UMONS Université de Mons

materials UMONS RESEARCH INSTITUTE FOR MATERIALS SCIENCE AND ENGINEERING

CIRMAP

Mesures quantitatives des propriétés mécaniques de matériaux mous

Philippe LECLERE

REMISOL

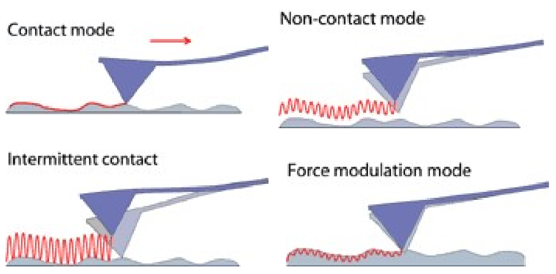
GT Nanomécanique
October 16, 2018
Montpellier (France)

Outline

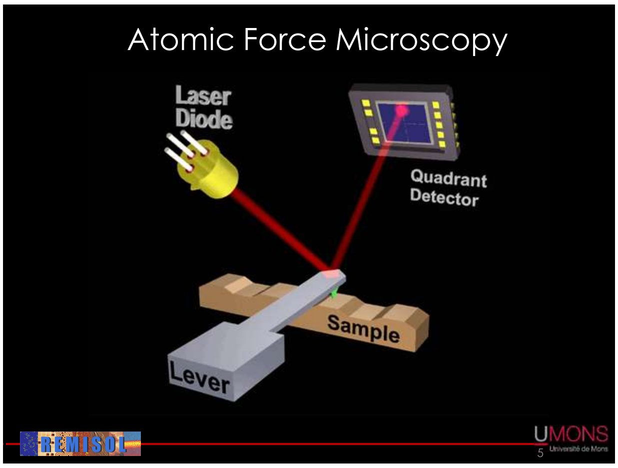
- Introduction – Scanning Probe Microscopy
- Beyond imaging the morphology …
- … Mechanical Properties
- Sub Resonance Tapping
- Intermodulation AFM
- Back to Contact Resonance
- Conclusions

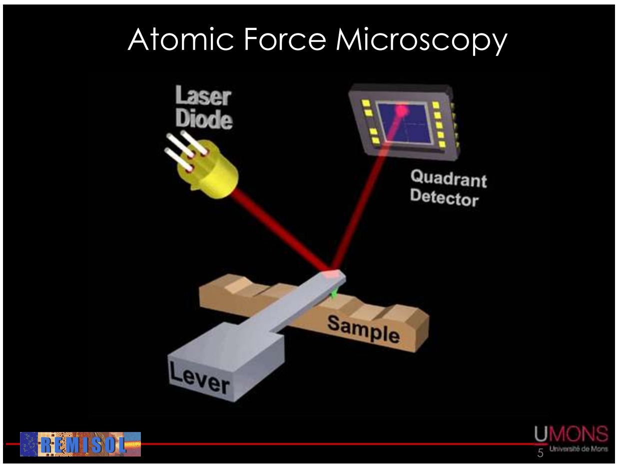
REMISOL 2 UMONS Université de Mons

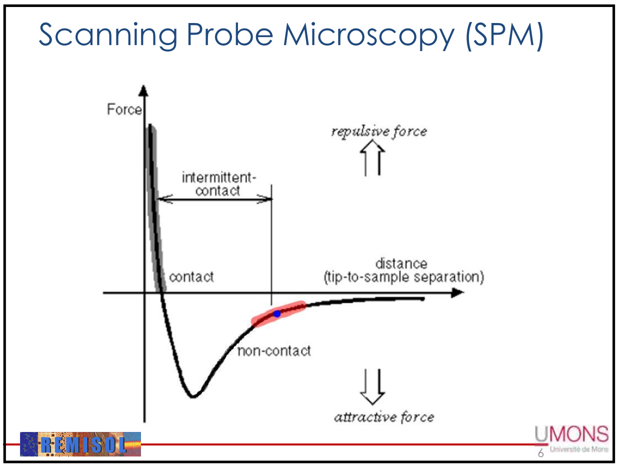
Imaging Modes

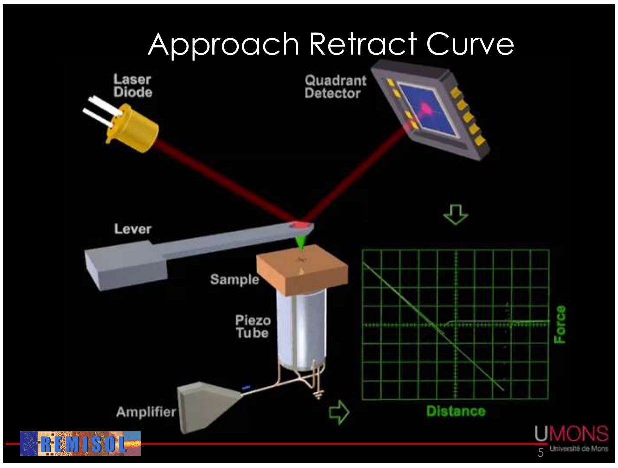


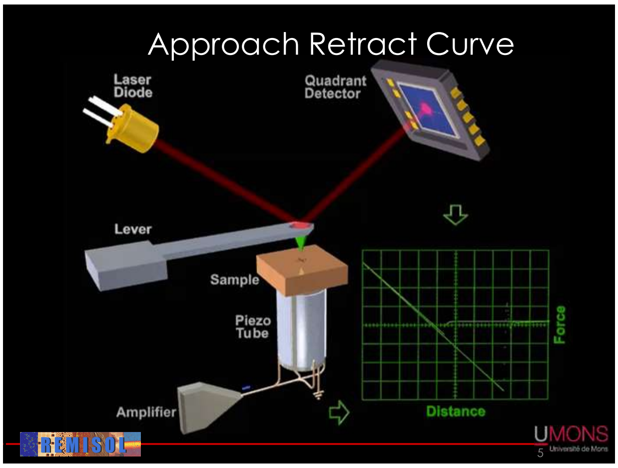
REMISOL 3 UMONS Université de Mons

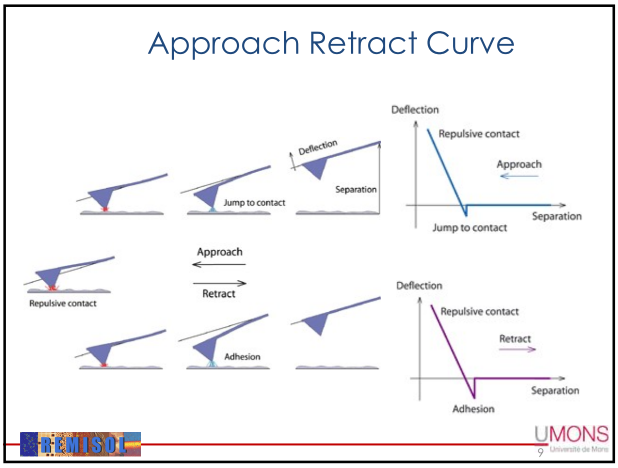

Atomic Force Microscopy
Laser
Diode
Quadrant
Detector
Sample
Lever
REMISOL
UMONS
Université de Mons
5


Atomic Force Microscopy
Laser
Diode
Quadrant
Detector
Sample
Lever
REMISOL
UMONS
Université de Mons
5

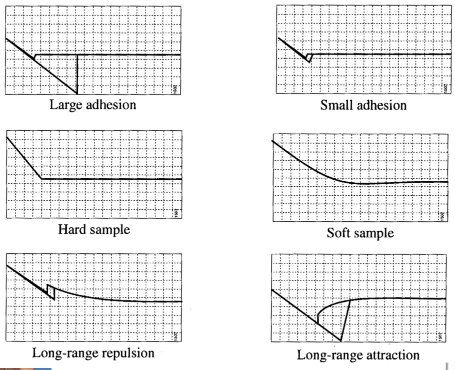

Scanning Probe Microscopy (SPM)
Force
repulsive force
intermittent-
contact
contact
distance
(tip-to-sample separation)
non-contact
attractive force
REMISOL
UMONS
Université de Mons
6


Approach Retract Curve
Laser Diode
Quadrant Detector
Lever
Sample
Piezo Tube
Amplifier
Force
Distance
REMISOL
UMONS
Université de Mons
5

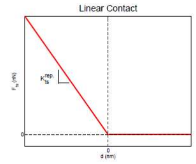

Approach Retract Curve
Laser Diode
Quadrant Detector
Lever
Sample
Piezo Tube
Amplifier
Force
Distance
REMISOL
UMONS
Université de Mons
5


Approach Retract Curve
Jump to contact
Deflection
Separation
Deflection
Repulsive contact
Approach
Jump to contact
Separation
Repulsive contact
Approach
Retract
Adhesion
Deflection
Repulsive contact
Retract
Separation
Adhesion
REMISOL
UMONS
9

Approach Retract Curve



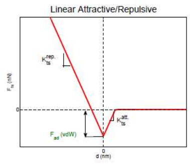
Models for tip-sample interactions



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

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

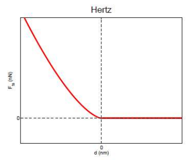
VEDA: A web-based virtual environment for dynamic atomic force microscopy



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

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

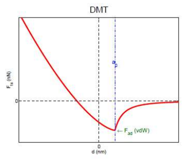
Models for tip-sample interactions



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

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

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



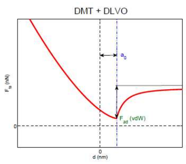
Tip-sample force versus gap for the DMT contact model.

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

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

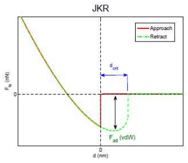
H = Hamaker constante

Models for tip-sample interactions



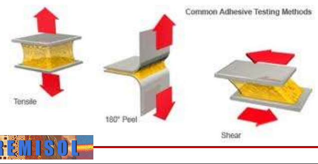
$$F_{DLVO+DMT}(d) = \begin{cases} \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D d} - \frac{HR}{6d^2}, & d > a_0 \\ \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D a_0} - \frac{HR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}(a_0-d)^{3/2}, & d \leqslant a_0 \end{cases}$$

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



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

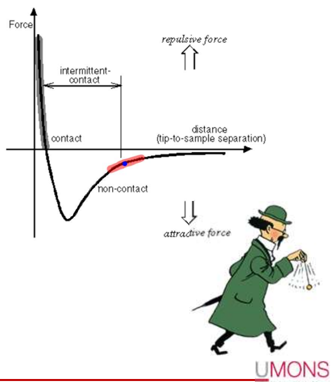
Mechanical Properties



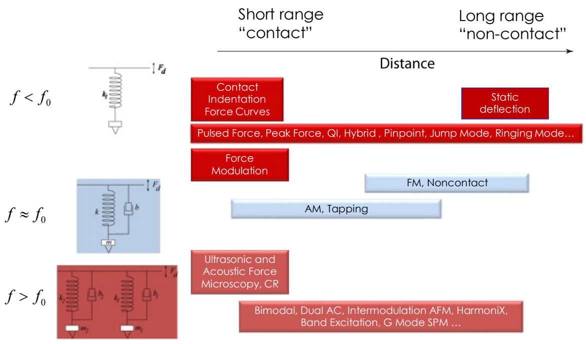
Scanning Probe Microscopy (SPM)

Morphology
- Contact AFM
- AM-AFM (Tapping Mode)
- FM-AFM (nc-AFM)

Mechanical Properties
- Friction Force Microscopy
- Force Modulation
- Contact Resonance
- HarmoniX
- Bimodal Dual AC
- Peak Force Tapping
- Intermodulation AFM
- Band Excitation
- …



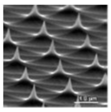
AFM Measurements



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

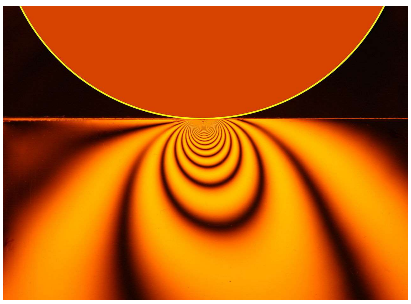
- DMT model, JKR model, Sneddon model, ...

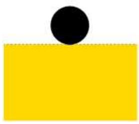
A signal giving access to the tip-surface contact stiffness

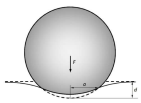
- "slope" of force-curve in the contact region,
- modulated cantilever vibration,
- phase-shift in AM-AFM,
- contact resonance frequency,
- higher harmonics vibration amplitude,
- In phase and quadrature signals, ...

Contact Mechanics Forces

Basic Hertz's elastic solution (1881)







Solid-state deformations

Several classes of deformations in elastic materials are the following:

Elastic: The material recovers its initial shape after deformation.

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).

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.

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.

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

UMONS Université de Mons

19

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 surfaces

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

UMONS Université de Mons

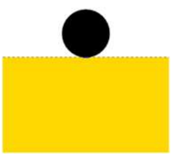
20

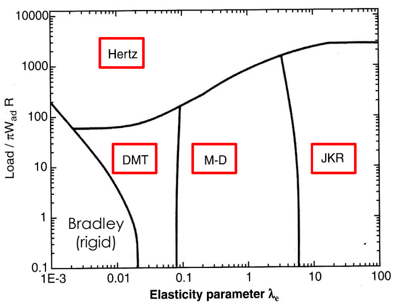
Contact Mechanics Forces

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

M-D = Maugis - Dugdale

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



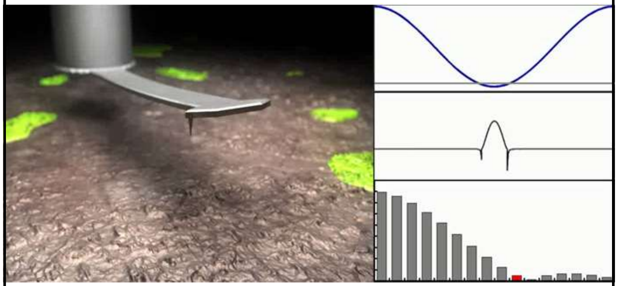


Johnson, Greewood, J. Colloid Interface Sci., 1997, 192, 326.

UMONS Université de Mons

21

Force Curves during Tapping Mode



HarmoniX

Adapted from Bruker

HarmoniX …
Force Curves during Tapping Mode

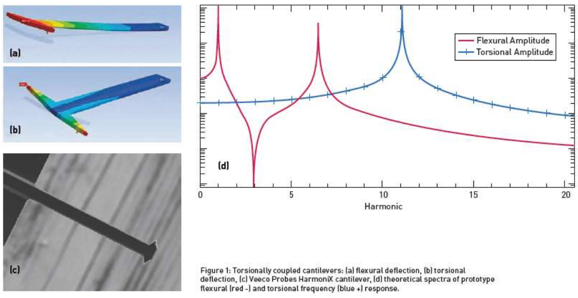
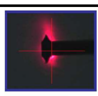
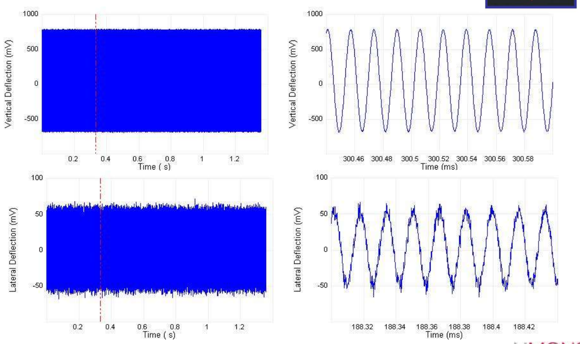


Figure 1: Torsionally coupled cantilevers: (a) flexural deflection, (b) torsional deflection, (c) Veeco Probes HarmoniX cantilever, (d) theoretical spectra of prototype flexural (red -) and torsional frequency (blue +) response.

Adapted from Bruker

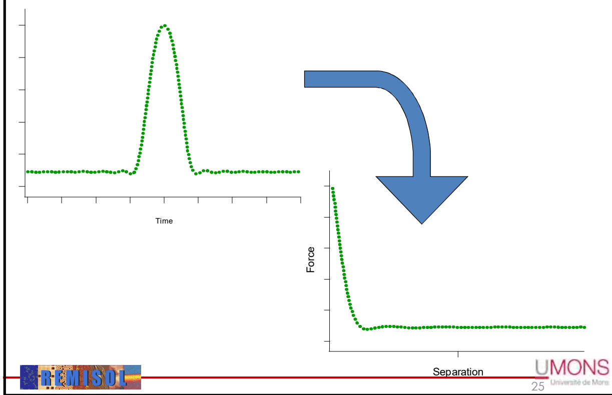
HSDC…



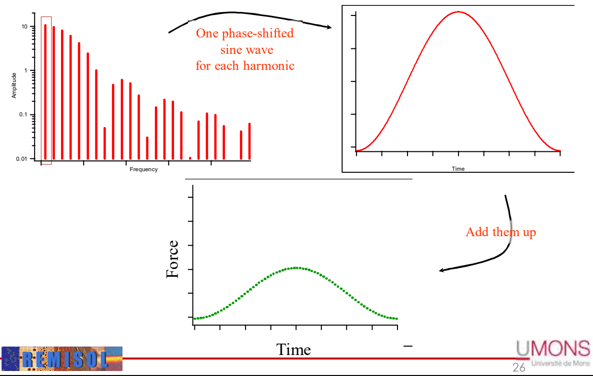


Adapted from Bruker

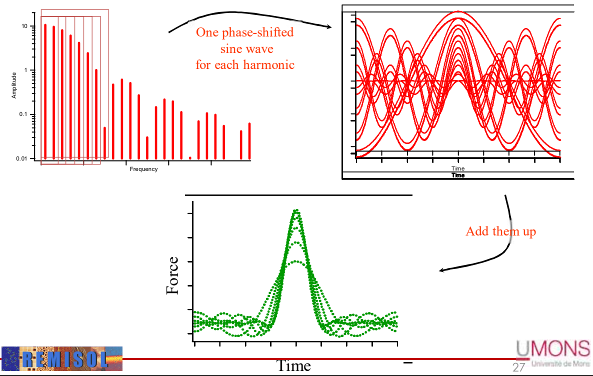
Force vs Time to Force Curve



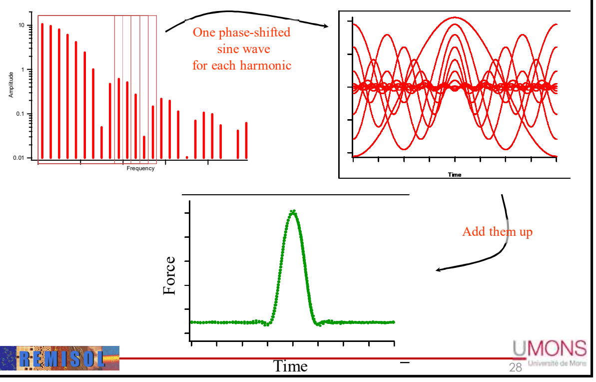
Reconstruct any Periodic Waveform from Fourier Series



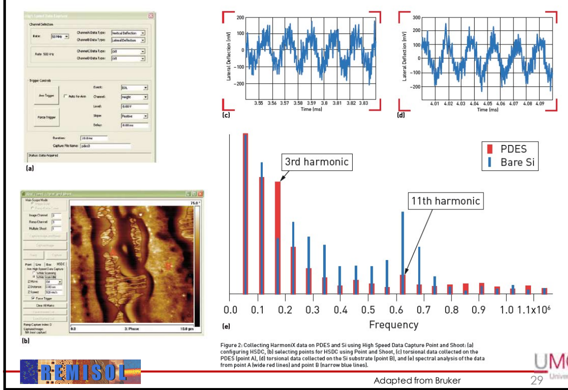
Reconstruct any Periodic Waveform from Fourier Series



Reconstruct any Periodic Waveform from Fourier Series

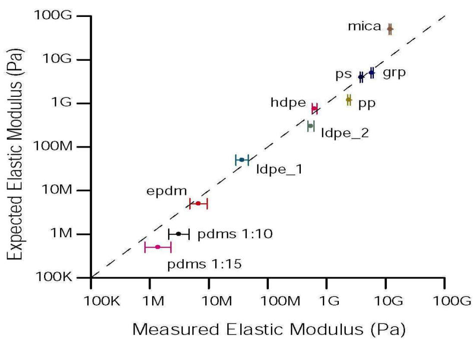


HarmoniX …
Force Curves during TappingMode



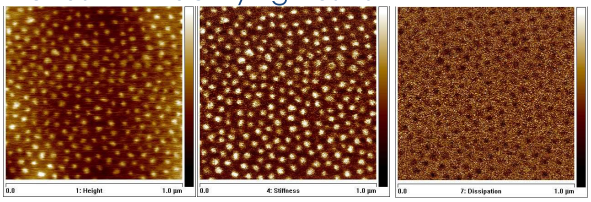
Adapted from Bruker

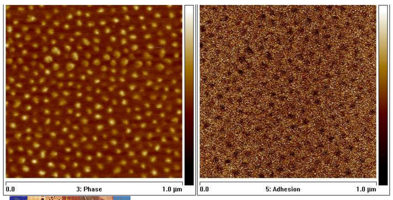
Quantitative: Comparing Modulus Results



Data courtesy O. Sahin, Rowland Institute at Harvard

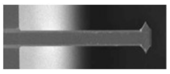
Blends with Tackifying Resins





Average adhesion
135 nN

RADIAL (50-10)$_4$

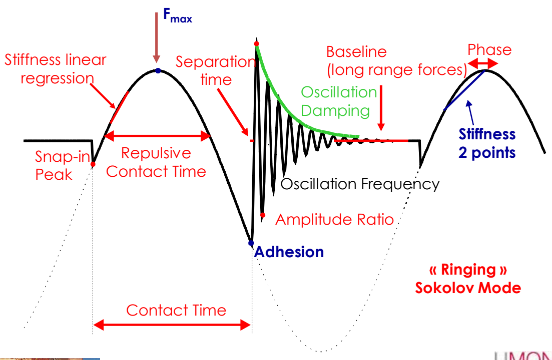


31

Sub Resonance Tapping

aka PeakForce Tapping, Jump Mode, Hybrid^{TM}, Pinpoint^{TM}, QI^{TM}, « Ringing » Mode AFM, …

Information contained in a PFM Curve



Adapted from Witec

33

Comparing various modes when imaging of soft materials with AFM

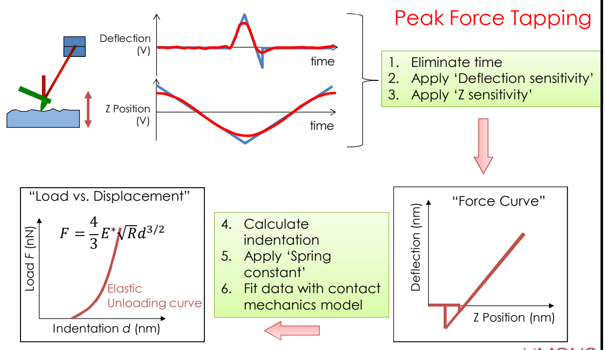
	Contact	Tapping	Sub-resonance
Contact area	Unstable contact	Small but hard to control	Small
Lateral Resolution	Low	Good*	Good*
Friction artifacts	Stick-slip	Minimum to none	Minimum to none
Sample safe	Potentially destructive	Non-destructive	Non-destructive
Force control	Excellent	Hard to control	Good
Quantitative physical info	Yes (force-volume mode)	No	Yes**

* Depends on material
** Accuracy is yet to be verified

UMONS Université de Mons 34

Analyzing Force Curves

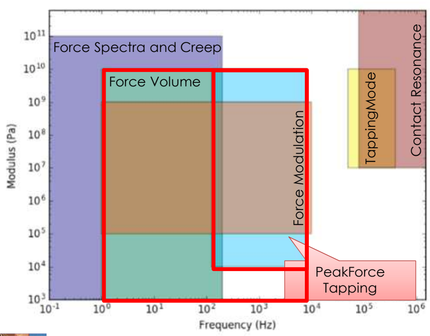
From Deflection and Z to modulus



Adapted from Bruker

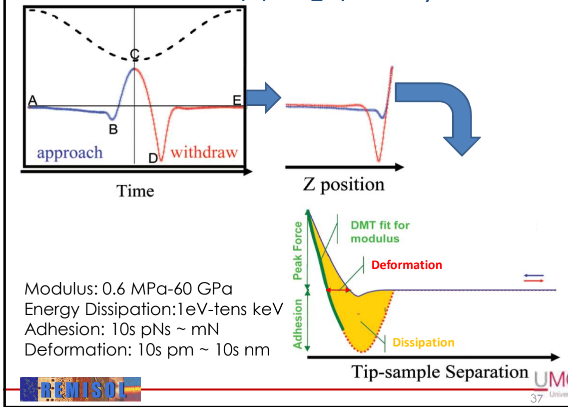
UMONS Université de Mons 35

AFM frequency and modulus ranges Force Volume and PeakForce Tapping



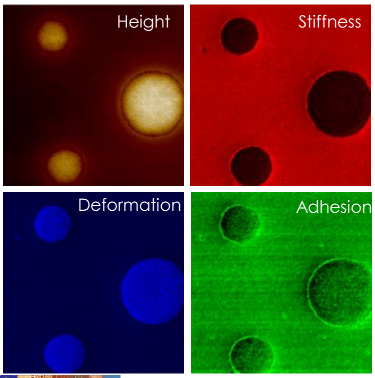
UMONS Université de Mons 36

Peak Force Tapping (QNM)



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

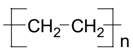
Blend of PS/LDPE



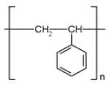
Macrophase separation

Information about mechanical properties at the nanoscale

LDPE

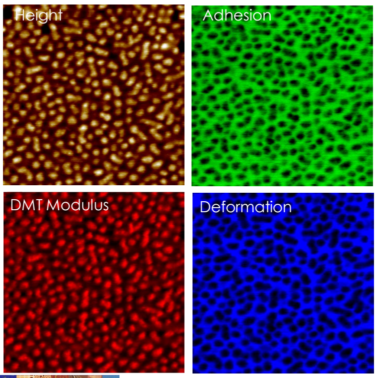


PS



Scan Size : 3.0 µm

Peak Force Tapping (QNM)

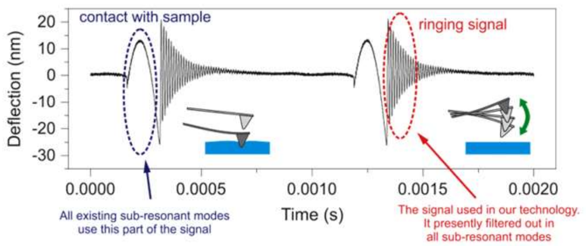


Microphase separation

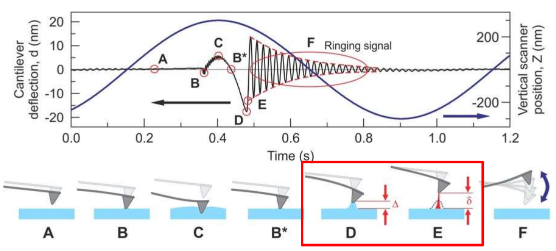
PSA

Scan size 1.0 µm

Ringing Mode …



Ringing Mode …



Ringing Mode

Why Ringing mode?

	Contact/DC	Tapping/AC	Sub-resonance	Ringing
# of channels	3	3/4	6	6+8
Description	Height, error, friction	Height, amplitude, Phase (deflection)	Height, error, adhesion, Stiffness, Visc. Losses, Deformation	All sub-resonance + 8 more
Physical channels to unambiguously characterize materials	2	1	5	5+7

Ringing Mode

Why Ringing mode?

	Contact/DC	Tapping/AC	Sub-resonance	Ringing*
# of channels	3	3/4	6	6+8
Description	Height, error, friction	Height, amplitude, Phase (deflection)	Height, error, adhesion, Stiffness, Visc. Losses, Deformation	All sub-resonance + 8 more
Physical channels to unambiguously characterize materials	2	1	5	5+7

Ringing Mode

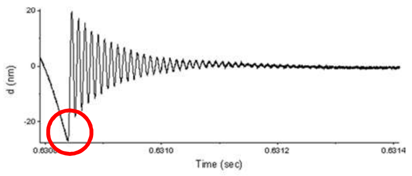
New Data Channels of Ringing Mode

1. Restored (averaged) adhesion
2. Adhesion height
3. Disconnection height
4. Zero-force height (*)
5. Pull-off neck height
6. Disconnection distance
7. Disconnection energy loss
8. Dynamic creep phase shift

(*) This channel, though, is available in some commercial AFMs.

Ringing Mode

1. Restored (averaged) adhesion



$$Aver\ F_{Ra} = \frac{1}{N}\sum_{k=1}^{N}\frac{\text{cantilever rebound signal}}{Exp(-\pi f_0 t_k / Q)\left|Sin(2\pi f_0 t_k + \varphi)\right|}$$

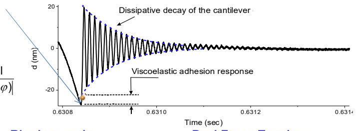
The image above is a self-explanatory definition of averaged restored adhesion. Because the ringing signal is proportional to the original adhesion (pull-off force), it can be "restored" using the formula shown above.

Ringing Mode

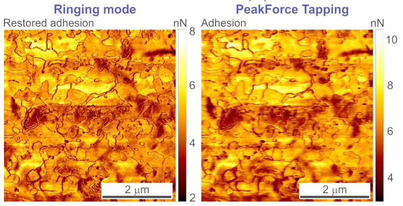
1. Restored (averaged) adhesion

Formula to calculate:

$$Aver\ F_{Ra} = \frac{1}{N}\sum_{k=1}^{N}\frac{\text{cantilever rebound signal}}{Exp(-\pi f_0 t_k / Q)\left|Sin(2\pi f_0 t_k + \varphi)\right|}$$



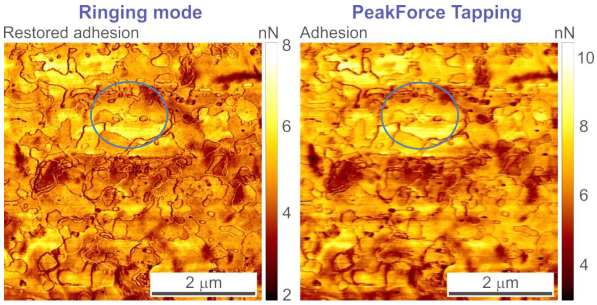
<u>Less noise</u> due to multiple averaging: *Ringing rest. adhesion* vs *Regular adhesion* in *PeakForce Tapping*



Scientific Reports **7**, Article number: 11828 (2017)

Ringing Mode

1. Restored (averaged) adhesion

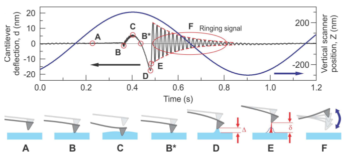


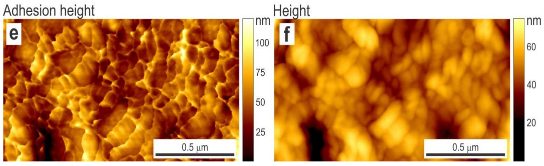
<u>Note</u>*: *both channels are recorded simultaneously

Scientific Reports **7**, Article number: 11828 (2017)

Ringing Mode

2. Adhesion height





A375 human melanoma cells

Scientific Reports **7**, Article number: 11828 (2017)

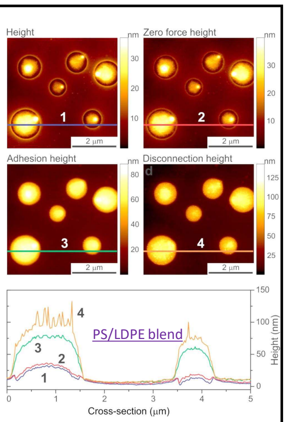
Ringing Mode

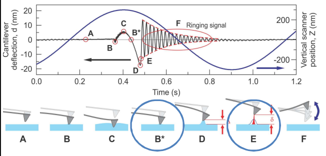
3. Disconnection height

The height at the moment of final disconnection (point E)

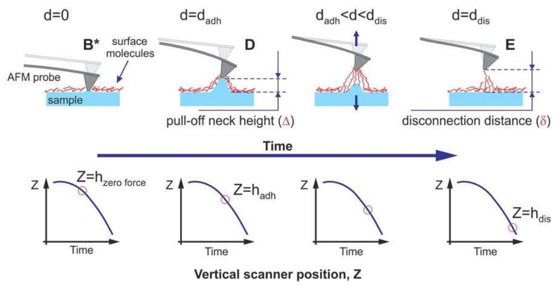
4. Zero-force height

The height at the moment of final disconnection (point B*)



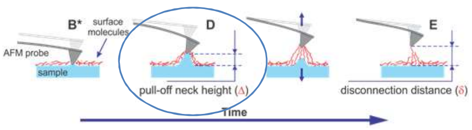


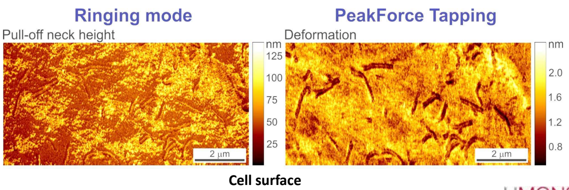
Ringing Mode …



Ringing Mode

5. Pull-off neck height

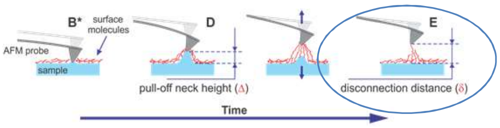


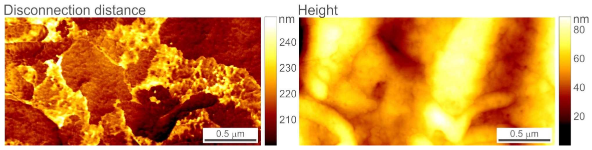


Cell surface

Ringing Mode

6. Disconnection distance

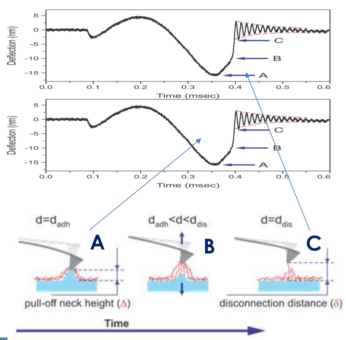


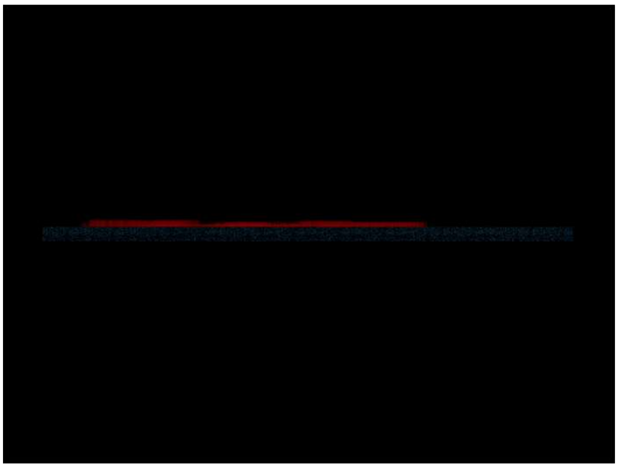


Cell surface

Ringing Mode

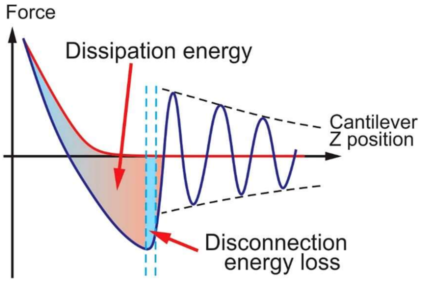
Rupturing of molecular bonds





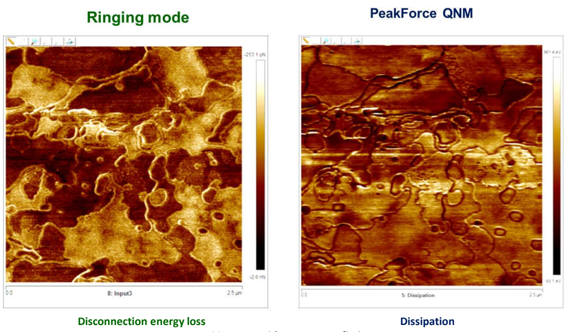
Ringing Mode …

7. Disconnection energy loss



Ringing Mode

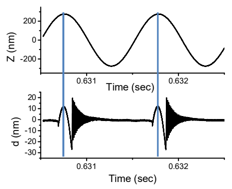
7. Disconnection energy loss



Human skin cornea flake

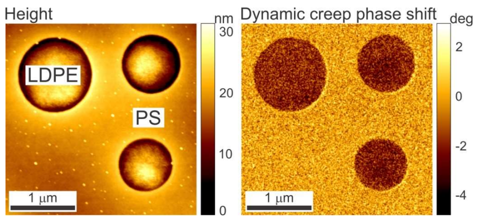
Ringing Mode

8. Dynamic creep phase shift

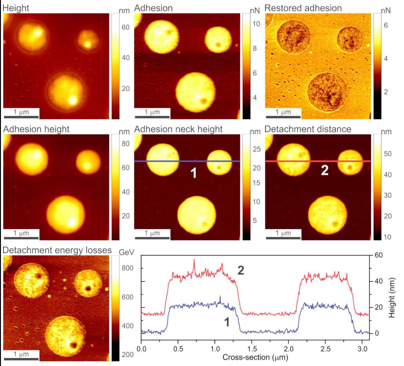


The phase difference in the max of the scanner max **Z** and the max of the of the cantilever deflection **d** .

PS/LDPE blend



Ringing Mode



An example of simultaneous imaging of different Ringing Mode channels.

The cross-sections lines shown in the images are presented in the bottom panel.

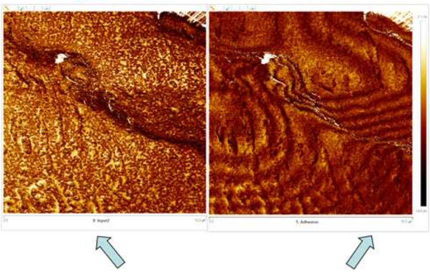
PS-LDPE calibration sample. The scan rate of 1 Hz is used.

Scientific Reports **7**, Article number: 11828 (2017)

58

Ringing Mode

Ringing mode **PeakForceQNM mode**



Restored adhesion (FRa) Standard adhesion map.

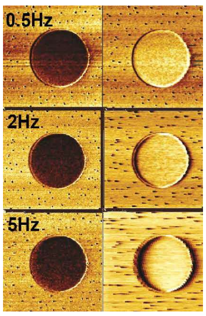
The scan rate is 0.1 Hz (fixed human epithelial cell).

Scientific Reports **7**, Article number: 11828 (2017)

59

Ringing Mode

Faster …

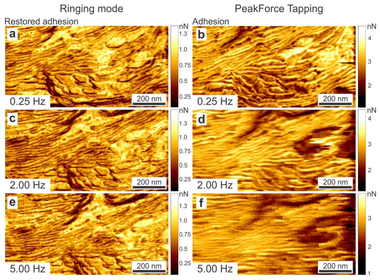


http://www.afm-nss.com

60

Ringing Mode

Advantage: Speed



Comparison of the restored adhesion (a,c,e; left column) and adhesion images (b,d,f; right column) obtained with ringing and PeakForce Tapping modes, respectively, recorded at different scanning speeds.
Maps of polystyrene-polycaprolactone composite polymeric material are shown.

REMISOL — UMONS Université de Mons — 61

Multifrequency AFM

Bimodal AFM = Dual AC Mode

APPLIED PHYSICS LETTERS VOLUME 84, NUMBER 3 19 JANUARY 2004

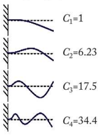
Compositional mapping of surfaces in atomic force microscopy by excitation of the second normal mode of the microcantilever

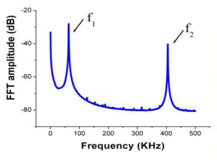
Tomás R. Rodríguez and Ricardo García[a)]
Instituto de Microelectrónica de Madrid, CSIC, Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain

(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]

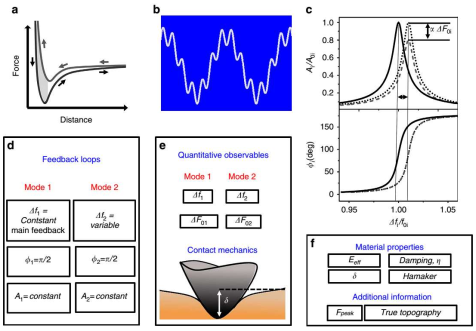
$\omega_i = \omega_1 C_i$





REMISOL — UMONS Université de Mons — 63

Bimodal AFM = Dual AC Mode



Bimodal AFM = Dual AC Mode

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

$$d_m = z_c - A_1 - A_2$$

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

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

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

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

Young's Modulus

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

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

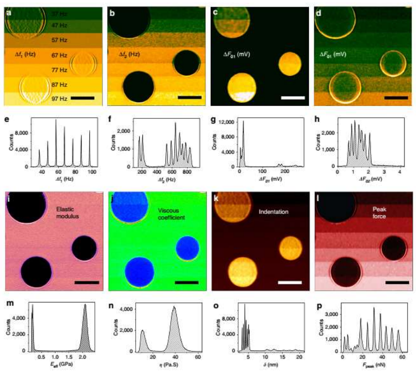
Viscosity

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

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

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

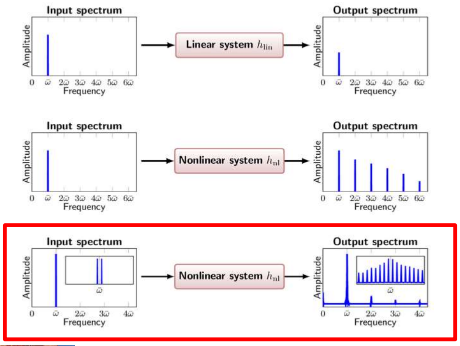
Bimodal AFM = Dual AC Mode



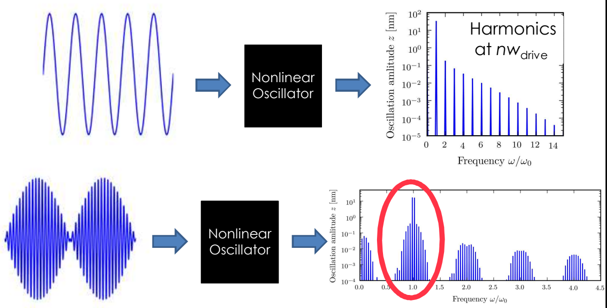
Intermodulation AFM

The methodology

Intermodulation AFM



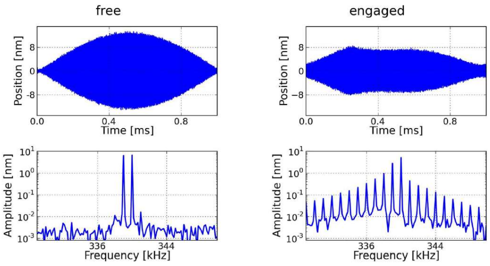
Harmonics, Intermodulation AFM



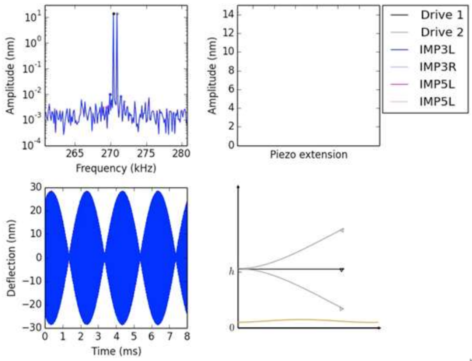
Intermodulation products near resonance

Intermodulation AFM

- Cantilever driven with two pure drive tones close to resonance
- Nonlinear tip-surface force creates new components in the spectrum (**Intermodulation products**)

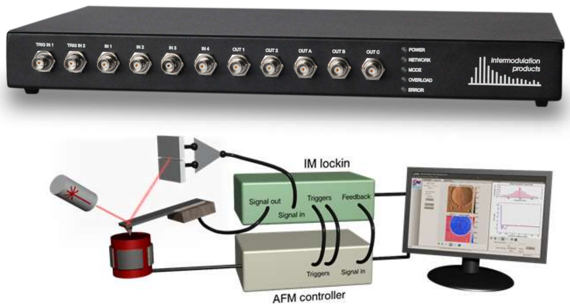


Intermodulation AFM



www.intermodulation-products.com

Intermodulation AFM

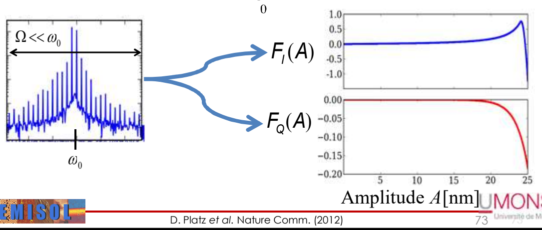


Force Quadratures

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

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

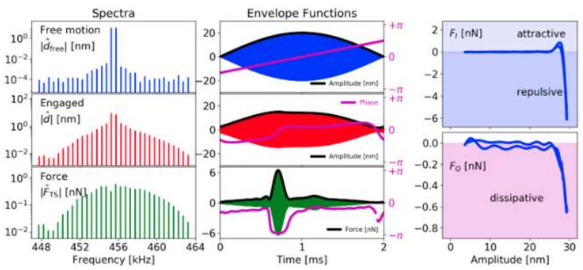
quadrature (dissipative): $F_Q(A) = \int_0^{2\pi} F_{ts}(z,\dot{z})\sin(\omega_0 t)dt$



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

REMISOL UMONS 73

Force Quadratures

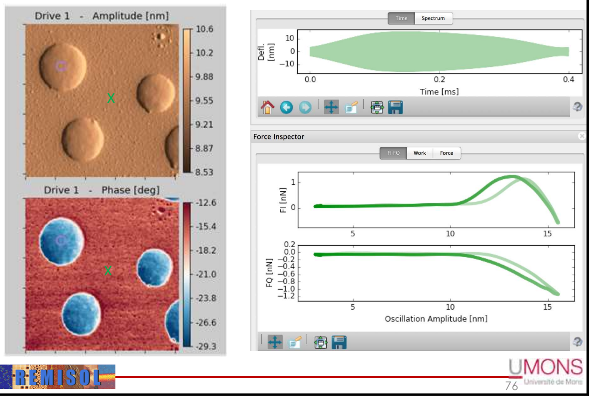


REMISOL UMONS 74

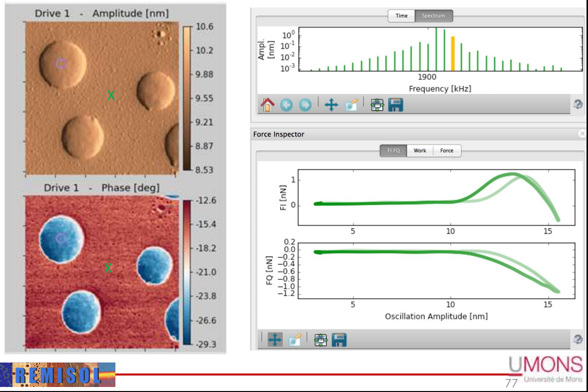
Intermodulation AFM

Some results

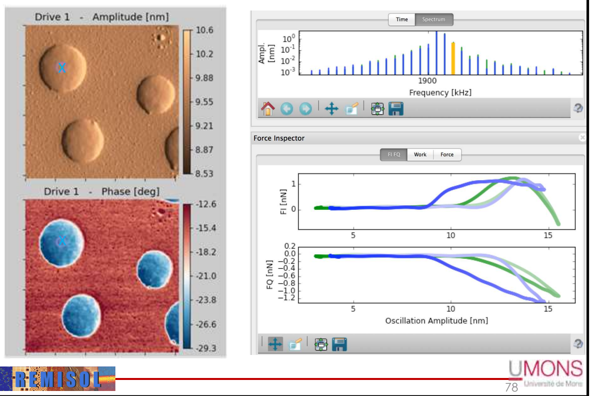
Blend of PS/LDPE



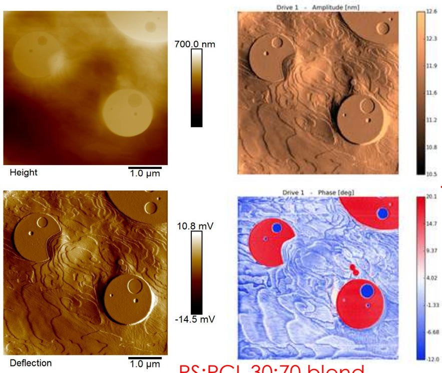
Blend of PS/LDPE



Blend of PS/LDPE



Blend of PS/PCL



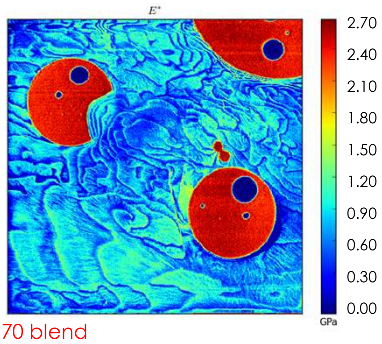
+ 41 others !

PS:PCL 30:70 blend

Soft Matter (2016), 12, 619.

UMONS 79

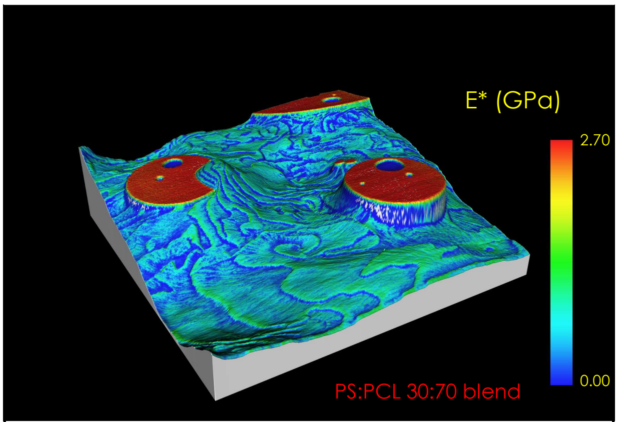
Blend of PS/PCL



PS:PCL 30:70 blend

Soft Matter (2016), 12, 619.

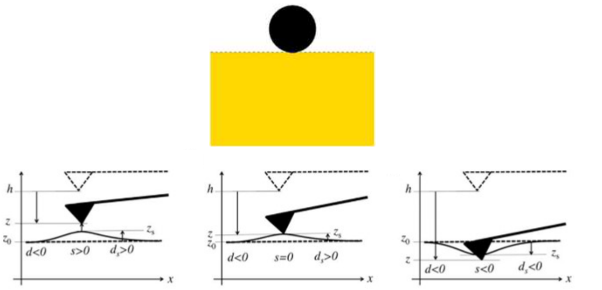
UMONS 80



Soft Matter (2016), 12, 619.

UMONS 81

Moving surface Model



Soft Matter (2016), 12, 619. 82

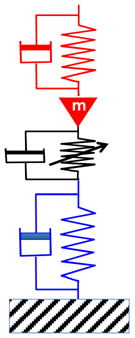
Moving surface Model

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

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

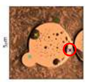
separation $s=(d-d_s)+h-z_0$

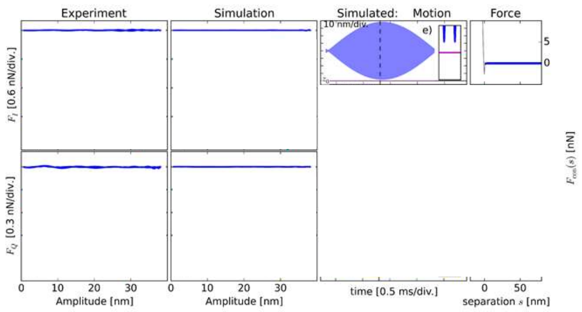
$$F_{\text{TS}}(s,\dot{s}) = \begin{cases} 0 & \text{if } s>0 \\ -F_{\text{ad}} - k_{\text{v}}s - \eta_{\text{v}}\dot{s} & \text{if } s\leq 0 \end{cases}$$



Soft Matter (2016), 12, 619. 83

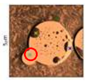
Fit to moving surface model

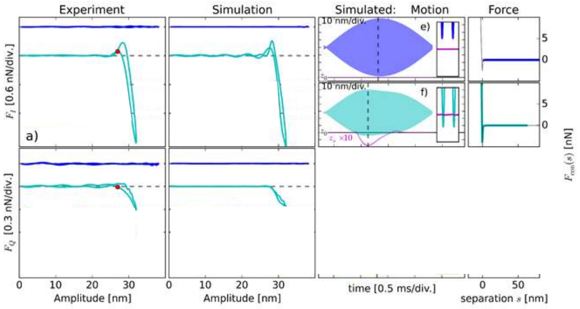




Soft Matter (2016), 12, 619. 84

Fit to moving surface model



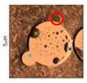


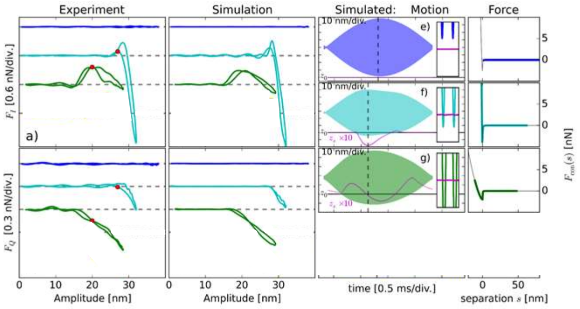
Soft Matter (2016), 12, 619.

UMONS

85

Fit to moving surface model



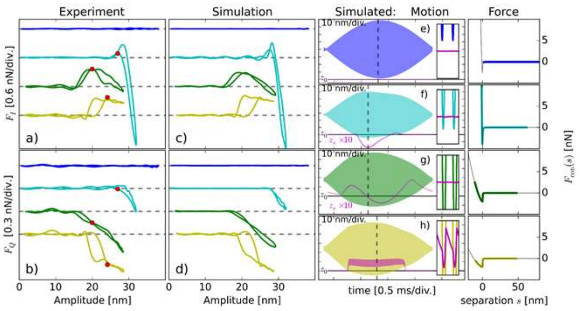


Soft Matter (2016), 12, 619.

UMONS

86

Fit to moving surface model



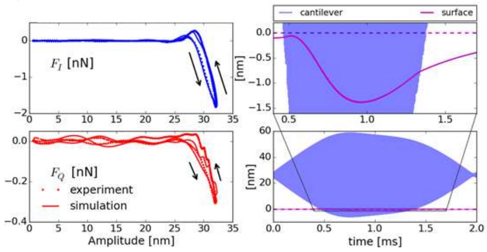
Soft Matter (2016), 12, 619.

UMONS

87

Fit to moving surface model

PS phase



surface stiffness k_s = 5.35 10^{-1}[N/m]
surface time constant $\tau_s = \eta_s / k_s$ = 5.4 10^{-4}[s]

REMISOL

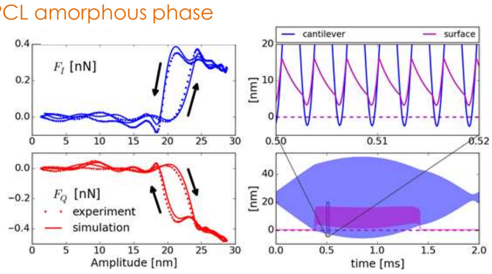
Soft Matter (2016), 12, 619.

UMONS Université de Mons

88

Fit to moving surface model

PCL amorphous phase



surface stiffness k_s = 5.10 10^{-3}[N/m]
surface time constant $\tau_s = \eta_s / k_s$ = 1.8 10^{-6}[s]

REMISOL

Soft Matter (2016), 12, 619.

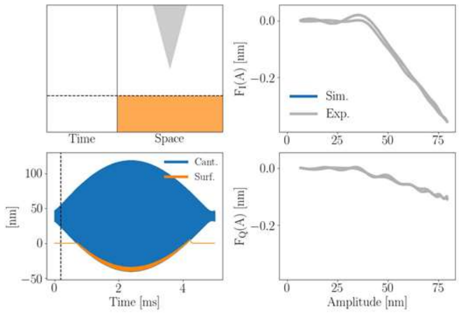
UMONS Université de Mons

89

Fit to moving surface model

Courtesy of P.A. Thoren

PS phase



REMISOL

Soft Matter (2016), 12, 619.

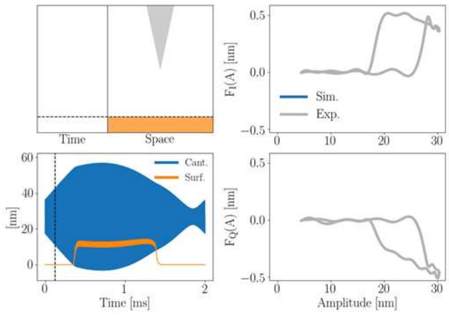
UMONS Université de Mons

90

Fit to moving surface model

Courtesy of P.A. Thoren

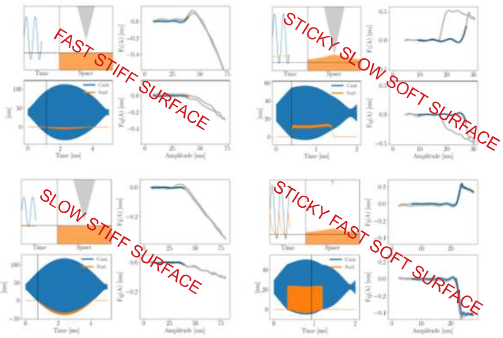
PCL amorphous phase



Soft Matter (2016), 12, 619.

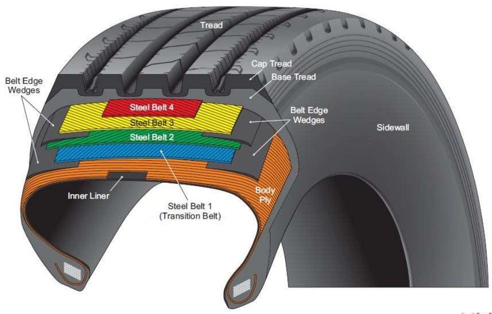
UMONS 91

Fit to moving surface model



UMONS 92

Automotive applications …



UMONS 93

DVA Inner layer

The inner liner is an extruded rubber sheet compounded with additives that result in low air permeability. The inner liner assures that the tire will hold high-pressure air inside, without the air gradually diffusing through the rubber structure.

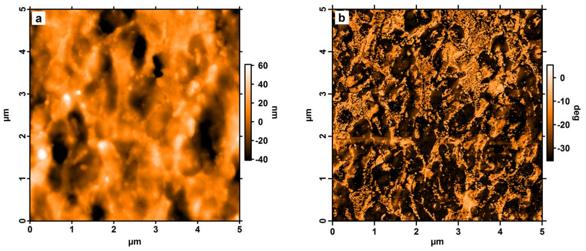
The inner layer of the tire is made with DVA (Dynamically Vulcanized Alloy,) a technology developed by ExxonMobil Chemical, to increase the IPR (Inflation Pressure Retention – used to measure of tire air pressure loss over time), more efficiently that regular tires.

The sample used in this study is a DVA of rubber domains (Brominated Poly(Isobutylene-co-p-Methylstyrene), BIMSM) dispersed in a polyamide (PA, also referred to as nylon) continuous phase.

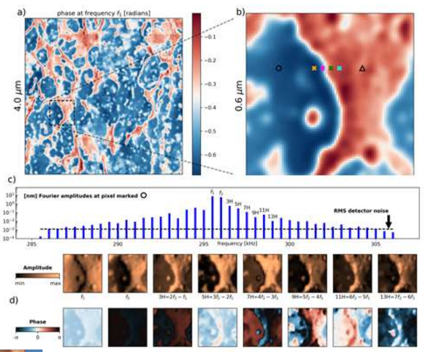
The sample was cryomicrotomed.

DVA Inner layer

Tapping Mode AFM

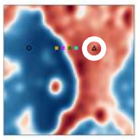


DVA Inner layer

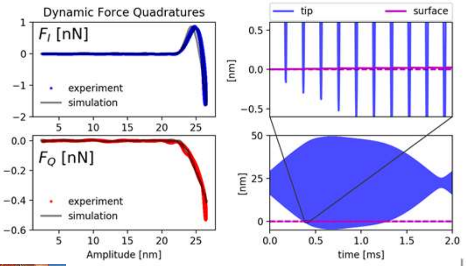


DVA layer

Im AFM



Scan size : 600 nm

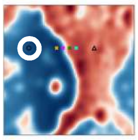


Polymer 135 (2018), 348-354

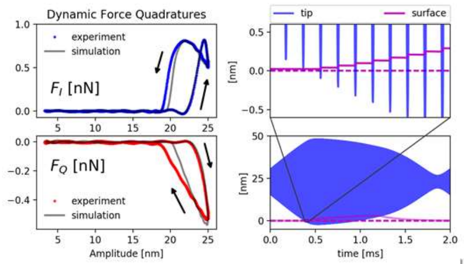
97

DVA layer

Im AFM



Scan size : 600 nm

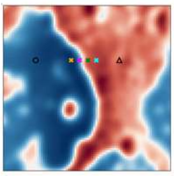


Polymer 135 (2018), 348-354

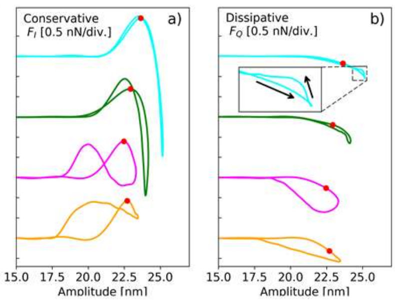
98

DVA Inner layer

Im AFM

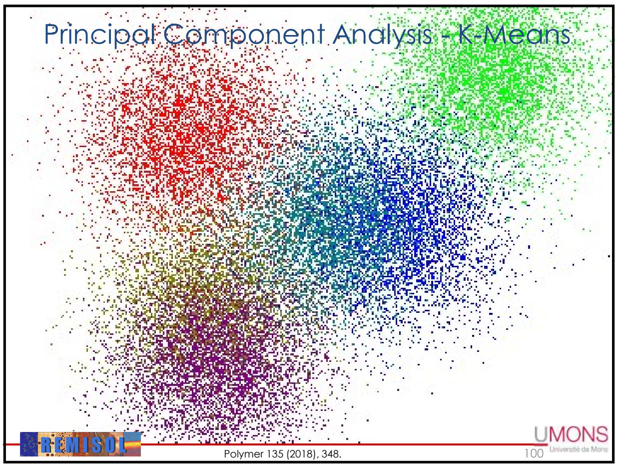


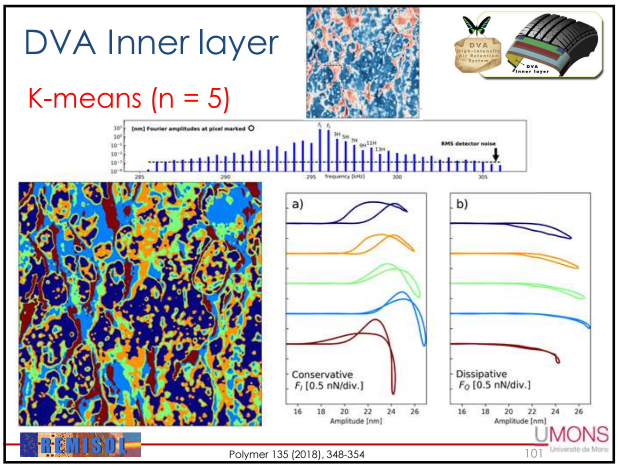
Scan size : 600 nm

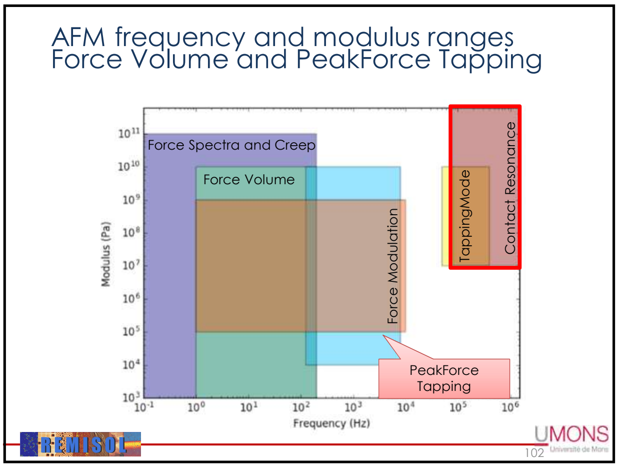


Polymer 135 (2018), 348-354

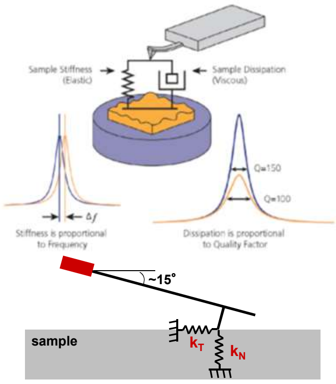
99


Principal Component Analysis - K-Means
REMISOL
Polymer 135 (2018), 348.
UMONS
100


DVA Inner layer
K-means (n = 5)
DVA
Inner layer
RMS detector noise
a)
b)
Conservative
F_I [0.5 nN/div.]
Dissipative
F_Q [0.5 nN/div.]
Amplitude [nm]
REMISOL
Polymer 135 (2018), 348-354
UMONS
101


AFM frequency and modulus ranges
Force Volume and PeakForce Tapping
Force Spectra and Creep
Force Volume
Force Modulation
TappingMode
Contact Resonance
PeakForce Tapping
Modulus (Pa)
Frequency (Hz)
REMISOL
UMONS
102

Contact Resonance



REMISOL
Adapted from Asylum Research 103
UMONS Université de Mons

How to measure Frequency & Q ?

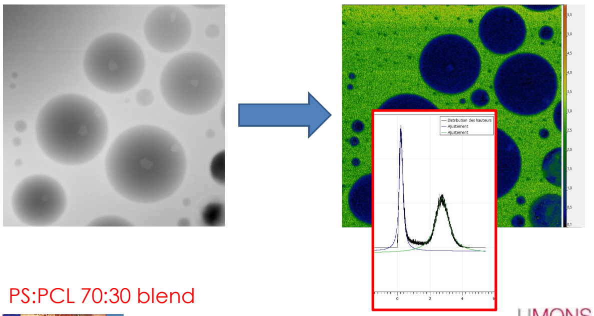
Measuring the resonance frequency

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.

REMISOL
From Asylum Research (CR-AFM application note) 105
UMONS Université de Mons

Contact Resonance

Scan size : 3.0 µm



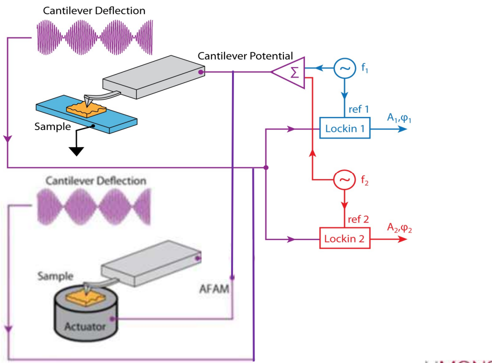
PS:PCL 70:30 blend

REMISOL

Data obtained by Michel Ramonda

106 UMONS Université de Mons

Contact Resonance : Tip or Sample ?



REMISOL

Adapted from Asylum Research

107 UMONS Université de Mons

Contact Resonance

Difficult task … or not !!!

REMISOL

108 UMONS Université de Mons

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.

REMISOL UMONS Université de Mons 109

Data processing …

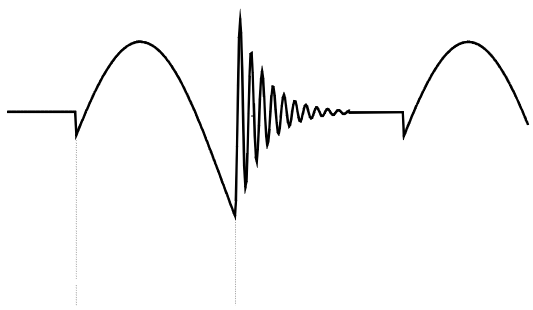
Mechanical Properties

Techniques	Benefits
DataCube Mode	Multidimensional data cube Soft and fragile matter Correlation to mechanical properties
PeakForce Tapping	Soft and fragile matter Correlation to mechanical properties
Tapping Mode	First technique available
Contact Mode	First technique available

Adapted from Bruker

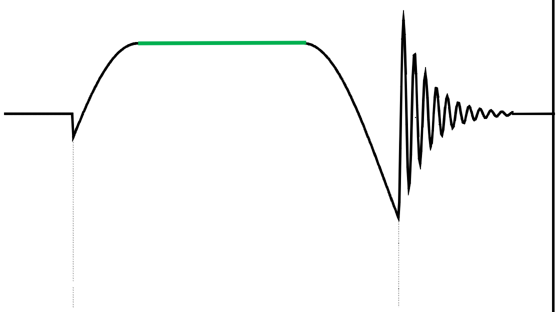
REMISOL UMONS Université de Mons 110

Back to Sub Resonance Tapping …



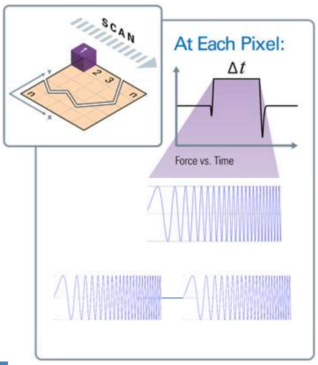
REMISOL UMONS Université de Mons 111

PFT - DataCube



Data processing …

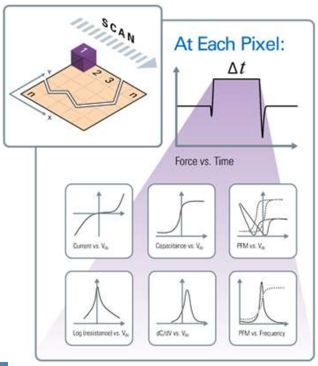
Mechanical Properties



Adapted from Bruker

Data processing …

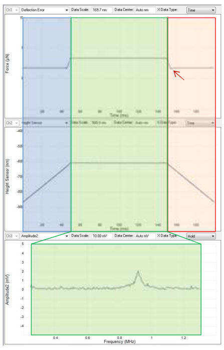
Electrical Properties



Adapted from Bruker

Peak Force Tapping - Contact Resonance

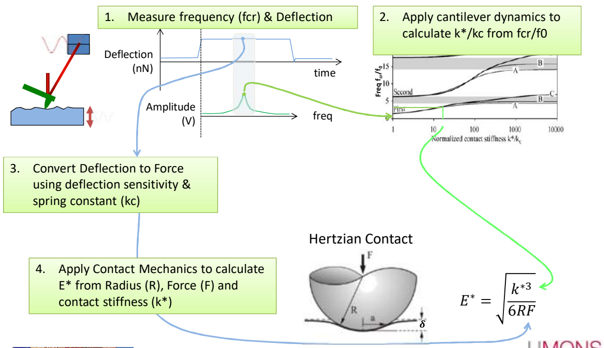
- CR is based on *FAST*Force Volume
  - Provides standard force curve for comparison for each pixel in map
    - Approach
    - Hold Force and sweep frequency
    - Retract
  - **More repeatable**: lateral force on tip is minimized, reducing tip wear
  - **More information**: allows measurement of adhesion 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

Contact Resonance

From Frequency and Deflection to modulus



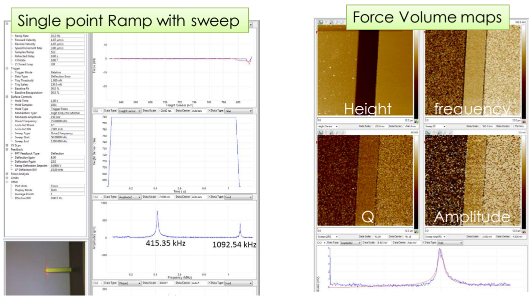
$$E^* = \sqrt{\frac{k^{*3}}{6RF}}$$

Adapted from Bruker

Peak Force Tapping Contact Resonance

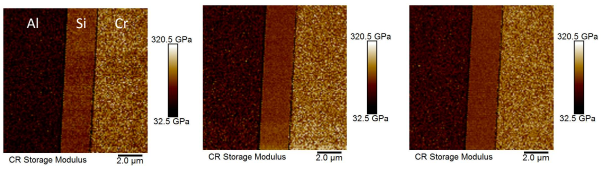
Real-time Contact Resonance Sweeping

Force Volume for mapping, Ramp for single points



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

Contact Resonance

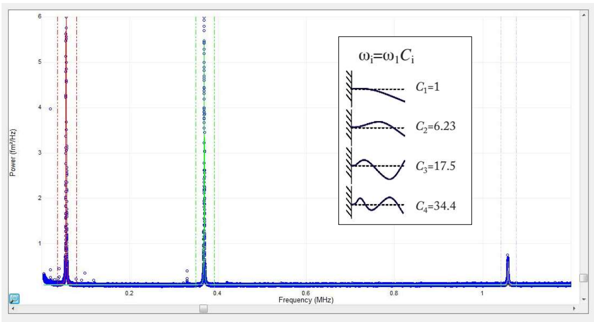


Load=200nN
Si: 165±15 GPa
Al: 85±24 GPa
Cr: 192±31 GPa

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

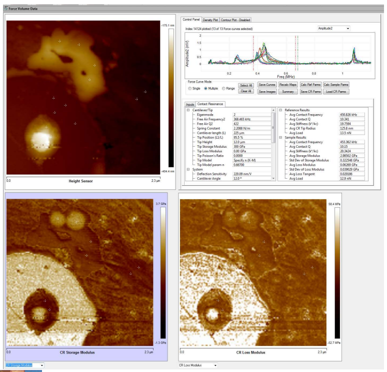
Load=1000nN
Si: 165±7 GPa
Al: 103±25 GPa
Cr: 202±26 GPa

Peak Force Tapping - Contact Resonance



Peak Force Tapping - Contact Resonance

PS-PCL

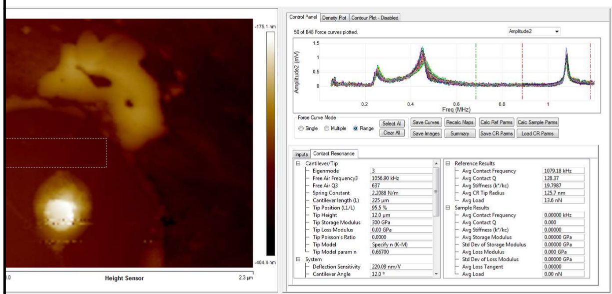


2^{nd} peak

In collaboration with Bede Pittinger 121

Peak Force Tapping - Contact Resonance

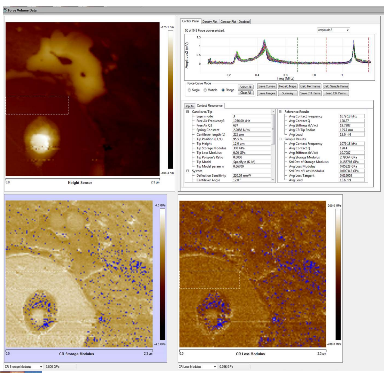
PS-PCL



In collaboration with Bede Pittinger 122

Peak Force Tapping - Contact Resonance

PS-PCL

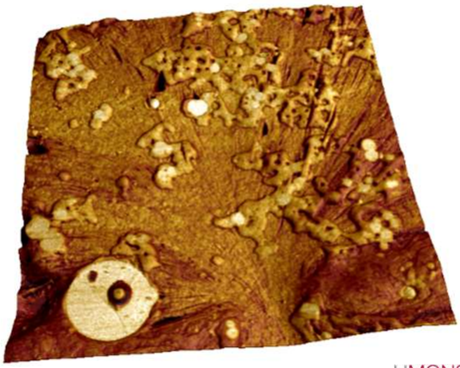


3^{rd} peak

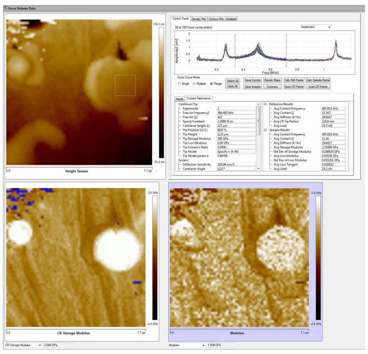
In collaboration with Bede Pittinger 123

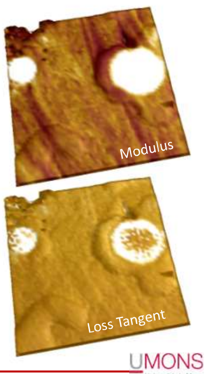
Peak Force Tapping - Contact Resonance

PS-PCL



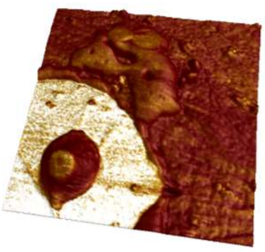
Peak Force Tapping - Contact Resonance



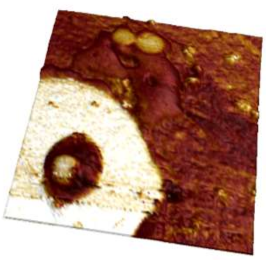


Comparing PFTQNM and CR

- PFTQNM



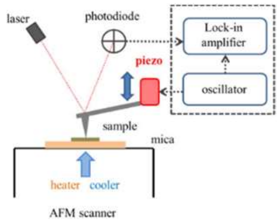
- CR 128x128

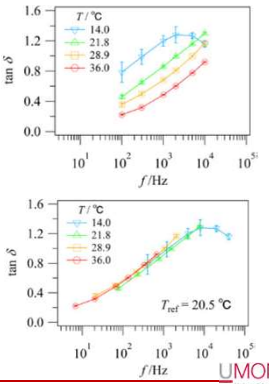


Perspectives

Nanorheological AFM

Vulcanized SBR



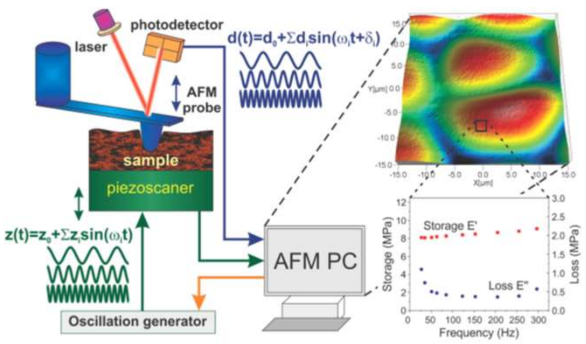


Williams–Landel–Ferry (WLF) equation

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

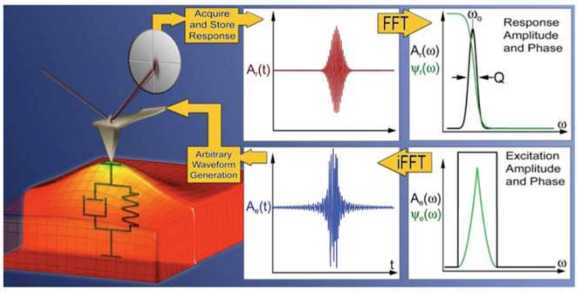
Japanese Journal of Applied Physics 57, 08NB08 (2018)

FT-NanoDMA



Scientific Reports | 5:12630 | DOI: 10.1038/srep12630

Band Excitation (BE)

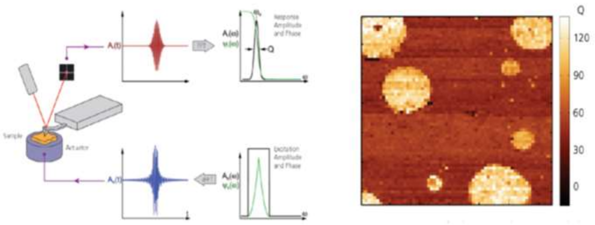


And Google Mode SPM …

S. Jesse, S.V. Kalinin, R. Proksch, A.P. Baddorf, and B.J. Rodriguez, Nanotechnology 18, 435503 (2007).

UMONS 130

Band Excitation (BE)



UMONS 131

Conclusions

Conclusions

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

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

For instance, recorc  ormation and adhesion maps in parallel to d phase images is now possible with quantit

New methods (such) are able to « rapidly » map the mechanic erties at the nanometer scale due to the cquisition and analysis processes.

REMISOL — UMONS Université de Mons — 133

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

REMISOL — UMONS Université de Mons — 134

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

REMISOL — UMONS Université de Mons — 135


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

Questions ?