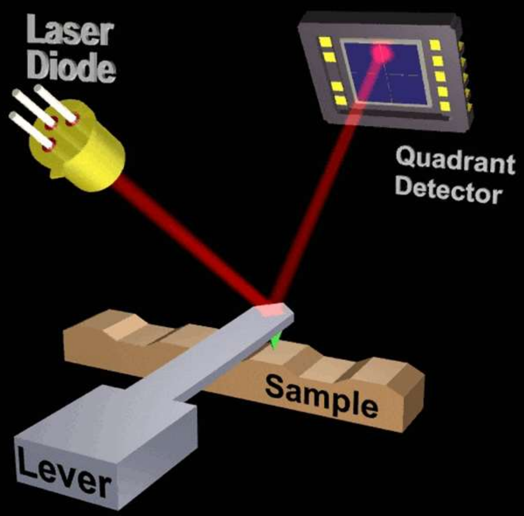
- Sub Resonance Tapping (PFT, …)
- Bimodal AFM
- Contact Resonance (CR-AFM)
- Nano Dynamical Mechanical Mechanics (nDMA)
- *Intermodulation AFM (ImAFM)*

Discussions - Conclusions

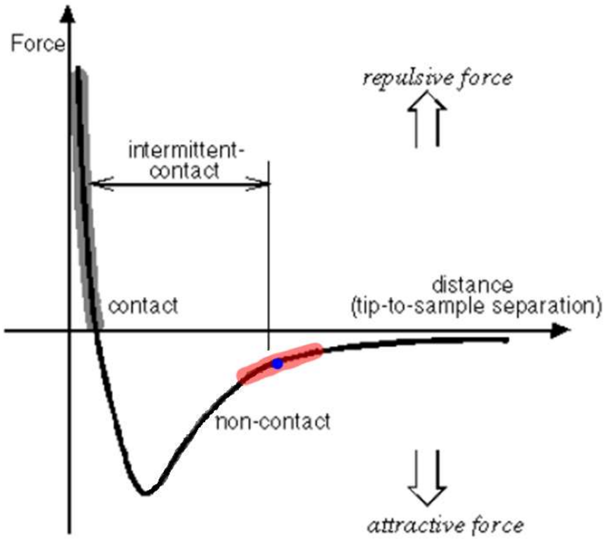
Imaging Modes



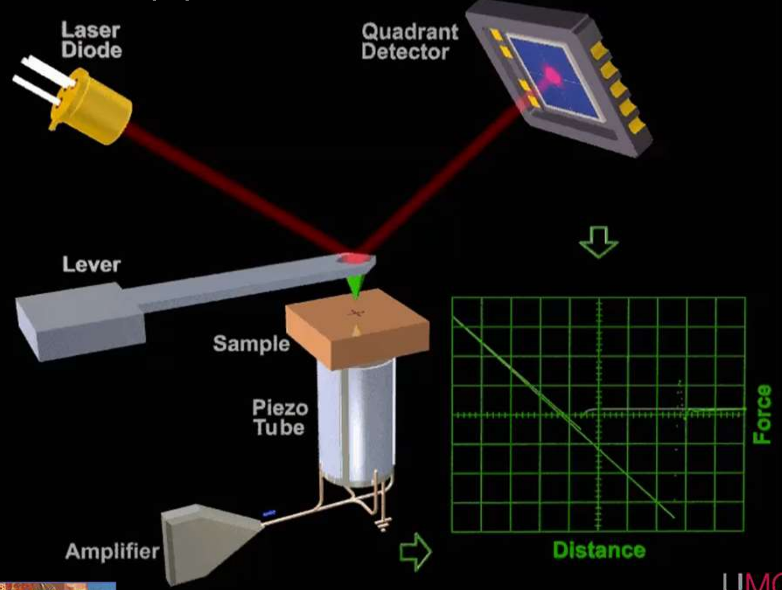
Atomic Force Microscopy



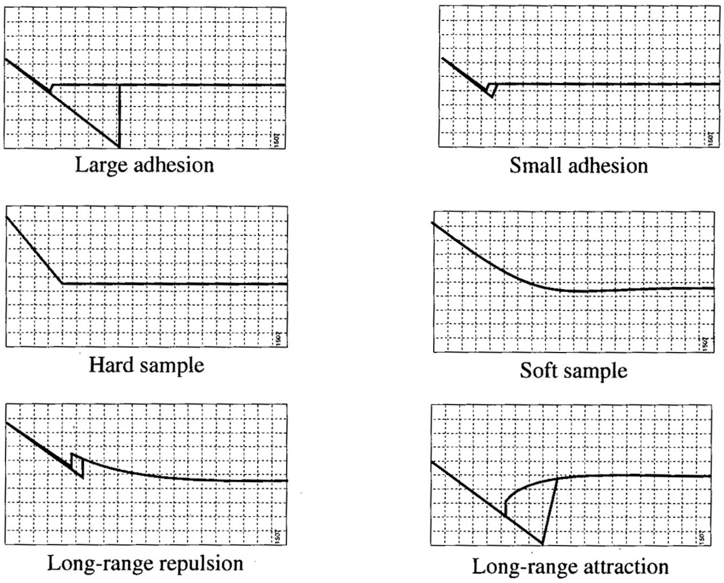
Scanning Probe Microscopy (SPM)



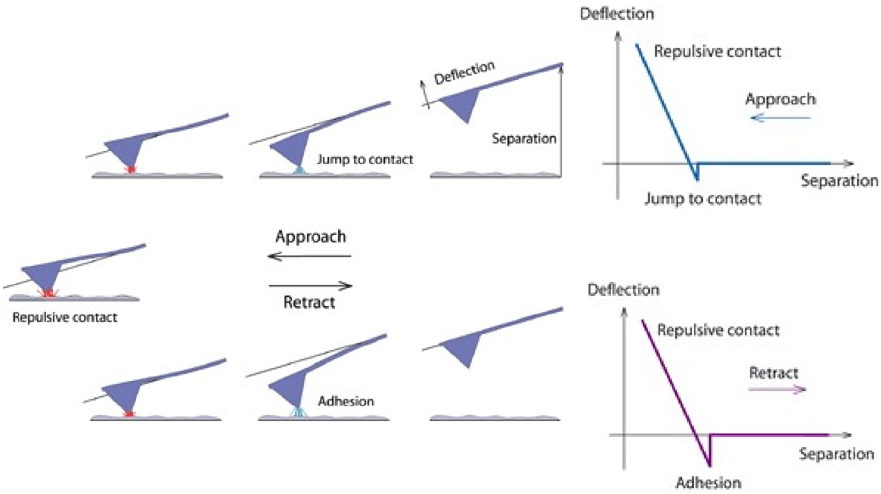
Approach Retract Curve



Scanning Probe Microscopy (SPM)



Scanning Probe Microscopy (SPM)



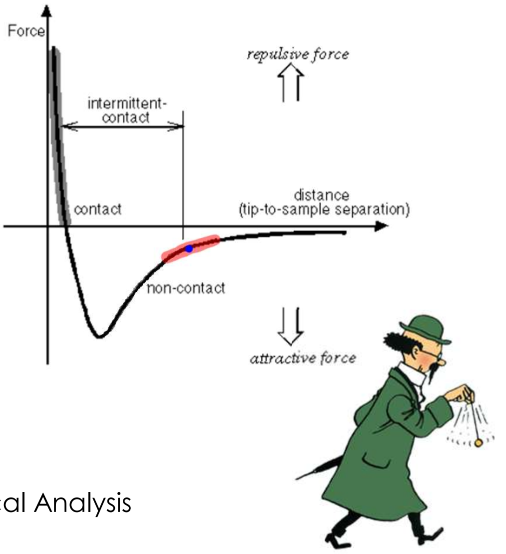
Scanning Probe Microscopy (SPM)

Morphology

- Contact AFM
- AM-AFM (Tapping Mode)
- FM-AFM (nc-AFM)
- « Multifrequency » AFM

Mechanical Properties

- Friction Force Microscopy
- Force Modulation
- Contact Resonance
- HarmoniX
- Bimodal Dual AC
- Peak Force Tapping
- Sub resonance AFM
- Intermodulation AFM
- Band Excitation
- nanoDynamical Mechanical Analysis
- …



Scanning Probe Microscopy (SPM)

Morphology

- Contact AFM
- AM-AFM (Tapping Mode)
- FM-AFM (nc-AFM)
- « Multifrequency » AFM

Mechanical Properties

- Friction Force Microscopy
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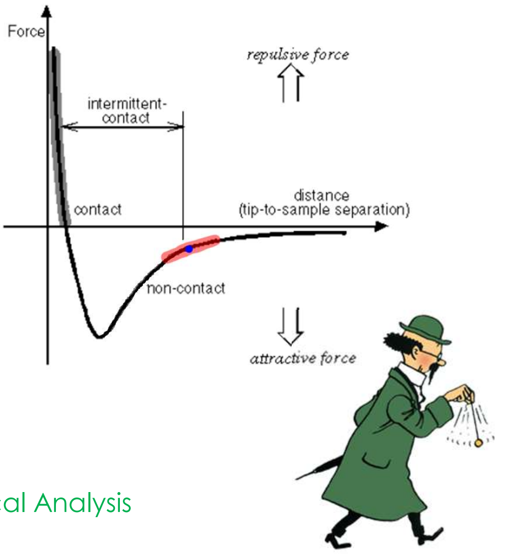
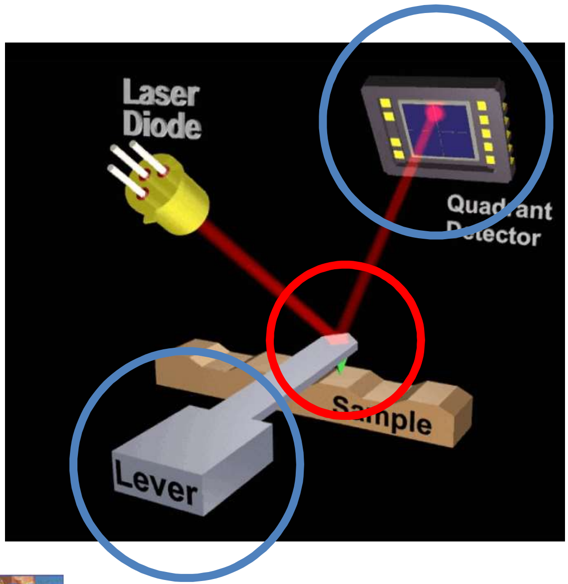
- nanoDynamical Mechanical Analysis
- …



The ingredients …

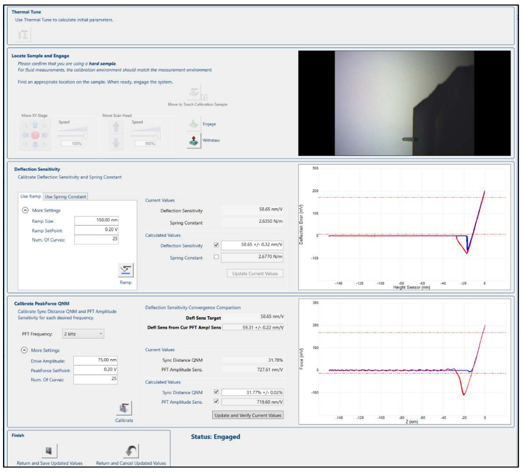


See Olivier's Talk !!!

What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **scanner, photodetector sensitivities** :
  - approach-retract curve on stiff sample (silicon, sapphire, ...), …

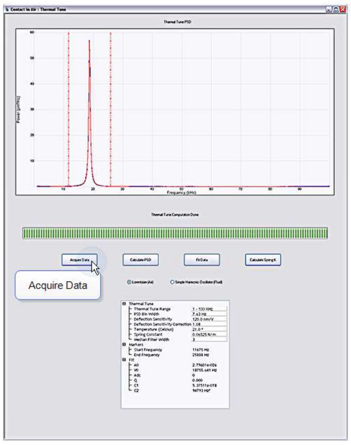


What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever)**: spring constant, resonance frequency, Quality factor.

Thermal Tune



- **Simple Harmonic Oscillator**, for use in fluid:

$$A(\nu) = A_0 + A_{DC} \cdot \frac{\nu_0^2}{\sqrt{(\nu_0^2 - \nu^2)^2 + \frac{\nu_0^2 \nu^2}{Q^2}}}$$

where:

$A(\nu)$ = amplitude as a function of frequency, ν

A_0 = baseline amplitude

A_{DC} = amplitude at DC (zero frequency)

ν_0 = center frequency of the resonant peak

Q = quality factor

- **Lorentzian**, for use in air:

$$A(\nu) = A_0 + \frac{C_1}{(\nu - \nu_0)^2 + C_2}$$

where:

$A(\nu)$ is the amplitude as a function of frequency, ν

A_0 is the baseline amplitude

ν_0 is the center frequency of the resonant peak

C_1 is a Lorentzian fit parameter

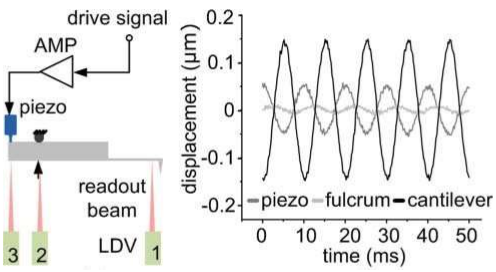
C_2 is a Lorentzian fit parameter

What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever)**: spring constant, resonance frequency, Quality factor.

Laser Doppler Vibrometry



What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever):** spring constant, resonance frequency, Quality factor.

Sader Method

The spring constant, k, is evaluated using the Sader Method (Ref. 1):

$$\boxed{k_{\text{Sader}} = A\,Q\,f_R^{1.3}}$$

which requires only the resonant frequency, f_R, and quality factor, Q, of the uncalibrated cantilever in air, measured far from any surface.

The coefficient, A, is universal for a particular cantilever geometry, regardless of cantilever thickness or coatings, and is obtained from measurements of a reference cantilever:

$$A = \frac{k_{\text{ref}}}{Q_{\text{ref}}\,f_{R,\text{ref}}^{1.3}}$$

where the subscript 'ref' refers to the reference cantilever. Multiple reference cantilevers are used to determine the A-coefficient (Ref. 2):

$$A = \frac{1}{N}\sum_{i=1}^{N} A_i = \frac{1}{N}\sum_{i=1}^{N}\frac{k_{\text{ref},i}}{Q_{\text{ref},i}\,f_{R,\text{ref},i}^{1.3}}$$

where N is the total number of measurements and the subscript i refers to an individual measurement. This average systematically reduces uncertainty in the A-coefficient which is used to standardise calibration.

J. E. Sader *et al.*, Rev. Sci. Instrum. **87**, 093711 (2016).

What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever):** spring constant, resonance frequency, Quality factor.

Sader Method

REVIEW OF SCIENTIFIC INSTRUMENTS 87, 093711 (2016)

A virtual instrument to standardise the calibration of atomic force microscope cantilevers

John E. Sader,[1,a)] Riccardo Borgani,[2] Christopher T. Gibson,[3] David B. Haviland,[2] Michael J. Higgins,[4] Jason I. Kilpatrick,[5] Jianing Lu,[6] Paul Mulvaney,[6] Cameron J. Shearer,[3] Ashley D. Slattery,[3] Per-Anders Thorén,[2] Jim Tran,[1] Heyou Zhang,[6] Hongrui Zhang,[4] and Tian Zheng[4]
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[4]ARC Centre of Excellence for Electromaterials Science, Australian Institute for Innovative Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia
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(Received 26 May 2016; accepted 2 September 2016; published online 27 September 2016)

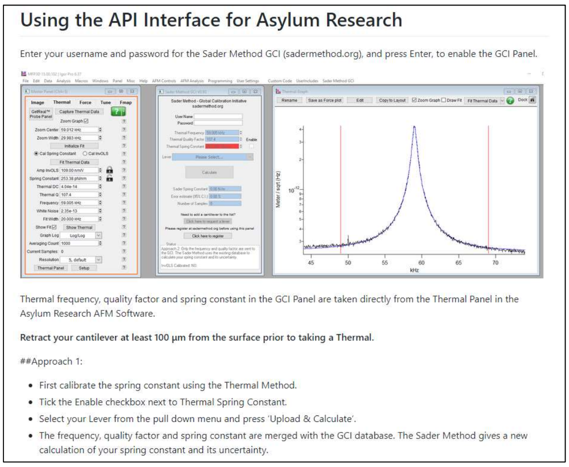
https://sadermethod.org/

What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever)**: spring constant, resonance frequency, Quality factor.

Sader Method

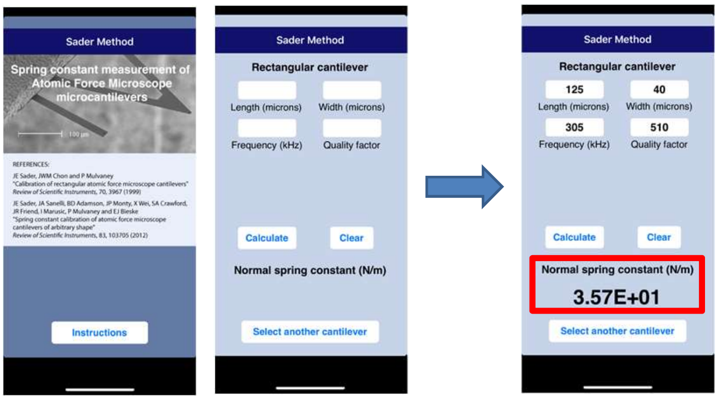


What do we need ?

A proper calibration of the AFM and the cantilever/probe

- **Probe (cantilever)**: spring constant, resonance frequency, Quality factor.

Sader Method

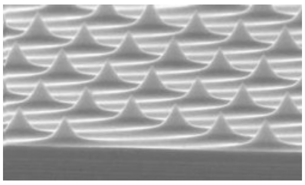


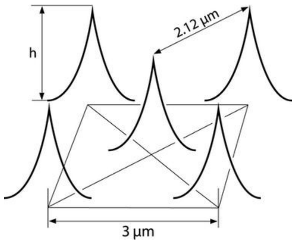
What do we need ?

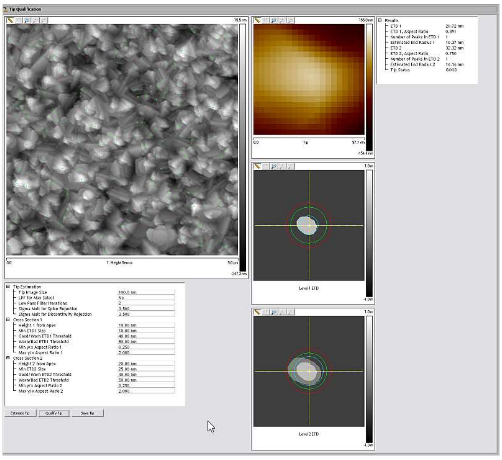
A proper calibration of the AFM and the cantilever/probe

- **Probe :** tip geometry and dimension (tip radius).

Test grating TGT1







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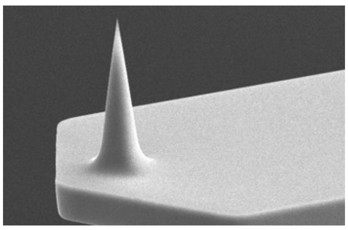
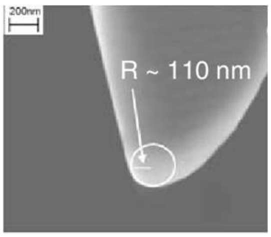
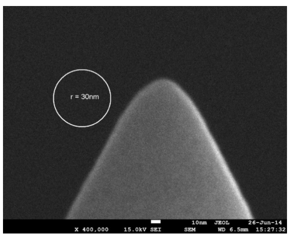
A proper calibration of the AFM and the cantilever/probe

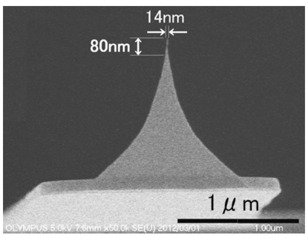
- **Probe :** tip geometry and dimension (tip radius).

Scanning Electron Microscopy





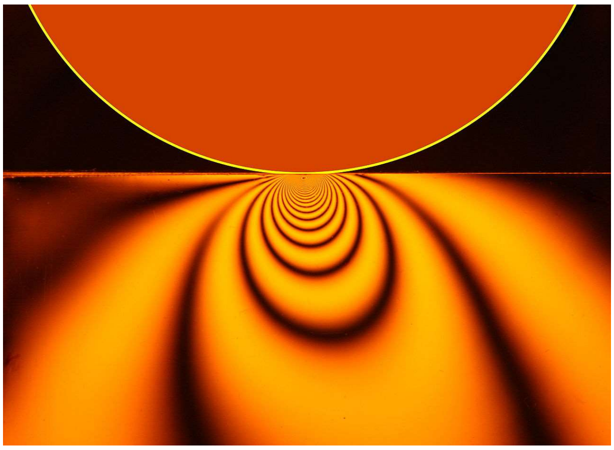


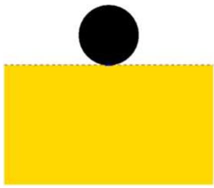


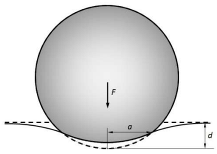
What do we need ?

A suitable contact mechanics model

Basic Hertz's elastic solution (1881)







What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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

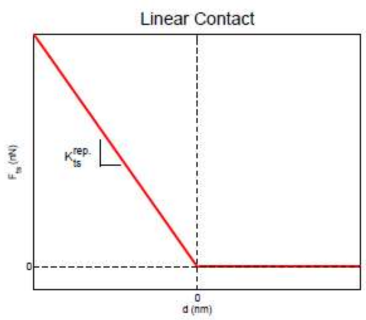


FIG. 66: Tip-sample force versus gap for the piecewise linear contact model.

$$F_{ts}(d) = \begin{cases} 0, & d > 0 \\ -k_{ts}^{rep} d, & d \leqslant 0 \end{cases}$$

VEDA: A web-based virtual environment for dynamic atomic force microscopy

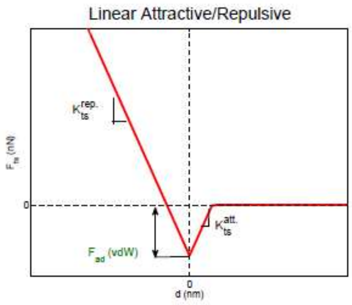
https://nanohub.org/resources/veda

What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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



$$F_{ts}(d) = \begin{cases} 0, & d < L_0 \\ k_a(d - L_0), & L_0 < d < 0 \\ -k_{ts} d, & d \geqslant 0 \end{cases}$$

FIG. 67: Tip-sample force versus gap for the piecewise linear attractive/repulsive contact model.

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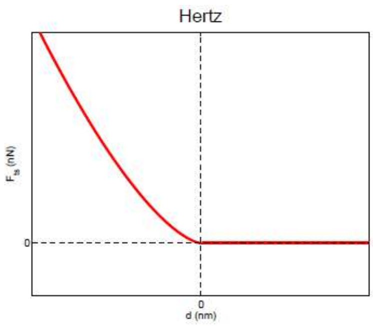
What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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



$$F_{ts}(d) = \begin{cases} 0, & d > 0 \\ \frac{4}{3} E^* \sqrt{R}(-d)^{3/2}, & d \leqslant 0 \end{cases}$$

$$E^* = \left[\frac{1 - \nu_{tip}^2}{E_{tip}} + \frac{1 - \nu_{sample}^2}{E_{sample}} \right]^{-1}.$$

FIG. 68: Tip-sample force versus gap for the Hertz contact model.

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What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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

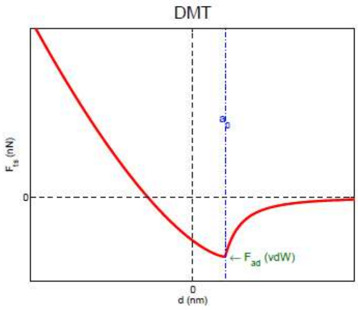

FIG. 69: Tip-sample force versus gap for the DMT contact model.

$$F_{DMT}(d) = \begin{cases} -\frac{HR}{6d^2}, & d > a_0 \\ -\frac{HR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}(a_0 - d)^{3/2}, & d \leqslant a_0 \end{cases}$$

$$E^* = \left[\frac{1-\nu_{tip}^2}{E_{tip}} + \frac{1-\nu_{sample}^2}{E_{sample}}\right]^{-1}.$$

H = Hamaker constante

VEDA: A web-based virtual environment for dynamic atomic force microscopy

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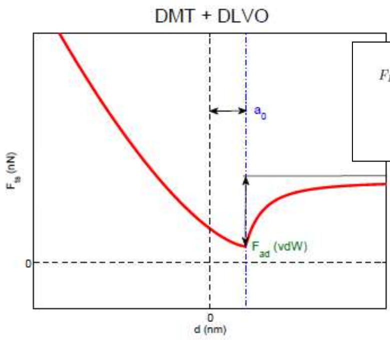
What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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



$$F_{DLVO+DMT}(d) = \begin{cases} \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D d} - \frac{HR}{6d^2}, & d > a_0 \\ \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D a_0} - \frac{HR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}(a_0 - d)^{3/2}, & d \leqslant a_0 \end{cases}$$

$$E^* = \left[\frac{1-\nu_{tip}^2}{E_{tip}} + \frac{1-\nu_{sample}^2}{E_{sample}}\right]^{-1}.$$

VEDA: A web-based virtual environment for dynamic atomic force microscopy

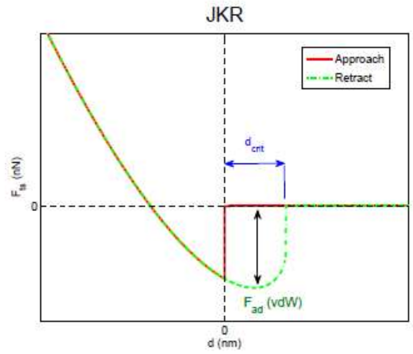
https://nanohub.org/resources/veda

What do we need ?

See Olivier's Talk !!!

A suitable contact mechanics model

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



JKR is nonconservative and includes a dependency to the history of the tip-sample contact.

VEDA: A web-based virtual environment for dynamic atomic force microscopy

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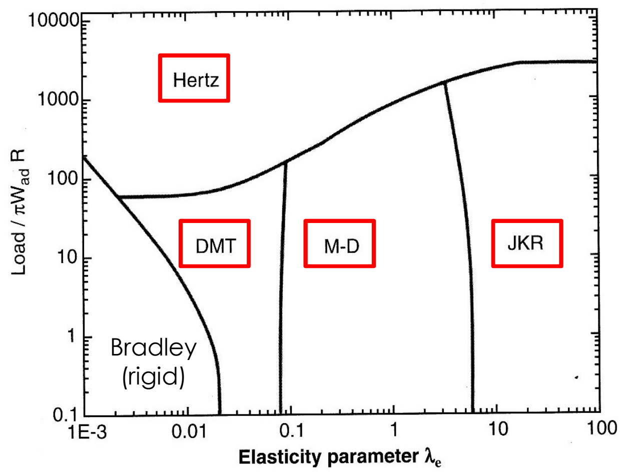
Contact Mechanics Forces

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

M-D = Maugis - Dugdale

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



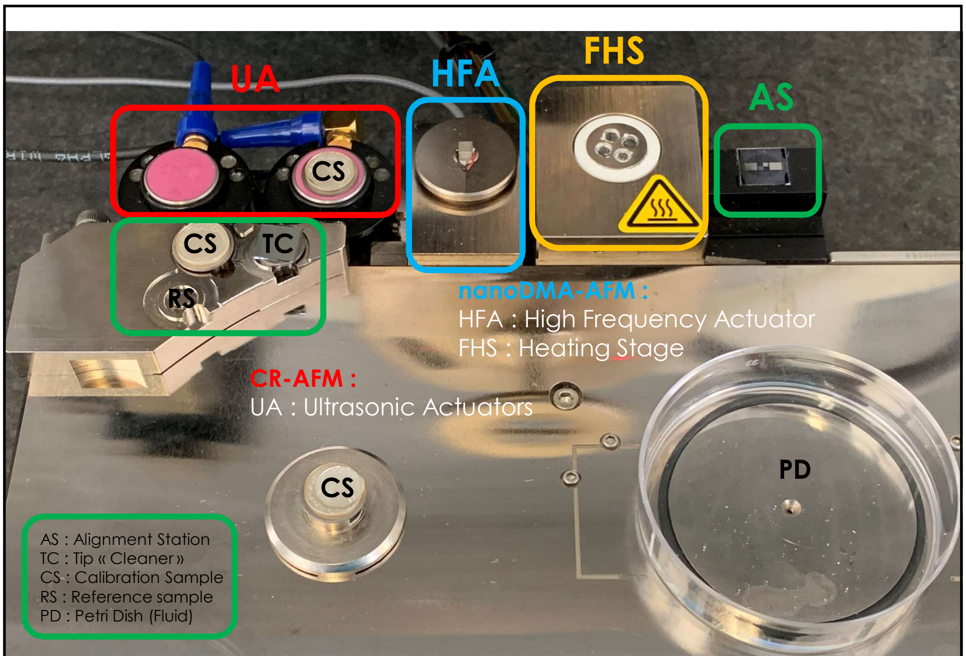
Johnson, Greewood, J. Colloid Interface Sci., 1997, 192, 326.

What do we need ?

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 (Tapping Mode AFM)
- Frequency shift & bandwidth (Q)
- Contact resonance frequency (CR-AFM)
- Higher harmonics vibration amplitude (HarmoniX)
- In phase and Quadrature signals (ImAFM)

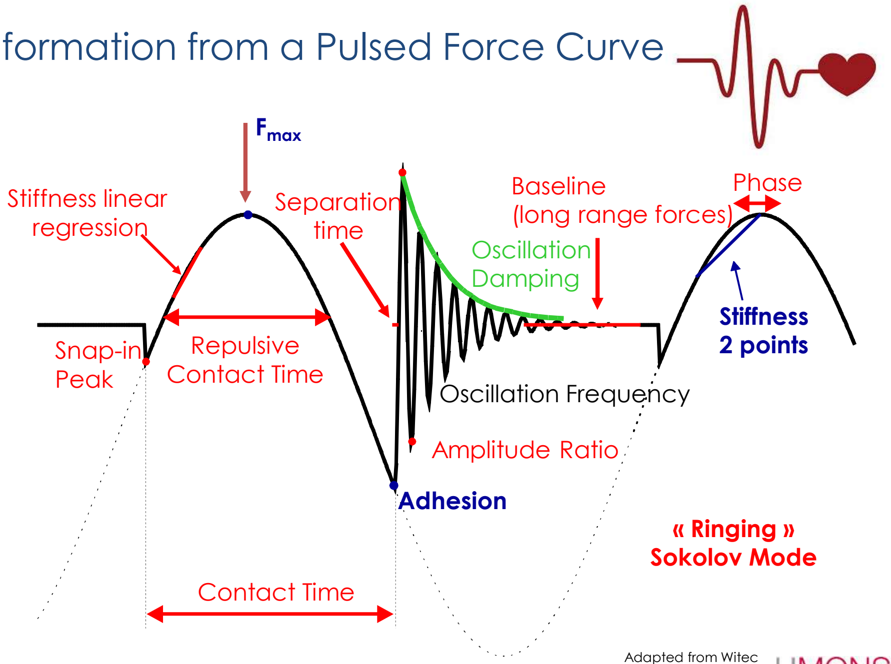
Observables !!



Sub Resonance Tapping

aka Pulsed Force, PeakForce Tapping, Jump Mode, Hybrid™, Pinpoint™, QI™, « Ringing » Mode AFM, …

Information from a Pulsed Force Curve



Adapted from Witec

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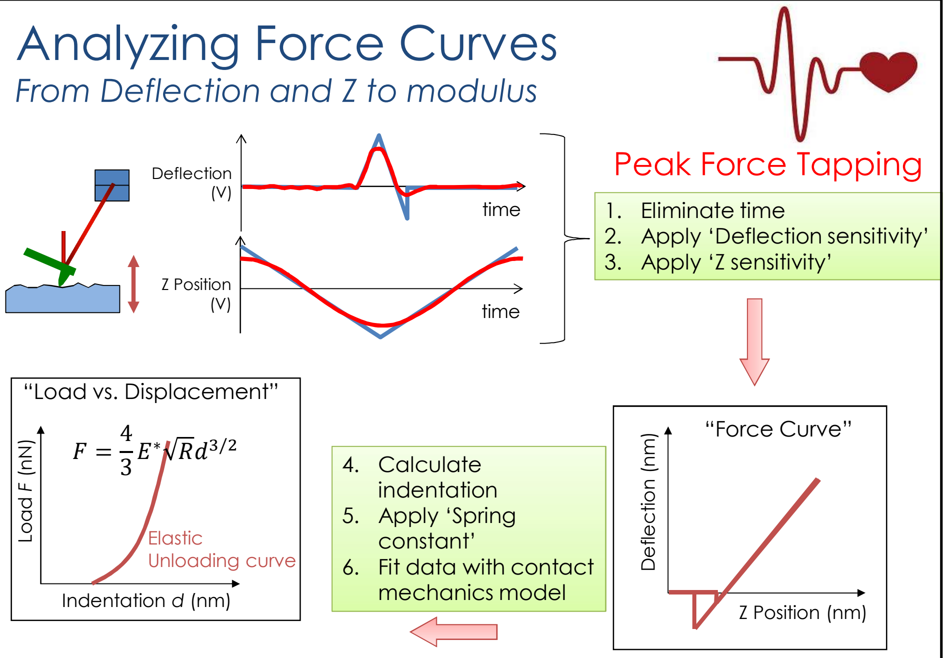
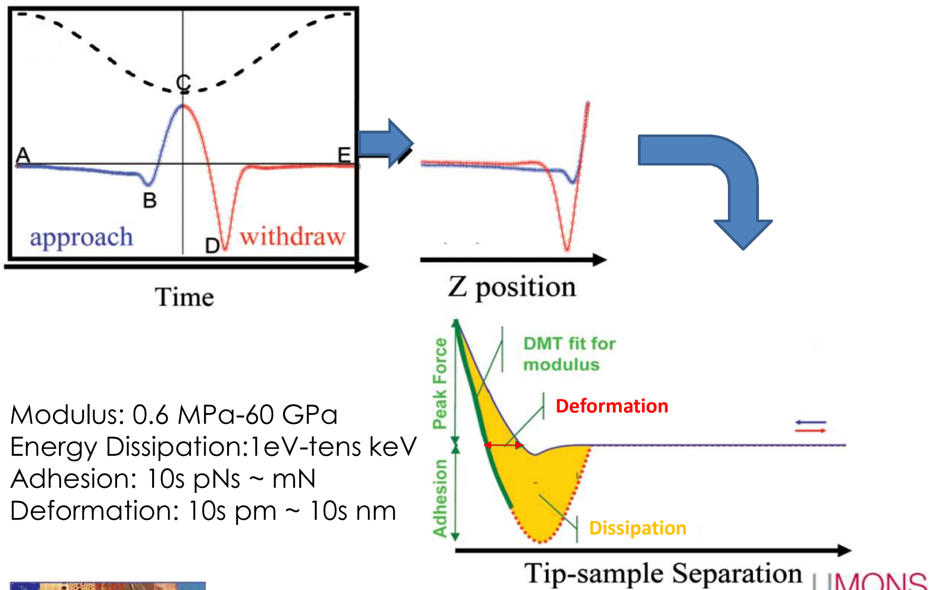
Analyzing Force Curves

From Deflection and Z to modulus

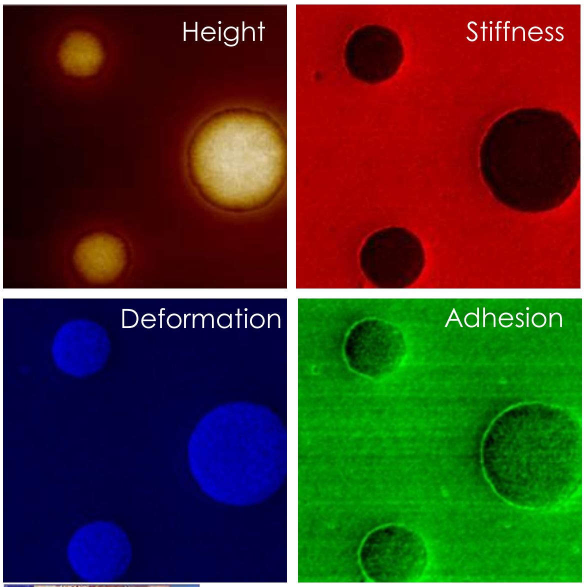


Peak Force Tapping (QNM)



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

Blend of PS/LDPE



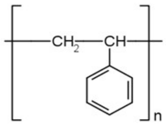
Macrophase separation

Information about mechanical properties at the nanoscale

LDPE

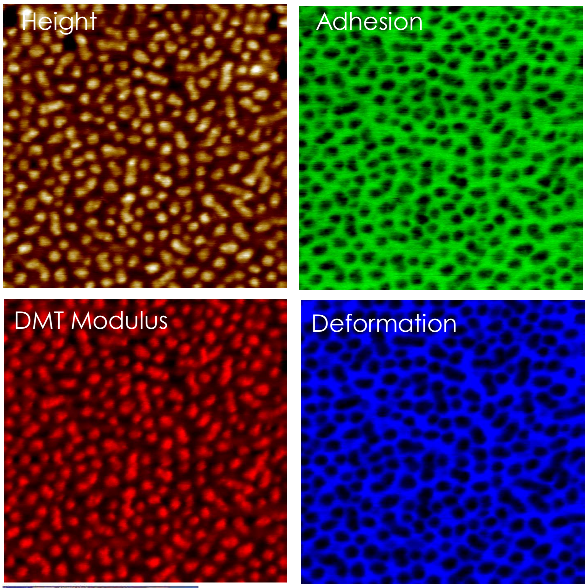
$\left[CH_2 - CH_2 \right]_n$

PS



Scan Size : 3.0 µm

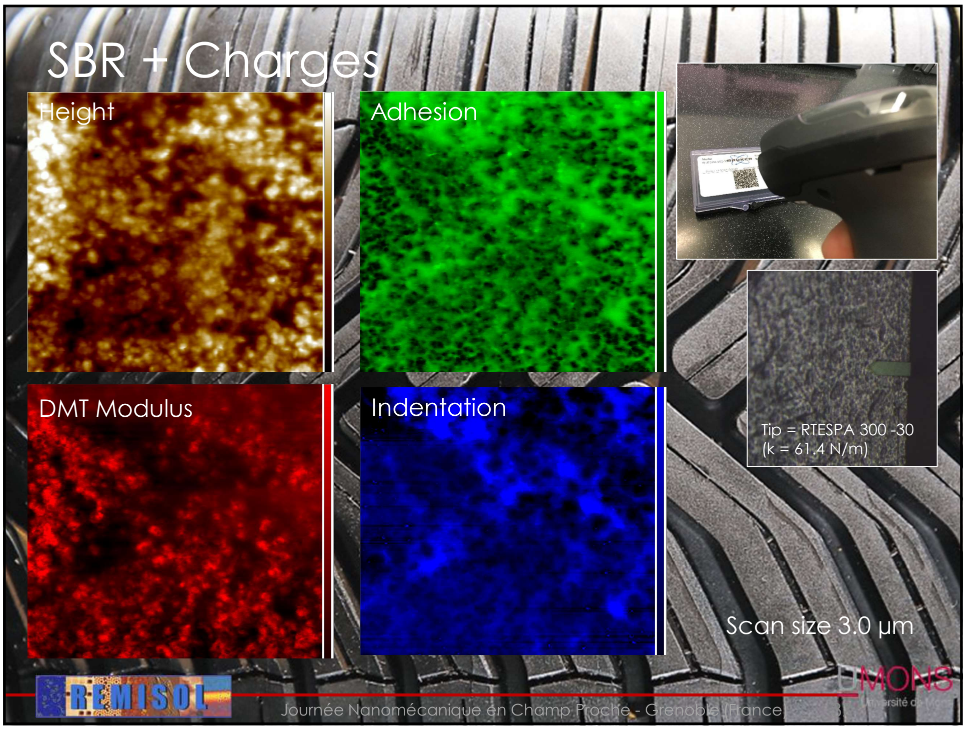
Pressure Sensitive Adhesive

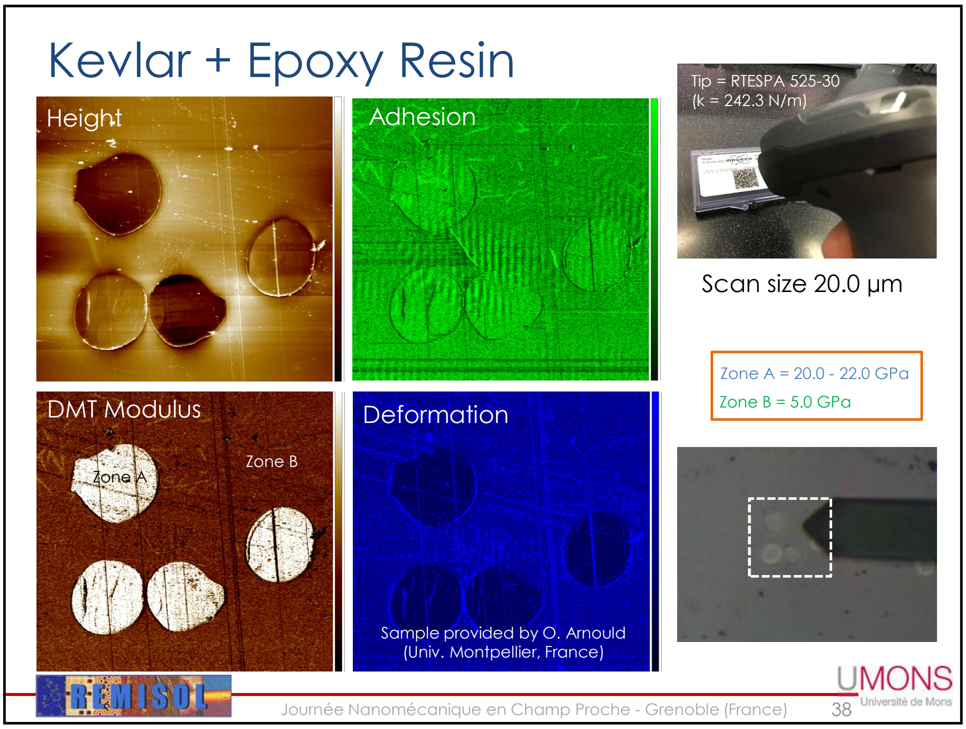


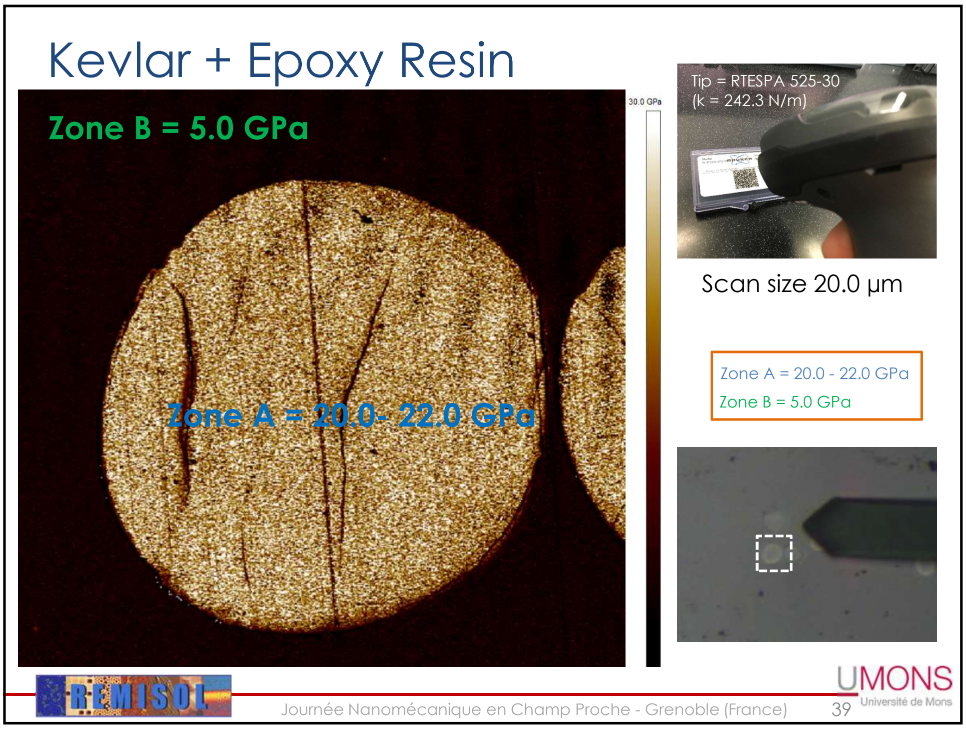
Microphase separation

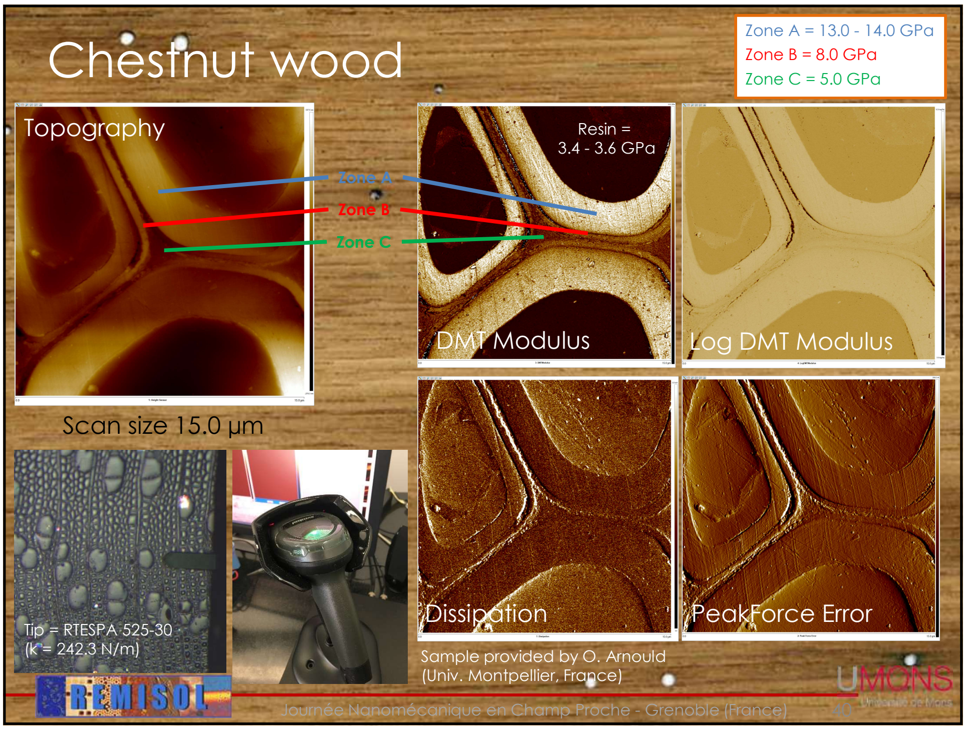
PSA

Scan size 1.0 µm

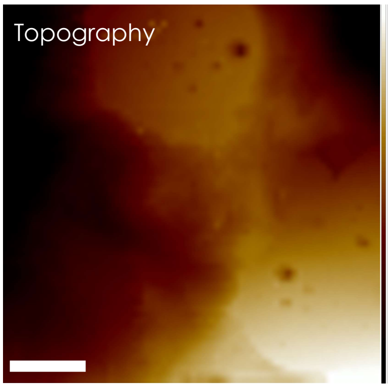

SBR + Charges
Height
Adhesion
DMT Modulus
Indentation
Tip = RTESPA 300 -30
(k = 61.4 N/m)
Scan size 3.0 µm
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
UMONS

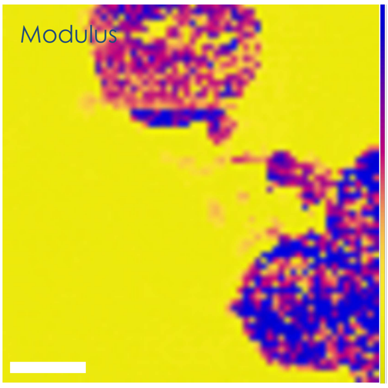

Kevlar + Epoxy Resin
Height
Adhesion
DMT Modulus
Zone A
Zone B
Deformation
Sample provided by O. Arnould
(Univ. Montpellier, France)
Tip = RTESPA 525-30
(k = 242.3 N/m)
Scan size 20.0 µm
Zone A = 20.0 - 22.0 GPa
Zone B = 5.0 GPa
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
38
UMONS
Université de Mons


Kevlar + Epoxy Resin
Zone B = 5.0 GPa
Zone A = 20.0- 22.0 GPa
30.0 GPa
Tip = RTESPA 525-30
(k = 242.3 N/m)
Scan size 20.0 µm
Zone A = 20.0 - 22.0 GPa
Zone B = 5.0 GPa
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
39
UMONS
Université de Mons


Chestnut wood
Zone A = 13.0 - 14.0 GPa
Zone B = 8.0 GPa
Zone C = 5.0 GPa
Topography
Zone A
Zone B
Zone C
Resin =
3.4 - 3.6 GPa
DMT Modulus
Log DMT Modulus
Scan size 15.0 µm
Dissipation
PeakForce Error
Tip = RTESPA 525-30
(k = 242.3 N/m)
Sample provided by O. Arnould
(Univ. Montpellier, France)
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
UMONS

PS – PCL (25:75)





Force volume

64 x 64 pixels
Scale bar = 1.0 µm

Tip : RTESPA 300 – 30

k = 39.22 N/m
Radius = 30 nm

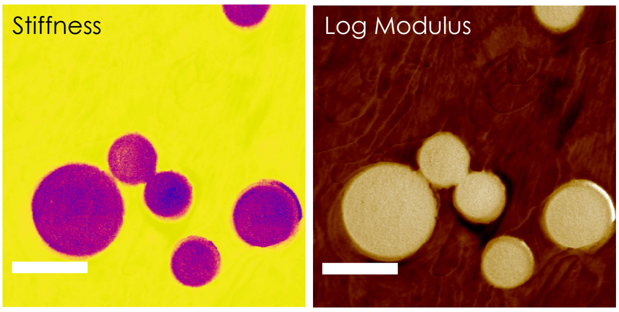
PS – PCL (25:75)

Tip : RTESPA 300 – 125

k = 29.22 N/m
Radius = 125 nm

PeakForce Tapping

512 x 512 pixels, PFSP = 15 nN
Scale bar = 2.0 µm



Viscoelastic Properties

Solid-state deformations

Several classes of deformations in materials are the following:

Elastic**: The material recovers its initial shape after deformation.**

Plastic**: The applied force induces non-recoverable deformations in the material when the stress (or elastic strain) reaches a critical magnitude, called the yield point.**

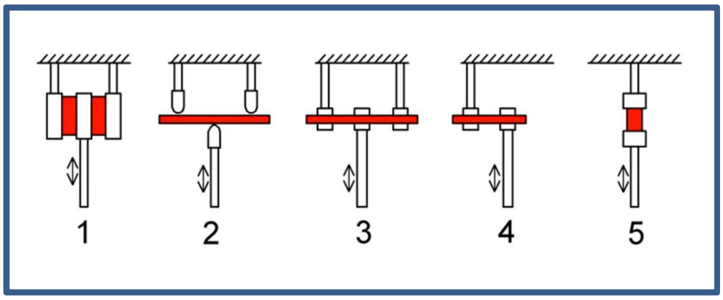
Viscoelastic**: If the time-dependent resistive contributions are large, and cannot be neglected. Rubbers and plastics have this property, and certainly do not satisfy Hooke's law. In fact, elastic hysteresis occurs.**

Anelastic: if the material is close to elastic, but the applied force induces additional time-dependent resistive forces (i.e. depend on rate of change of extension/compression, in addition to the extension/compression).

Hyperelastic: The applied force induces displacements in the material following a strain energy density function.

Viscoelastic Properties

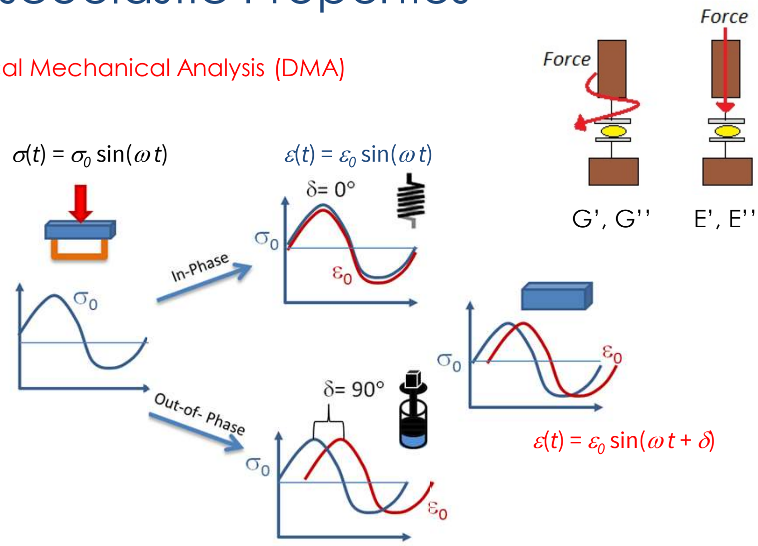
Dynamical Mechanical Analysis (DMA)



1 Shear
2 3-point bending
3 Dual cantilever
4 Single cantilever
5 Tension or Compression

Viscoelastic Properties

Dynamical Mechanical Analysis (DMA)



$d\sigma/dt = \varepsilon\, \sigma_0 \cos(\omega t) = \varepsilon_0 \sin(\omega t + \pi/2)$

Viscoelastic Properties

Dynamical Mechanical Analysis (DMA)

The behavior of viscoelastic materials lies between these two limits, that is, the difference between the applied stress and the resultant strain is an angle, δ

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta)$$

This equation can be rewritten as :

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t) \cos(\delta) + \varepsilon_0 \cos(\omega t) \sin(\delta) = \varepsilon' \sin(\omega t) + \varepsilon'' \cos(\omega t)$$

or

$$\boldsymbol{\sigma(t) = \varepsilon_0 E^* [\sin(\omega t) \cos(\delta) + \cos(\omega t) \sin(\delta)] = \varepsilon_0 \sin(\omega t) E' + \varepsilon_0 \cos(\omega t) E''}$$

- E^* is the ratio of maximum stress σ_0 to maximum strain ε_0,
- $\sigma_0 \cos(\delta)/\varepsilon_0$ and $\sigma_0 \sin(\delta)/\varepsilon_0$ are the storage and loss modulus (E', E'').
- The two moduli are also known as the *elastic* and *viscous modulus*.

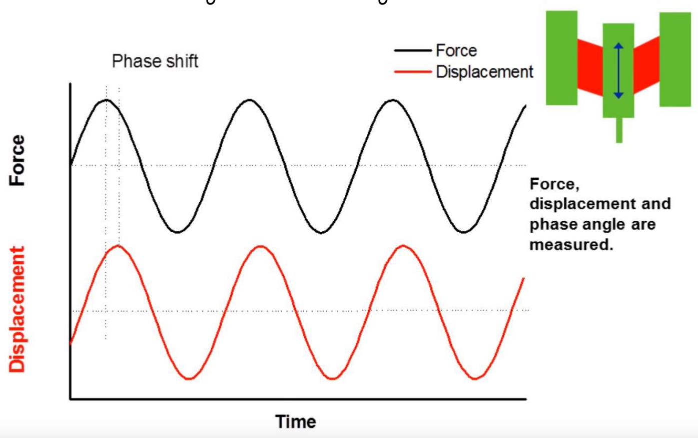
The ratio of the loss to the storage modulus is the phase angle and is called damping:

$$\tan(\delta) = E'' / E'$$

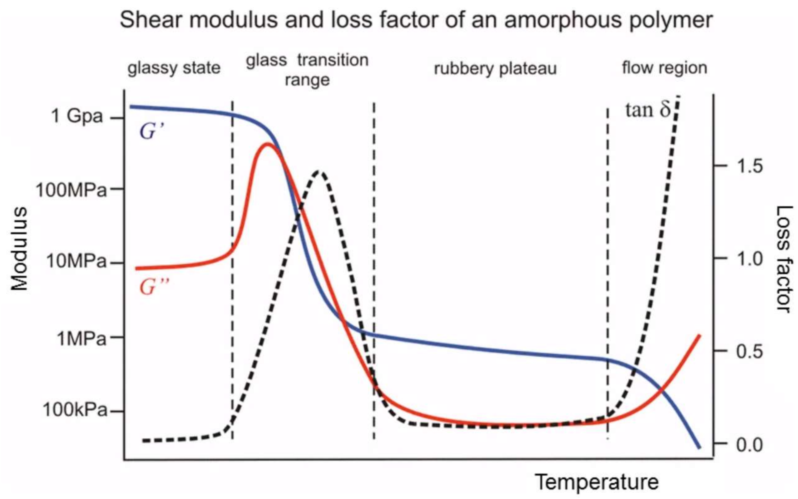
Viscoelastic Properties

Dynamical Mechanical Analysis (DMA)

$$\sigma = \varepsilon_o E' \sin \omega t + \varepsilon_o E'' \cos \omega t$$

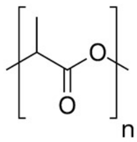


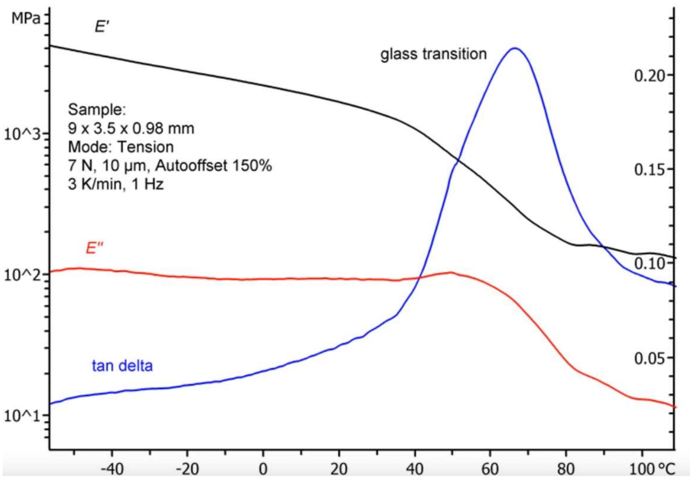
Viscoelastic Properties



Viscoelastic Properties

Poly(lactic acid) - PLA





Multifrequency AFM

Bimodal AFM

The methodology

European Polymer Journal
Volume 49, Issue 8, August 2013, Pages 1897-1906

Feature Article

Nanomechanical mapping of soft matter by bimodal force microscopy

Ricardo Garcia [a], Roger Proksch [b]

Bimodal AFM = Dual AC Mode

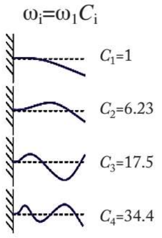
APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 3 19 JANUARY 2004

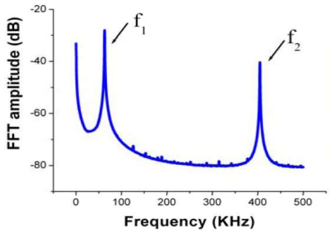
Compositional mapping of surfaces in atomic force microscopy by excitation of the second normal mode of the microcantilever

Tomás R. Rodríguez and Ricardo García[a)]
Instituto de Microelectrónica de Madrid, CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain

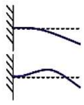
(Received 4 August 2003; accepted 20 November 2003)

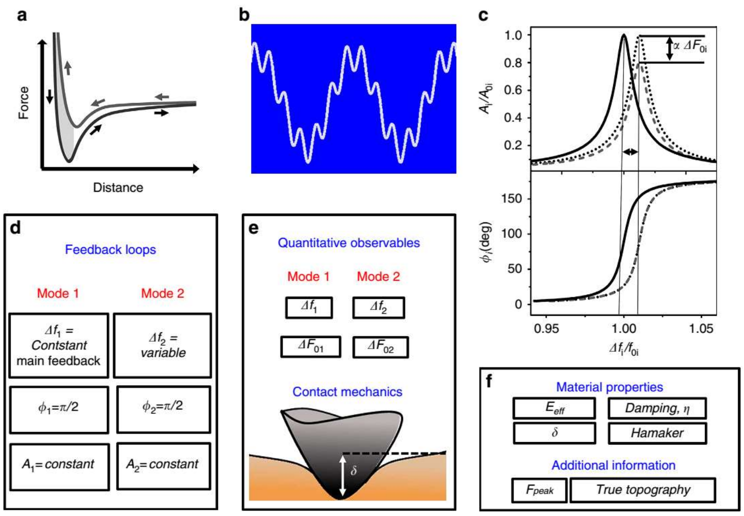
We propose a method for mapping the composition of a surface by using an amplitude modulation atomic force microscope operated without tip-surface mechanical contact. The method consists in exciting the first two modes of the microcantilever. The nonlinear dynamics of the tip motion, the coupling of its first two modes, and the sensitivity of the second mode to long-range attractive forces allows us to use this mode to probe compositional changes while the signal from the first mode is used to image the sample surface. We demonstrate that the second mode has a sensitivity to surface force variations below 10^{-11} N. © *2004 American Institute of Physics.*
[DOI: 10.1063/1.1642273]





Bimodal AFM = Dual AC Mode





Bimodal AFM = Dual AC Mode

$$\boxed{\Delta f_i(d_m) = -f_{0i}\frac{\langle F_{ts} z_i\rangle_{Ti}}{k_i A_i^2} = -\frac{f_{0i}}{k_i - A_i^2}\frac{1}{T_i}\int_{T-\frac{T_i}{2}}^{T+\frac{T_i}{2}} F_{ts}(z_c - z_1 - z_2) z_i dt}$$

$$d_{\mathrm{m}} = z_{\mathrm{c}} - A_1 - A_2$$

$$\Delta f_1(d_{\mathrm{m}}) = \frac{f_1}{k_1\sqrt{2\pi A_1^3}} I_{-}^{1/2} F(d_{\mathrm{m}})$$

$$\Delta f_2(d_{\mathrm{m}}) = \frac{f_2}{2k_2\sqrt{2\pi A_1}} D_{-}^{1/2} F(d_{\mathrm{m}})$$

$$I_{-}^{1/2} F(z) = \frac{1}{\Gamma(1/2)}\int_z^{\infty}\frac{F(z)}{(t-z)^{1/2}}\mathrm{d}t$$

$$D_{-}^{1/2} F(z) = \frac{(-1)}{\Gamma(1/2)}\frac{\mathrm{d}}{\mathrm{d}z}\int_z^{\infty}\frac{F(z)}{(t-z)^{1/2}}\mathrm{d}t$$

Young's Modulus

$$\Delta f_1(d_{\mathrm{m}}) = \sqrt{\frac{R}{8A_1^3}\frac{f_{01}}{k_1}} E_{\mathrm{eff}}\delta^2 = \beta_1 E_{\mathrm{eff}}\delta^2$$

$$\Delta f_2(d_{\mathrm{m}}) = \sqrt{\frac{R}{8A_1}\frac{f_{02}}{k_2}} E_{\mathrm{eff}}\delta = \beta_2 E_{\mathrm{eff}}\delta$$

Viscosity

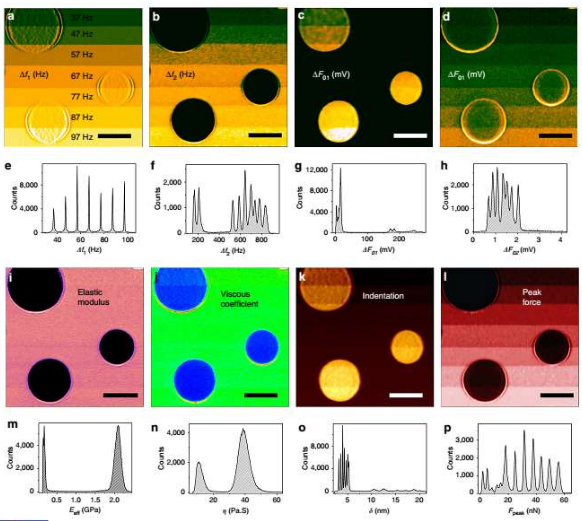
$$\Delta F_{01}(d_{\mathrm{m}}) = F_{01}\left(\frac{\Delta f_1(d_{\mathrm{m}})}{f_1} + \frac{\sqrt{2\pi} Q_1 f_1}{k_1 A_1^{3/2}} I_{-}^{1/2} B(d_{\mathrm{m}})\right)$$

$$B(x) = 2\int \eta\sqrt{R\delta}\mathrm{d}x$$

$$I_{-}^{1/2} B(d_{\mathrm{m}}) = 0.5\sqrt{\pi R}\eta\delta^2$$

Bimodal AFM = Dual AC Mode

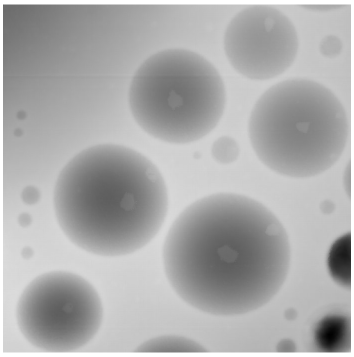
PS:LDPE polymer blend



Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm



Japanese Journal of Applied Physics 55, 08NB06 (2016)
http://doi.org/10.7567/JJAP.55.08NB06

Elastic and viscoelastic characterization of inhomogeneous polymers by bimodal atomic force microscopy

Hung K. Nguyen[1], Makiko Ito[1], and Ken Nakajima[1,2*]

$$\Delta f_1 = f_{01}\left(\sqrt{1+\frac{A_{01}}{QA_1}\cos\varphi_1}-1\right)$$

$$E = (1-\nu^2)\sqrt{\frac{8}{RA_1}\frac{k_2^2 f_{01}}{k_1 f_{02}^2}\frac{\Delta f_2^2}{\Delta f_1}}$$

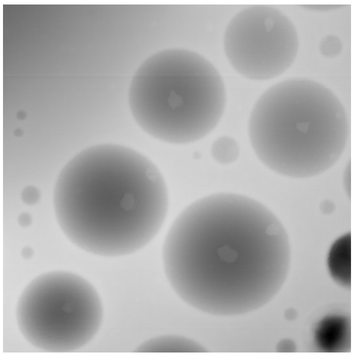
$$\tan\delta = \frac{\sin\varphi_1 - A_1/A_{01}}{\cos\varphi_1}$$

Data obtained by Michel Ramonda (Univ. Montpellier) - michel.ramonda@umontpellier.fr

Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm



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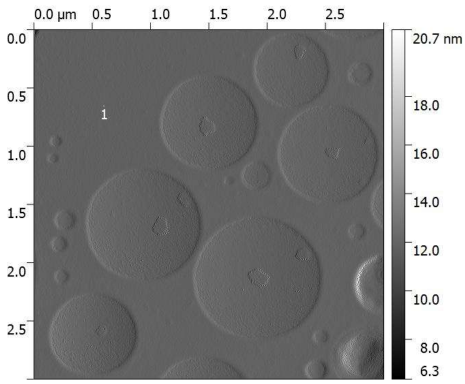


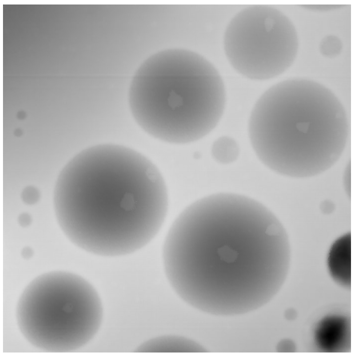
Amplitude (A_1)

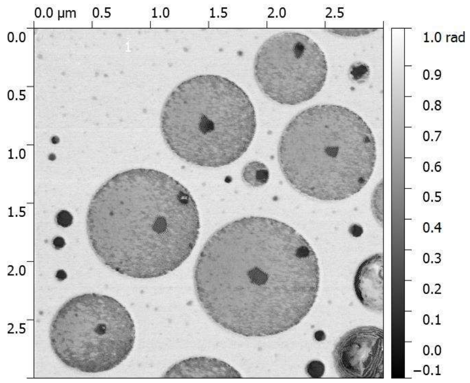
Data obtained by Michel Ramonda (Univ. Montpellier) - michel.ramonda@umontpellier.fr

Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm





Phase (φ_1)

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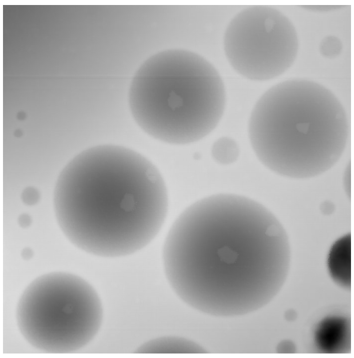
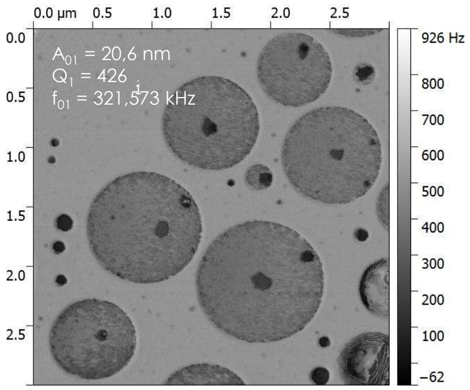
Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm





Δf_1

$$\Delta f_1 = f_{01}\left(\sqrt{1+\frac{A_{01}}{Q_1 A_1}\cos\varphi_1}-1\right)$$

Japanese Journal of Applied Physics 55, 08NB06 (2016)
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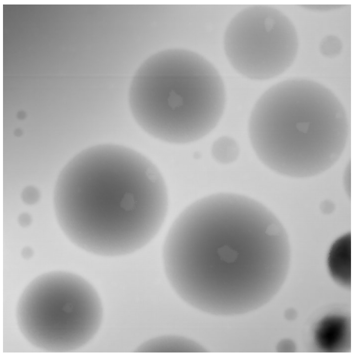
Hung K. Nguyen[1], Makiko Ito[1], and Ken Nakajima[1,2*]

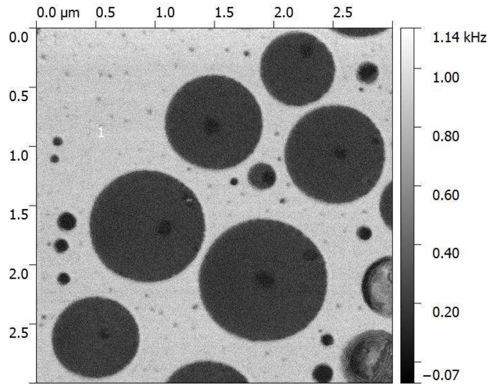
Data obtained by Michel Ramonda (Univ. Montpellier) - michel.ramonda@umontpellier.fr

Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm





Δf_2

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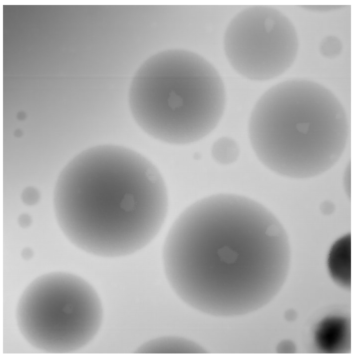
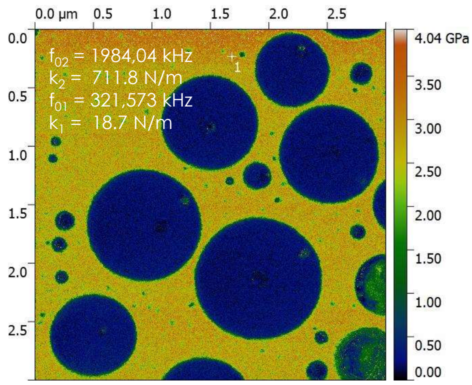
Data obtained by Michel Ramonda (Univ. Montpellier) - michel.ramonda@umontpellier.fr

Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 µm





$$E = (1-\nu^2)\sqrt{\frac{8}{RA_1}\,\frac{k_2^2 f_{01}}{k_1 f_{02}^2}\,\frac{\Delta f_2^2}{\Delta f_1}}$$

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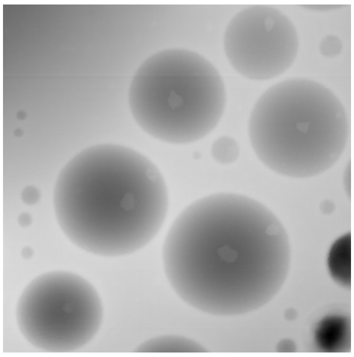
Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 μm



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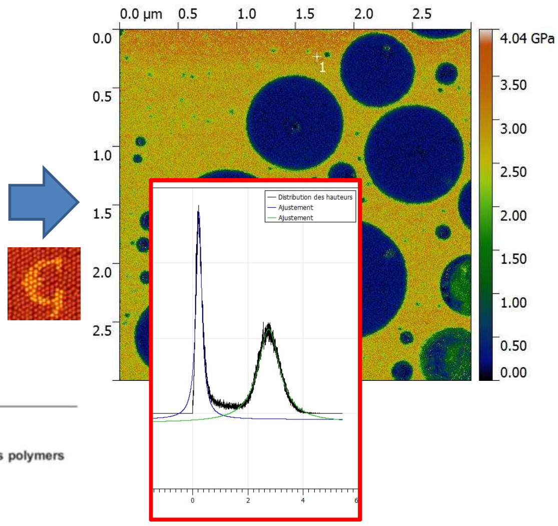
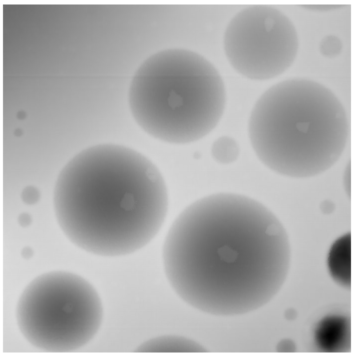


Data obtained by Michel Ramonda (Univ. Montpellier) - michel.ramonda@umontpellier.fr

Bimodal AFM

PS:PCL 70:30 blend

Scan size : 3.0 μm



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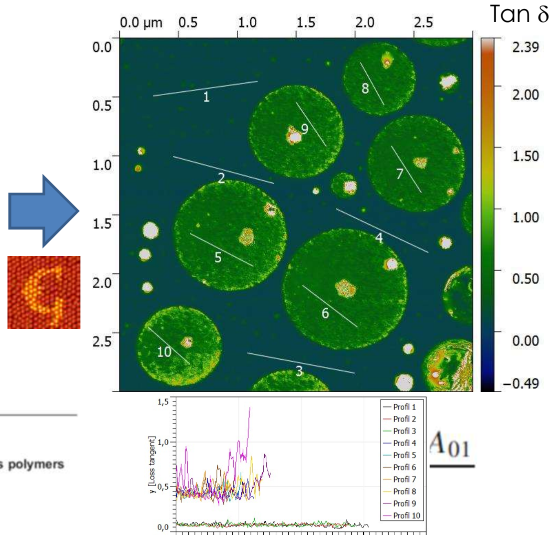
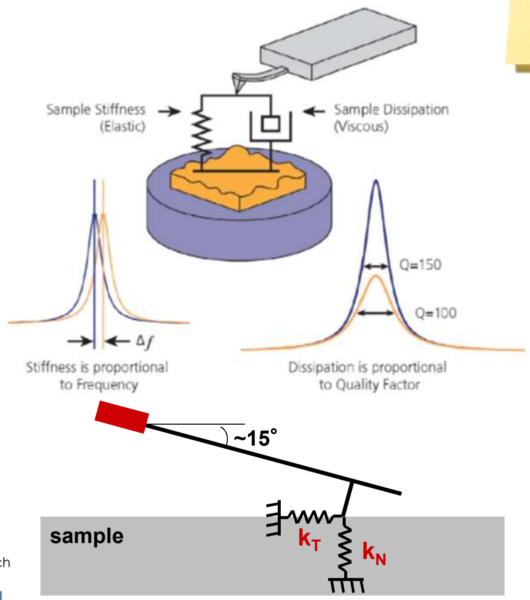


Data obtained by Michel Ramonda (Univ. Mc

Contact Resonance AFM

Contact Resonance

See Olivier's Talk !!!



Adapted from Asylum Research

Contact Resonance

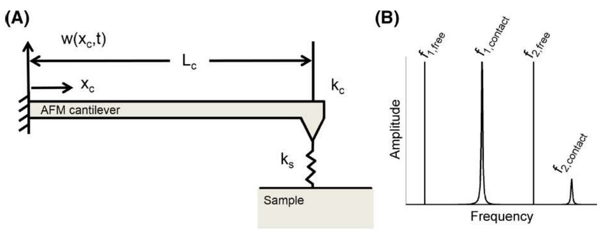
See Olivier's Talk !!!

Cellulose (2016) 23:1031–1041
DOI 10.1007/s10570-016-0883-4

ORIGINAL PAPER

Mechanical properties of cellulose nanomaterials studied by contact resonance atomic force microscopy

Ryan Wagner · Robert J. Moon · Arvind Raman



Measuring the resonance frequency

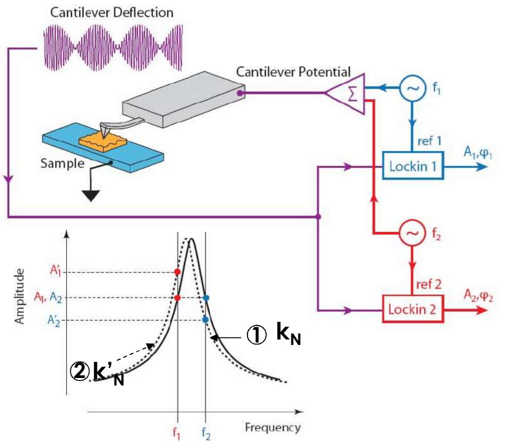
Methods	What it does	Benefits	Disadvantages
Fixed frequency[2]	The cantilever response is measured at a fixed frequency, which varies as the contact resonance frequency shifts.	Simple to implement and produces elastic contrast images.	Produces only qualitative results since the frequency shift itself 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 Research (CR-AFM application note)

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

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

② Stiffness k'_N

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

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

Resonance tracking:

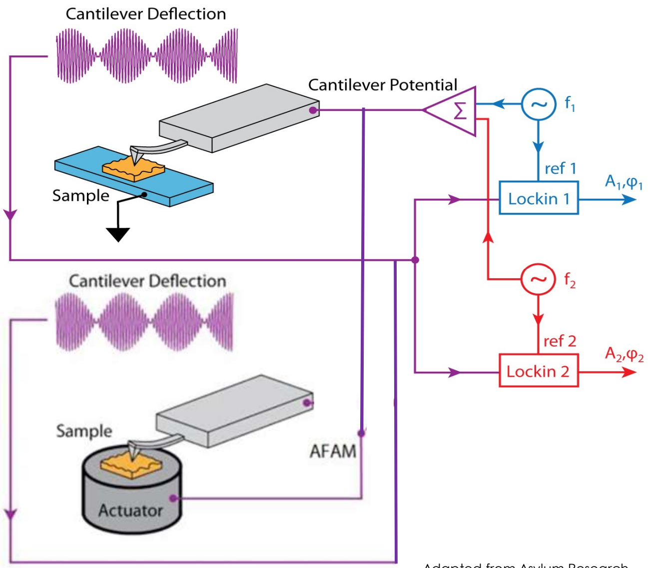
$\Delta f = f_1 - f_2 = $ constant

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

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

Adapted from Asylum Research

Contact Resonance : Tip or Sample ?



Adapted from Asylum Research

Contact Resonance

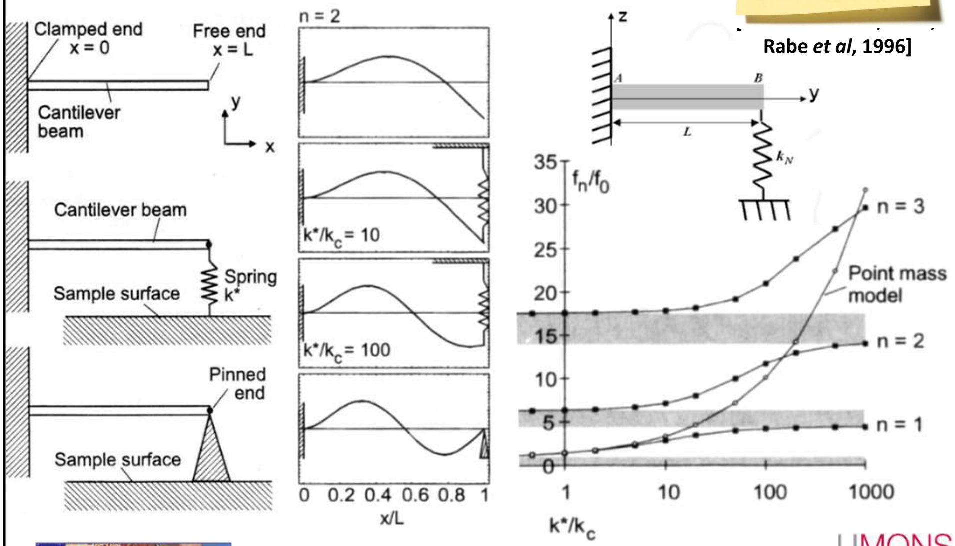
Difficult task … or not !!!

Cantilever dynamic: models

Clamped beam coupled with a normal spring

See Olivier's Talk !!!

Rabe *et al*, 1996]



Cantilever dynamic: models

See Olivier's Talk !!!

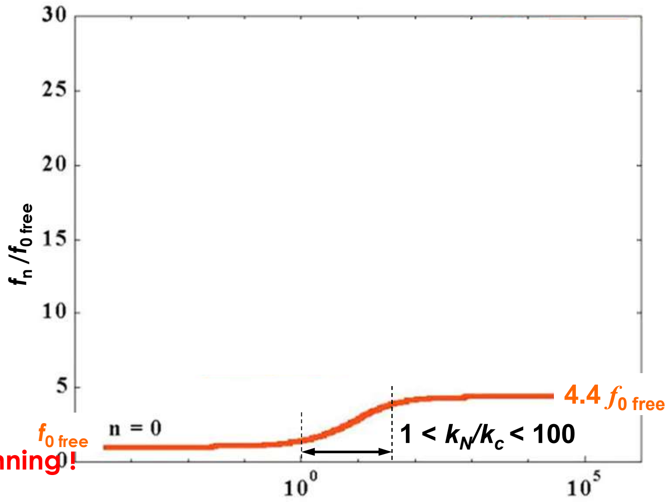
Sensitivity of the cantilever contact stiffness and considered mode

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

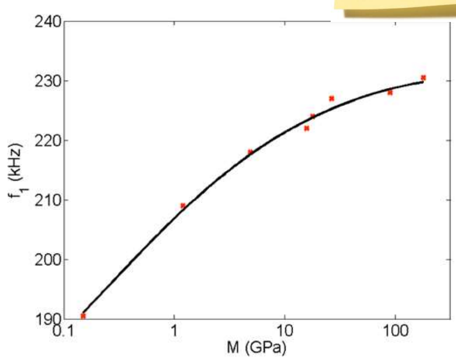
"Hard" sample (Si)
$k_N \approx 1000$ N/m
Not OK using n = 0
OK using n > 0
with low applied static force for scanning!



Cantilever dynamic: calibration

See Olivier's Talk !!!

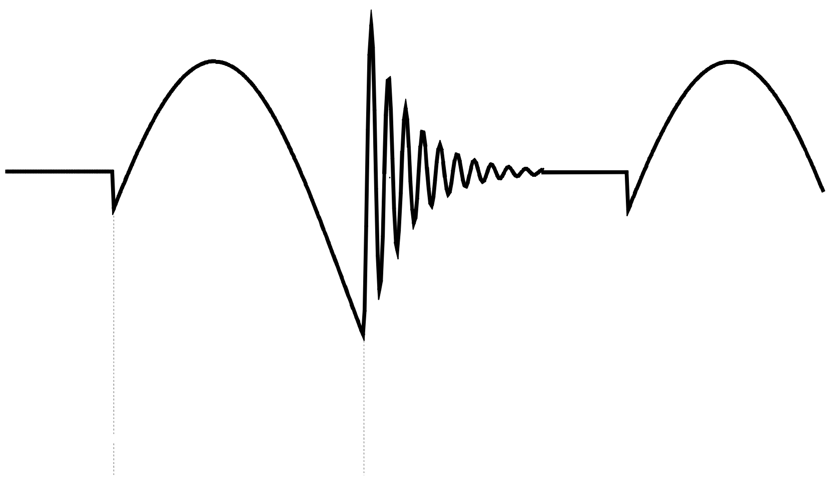
- Pointe utilisée (Bruker MPP-32120-10) :
  - Raideur : k = 0.1 N/m
  - f_0 = 14 kHz (à l'air)
  - Rotated tip
- Calibration sur :
  - PU3455 (0.15 GPa)
  - PE1 (1.2 GPa)
  - PMMA (4.9 GPa)
  - Soufre 010 (15.8 GPa)
  - HOPG (18.0 GPa)
  - Soufre 001 (26.5 GPa)
  - Calcite (90.0 GPa)
  - Silicium (181.0 GPa)



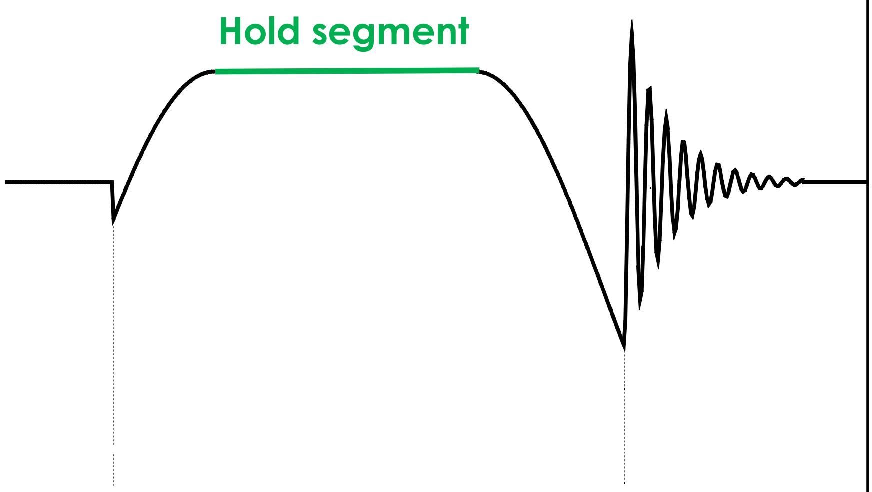
- Force d'appui ~20 nN et force d'adhésion ~ 20 nN
- Loi de régression : $f_1 = f_{as}\left(1 - exp\left(\frac{M - M'}{M_0}\right)^{1/\alpha}\right)$

Courtesy of O. Arnould, M. Ramonda & R. Arinero

Back to Sub Resonance Tapping …

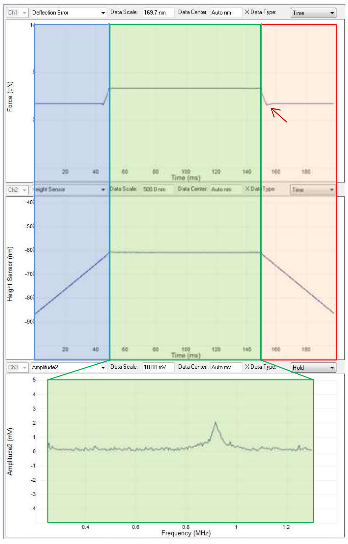


PFT – DataCube – Contact Resonance



Peak Force Tapping - Contact Resonance

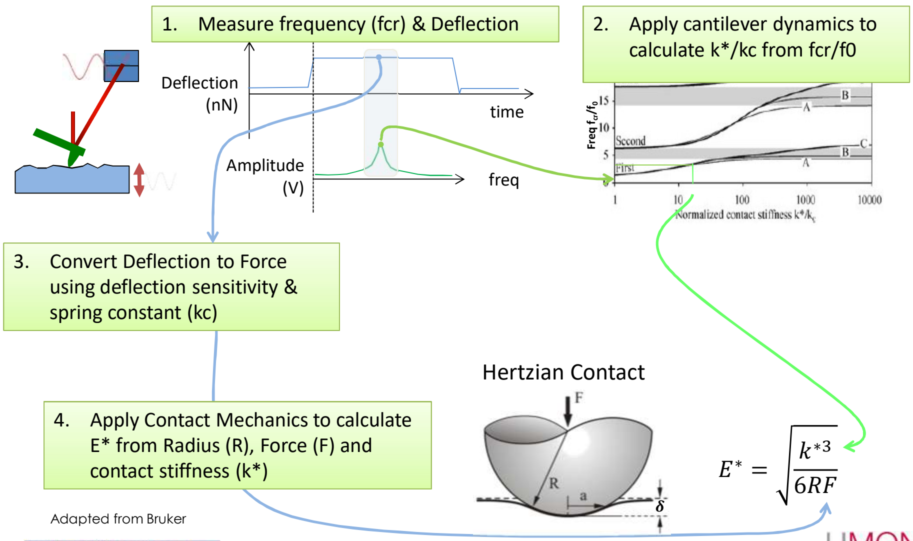
- CR is based on *FAST*Force Volume
  - Provides standard force curve for comparison for each pixel in map
    - Approach
    - Hold Force and sweep frequency
    - Retract
  - **More repeatable**: lateral force on tip is minimized, reducing tip wear
  - **More information**: allows measurement of adhesion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



Adapted from Bruker

Peak Force Tapping - Contact Resonance

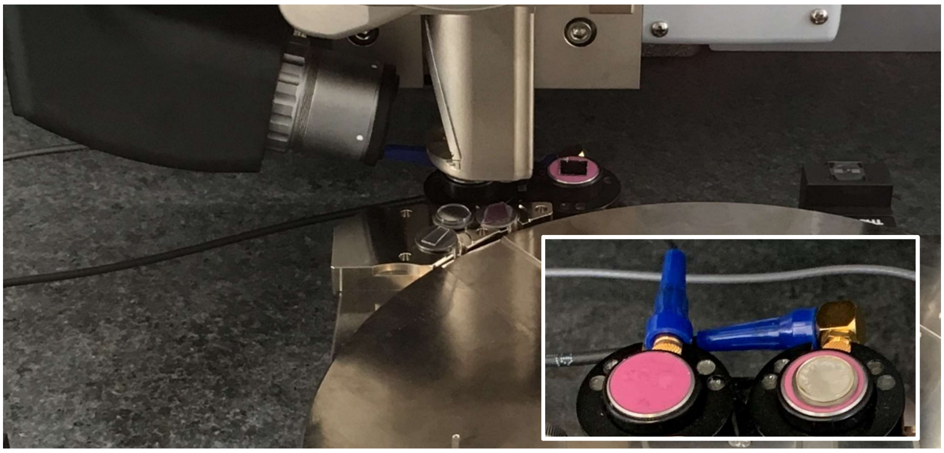
From Frequency and Deflection to modulus



Adapted from Bruker

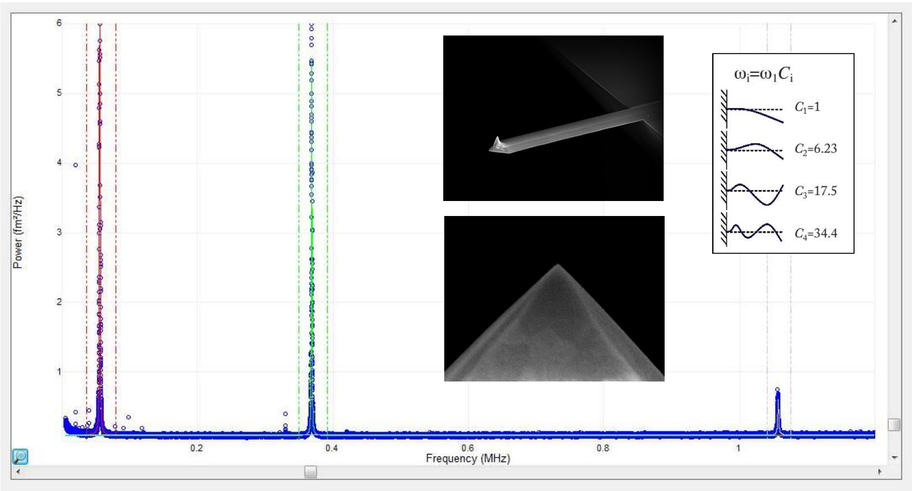
Peak Force Tapping - Contact Resonance

Hardware



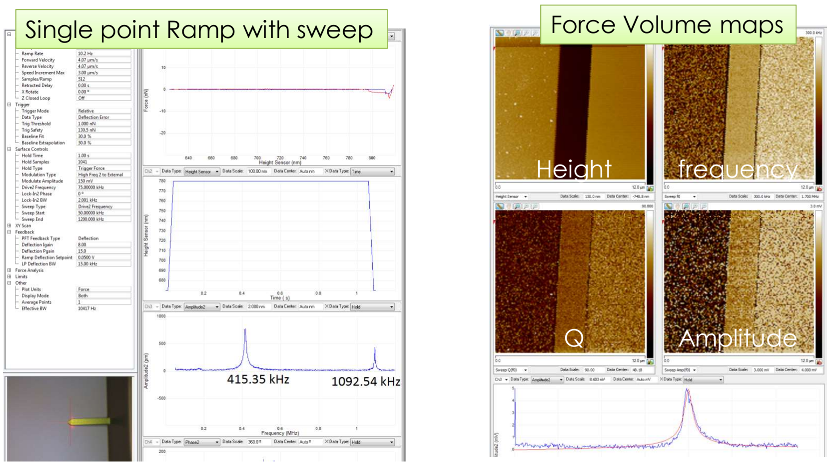
Peak Force Tapping - Contact Resonance

Hardware



Adama innovations

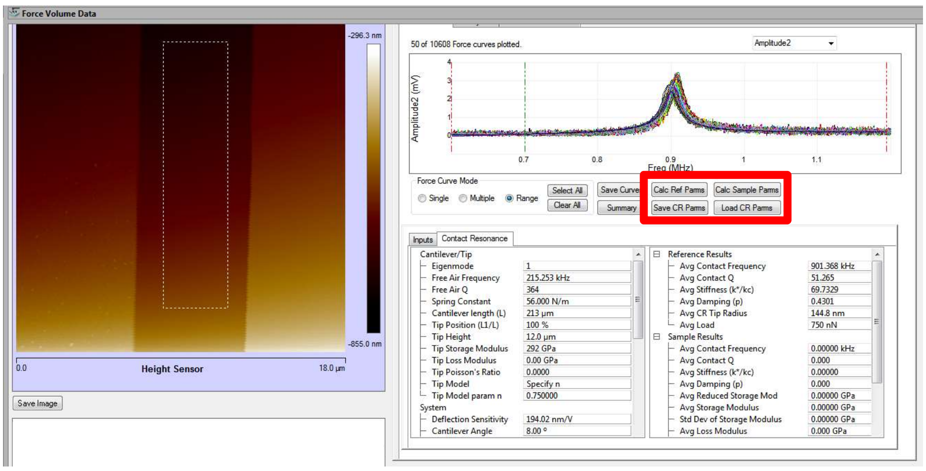
Peak Force Tapping - Contact Resonance



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

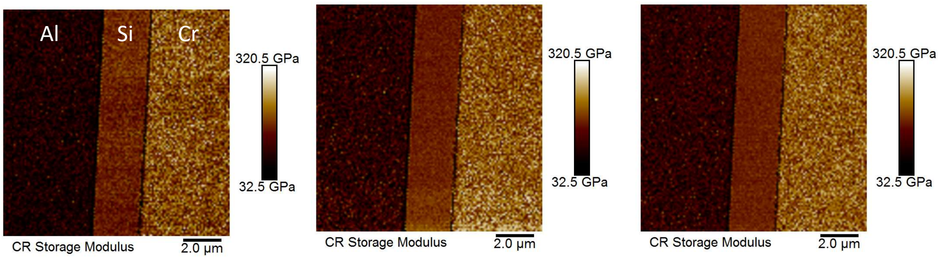
Real-time Contact Resonance Sweeping

Force Volume for mapping, Ramp for single points



Peak Force Tapping - Contact Resonance

Calibration on known modulus materials



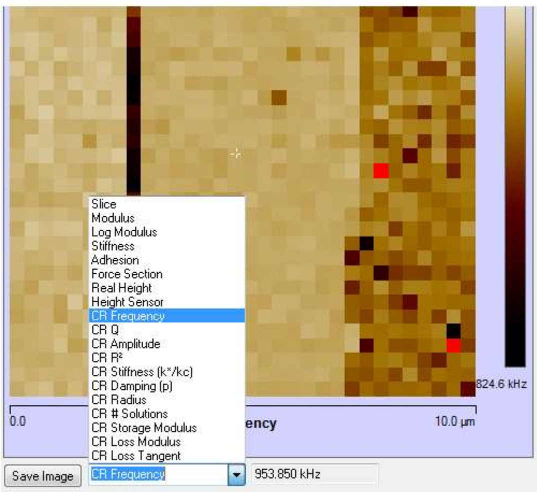
Load=200nN
Si: 165±15 GPa
Al: 85±24 GPa
Cr: 192±31 GPa

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

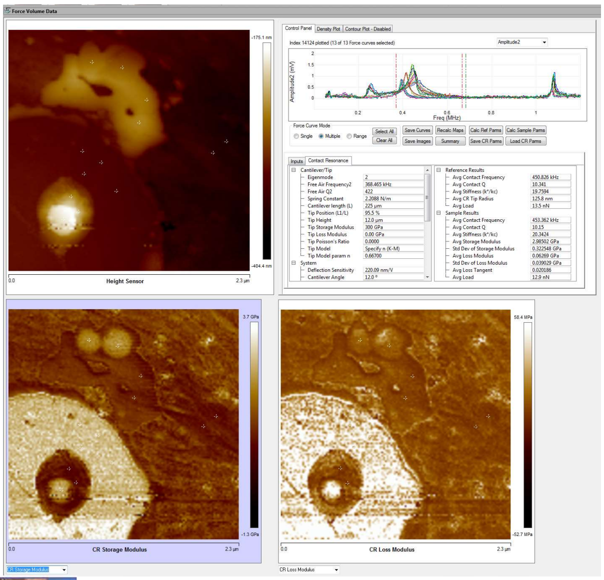
Peak Force Tapping - Contact Resonance

Property maps



Peak Force Tapping - Contact Resonance

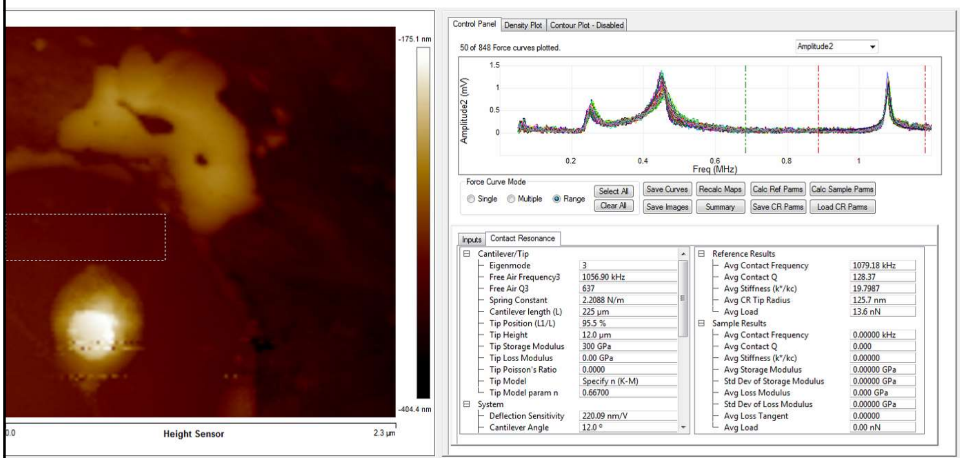
PS-PCL



2nd peak

Peak Force Tapping - Contact Resonance

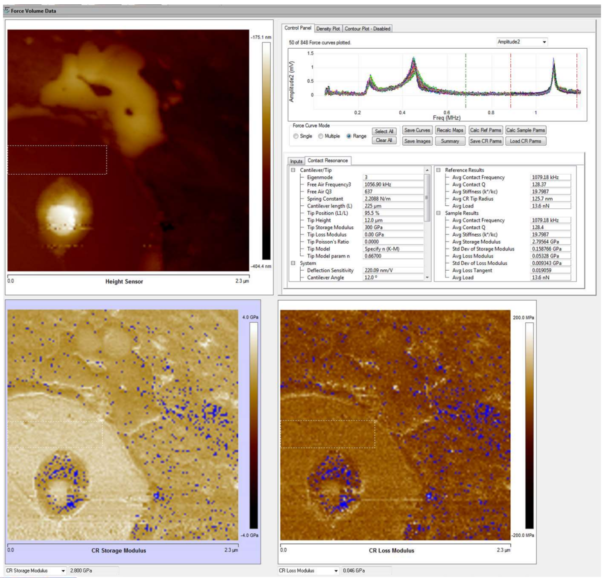
PS-PCL



Peak Force Tapping - Contact Resonance

PS-PCL

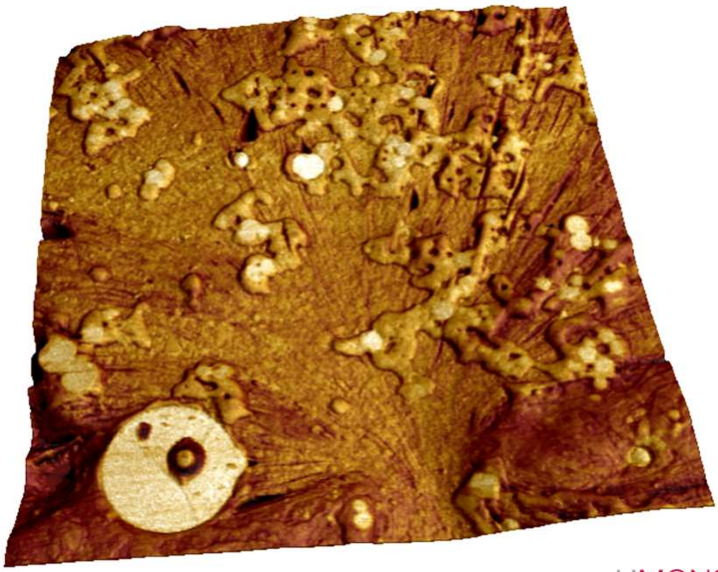
3rd peak



UMONS
Université de Mons

Peak Force Tapping - Contact Resonance

PS-PCL



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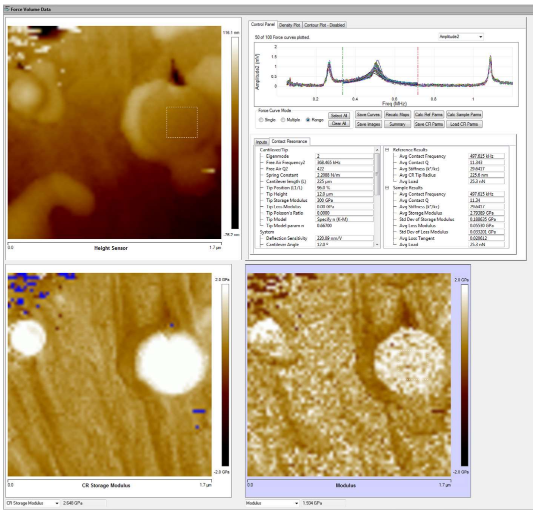
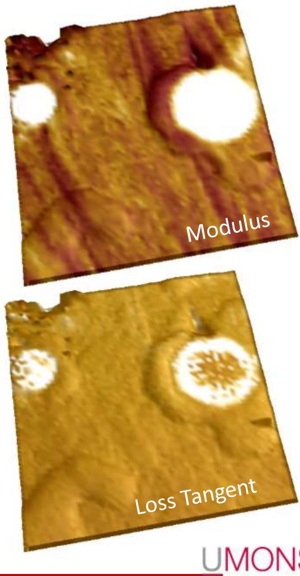
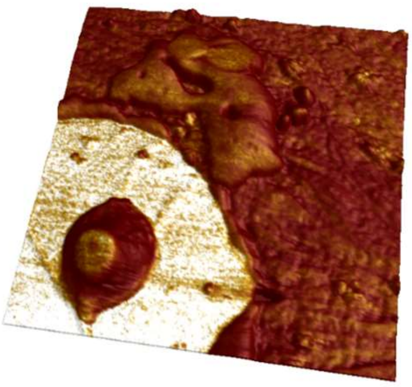
Peak Force Tapping - Contact Resonance

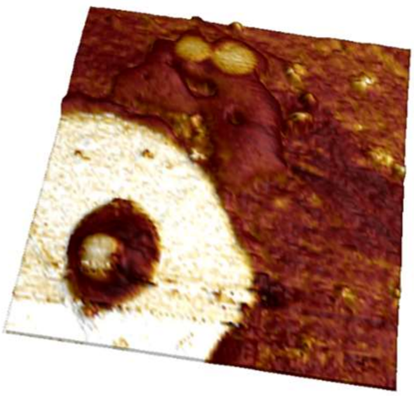




Comparing PFTQNM and CR

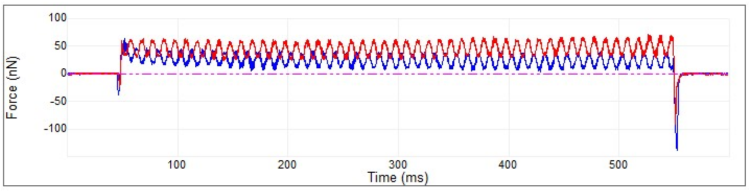
- PFTQNM
- CR 128x128





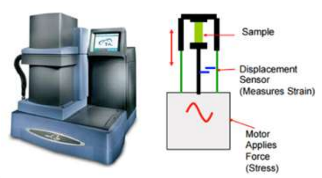
Nano Dynamical Mechanical Analysis

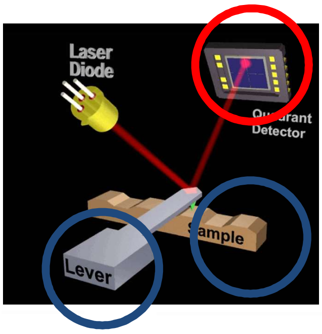
nDMA



The methodology

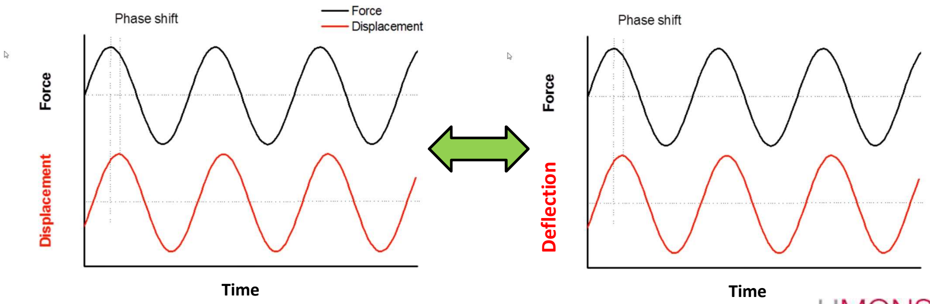
From DMA to nDMA …





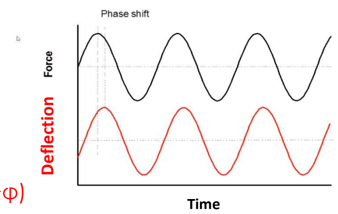
$D(t) = D_1\, e^{i(\omega t+\varphi)} + D_0$

$Z(t) = Z_1 e^{i(\omega t+\psi)} + Z_0$



nDMA - Equations

$Z(t) = Z_1 e^{i(\omega t+\psi)} + Z_0$ $D(t) = D_1\, e^{i(\omega t+\varphi)} + D_0$



Stiffness: $S^* = F^*/L^*$

Deformation: $L^* = Z_1\, e^{i(\omega t+\psi)} - D_1\, e^{i(\omega t+\varphi)}$

If the cantilever spring constant K is assumed to be calibrated and known :

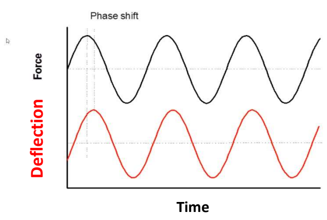
$$\boxed{F^* = K_C\, D_1\, e^{i(\omega t+\varphi)}}$$

$$\boxed{S^* = S' + iS'' = K_C\, D_1\, e^{i(\omega t+\varphi)} / [Z_1\, e^{i(\omega t+\psi)} - D_1\, e^{i(\omega t+\varphi)}]}$$

$$S' = \frac{K_C D_1}{Z_1} \frac{\cos(\varphi-\psi) - (D_1/Z_1)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi) + 1} \qquad S'' = \frac{K_C D_1}{Z_1} \frac{\sin(\varphi-\psi)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi) + 1}$$

nDMA - Equations

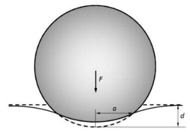
$\boxed{Z(t)=Z_1 e^{i(\omega t+\psi)} + Z_0}$ $\boxed{D(t)= D_1\, e^{i(\omega t+\varphi)} + D_0}$



$$S' = \frac{K_c D_1}{Z_1} \frac{\cos(\varphi-\psi)-(D_1/Z_1)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi)+1} \qquad S" = \frac{K_c D_1}{Z_1} \frac{\sin(\varphi-\psi)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi)+1}$$

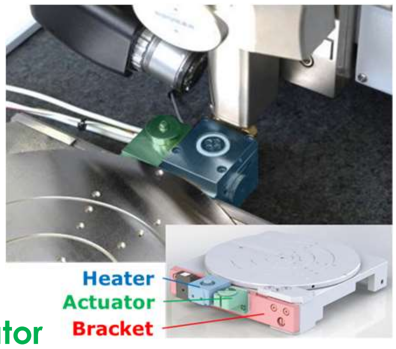
$$E' = \frac{S'}{\boxed{2a_c}} = \frac{K_c D_1}{2a_c Z_1} \frac{\cos(\varphi-\psi)-(D_1/Z_1)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi)+1}$$

$$E" = \frac{S"}{\boxed{2a_c}} = \frac{K_c D_1}{2a_c Z_1} \frac{\sin(\varphi-\psi)}{(D_1/Z_1)^2 - 2(D_1/Z_1)\cos(\varphi-\psi)+1}$$



$$\tan\delta = E"/E' = S"/S' = \frac{\sin(\varphi-\psi)}{\cos(\varphi-\psi)-(D_1/Z_1)}$$

nDMA - Hardware



Fast heating

nDMA **heater**

(RT-250 °C, 0.1Hz – 300 Hz)

Wide bandwidth actuation

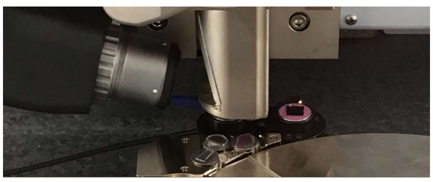
High frequency sample **actuator**

(RT measurements, 0.1Hz-20 kHz)

Pre-calibrated probes

Calibration sample

(Sapphire)



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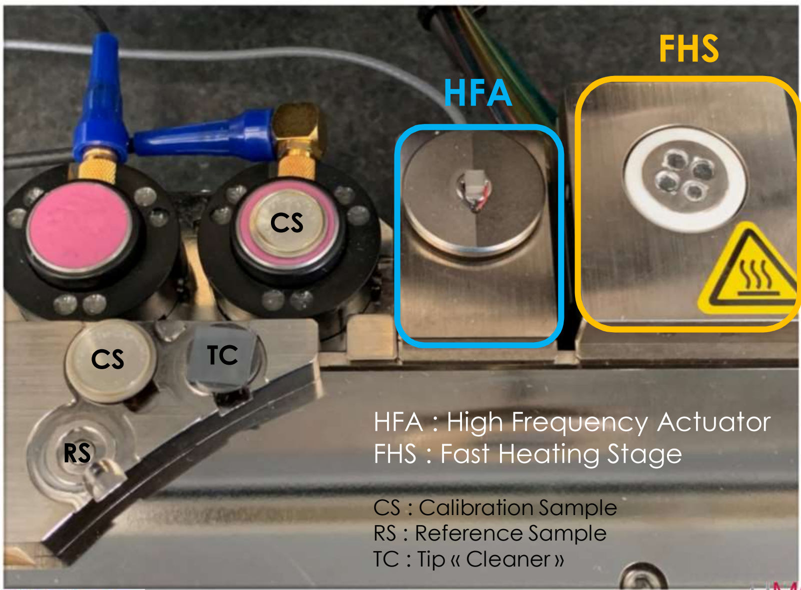

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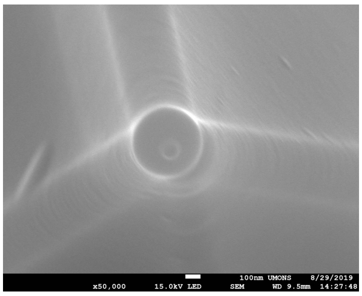
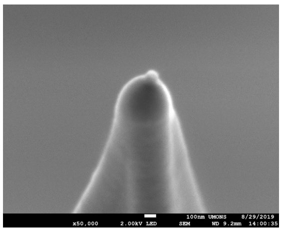
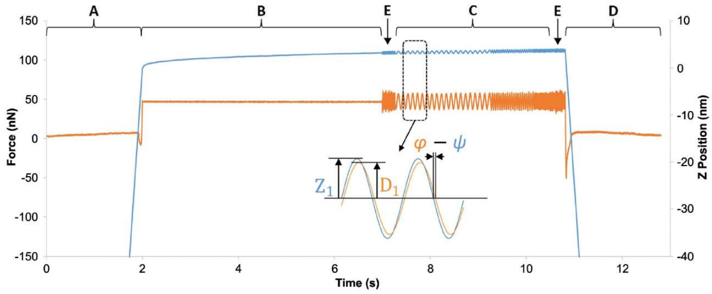
Pre-calibrated tips

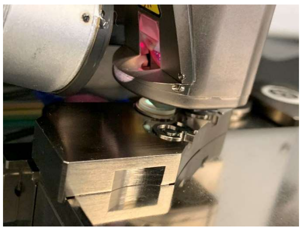




Probe Type	Spring Const. (N/m)	Tip Radius (nm)	min E' (MPa)	max E' (MPa)
SAA-HPI-DC-125	0.25	125	0.1	10
RTESPA150-125	5	125	2	200
RTESPA300-125	40	125	20	2,000
RFESPA-40-30	0.9	33	0.8	80
RTESPA150-30	5	33	4	400
RTESPA300-30	40	33	40	4,000
RTESPA525-30	200	33	200	20,000

nDMA – Ramp Scripting





Calibration on Sapphire in the exact same conditions !

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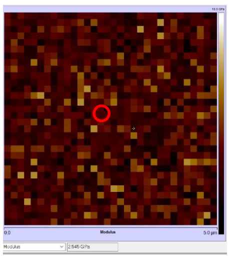
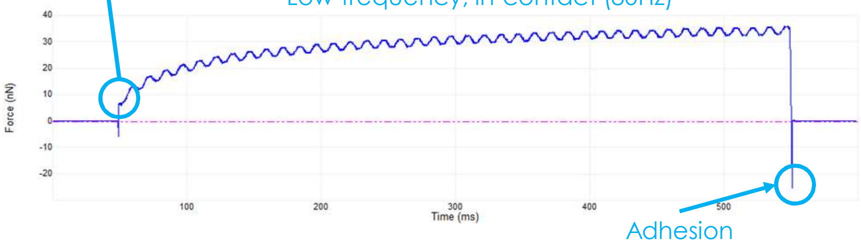


Preload control

Low-frequency, in-contact (80Hz)



Adhesion quantified

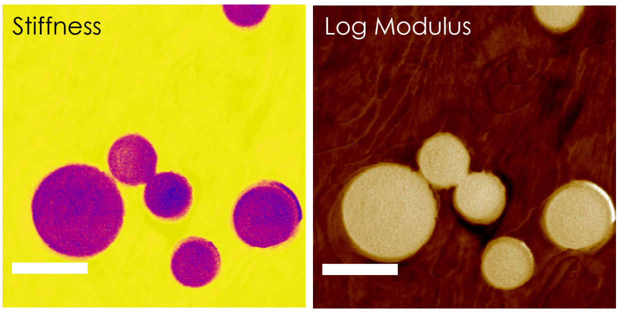
PS – PCL (25:75)

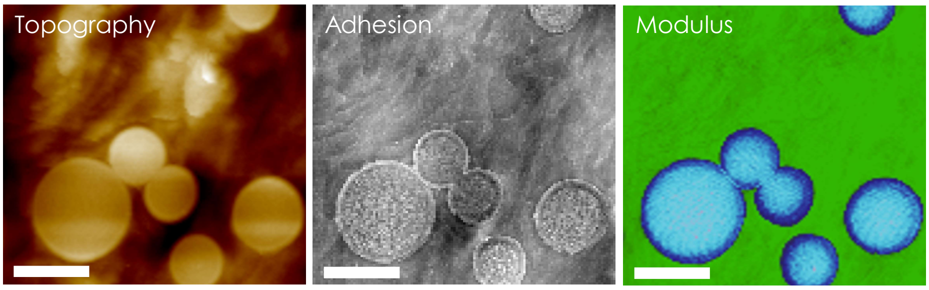
Tip : RTESPA 300 – 125

k = 29.22 N/m
Radius = 125 nm

PeakForce Tapping

512 x 512 pixels, PFSP = 15 nN
Scale bar = 2.0 µm



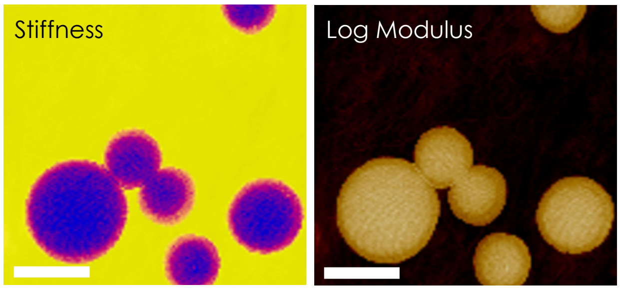


PS – PCL (25:75)

Tip : RTESPA 300 – 125

k = 29.22 N/m
Radius = 125 nm

PeakForce Tapping nanoDMA
128 x 128 pixels,
Frequency = 80 Hz
Scale bar = 2.0 µm

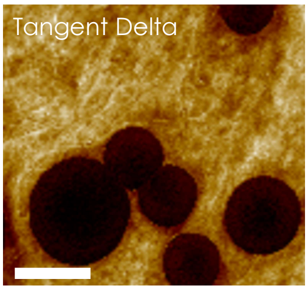


PS – PCL (25:75)

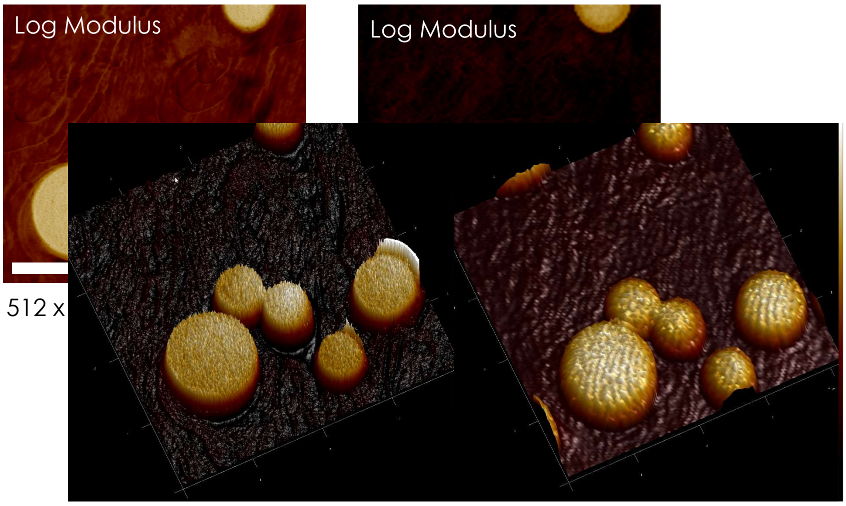
Tip : RTESPA 300 – 125

k = 29.22 N/m
Radius = 125 nm

PeakForce Tapping nanoDMA
128 x 128 pixels,
Frequency = 80 Hz
Scale bar = 2.0 µm



PFT vs. nDMA



512 x

PS:PCL 30:70 blend

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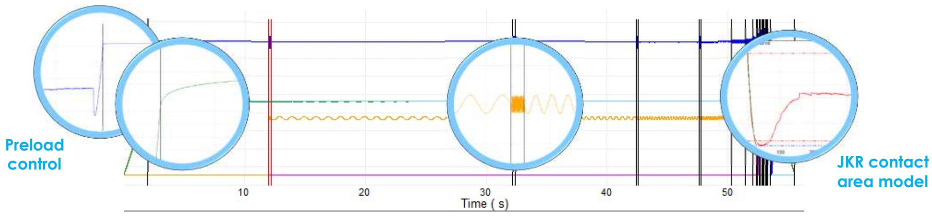
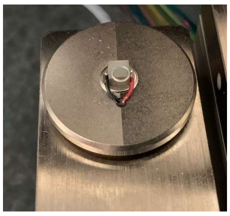


HFA



Modulated force, embedded in force curve
- Sub-nm amplitudes, stays in linear regime.
- No ripping out of contact during modulation

Imaging and point spectroscopy
- Quantitative data in both

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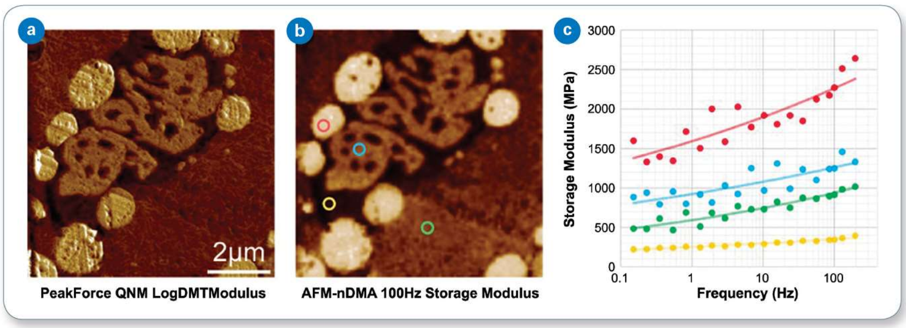

COC PE LDPE Elastomer

Adapted from Bruker

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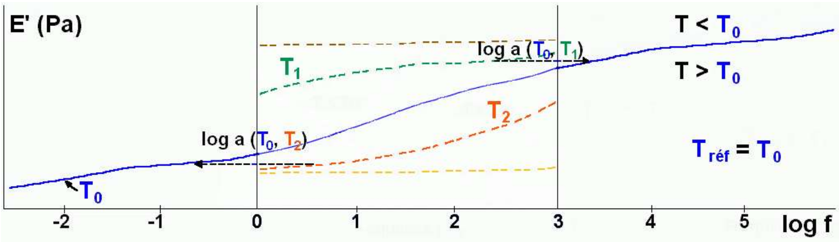
Time –Temperature Superposition (TTS)

The **time–temperature superposition principle** is a concept in polymer physics and in the physics of glass-forming liquids.
This superposition principle is used to determine temperature-dependent mechanical properties of linear viscoelastic materials from known properties at a reference temperature.



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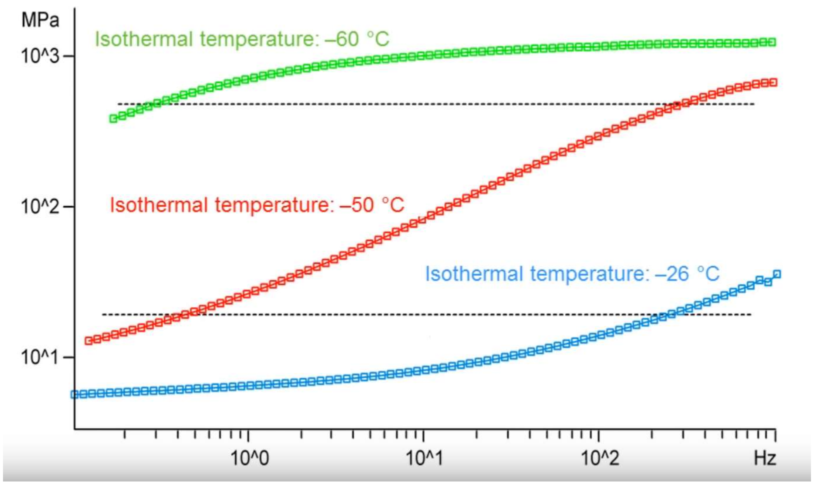
Time –Temperature Superposition (TTS)



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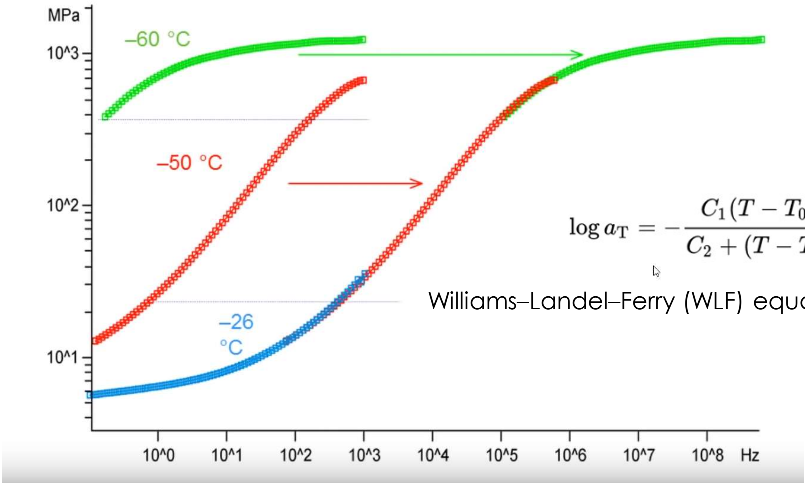
Time –Temperature Superposition (TTS)



$$\log a_T = -\frac{C_1(T-T_0)}{C_2+(T-T_0)}$$

Williams–Landel–Ferry (WLF) equation

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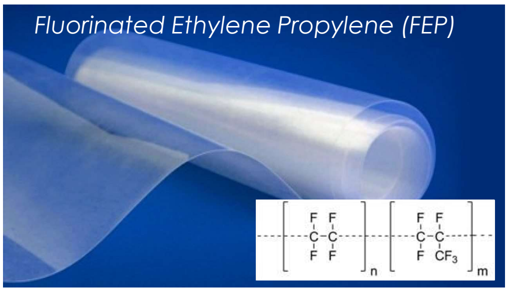
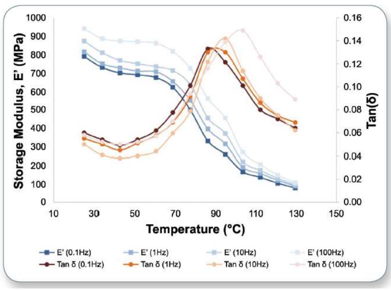
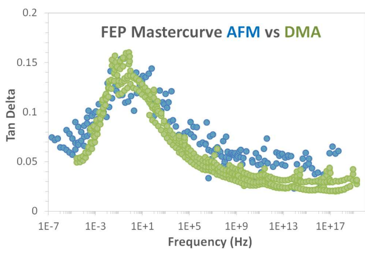
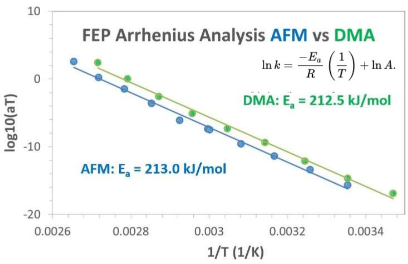






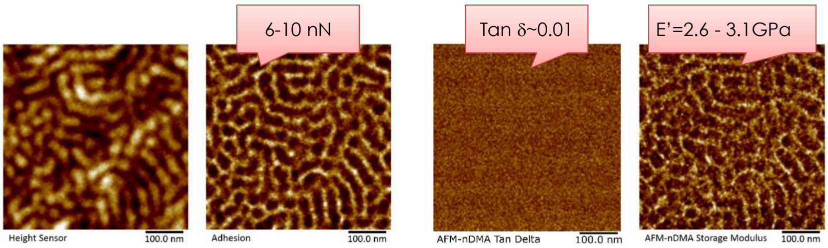


Adapted from Bruker

nanoDynamical Mechanical Analysis

Block Copolymer : PS-b-PMMA

- Both adhesion and loss tangent contribute to energy dissipation.
- Adhesion usually dominates in intermittent contact methods.



- E' map shows expected contrast correlating to 20 nm domains.

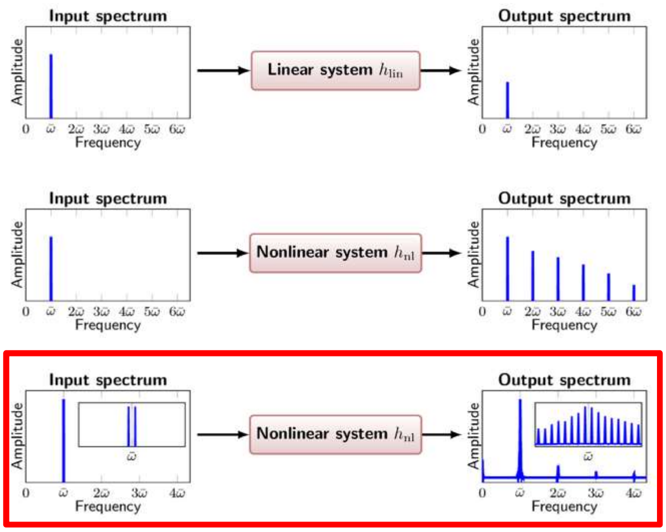
Decoupling adhesion from loss tangent !

AFM-nDMA measures Tan δ in contact → no adhesion artifact

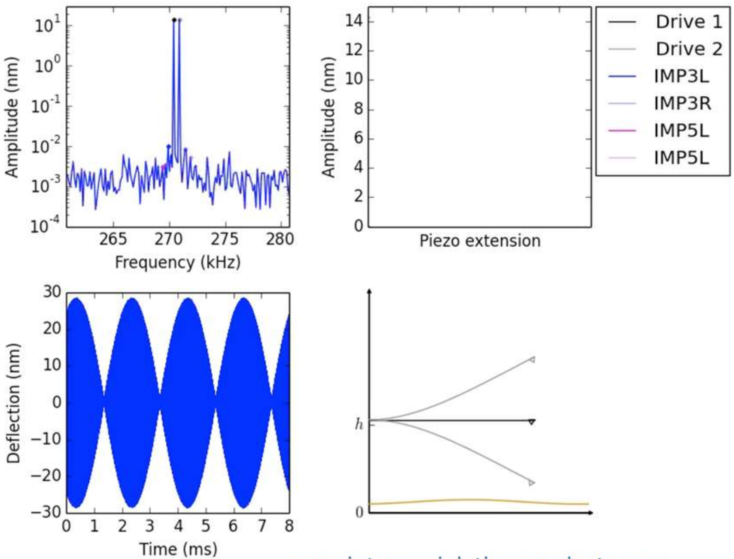
Intermodulation AFM

The methodology

Intermodulation AFM



Intermodulation AFM



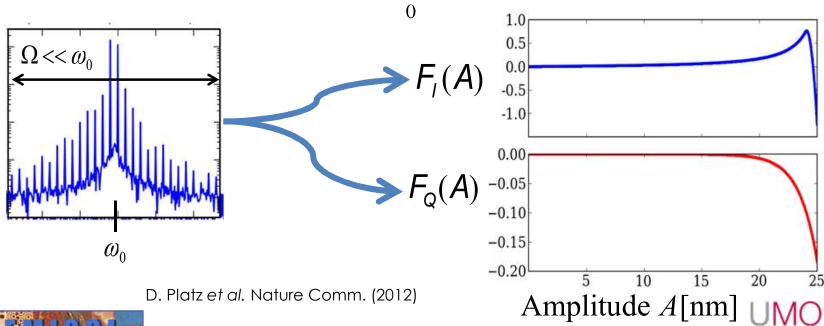
www.intermodulation-products.com

Force Quadratures

tip motion: $z(t) \cong h + A\cos(\omega_0 t)dt$

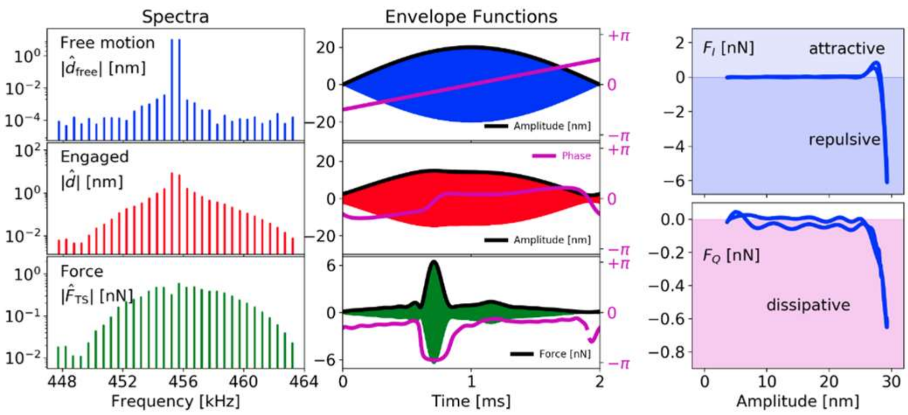
in-phase (conservative): $F_I(A) = \int_0^{2\pi} F_{ts}(z,\dot{z})\cos(\omega_0 t)dt$

quadrature (dissipative): $F_Q(A) = \int_0^{2\pi} F_{ts}(z,\dot{z})\sin(\omega_0 t)dt$

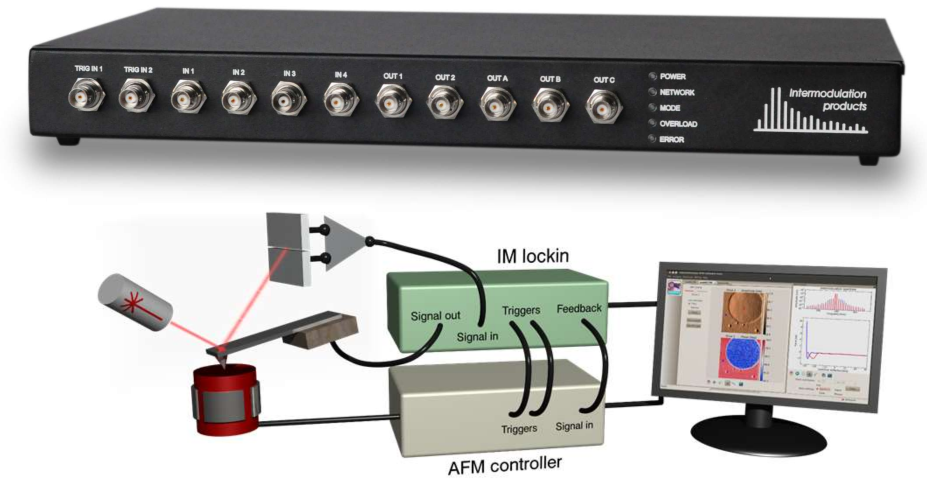


D. Platz *et al.* Nature Comm. (2012)

Force Quadratures



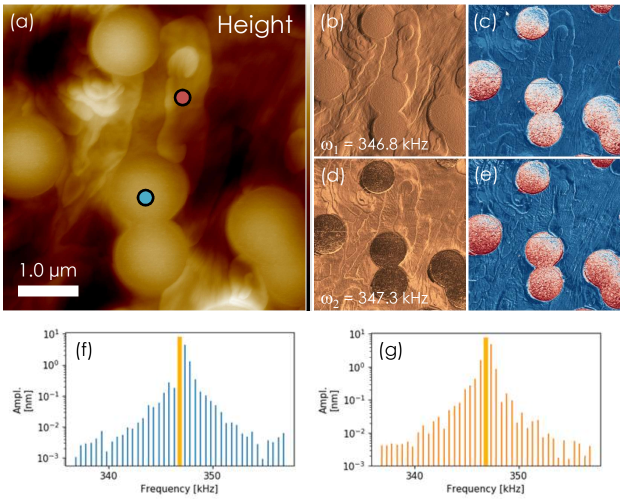
Intermodulation AFM



Intermodulation AFM

Some results

Blend of PS/PCL

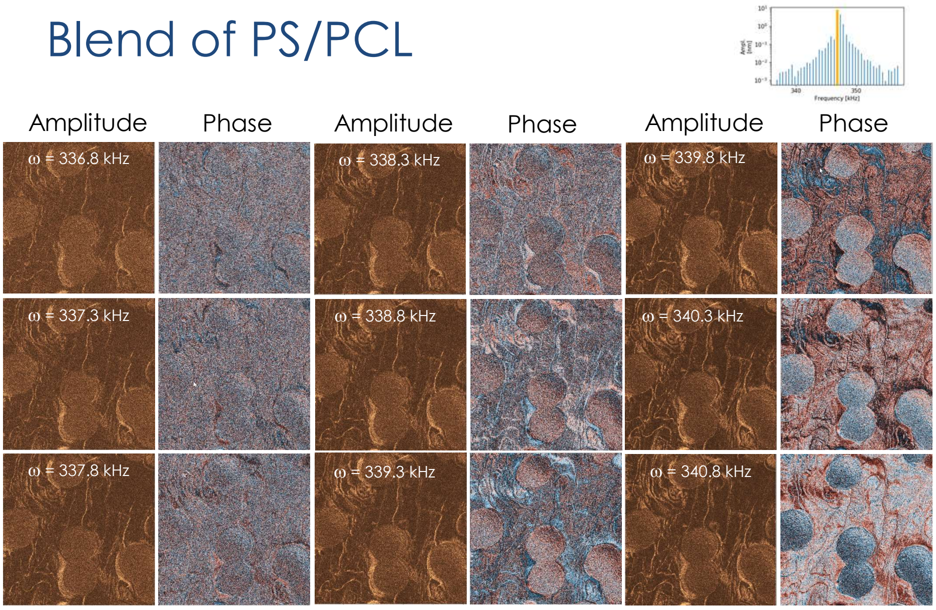


Soft Matter (2016), 12, 619.

PS:PCL 30:70 blend

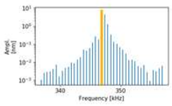
+ 40 others !

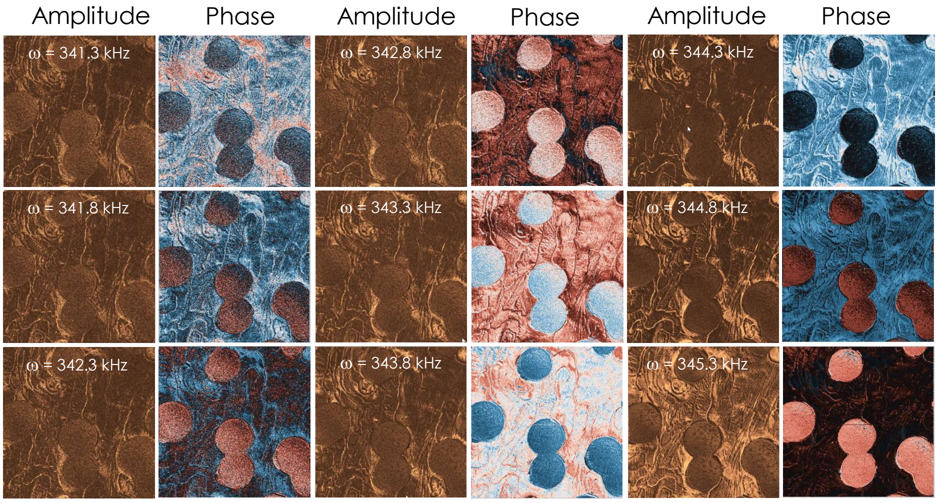
Blend of PS/PCL



PS:PCL 30:70 blend

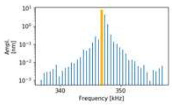
Blend of PS/PCL

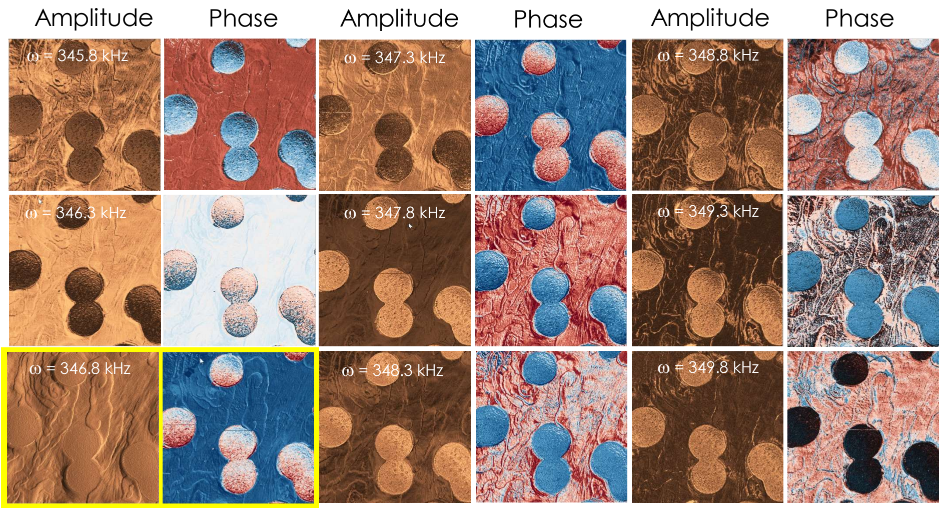




PS:PCL 30:70 blend

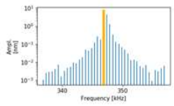
Blend of PS/PCL



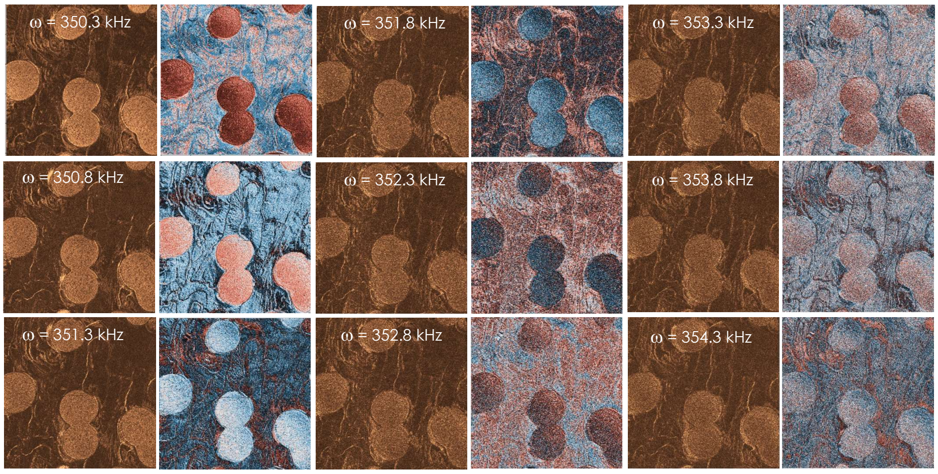


PS:PCL 30:70 blend

Blend of PS/PCL

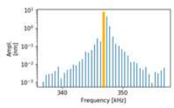


Amplitude | Phase | Amplitude | Phase | Amplitude | Phase

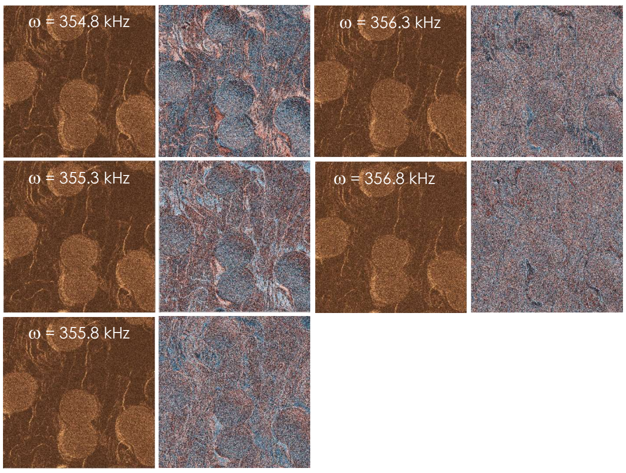


PS:PCL 30:70 blend

Blend of PS/PCL

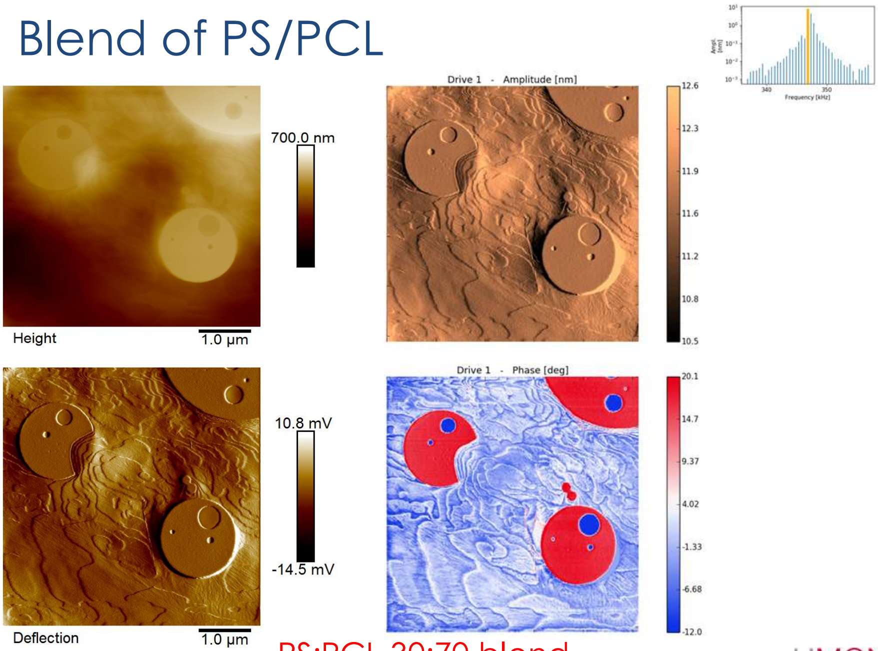


Amplitude | Phase | Amplitude | Phase



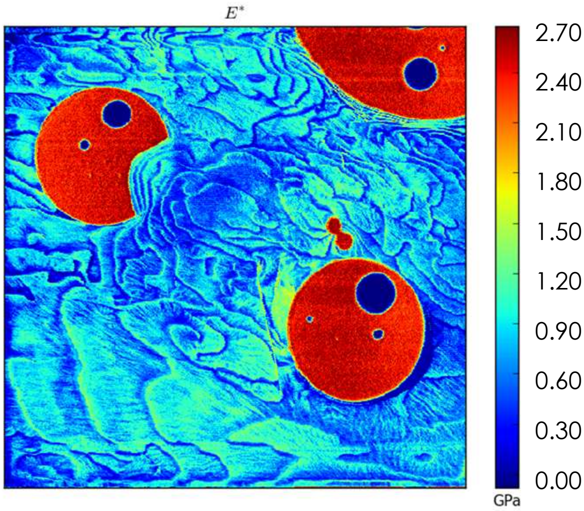
PS:PCL 30:70 blend

Blend of PS/PCL

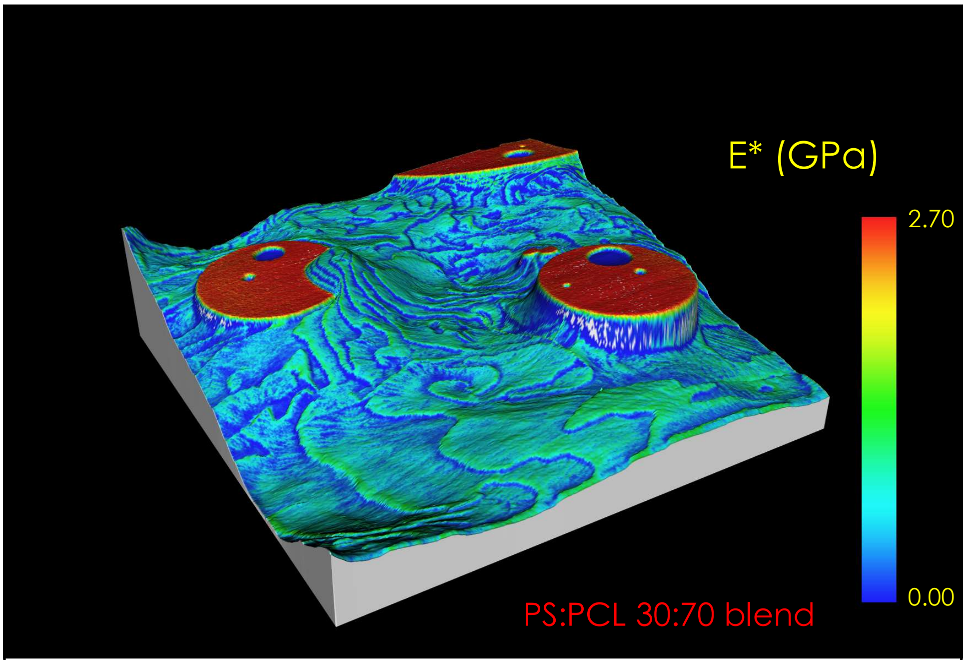


PS:PCL 30:70 blend

Blend of PS/PCL



PS:PCL 30:70 blend



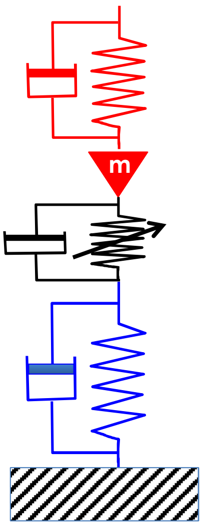
Moving Surface Model

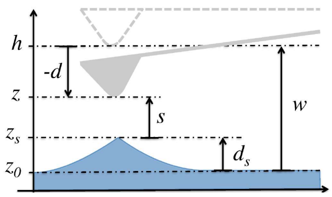
$$\boxed{m\ddot{d} + \gamma m\dot{d} + kd} = F_{TS}(s,\dot{s}) + F_{\text{drive}}$$

$$\boxed{\eta\dot{d}_s + k_s d_s} = -F_{TS}(s,\dot{s})$$

$$\text{separation} \quad s = (d - d_s) + h - z_0$$

$$F_{\text{TS}}(s,\dot{s}) = \begin{cases} 0 & \text{if } s > 0 \\ -F_{\text{ad}} - k_{\text{v}}s - \eta_{\text{v}}\dot{s} & \text{if } s \leq 0 \end{cases}$$

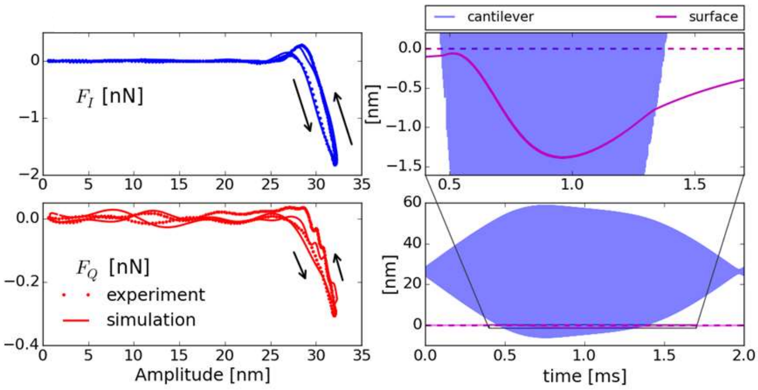




Soft Matter (2016), 12, 619.

Fit to moving surface model

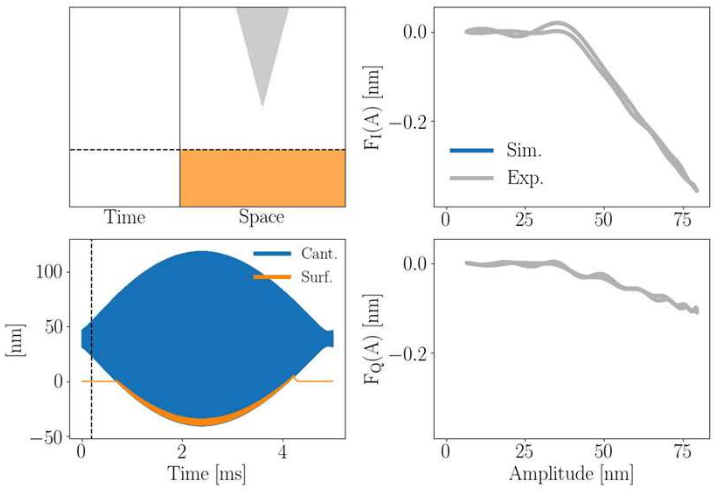
PS phase



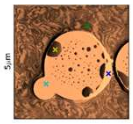
Fit to moving surface model

Courtesy of P.A. Thoren

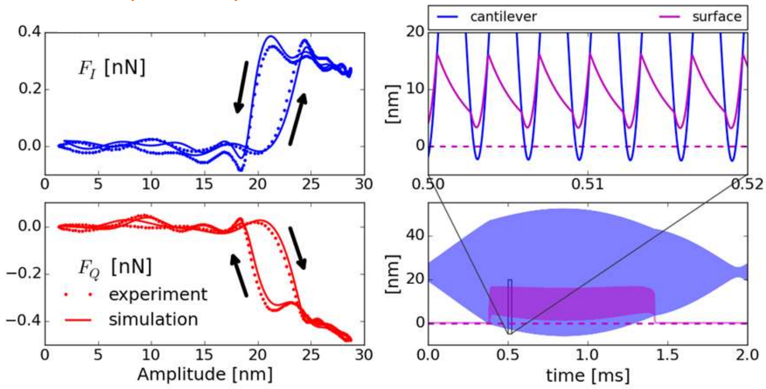
PS phase



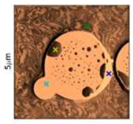
Fit to moving surface model



PCL amorphous phase

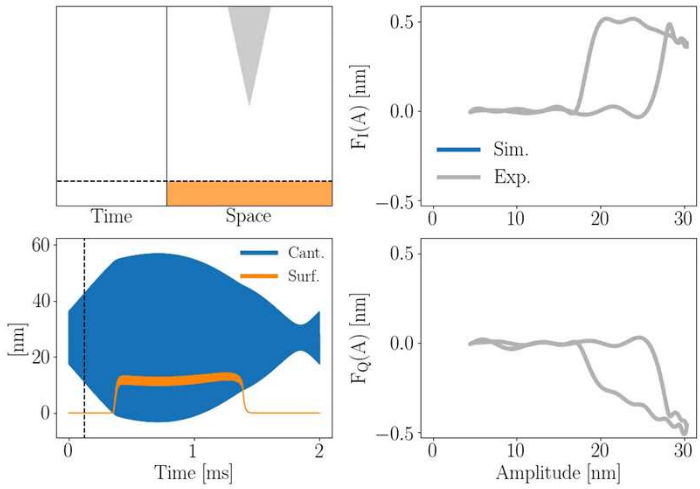


Fit to moving surface model

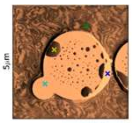


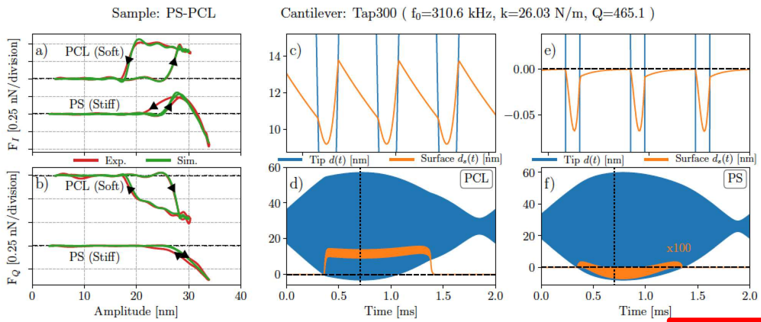
Courtesy of P.A. Thoren

PCL amorphous phase



Fit to moving surface model





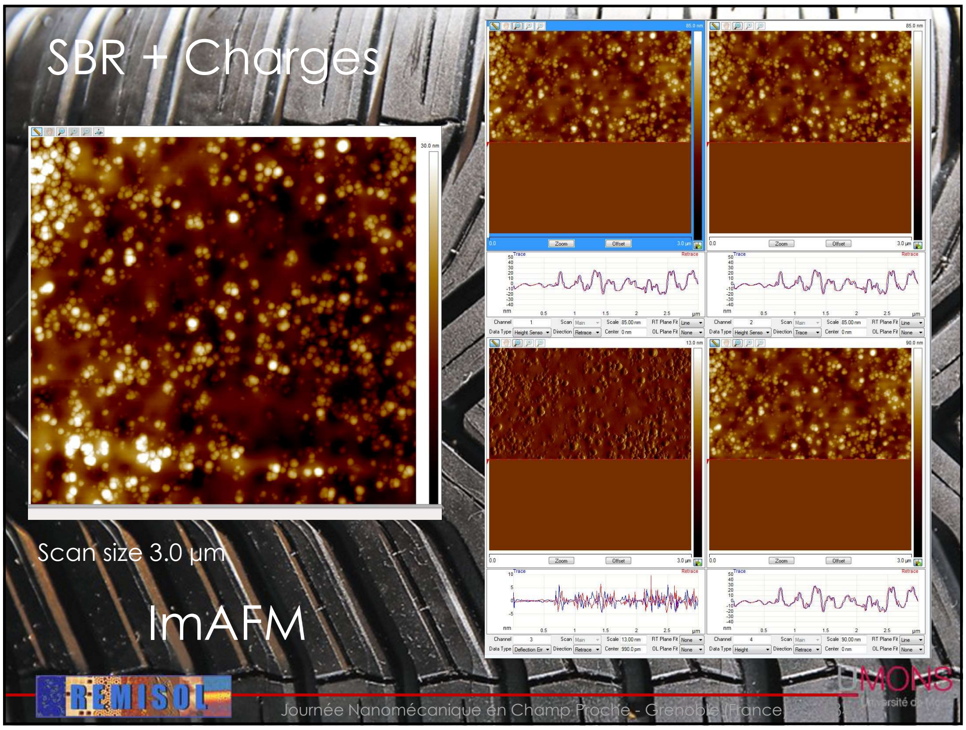
	h [nm]	τ_s [ns]	τ_v [ns]	k_s [N/m]	k_v [N/m]	F_{ad} [nN]	$K=k_s/k_v$	$R=\tau_s/\tau_v$
PCL	26.95	8118	580.3	0.0469	0.1557	2.859	0.3012	13.99
PS	25.98	735.2	152.8	32.53	1.097	3.88	29.65	4.811

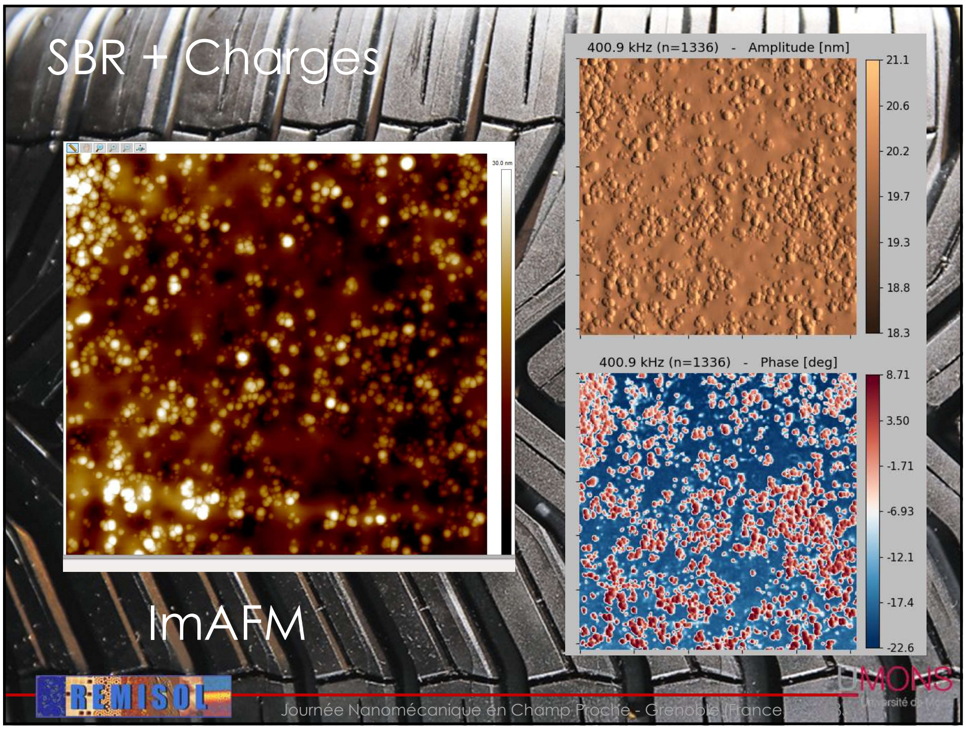
Impact-Rheology Factor

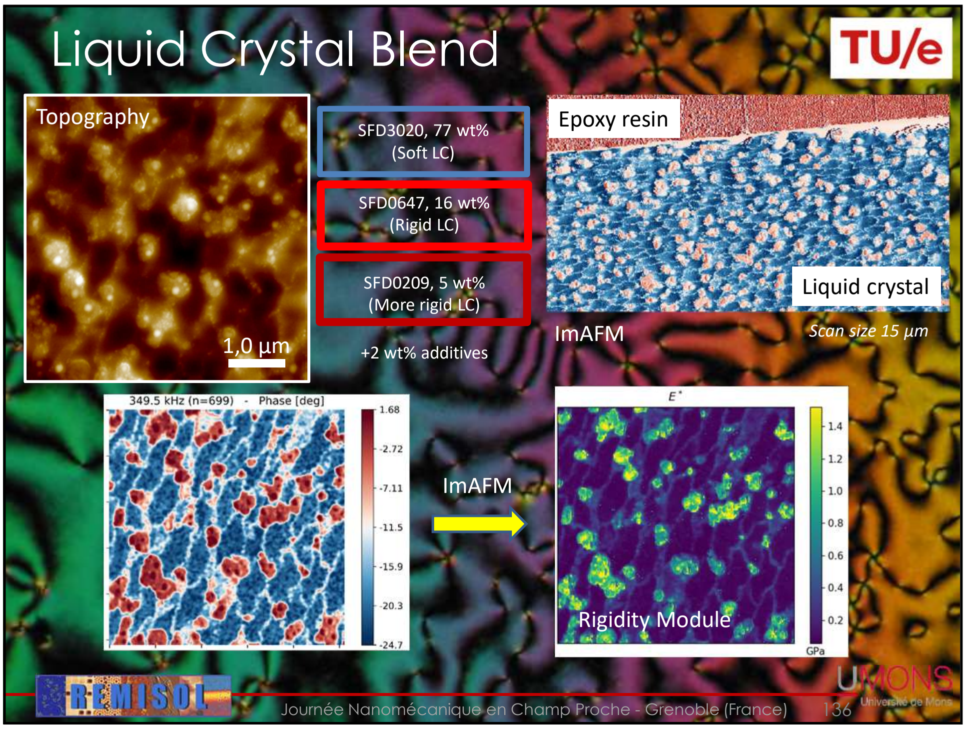
$$R=\frac{\tau_s}{\tau_v}=\frac{\eta_s}{k_s}\frac{k_v}{\eta_v}$$

REMISOL UMONS Université de Mons

Journée Nanomécanique en Champ Proche - Grenoble (France) 133

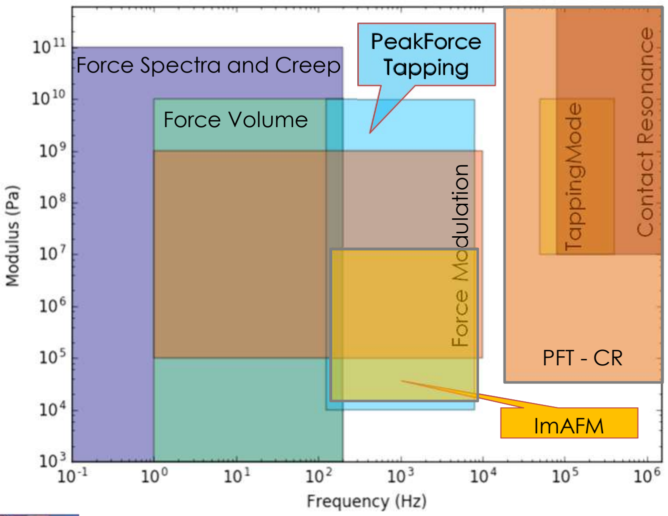



SBR + Charges
400.9 kHz (n=1336) - Amplitude [nm]
21.1
20.6
20.2
19.7
19.3
18.8
18.3
400.9 kHz (n=1336) - Phase [deg]
8.71
3.50
-1.71
-6.93
-12.1
-17.4
-22.6
ImAFM
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
UMONS


Liquid Crystal Blend
TU/e
Topography
1,0 µm
SFD3020, 77 wt% (Soft LC)
SFD0647, 16 wt% (Rigid LC)
SFD0209, 5 wt% (More rigid LC)
+2 wt% additives
Epoxy resin
Liquid crystal
ImAFM
Scan size 15 µm
349.5 kHz (n=699) - Phase [deg]
1.68
-2.72
-7.11
-11.5
-15.9
-20.3
-24.7
ImAFM
1.4
1.2
1.0
0.8
0.6
0.4
0.2
GPa
Rigidity Module
REMISOL
Journée Nanomécanique en Champ Proche - Grenoble (France)
136
UMONS
Université de Mons

Conclusions

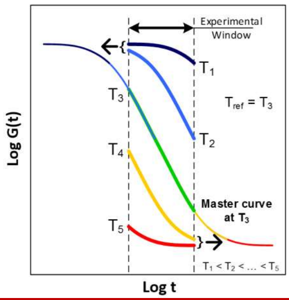
AFM frequency and modulus ranges



Take home message …

Combined, AFM measurements with non-resonant modes and resonant modes can provide :

- Huge range of properties covered including E', E'' and Tan δ.
- FV based Contact Resonance for stiff samples at higher frequencies.
- FV force curves, nDMA and ImAFM for soft samples at low frequencies.
- FV and PFT cover wide range of ramp rates for time-temperature studies.



Take home message …

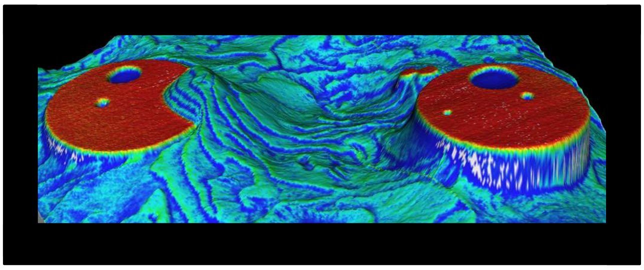
Understanding the relative contribution of the various error sources allows us to prioritize improvements to address them

- 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.

Conclusions

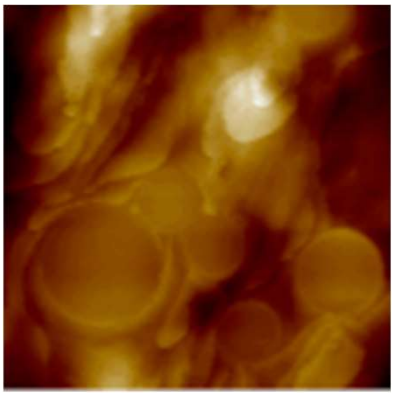
SPM is a powerful characterization tool for materials science and biology, capable of revealing surface structures with high resolution and provides useful information on the morphology of materials … complementary to other techniques.

Force distance curve-based analysis allow multiple material properties to be decoupled and measured independently … even of very soft materials !



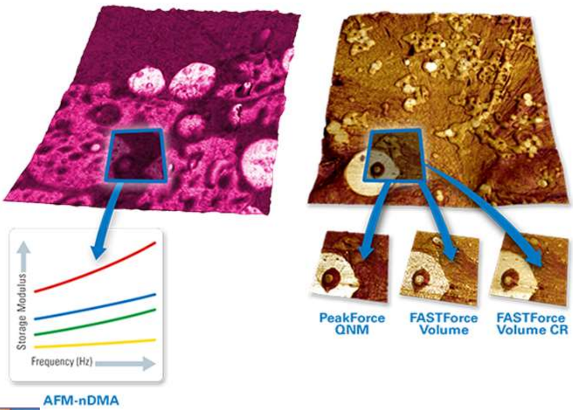
Conclusions

For instance, recording of stiffness, deformation, adhesion and viscoelastic (E', E'', tan δ) property maps in parallel to the topography image is now possible with quantitative values.



Conclusions

New methods (such HMX, PFT, BE, CR, nDMA…) are able to « rapidly » map the mechanical properties at the nanometer scale due to the (very) fast data acquisition and analysis processes.



Conclusions

A decade ago …

CR-AFM, ImAFM, nanoDMA, BE

	PeakForce QNM	HarmoniX	TappingMode Phase Imaging	Single Harmonic	Dual AC	Pulsed Force Mode	Force Volume
Young's modulus and adhesion mapping	Yes	Yes	Mixed & Parameter dependent	Mixed & Parameter dependent	Mixed & Parameter dependent	Qualitative	Possible offline
Deformation depth mapped?	Yes	Yes	No	No	No	No	Possible offline
Quantitative Modulus range	0.7 Mpa – 70 GPa	10 MPa – 79 GPa	–	–	–	–	<1 MPa – 100 GPa
Adhesion noise level	<10 pN	200 pN	–	–	–	<1 nN	<10 pN
Feedback on Peak Force?	Yes	No	No	No	No	Yes	Yes
Peak force	<100 pN	<5 pN	<3 nN	<10 nN	<5 nN	<20 nN	<50 nN
Lateral resolution	<5 nm	<10 nm	<5 nm	<10 nm	<10 nm	<50 nm	<100 nm
Simultaneous high resolution imaging	Yes	Yes	Yes	Yes	Yes	Moderate	No
Mapping Time	4 minutes	4 minutes	4 minutes	4 minutes	4 minutes	4 minutes	18 hours
Easy to use?	Yes	No	Yes	No	No	No	No

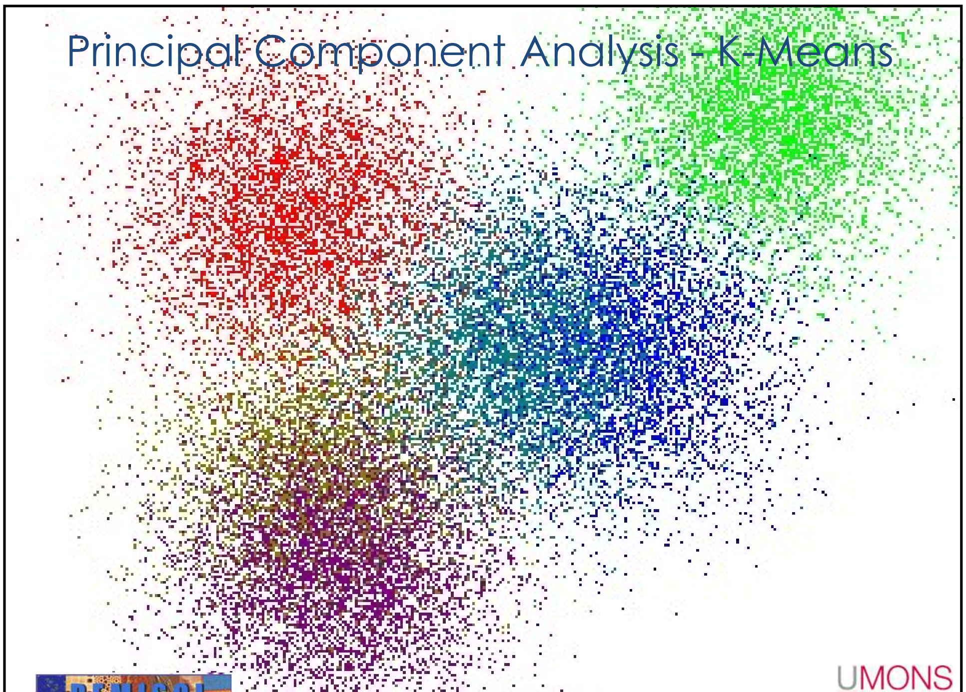
Viscoelastic properties (E', E'', tan δ)

Recent developments in data processing …

Big, Deep, Smart Data !!!

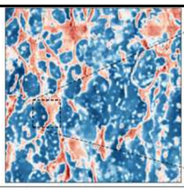
Recent modes further expand these capabilities by enabling the acquisition of multidimensional data cubes. For materials scientists and engineers, this breaks long-standing efficiency and characterization barriers.
These new capabilities provide simultaneous capture of nanometer-scale mechanical (and electrical) characteristics in **high-density data cubes**, previously impossible to attain in a single measurement.

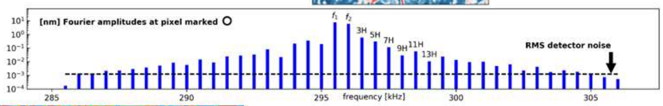
Principal Component Analysis - K-Means

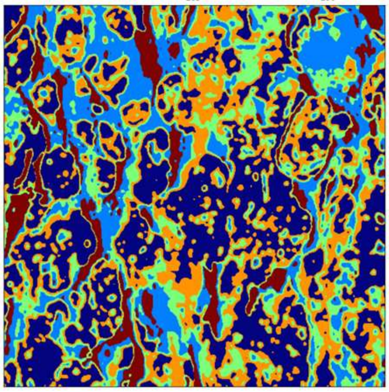


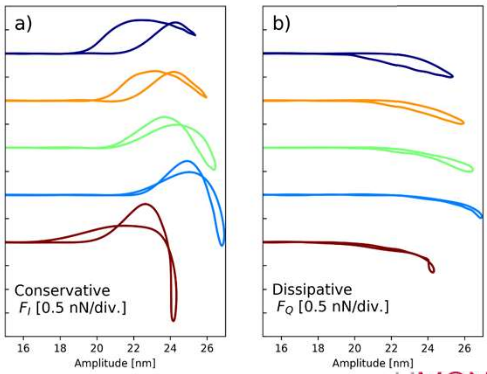
DVA Inner layer

K-means (n = 5)





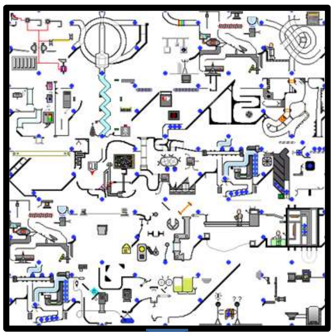




Polymer 135 (2018), 348-354

Conclusions

Multifrequency methods are extremely promising but also need some (new) models to provide quantitative parameters.
Data-driven materials development and design (machine learning, AI) are most probably the key issue to achieve this goal.



Property mapping


danke
謝謝
ngiyabonga
teşekkür ederim
спасибо
dank je
thank you
gracias
tapadh leat
bedankt
hvala
mauruuru
mochchakkeram
dziękuję
go raibh maith agat
obrigado
sagolun
sukriya
kop khun krap
grazie
arigatō
takk
dakujem
мерси
terima kasih
감사합니다
ευχαριστώ
merci

Questions ?