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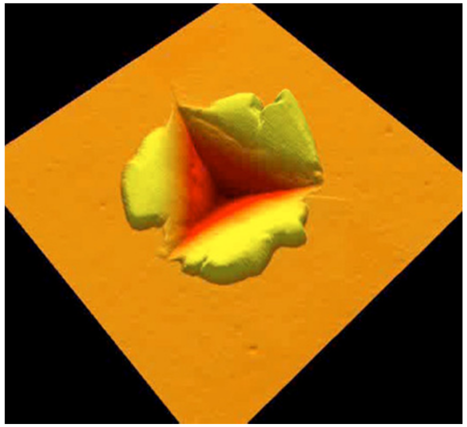
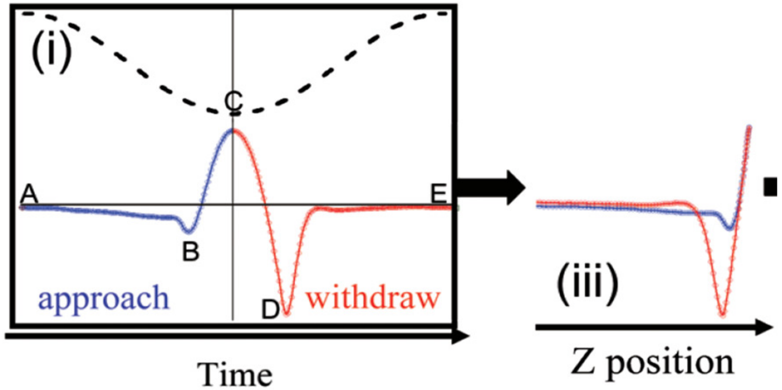
Propriétés (nano)mécaniques des matériaux : Courbes de forces et d'indentation





Philippe LECLERE

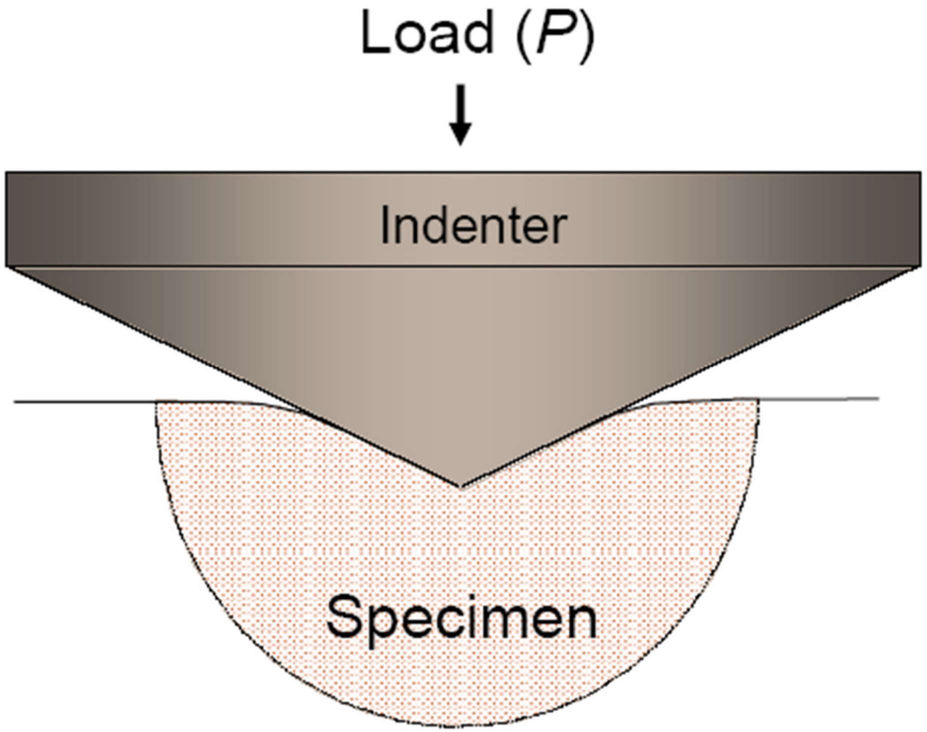
Forum des Microscopies à Sonde Locale
28 mars – 01 avril 2011
Ecully (France)

Menu

1. Microindentation et Nanoindentation
2. Courbes de force
3. Propriétés (nano)mécaniques
   a. Pulsed Force Mode
   b. HarmoniX
   c. Peak Force Tapping
   d. Multifrequency Methods
4. Remarques et conclusions

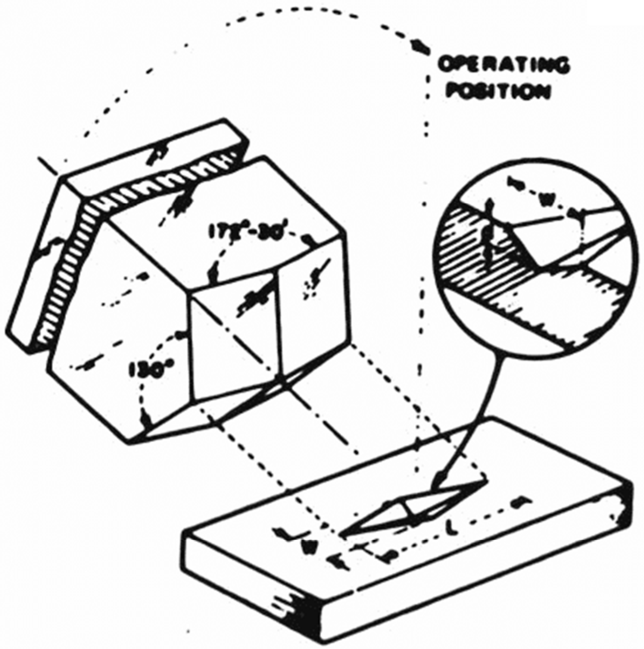
Part 1. Nanoindentation

Indentation test (Hardness test)

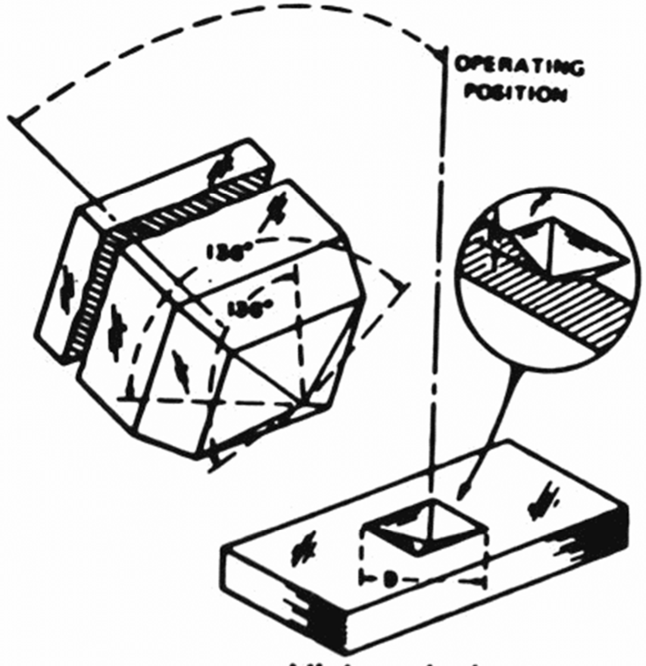


- Hardness – resistance to penetration of a hard indenter

Microhardness - Vickers and Knoop



Knoop Indenter



Vickers Indenter

Nanoindentation

- Nanoindentation is called as,
  - The depth sensing indentation
  - The instrumented indentation

- Nanoindentation method gained popularity with the development of :

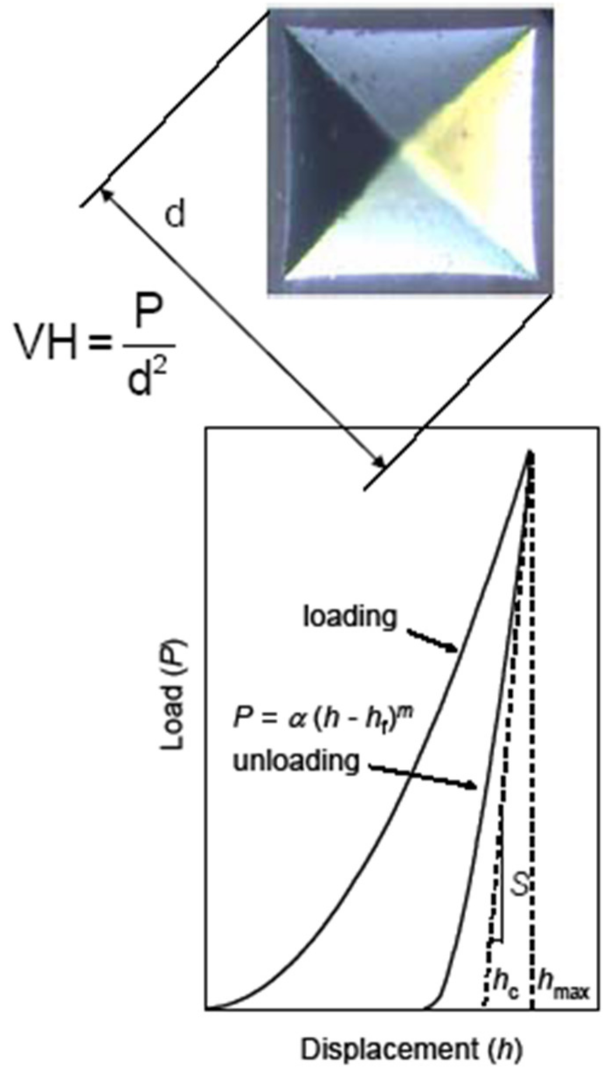
  - Machines that can record small load and displacement with high accuracy and precision

  - Analytical models by which the load-displacement data can be used to determine modulus, hardness and other mechanical properties.

Micro vs Nano Indentation

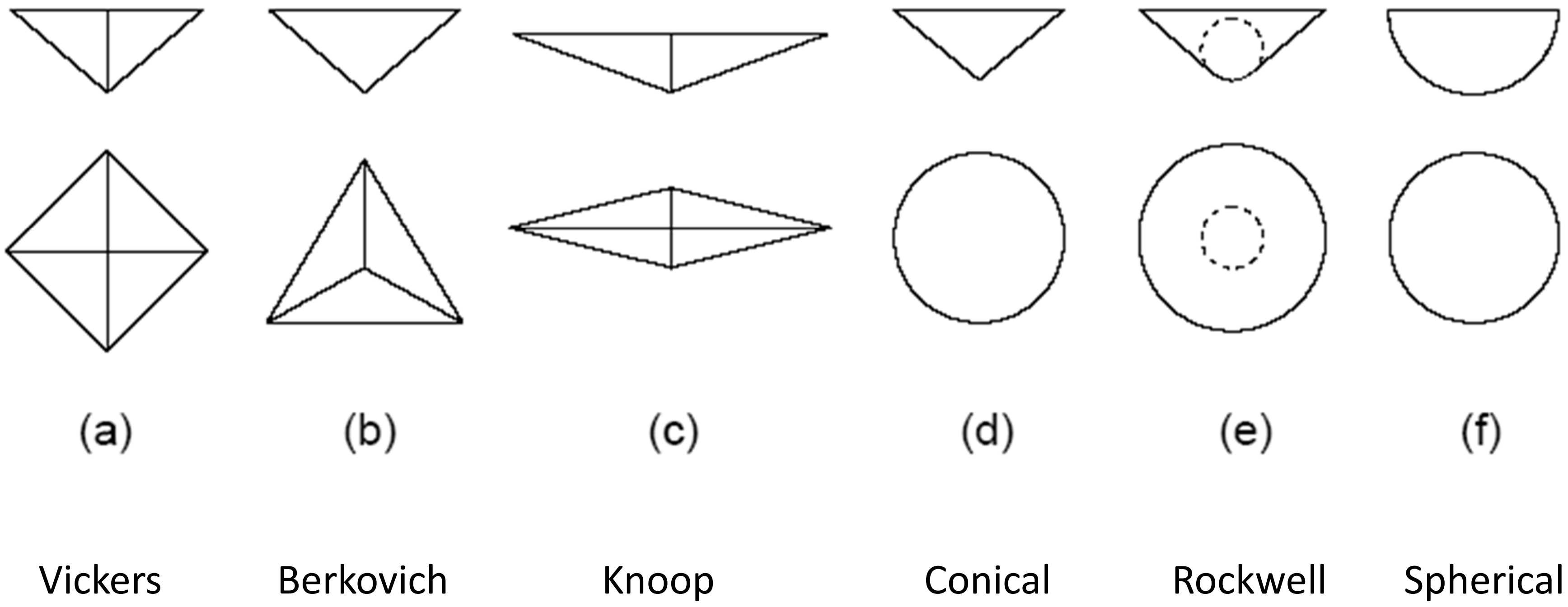
- Microindentation
  A prescribed load applied to an indenter in contact with a specimen and the load is then removed and the area of the residual impression is measured. The load divided by the area is called the hardness.

- Nanoindentation
  A prescribed load is applied to an indenter in contact with a specimen. As the load is applied, the depth of penetration is measured. The area of contact at full load is determined by the depth of the impression and the known angle or radius of the indenter. The hardness is found by dividing the load by the area of contact. Shape of the unloading curve provides a measure of elastic modulus.

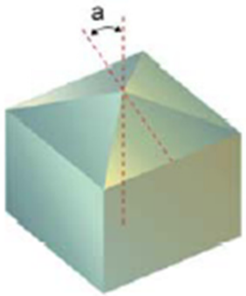
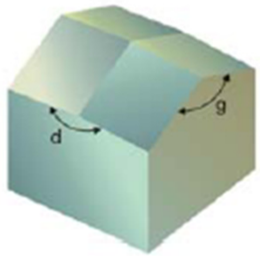
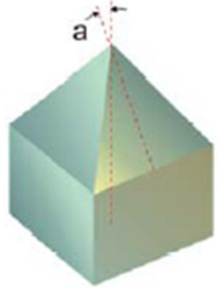


Anthony C. Fischer-Cripps, Principles of nanoindentation, training lecture

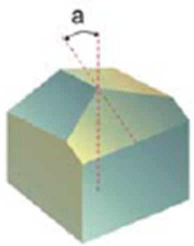
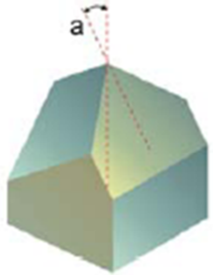
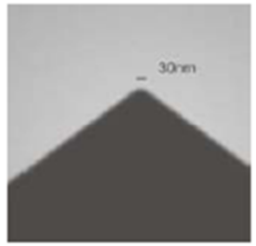
Schematics of indenter tips



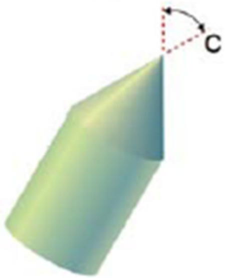
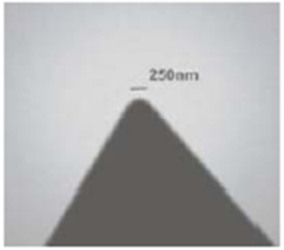
4-sided indenters

<table>
<tr>
<td>VICKERS
FV
</td>
<td>KNOOP INDENTER
FK
</td>
<td>4-SIDED CUSTOM
FD
</td>
<td>END LINE
TEM micrograph
</td>
</tr>
<tr>
<td>Standard Vickers indenter:
a = 68.00°
Available as
Traceable Standard</td>
<td>Standard Knoop indenter defined by 2 angles:
d = 172.50°, g = 130.00°</td>
<td>Custom 4-sided indenters:
80° > a > 20°</td>
<td>Micro Star indenters maximum line of conjunction: 400nm.</td>
</tr>
</table>

3-sided indenters

BERKOVICH **TB**  	**CUBE CORNER** **TC**  	**3-SIDED CUSTOM** **TD**  	**SHARPNESS** TEM micrograph 
Berkovich: a = 65.03° Mod. Berkovich: a = 65.27° Available as **Traceable Standard**	Cube corner: a = 35.26° Available as **Traceable Standard**	Custom 3-sided indenters: 80° > a > 20°	Micro Star 3-sided sharp indenters tip radius < 50nm.

Cone indenters

<table>
<tr>
<td>CONE TIP
VS

</td>
<td>POINT SHARPNESS
TEM micrograph

</td>
<td>FLAT END CONE
VP
</td>
<td>ROUND END CONE
VR
</td>
</tr>
<tr>
<td>Included conical angle:
20° > c > 140°</td>
<td>Micro Star sharp cone
radius less than 300nm.</td>
<td>Flat from 500nm diameter
to larger compatible sizes.</td>
<td>Spherical end radius 500nm
to larger compatible sizes.</td>
</tr>
</table>

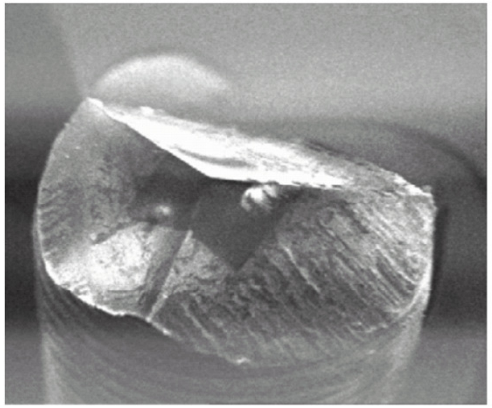
Indenter geometry

Indenter type	Projected area	Semi angle (θ)	Effective cone angle (α)	Intercept factor	Geometry correction factor (β)
Sphere	$A \approx \pi 2Rh_p$	N/A	N/A	0.75	1
Berkovich	$A = 3h_p^2\tan^2\theta$	65.3 °	70.2996 °	0.75	1.034
Vickers	$A = 4h_p^2\tan^2\theta$	68 °	70.32 °	0.75	1.012
Knoop	$A = 2h_p^2\tan\theta_1\tan\theta_2$	θ_1=86.25 ° θ_2=65 °	77.64 °	0.75	1.012
Cube Corner	$A = 3h_p^2\tan^2\theta$	35.26 °	42.28 °	0.75	1.034
Cone	$A = \pi h_p^2\tan^2\alpha$	α	α	0.72	1

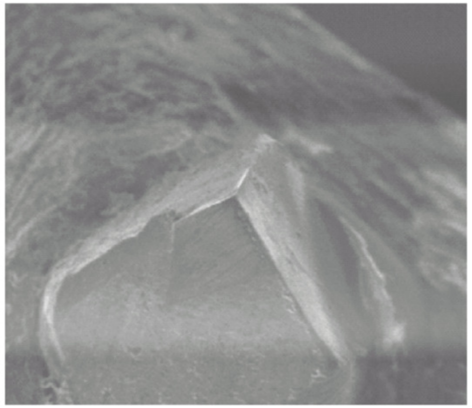
Anthony C. Fischer-Cripps, Nanoindentation, 2002, Springer

Nanoindenter tips

Three-sided pyramidal tips

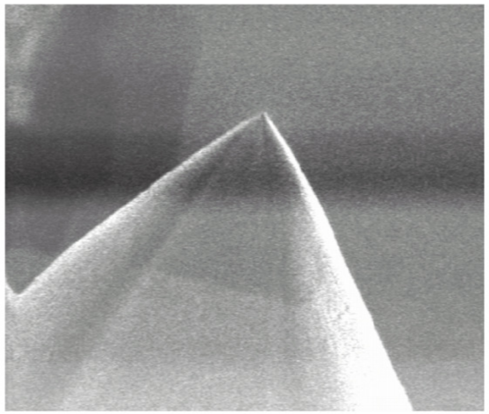


Berkovich

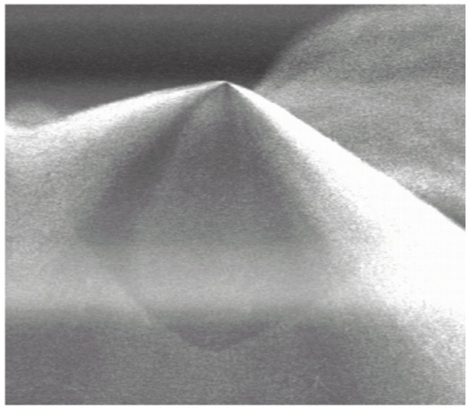


Cube-corner

Cono-spherical tips

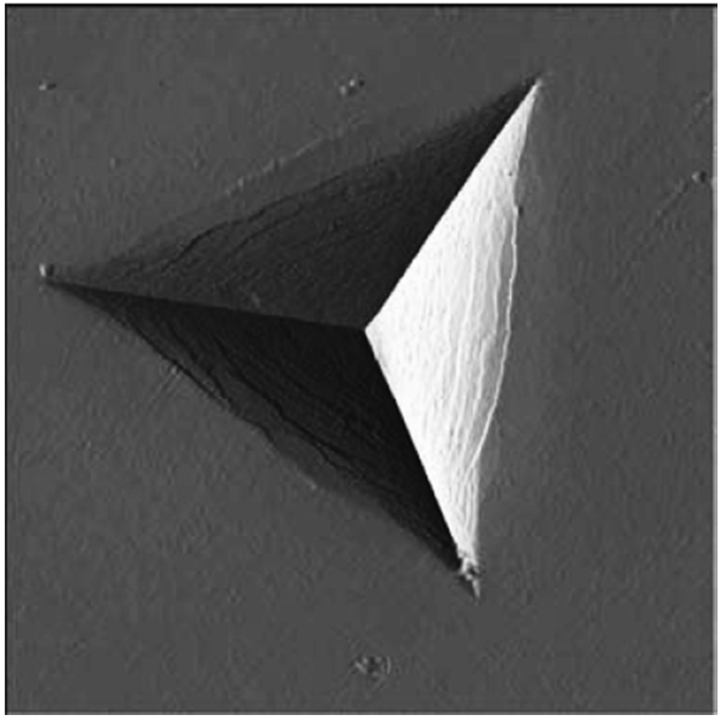


Conical (<3 μm)



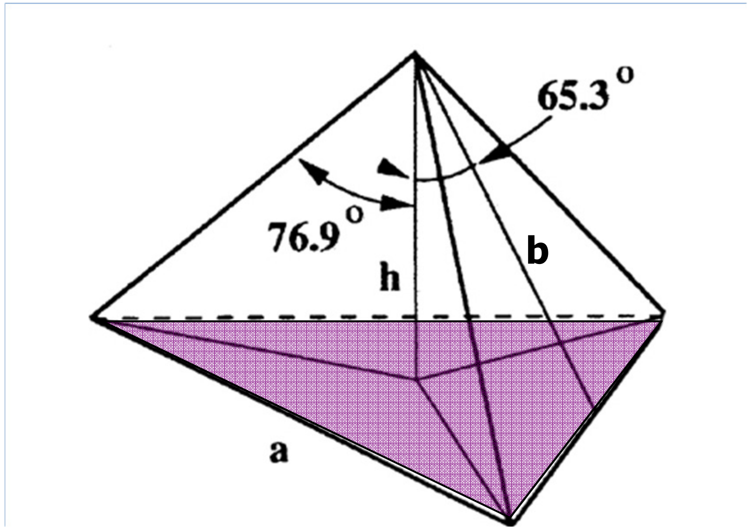
Conical (>3 μm)

Sharp indenter (Berkovich)

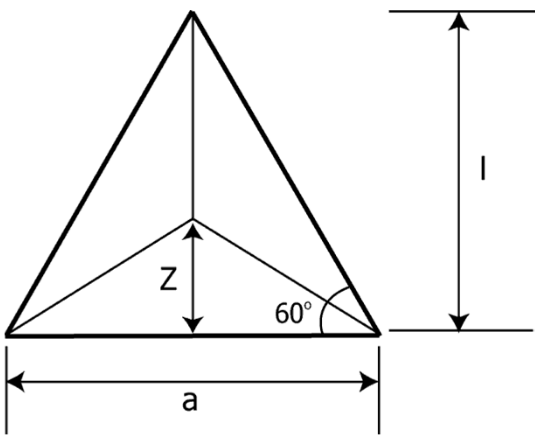


- Advantage
  - Sharp and well-defined tip geometry
  - Well-defined plastic deformation into the surface
  - Good for measuring modulus and hardness values
- Disadvantage
  - Elastic-plastic transition is not clear.

Berkovich indenter



Projected area



$$\tan 60^o = \frac{l}{a/2}$$

$$l = \frac{\sqrt{3}}{2}a$$

$$A_{proj} = \frac{al}{2} = \frac{\sqrt{3}}{4}a^2$$

$$\cos 65.27^o = \frac{h}{b}$$

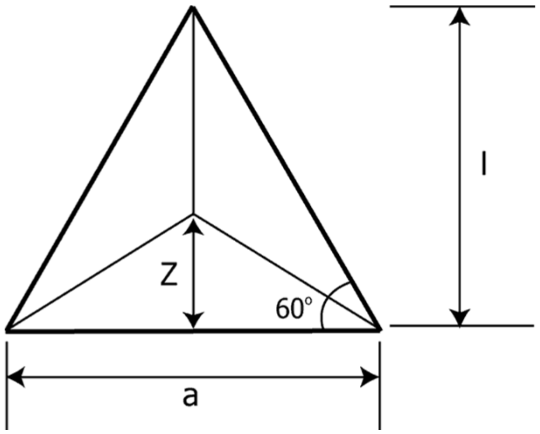
$$h = \frac{a\cos 65.3^o}{2\sqrt{3}\sin 65.3^o} = \frac{a}{2\sqrt{3}\tan 65.3^o}$$

$$a = 2\sqrt{3}h\tan 65.3^o$$

$$A_{proj} = 3\sqrt{3}h^2\tan^2 65.3^o = 24.56h^2$$

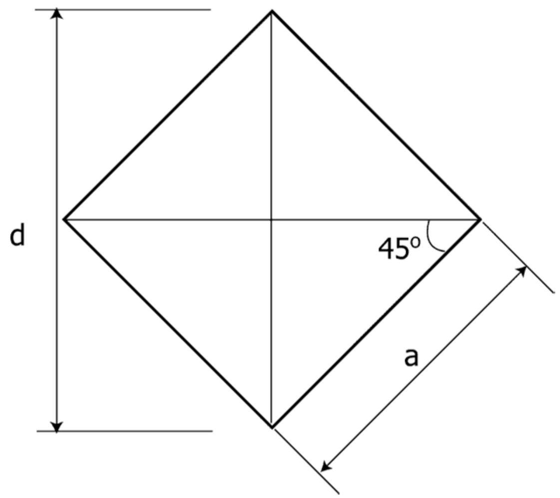
Berkovich vs Vickers indenter

• Berkovich projected area



$$A_{proj} = 3\sqrt{3}h^2 \tan^2 65.3^o = 24.56h^2$$

• Vickers projected area

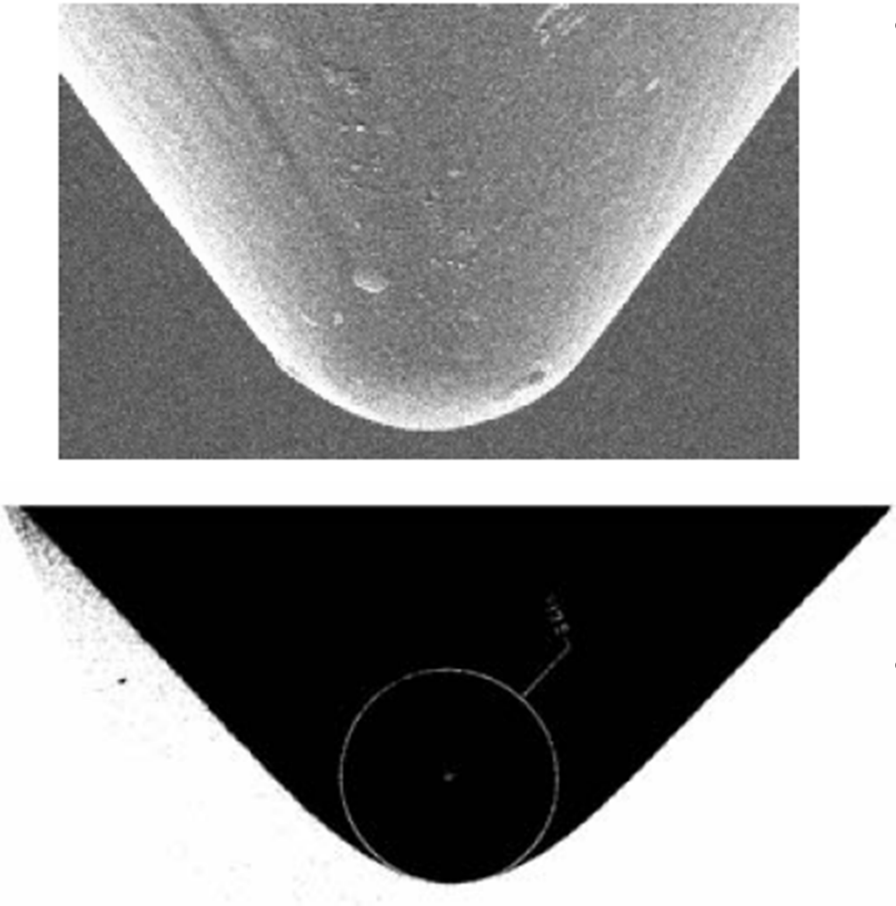


$$A_{proj} = 4h^2 \tan^2 68^o = 24.504h^2$$

- Face angle of Berkovich indenter: 65. 3 °
- Same projected area-to-depth ratio as Vickers indenter
- Equivalent semi-angle for conical indenter: 70.3 °

$$A = \pi h_p{}^2 \tan^2 \alpha$$

Blunt indenter - spherical tip

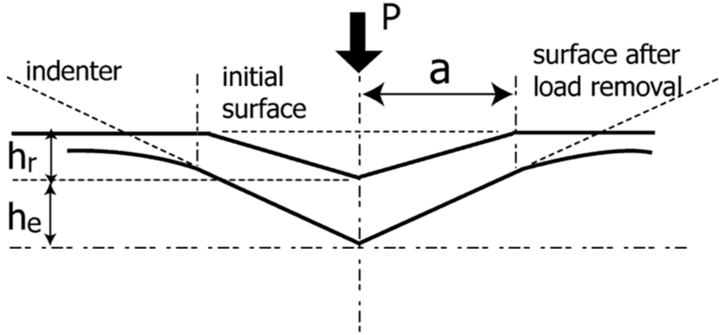


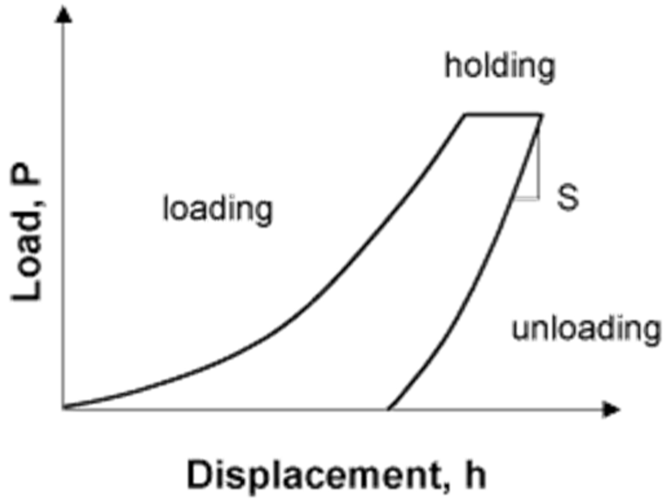
MTS Tech sheet for spherical tip

- Advantage
  - Extended elastic-plastic deformation
  - Load displacement results can be converted to indentation stress-strain curve.
  - Useful in determination of yield point

- Disadvantage
  - Tip geometry is not very sharp and the spherical surface is not always perfect.

Data Analysis





- *P* : applied load
- *h* : indenter displacement
- h_r : plastic deformation after load removal
- h_e : surface displacement at the contact perimeter

Analytical Model – Basic Concept

- Nearly all of the elements of this analysis were first developed by workers at the Baikov Institute of Metallurgy in Moscow during the 1970's (for a review see Bulychev and Alekhin).

- The basic assumptions of this approach are :
  - Deformation upon unloading is purely elastic
  - The compliance of the sample and of the indenter tip can be combined as springs in series

$$\frac{1}{E_r} = \frac{1-\upsilon_i^{\,2}}{E_i} + \frac{1-\upsilon_s^{\,2}}{E_s}$$

  - The contact can be modeled using an analytical model for contact between a rigid indenter of defined shape with a homogeneous isotropic elastic half space using

$$S = \frac{2\sqrt{A}}{\sqrt{\pi}} E_r$$

  where S is the contact stiffness and A the contact area.

  - This relation was presented by Sneddon. Later, Pharr, Oliver and Brotzen where able to show that the equation is a robust equation which applies to tips with a wide range of shapes.

Analysis result

- Reduced modulus

$$\frac{1}{E^*}=\frac{1-\upsilon^2}{E}+\frac{1-\upsilon'^2}{E'}$$

E: modulus of specimen
E': modulus of indenter

- Stiffness

$$\frac{dP}{dh}=2E^*\frac{\sqrt{A}}{\sqrt{p}}$$

- Contact area

$$A=3\sqrt{3}h_p{}^2\tan^2 65.3=24.5h_p{}^2$$

for Berkovich indenter

- Hardness

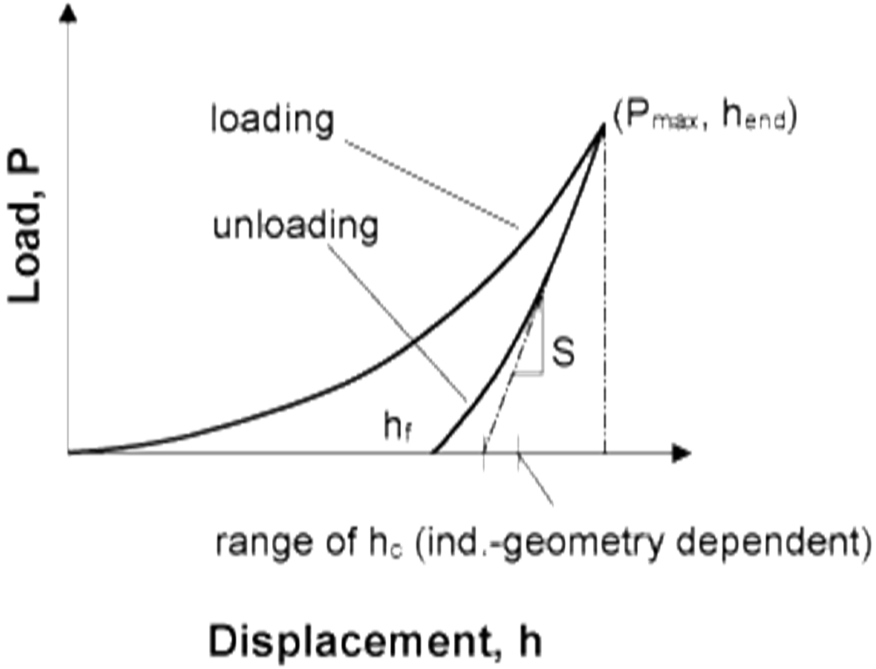
$$H=\frac{P}{24.5h_p{}^2}$$

- Elastic modulus

$$E^*=\frac{dP}{dh}\frac{1}{2h_p}\frac{1}{\beta}\sqrt{\frac{\pi}{24.5}}$$

$\beta=1.034$ for Berkovich indenter

Analytical Model – Oliver and Pharr



$$P = \alpha (h - h_f)^m$$

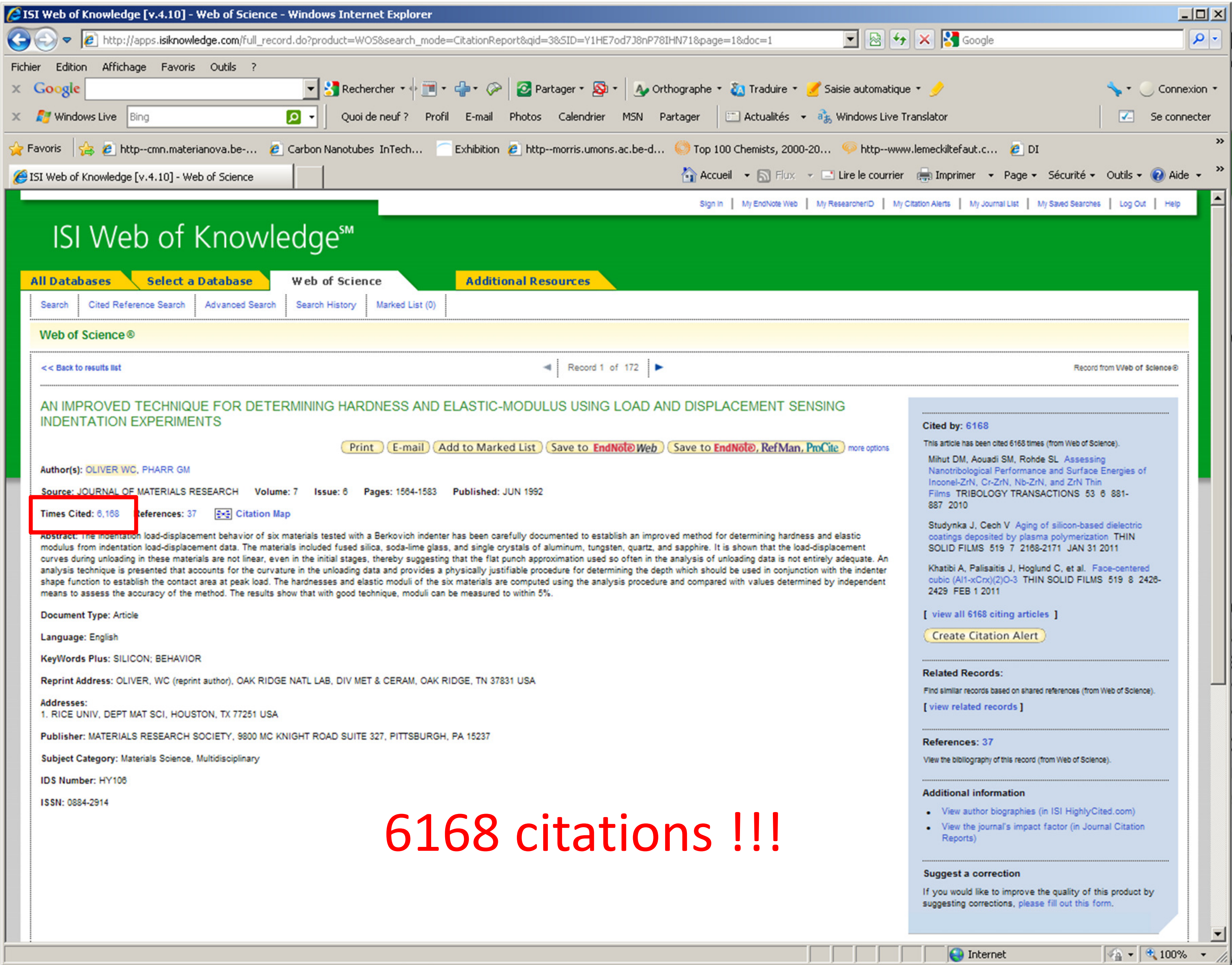
$$h_c = h_t - \varepsilon \frac{P}{S}$$

$$A_c = f(h_c)$$

ε = 0.72, 0.75 and 1, for cone-, sphere- and flat-punch-geometry, respectively.

Oliver & Pharr, J Mater Res, 1992

One of the most cited paper in Materials Science



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AN IMPROVED TECHNIQUE FOR DETERMINING HARDNESS AND ELASTIC-MODULUS USING LOAD AND DISPLACEMENT SENSING INDENTATION EXPERIMENTS

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Author(s): OLIVER WC, PHARR GM

Source: JOURNAL OF MATERIALS RESEARCH **Volume:** 7 **Issue:** 6 **Pages:** 1564-1583 **Published:** JUN 1992

Times Cited: 6,168 **References:** 37 Citation Map

Abstract: The indentation load-displacement behavior of six materials tested with a Berkovich indenter has been carefully documented to establish an improved method for determining hardness and elastic modulus from indentation load-displacement data. The materials included fused silica, soda-lime glass, and single crystals of aluminum, tungsten, quartz, and sapphire. It is shown that the load-displacement curves during unloading in these materials are not linear, even in the initial stages, thereby suggesting that the flat punch approximation used so often in the analysis of unloading data is not entirely adequate. An analysis technique is presented that accounts for the curvature in the unloading data and provides a physically justifiable procedure for determining the depth which should be used in conjunction with the indenter shape function to establish the contact area at peak load. The hardnesses and elastic moduli of the six materials are computed using the analysis procedure and compared with values determined by independent means to assess the accuracy of the method. The results show that with good technique, moduli can be measured to within 5%.

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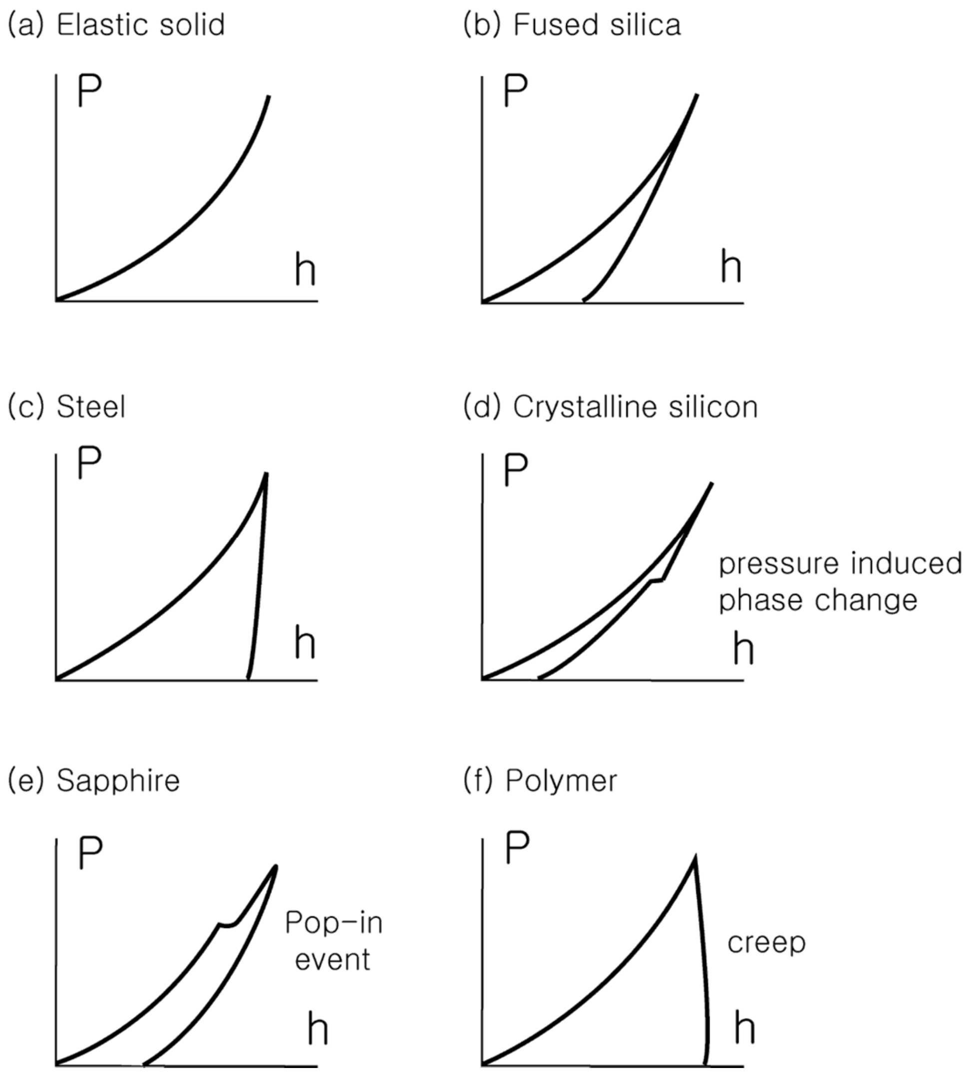
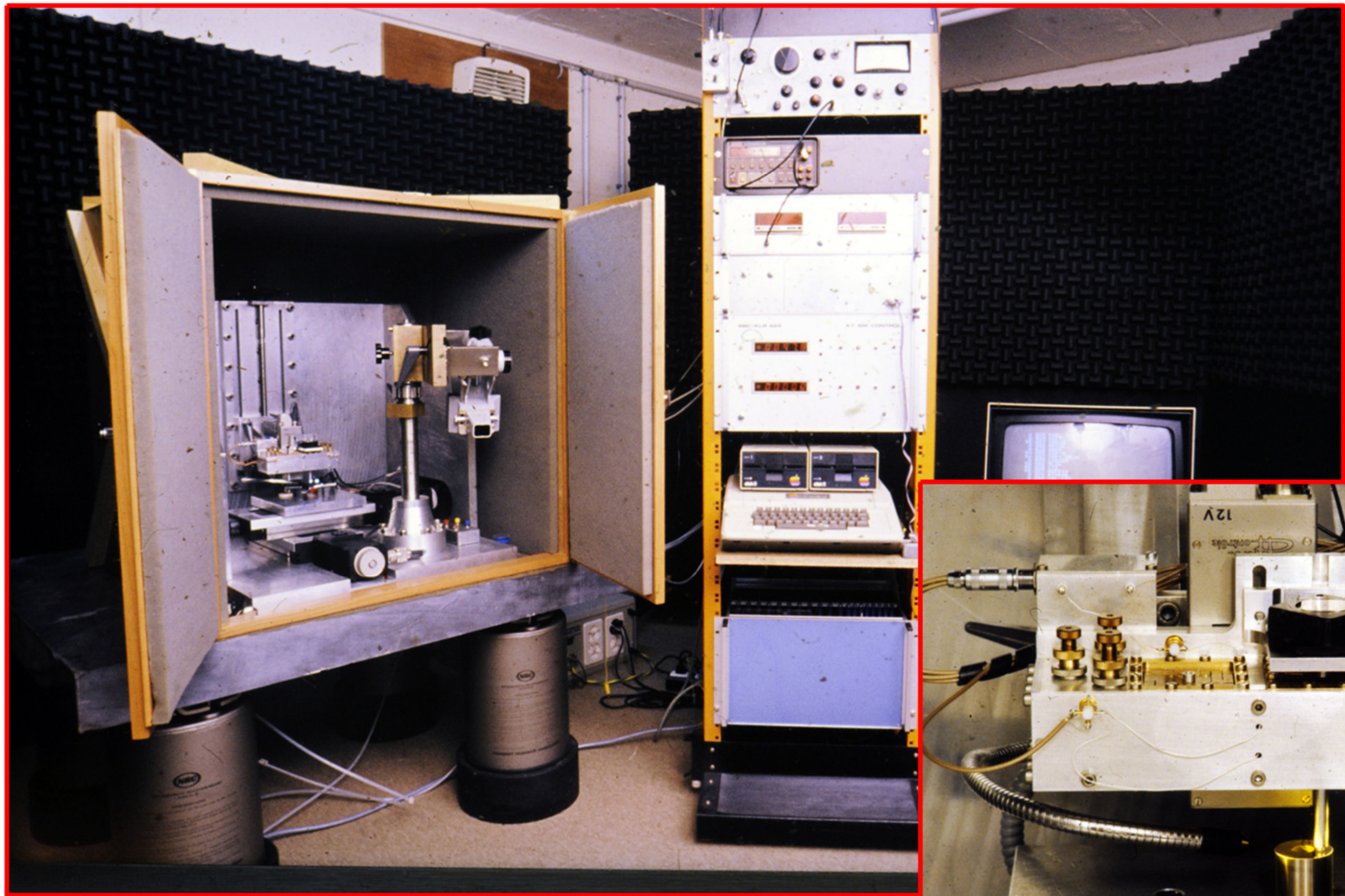
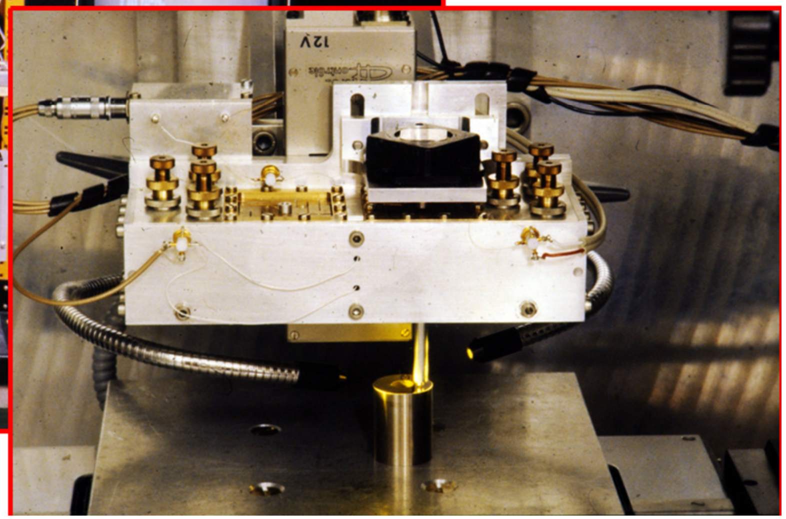


Anthony C. Fischer-Cripps, Nanoindentation, 2002, Springer

THE ORIGINAL NANOINDENTER

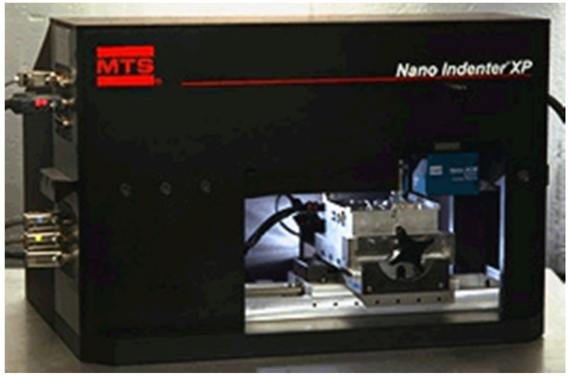
• Pethica, Hutchings, and Oliver, *Phil Mag A***48**, 593(1983)





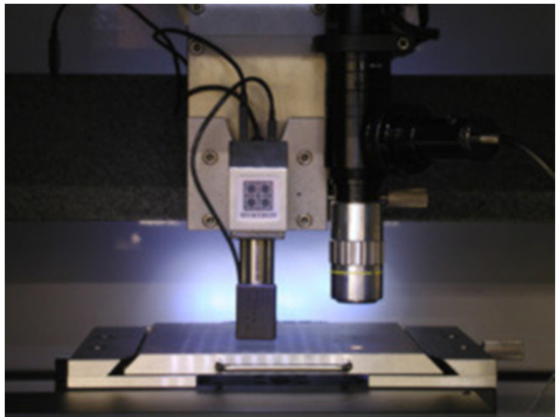
Commercial machines

- MTS_Nano-Indenter XP



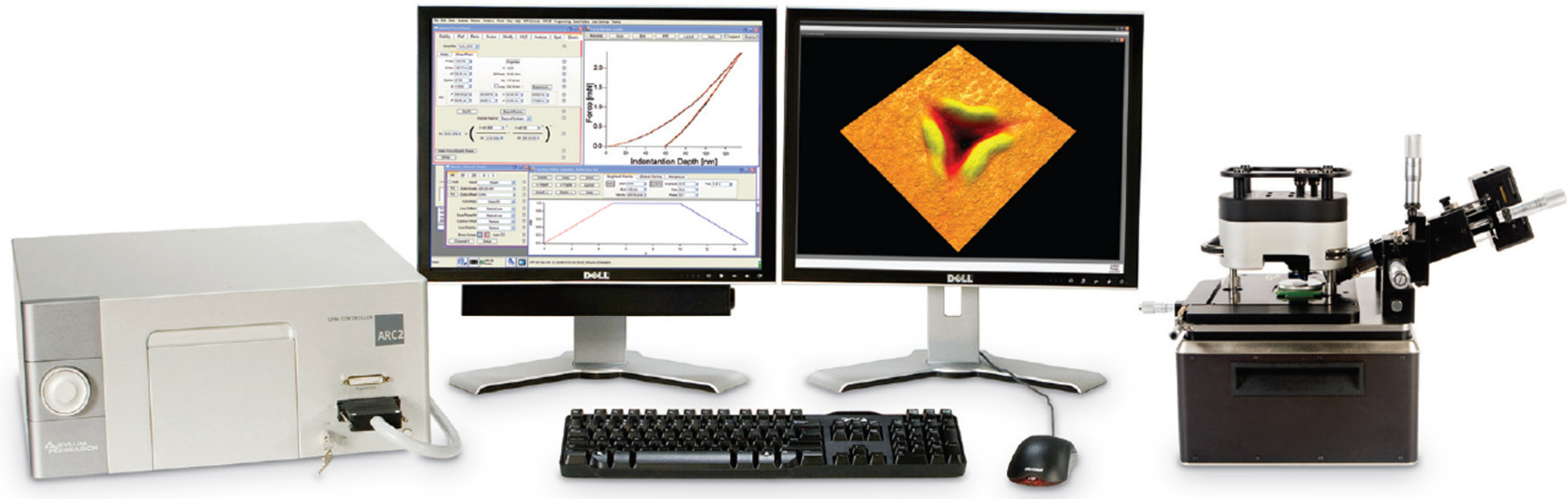
- CSIRO_UMIS
- (Ultra-Micro-Indentation System)

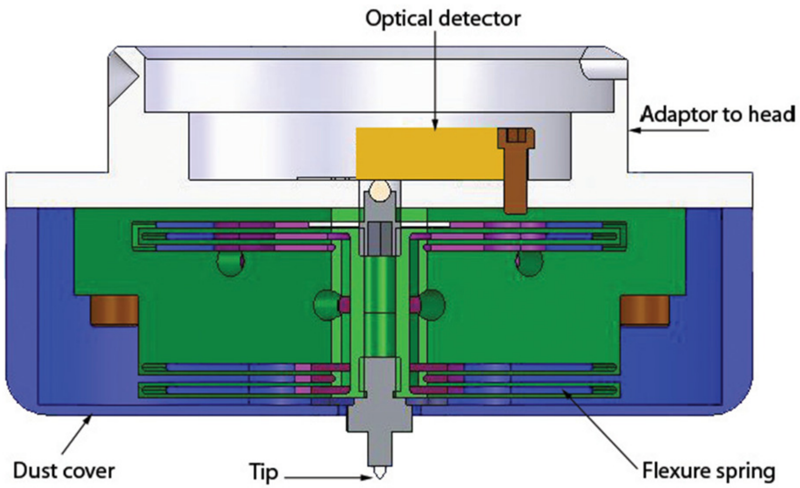
- Hysitron_Triboscope



- CSM_NHT
- (Nano-Hardness Tester)

Commercial machines





NanoIndenter Module

Sensored, Flexure based Z axis for precision, accuracy and quantitative measurements

Top View Head allows easy sample viewing

Uses commercially available indenter tips

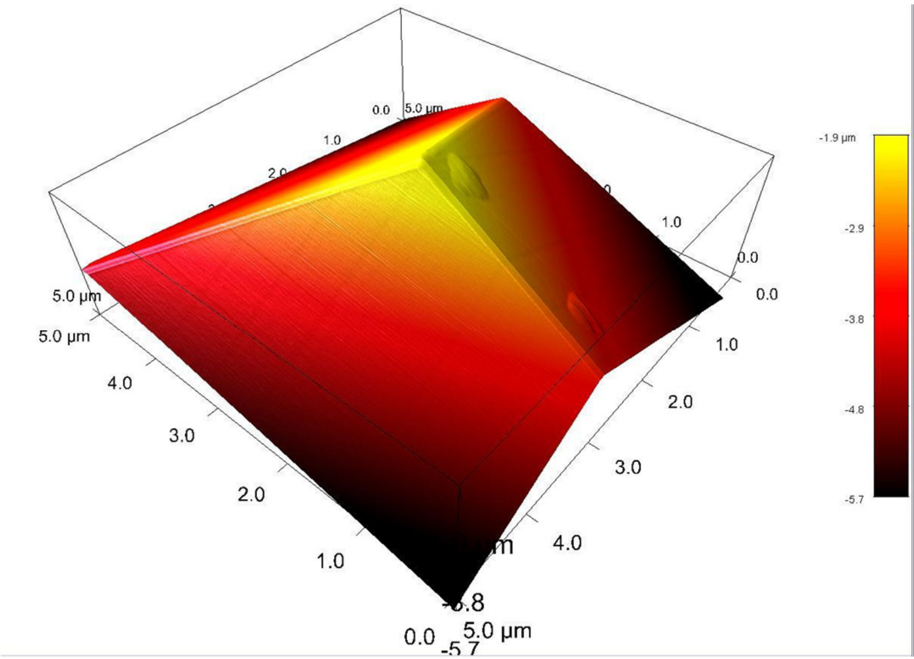
Tip Characterization through AFM imaging

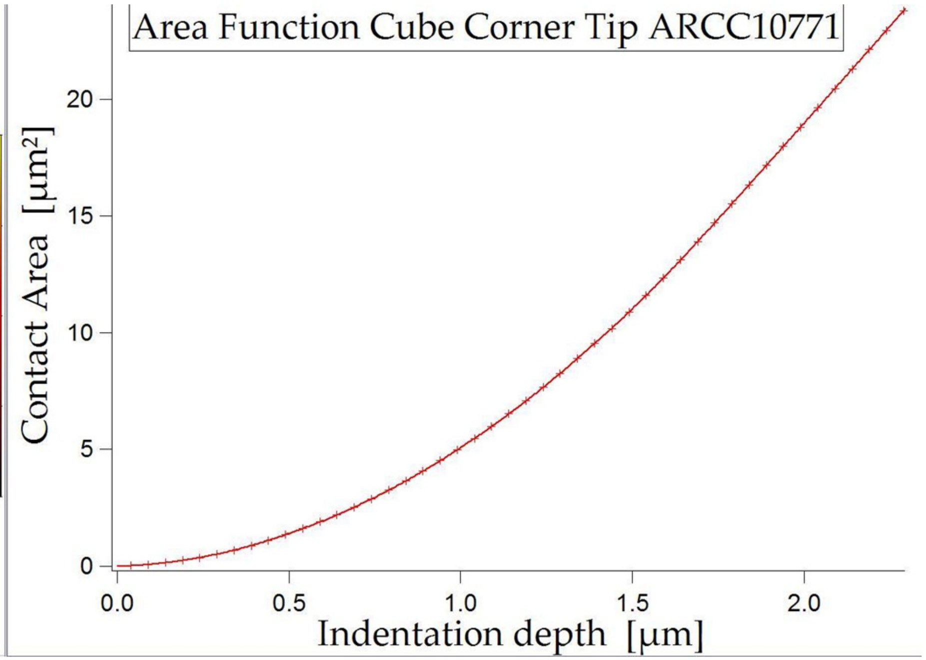
Depth resolution: 0.3 nm

Flexible software with open source adaptability

Asylum Research
Science First

Direct Measurement of Area Function

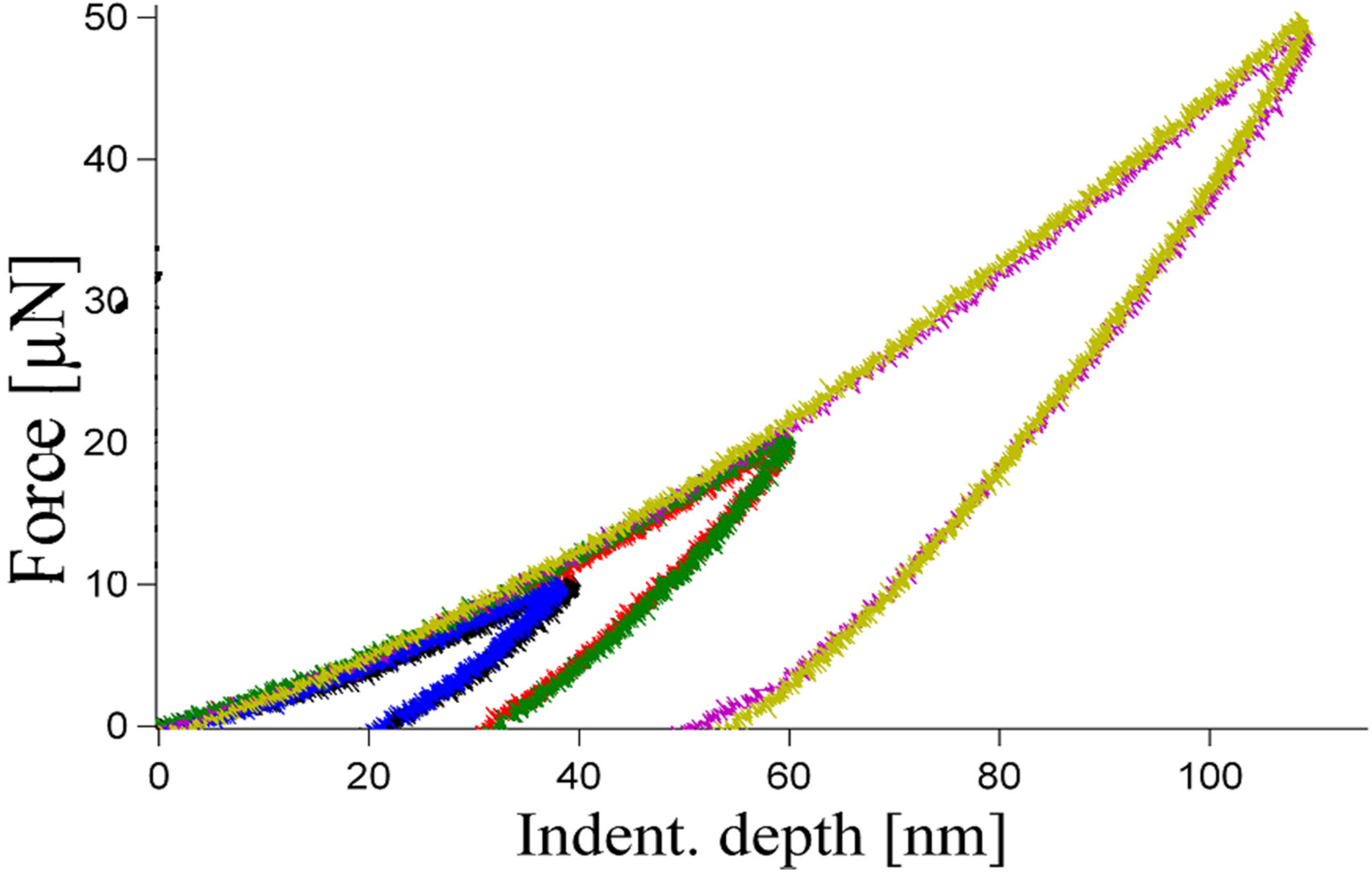




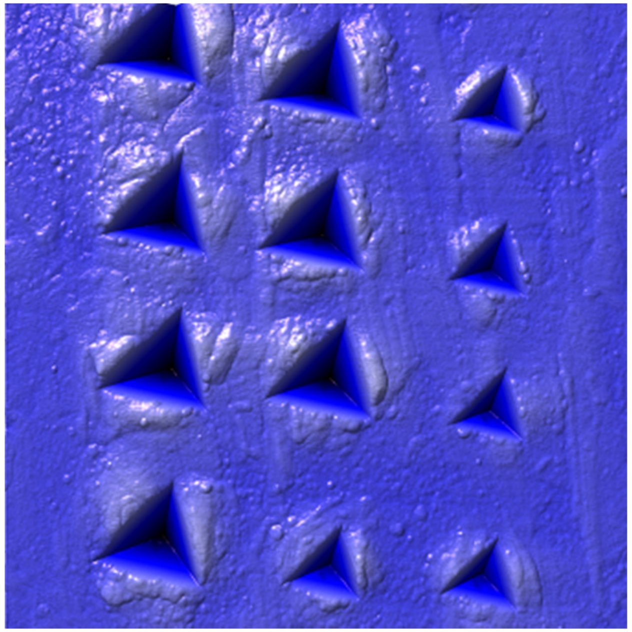
Indenting tip is placed as sample and imaged with high aspect ratio AFM tip. Tip can be checked for contamination/defects.

Results should be compared to standard methods for area function.

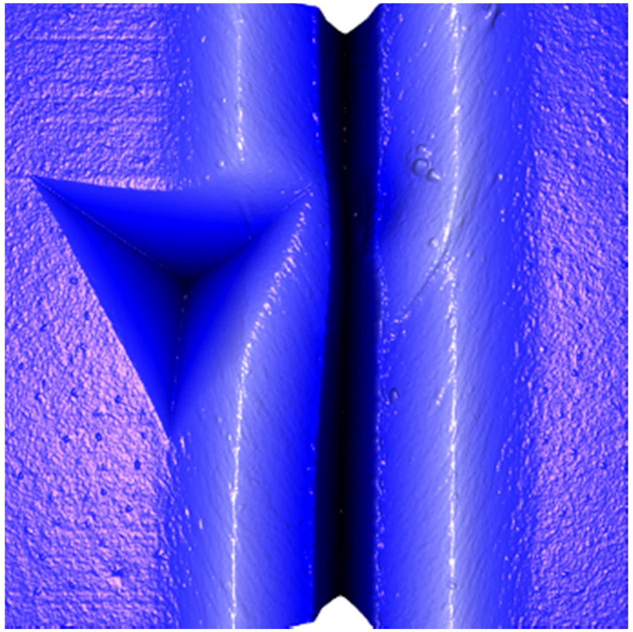
Polymer Indentation

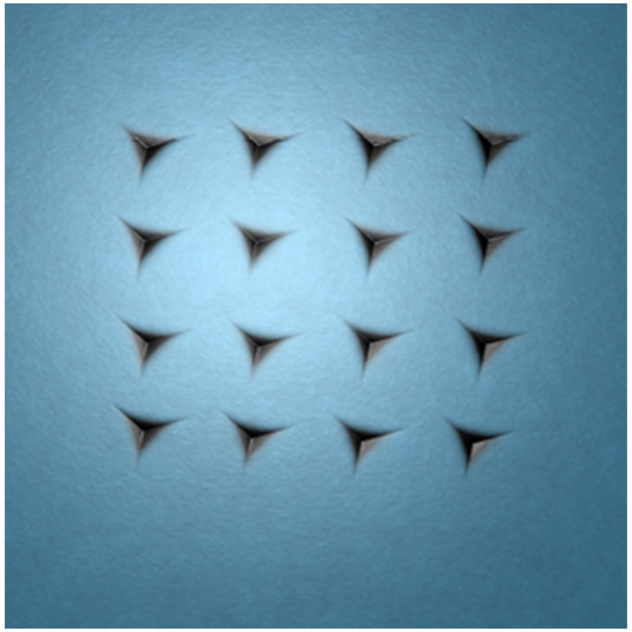


Indentation Imaging



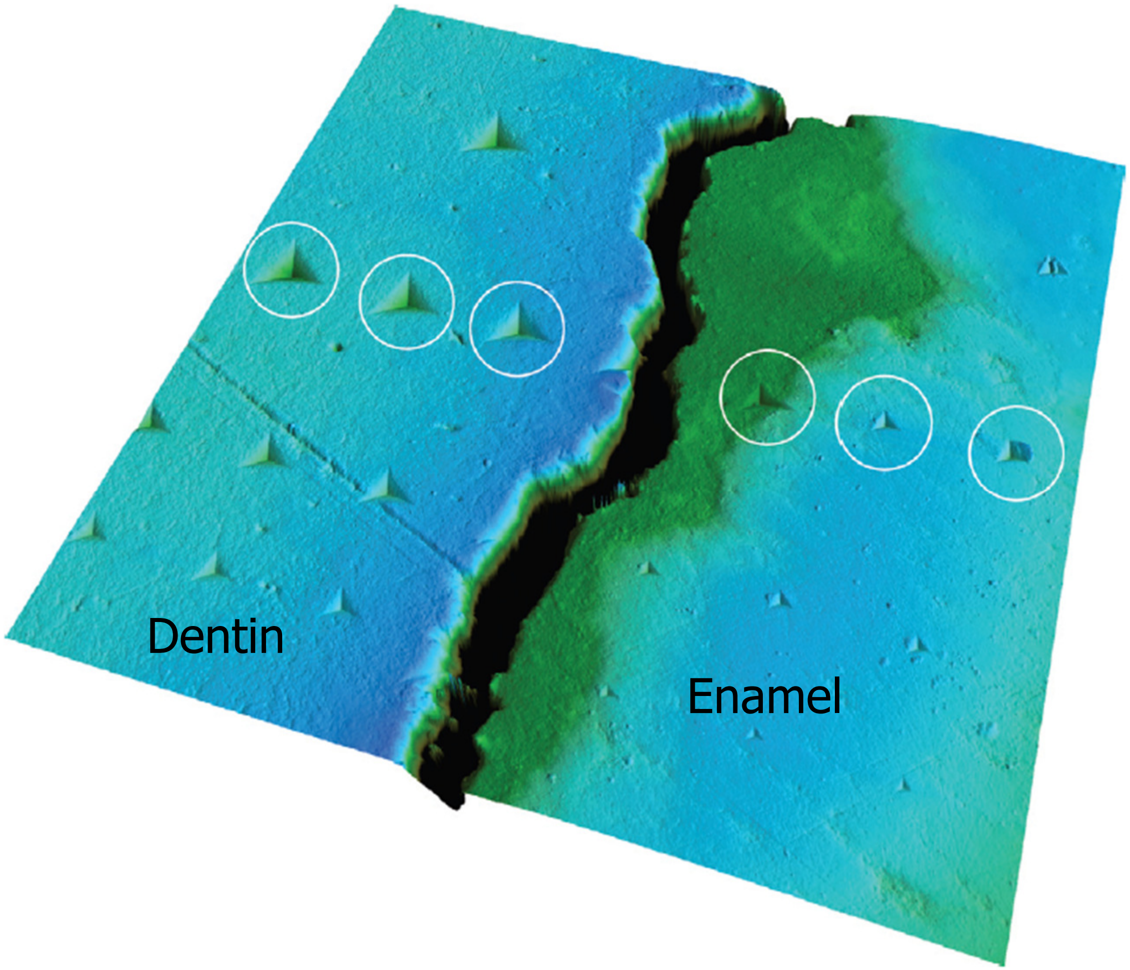
Accurate measurement of contact areas and volumes





Cube corner diamond tip indentation on copper, 20um scan.

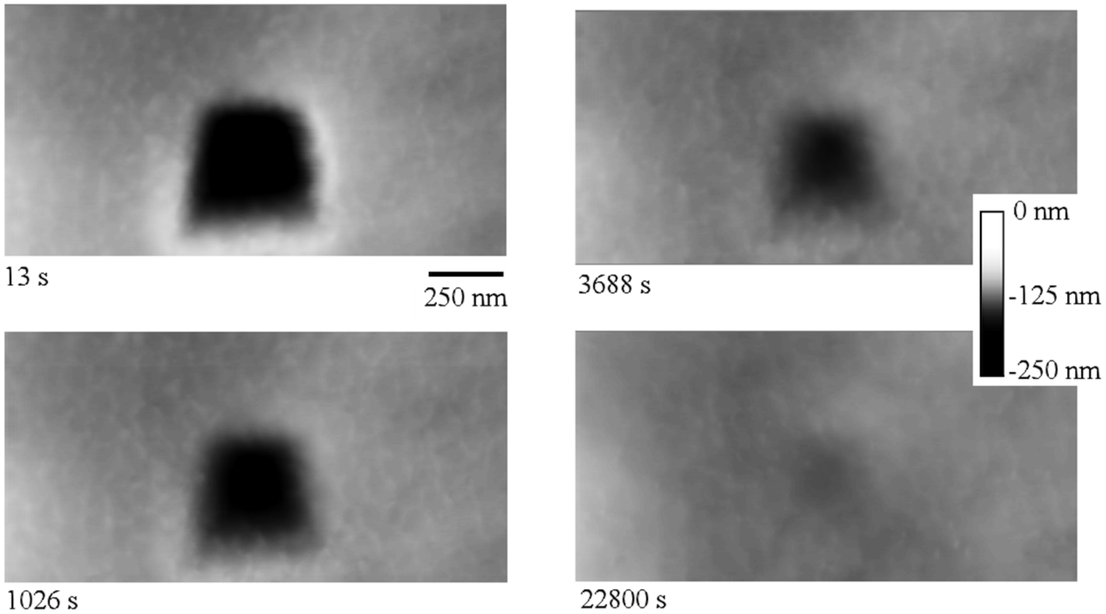
Nanoindentation of natural materials

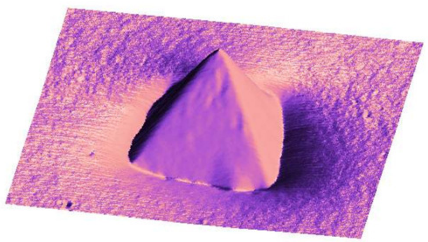


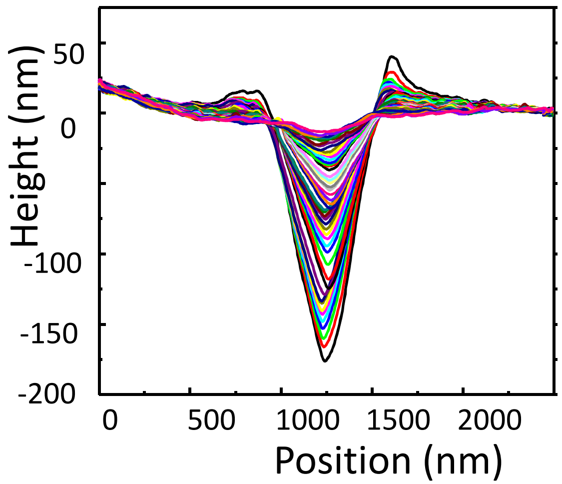
Indenting on dentin (left of crack), and enamel (right) on a human tooth sample. The indentations in each row (one row is circled) were all created with the same maximum force. The smaller indents on the enamel demonstrate that it is harder than the dentin, 70 μm scan.

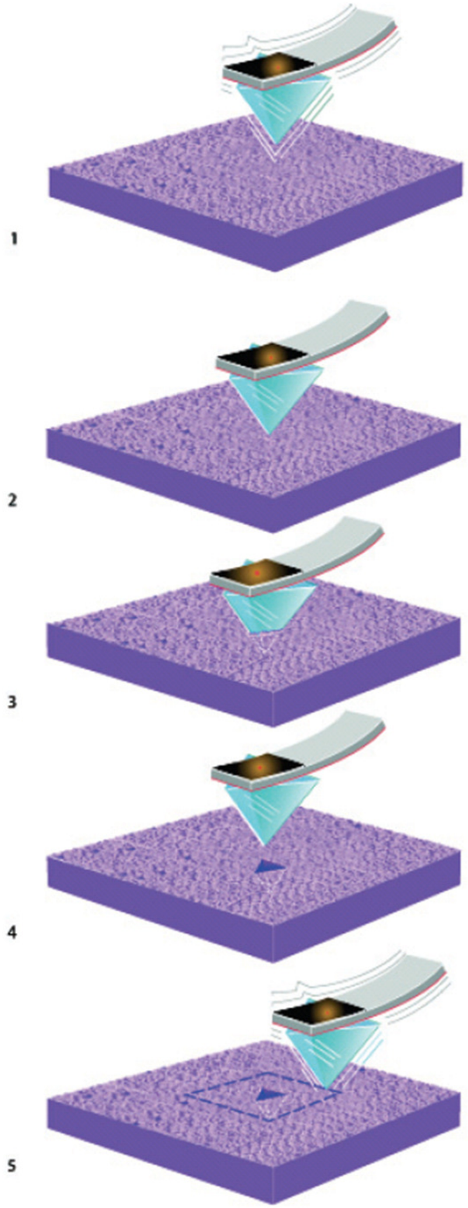
Sample courtesy D. Wagner and S. Cohen, Weizmann Institute of Science.

Polymer “Self-Healing”





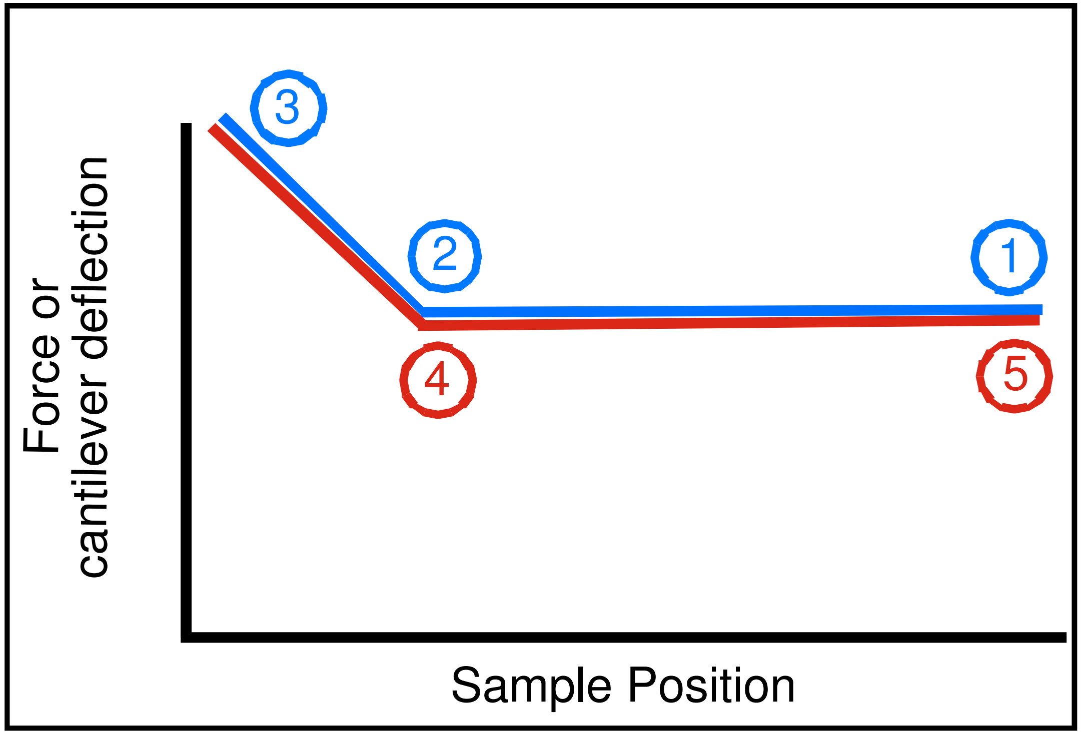




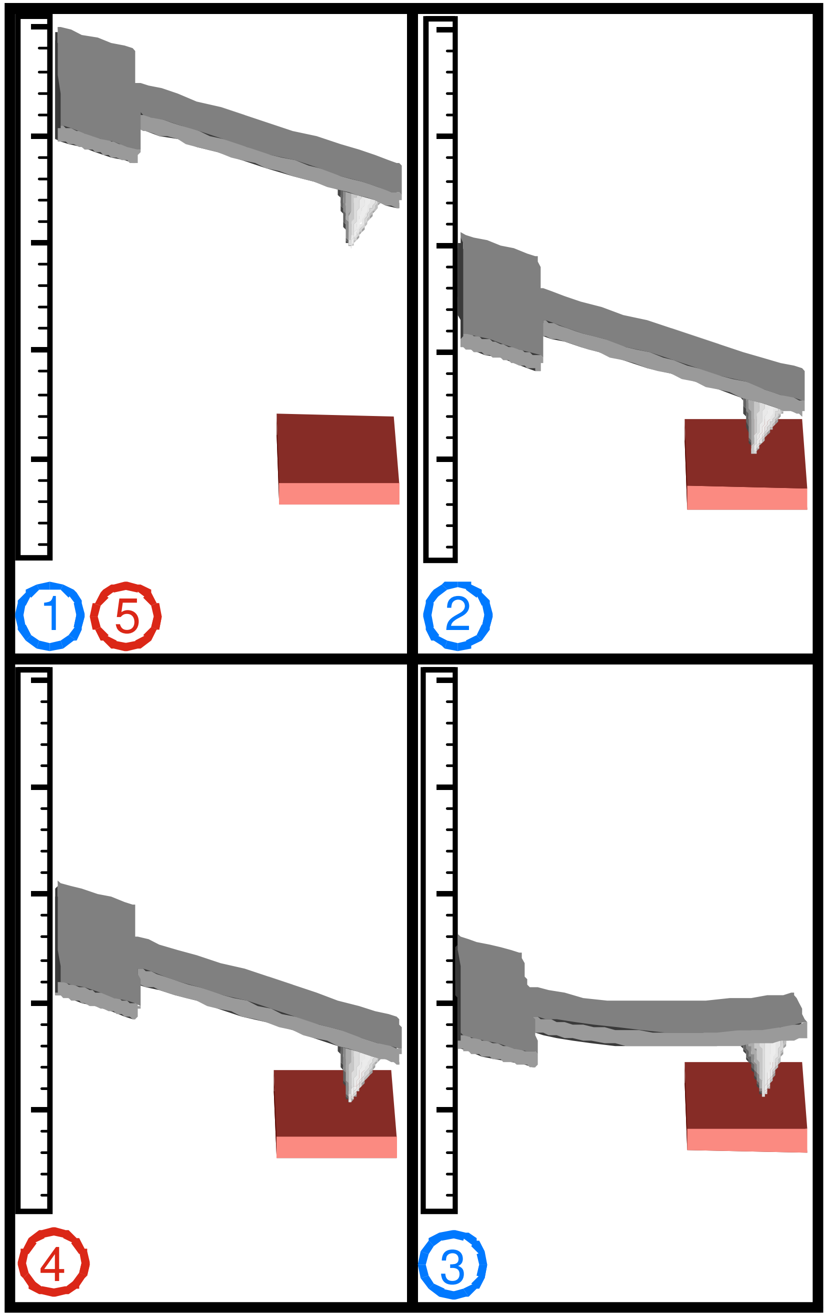
C.R. Acad. Sci. Paris IIb, **325** (1997) 211-220

Part 2. Force curves

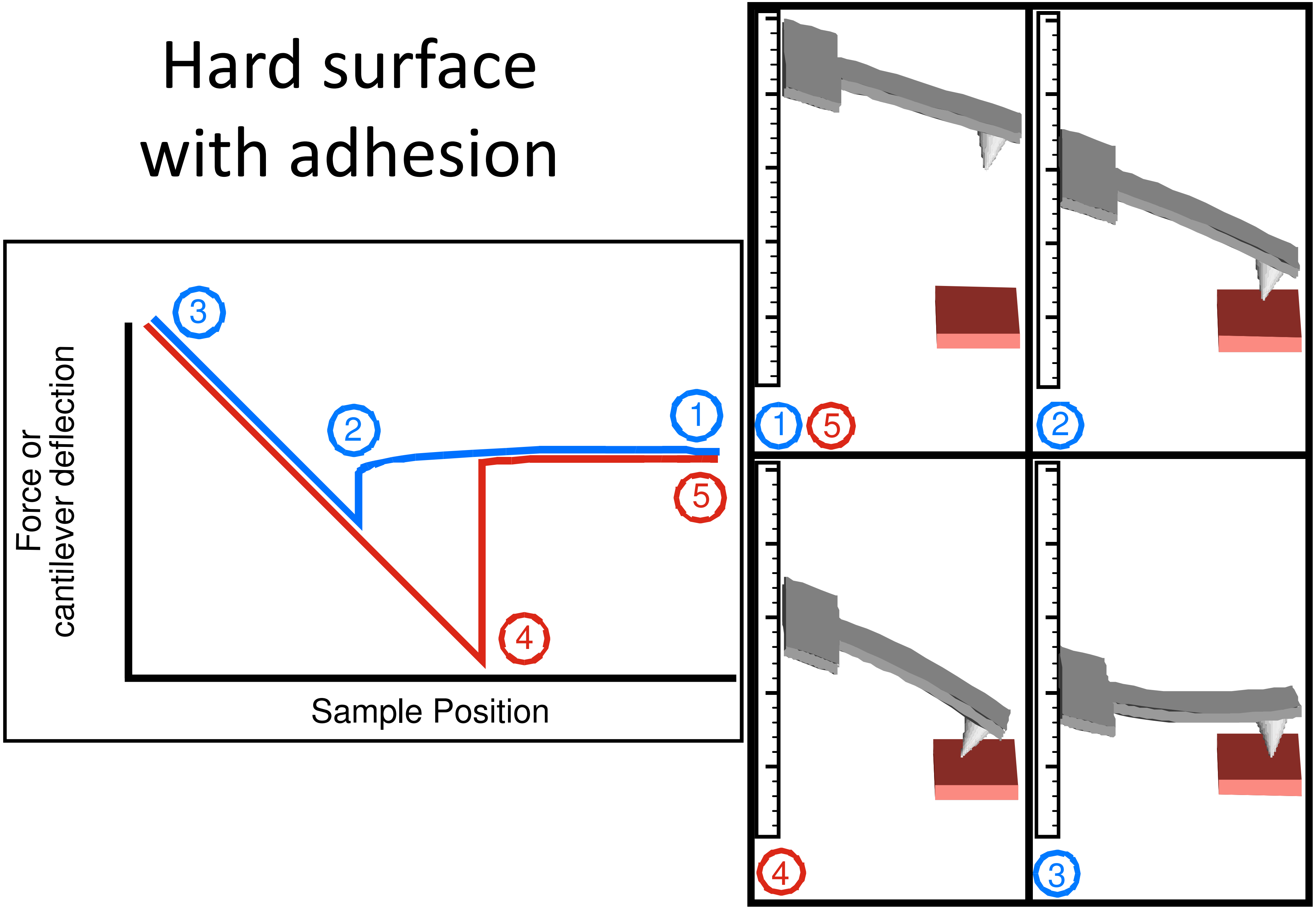
Hard surface, no interaction



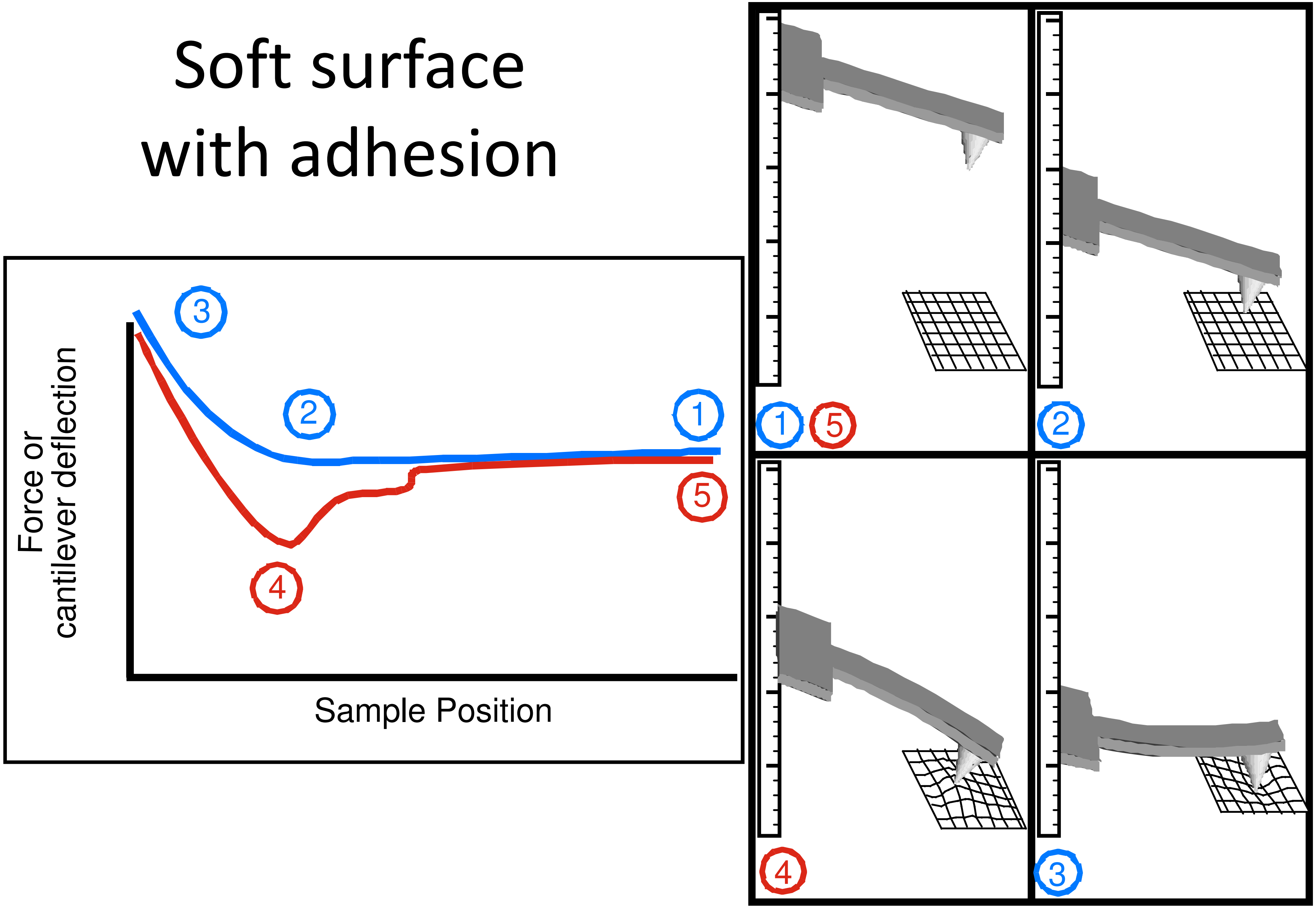
“The imaging dream curve”



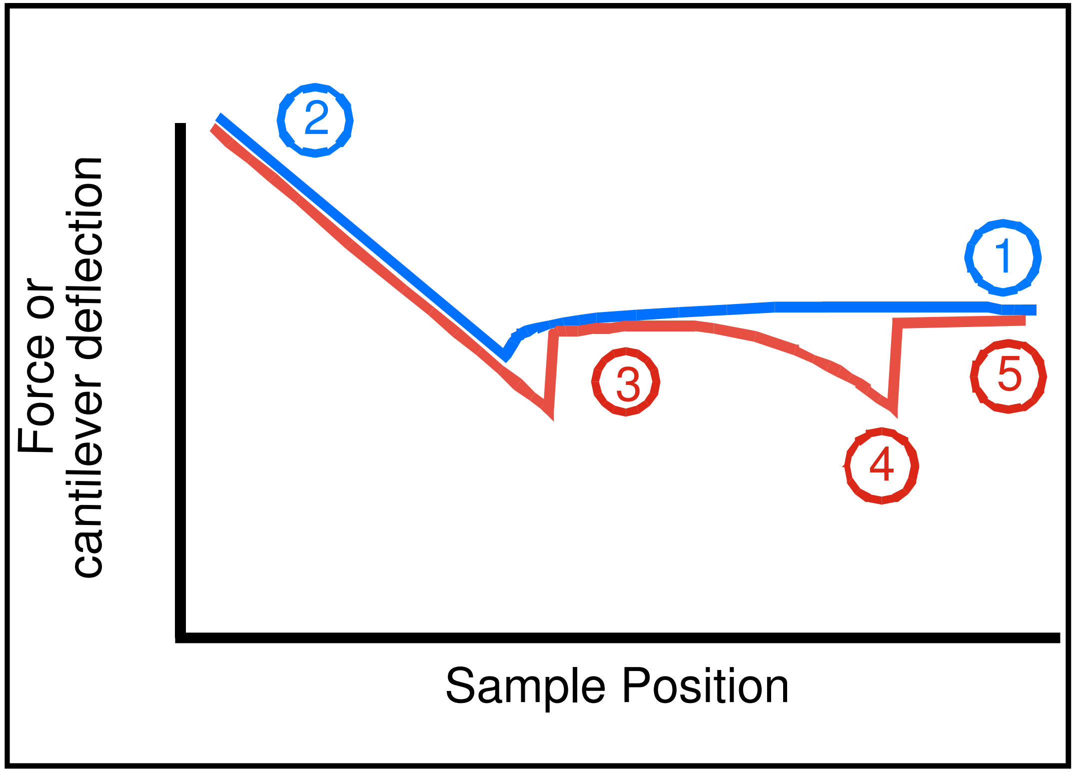
Hard surface with adhesion

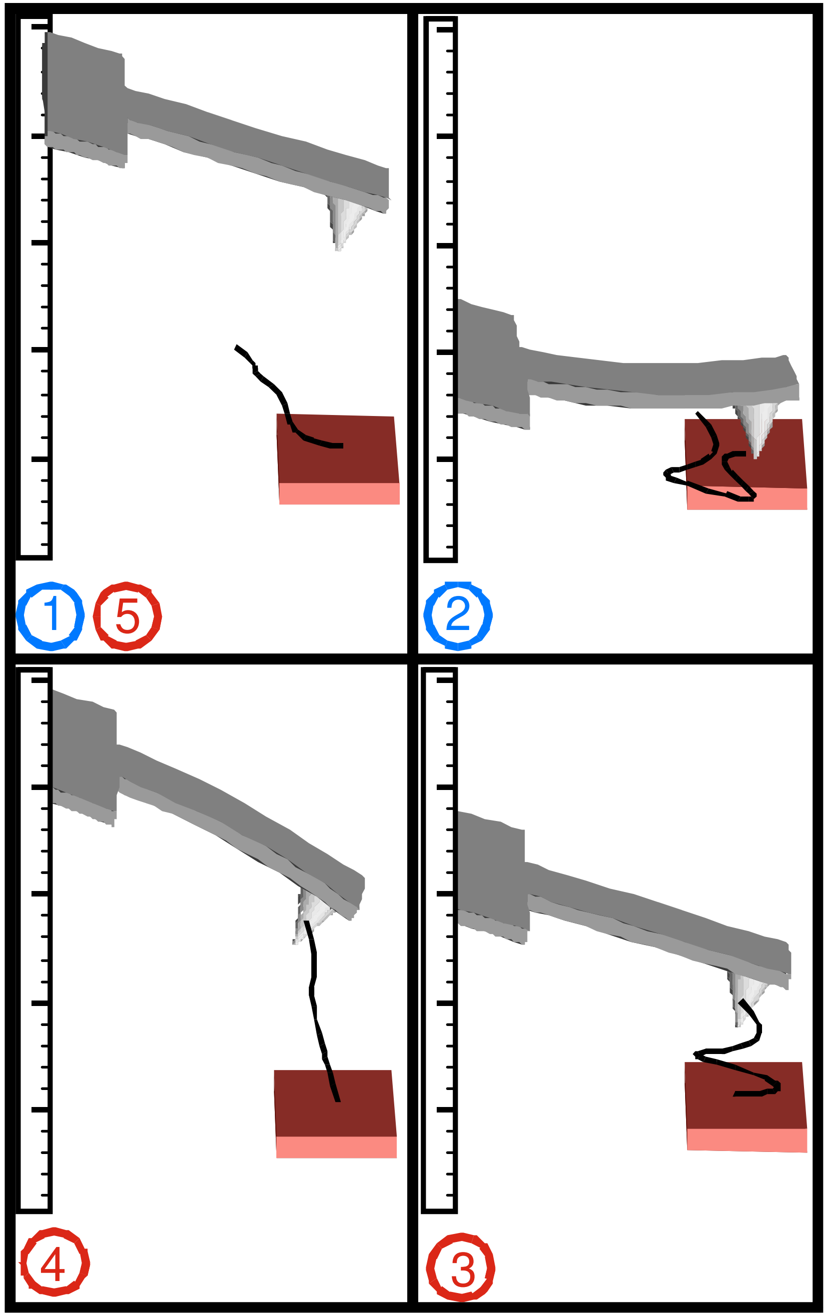


Soft surface with adhesion



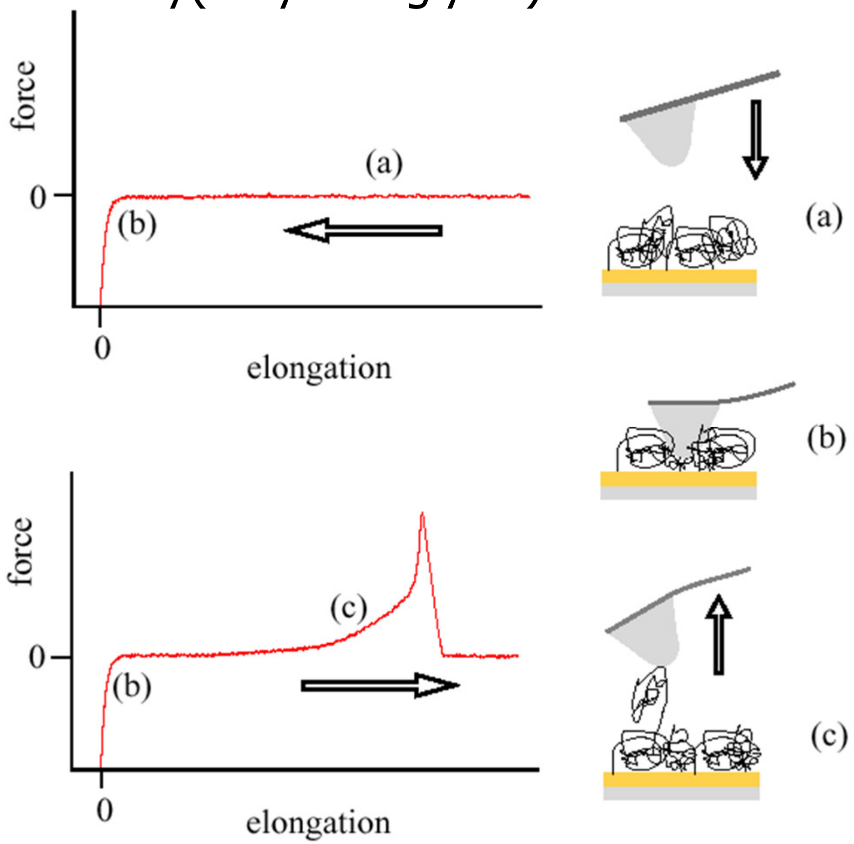
Tethered event



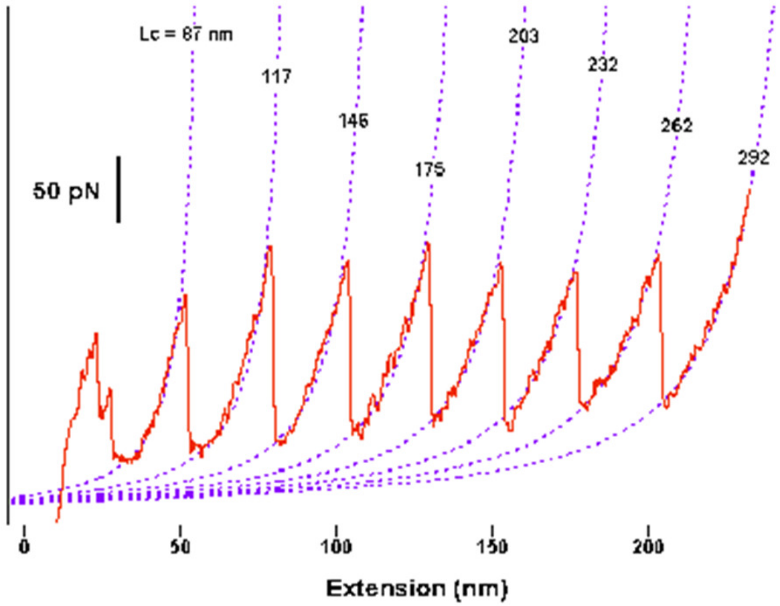


At the molecular scale …

Poly(ethylene-glycol) in water



Titin unfolding

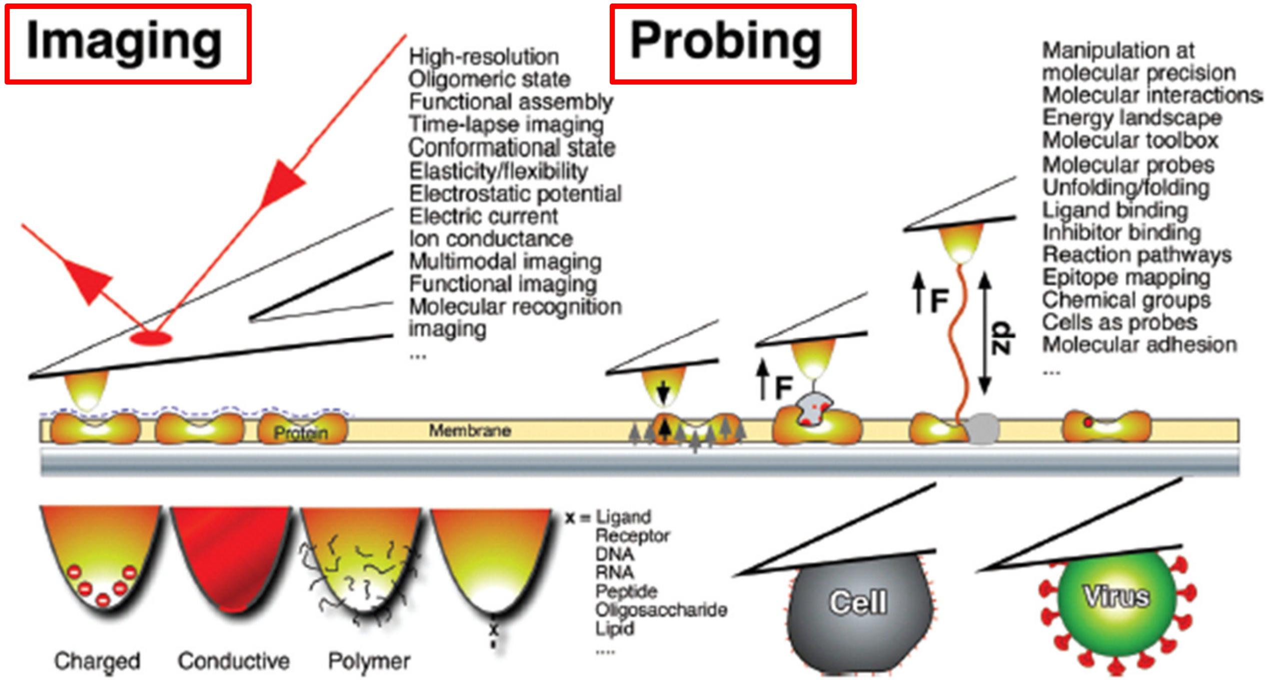


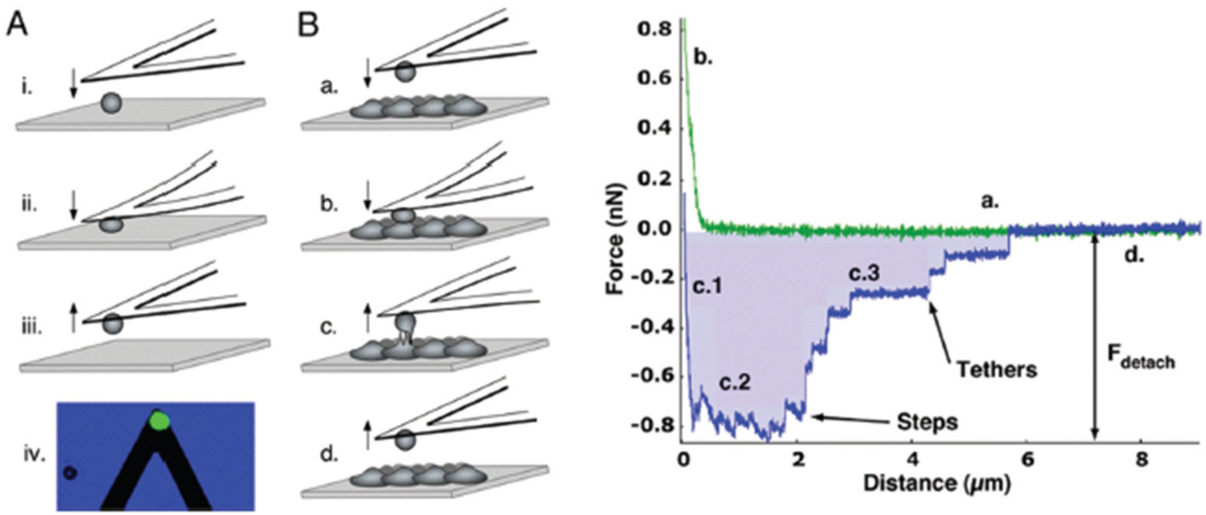
F. Oesterhelt, M. Rief et H.E. Gaub
New Journal of Physic**s** **1** (1999) 6.1–6.11

J. Clarke, S. Fowler et A. Steward
Cambridge University, UK.

In Biology …

D.J. Muller, Biochemistry (2008), **47**, 7986–7998

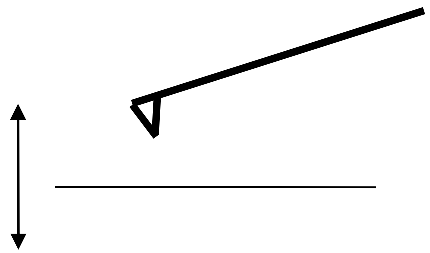




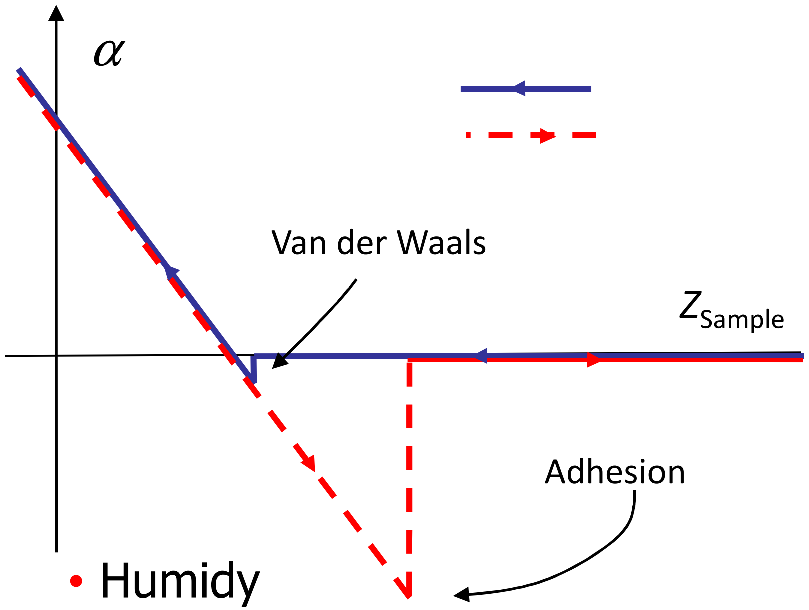
Force - Distance Curves

Saw teeth Z-modulation

measurement of the deflection

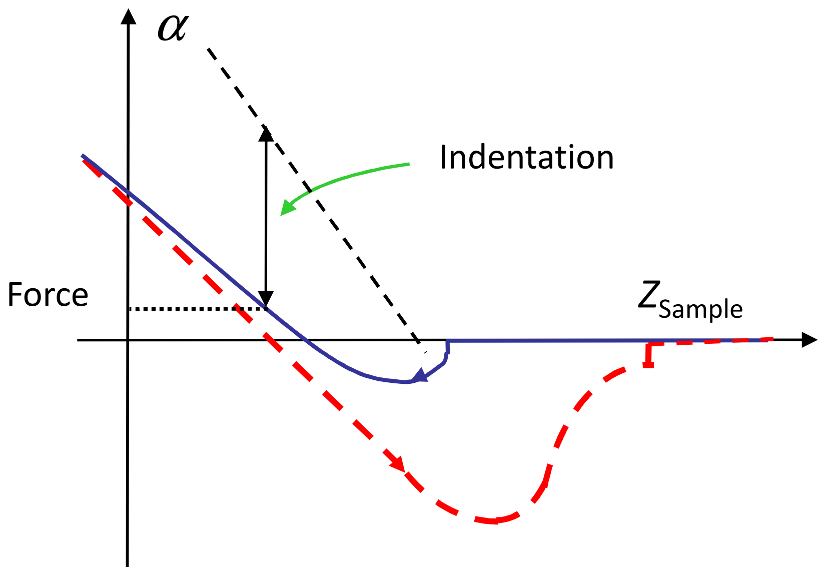


Hard Surface



- Humidy
- pH, ionic force
- Tip chemistry
- …

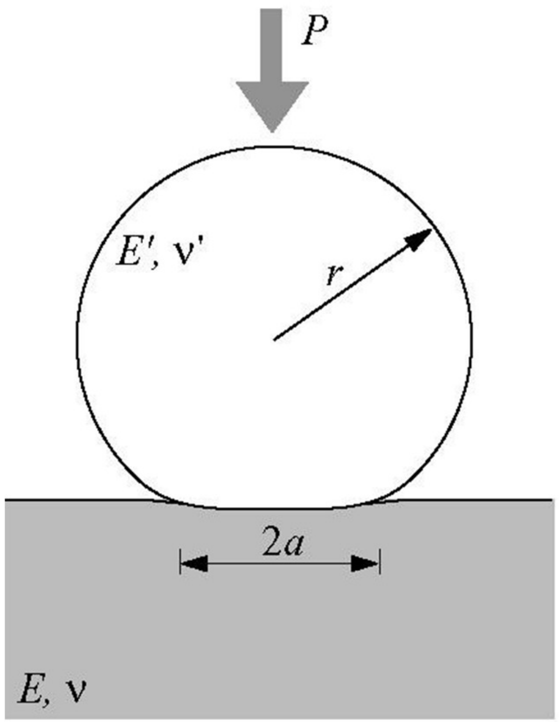
Soft (or compliant) Surface



- Frequency
- Tip shape
- Indentation depth…

Contact Mechanics Forces

Basic Hertz's elastic solution (1881)



- Contact radius

$$a^3 = 4kPr/3E$$

- Displacement

$$Z = (4k/3E)^{2/3} P^{2/3} r^{-1/3}$$

where $k = (9/16)[(1 - \nu^2) + (1 - \nu'^2)E/E']$

- Mean stress

$$p_o = P/\pi a^2$$

- Maximum tensile stress

$$\sigma_m = (1/2)(1 - 2\nu)p_o$$

$$\sigma_R = \sigma_m (a/R)^2$$

- Indentation stress - indentation strain

$$p_0 = (3E/4\pi k)\, a/r$$

Contact Mechanics Forces

To determine the deformation of two elastic objects in contact, we have to establish and resolve the relationship netween the stress Γ and strain ε 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

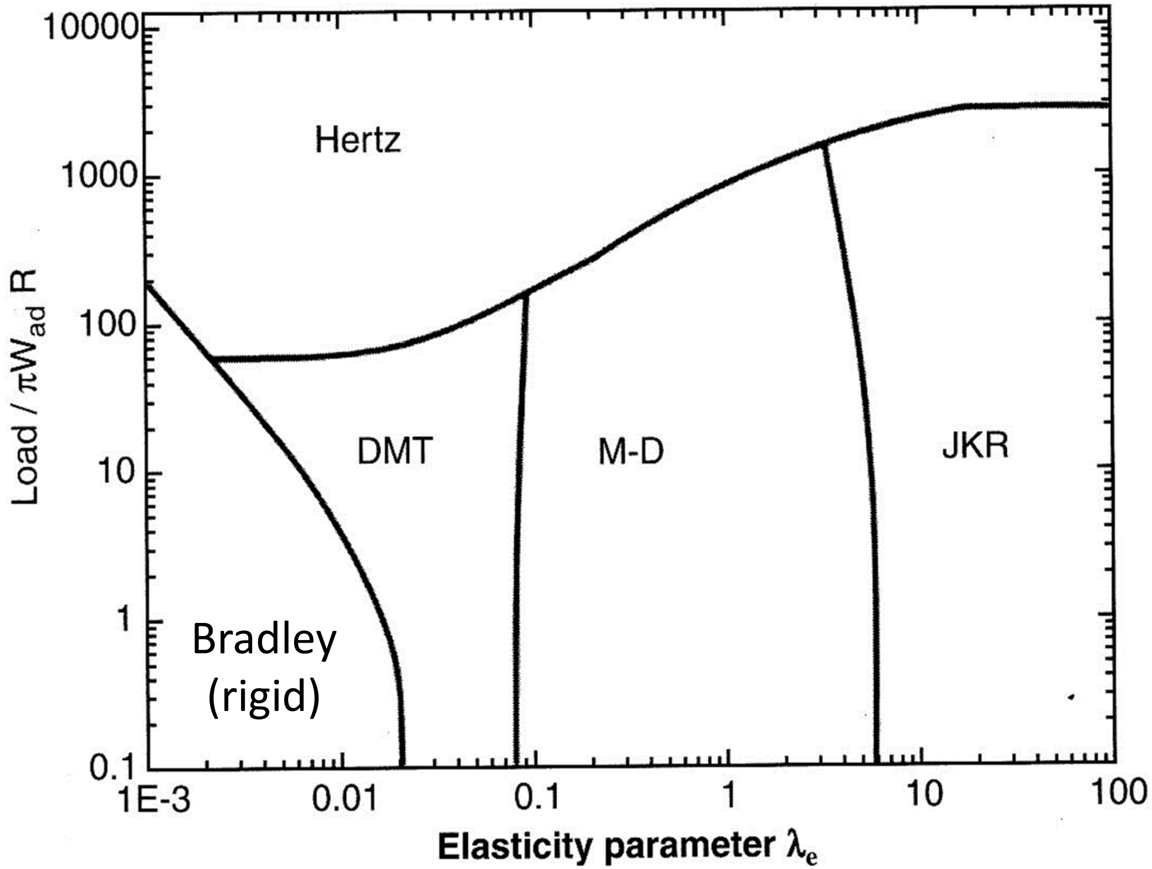
$$\frac{1}{E_{eff}} = \left(\frac{1-\nu_t^{\,2}}{E_t} + \frac{1-\nu_s^{\,2}}{E_s} \right)$$

Contact Mechanics Forces

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

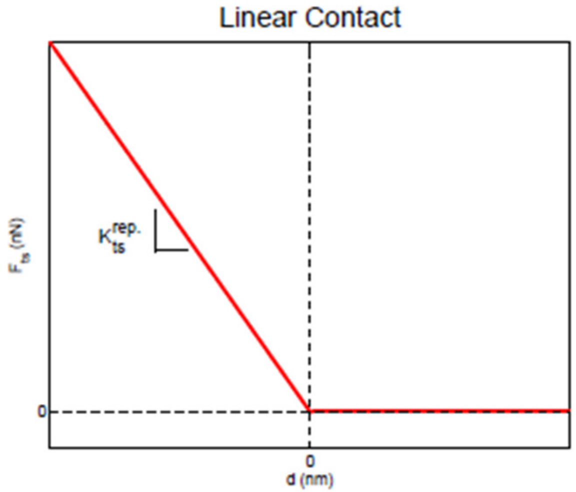
M-D = Maugis - Dugdale

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



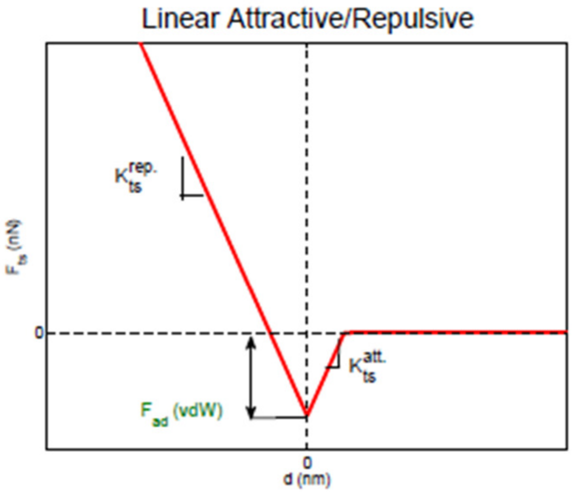
Johnson, Greewood, *J. Colloid Interface Sci.,* 1997, **192**, 326.

Models for tip-sample interactions



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

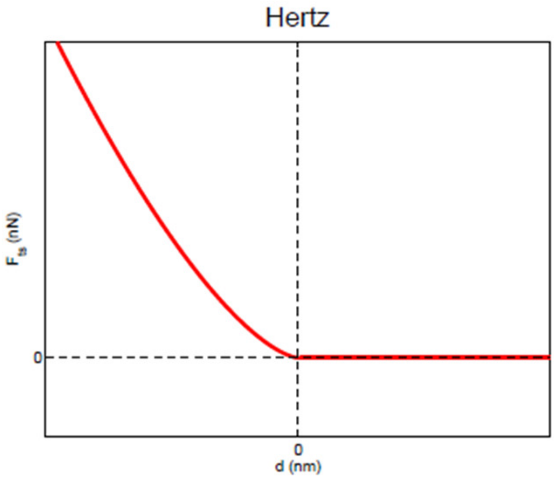
Tip-sample force versus gap for the piecewise linear contact model.



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

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

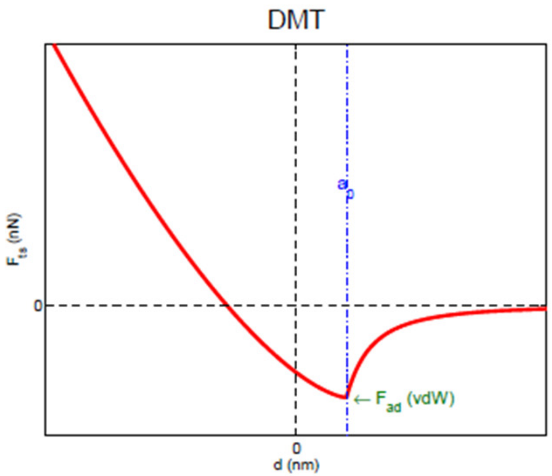
Models for tip-sample interactions



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

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

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



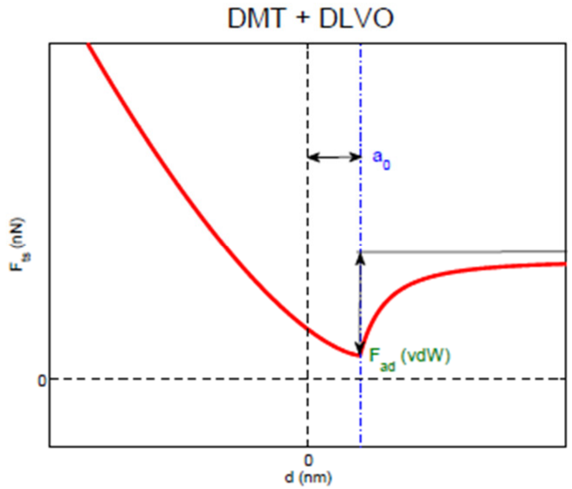
Tip-sample force versus gap for the DMT contact model.

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

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

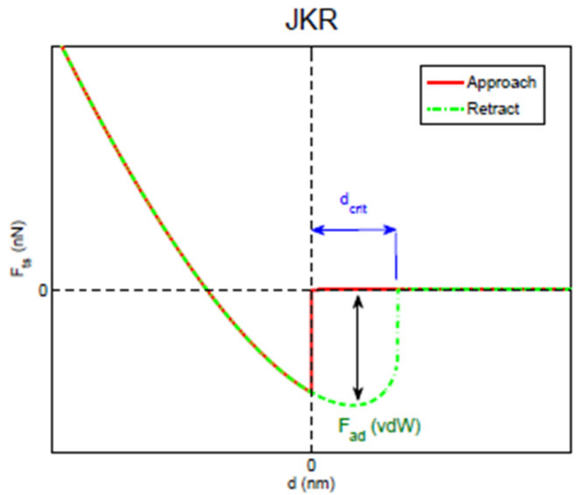
H = Hamaker constante

Models for tip-sample interactions



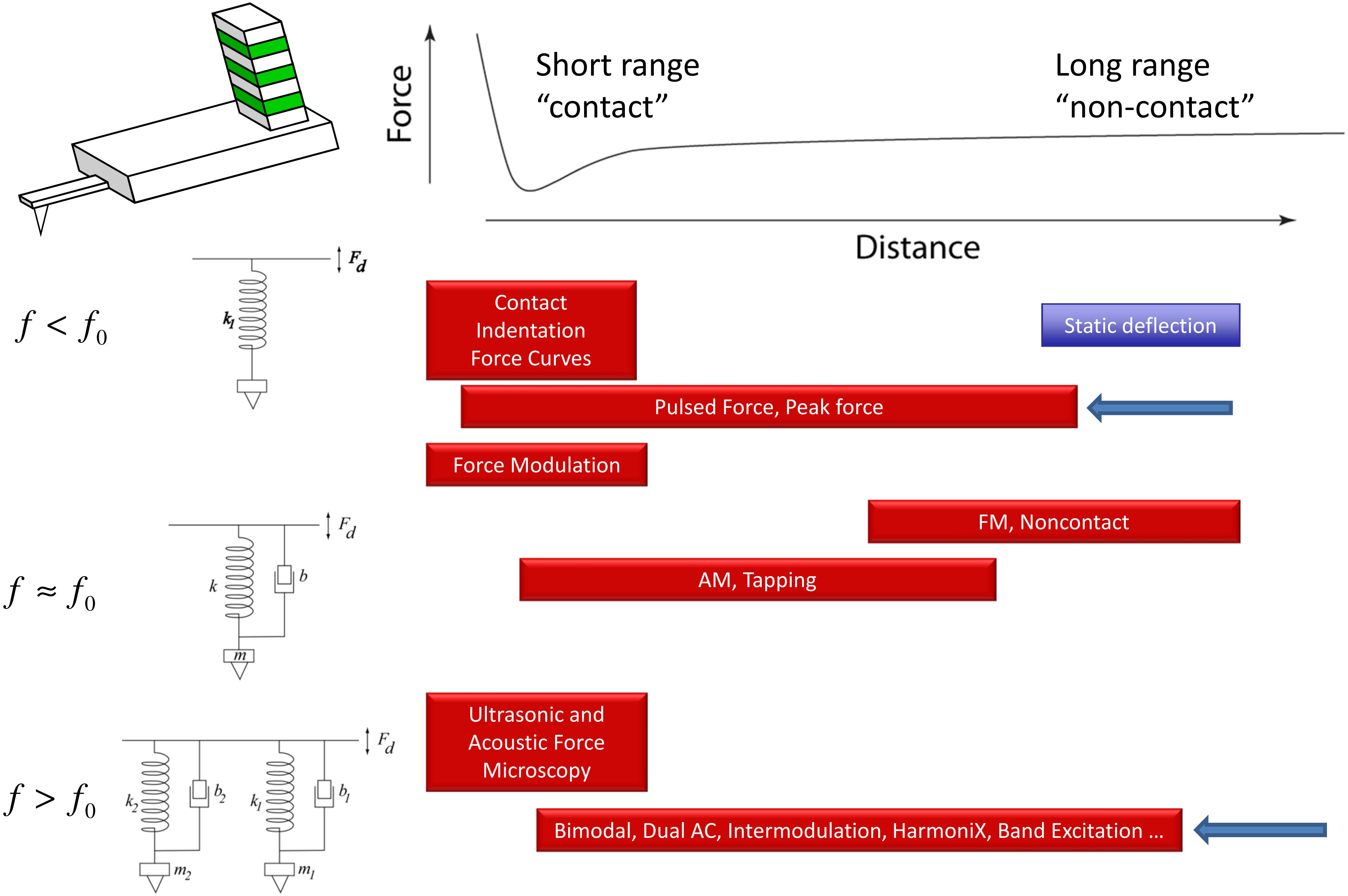
$$F_{DLVO+DMT}(d) = \begin{cases} \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D d} - \frac{HR}{6d^2}, & d > a_0 \\ \frac{4\pi R}{\epsilon\epsilon_0 K_D}\sigma_T\sigma_S e^{-K_D a_0} - \frac{HR}{6a_0^2} + \frac{4}{3}E^*\sqrt{R}(a_0 - d)^{3/2}, & d \leqslant a_0 \end{cases}$$

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



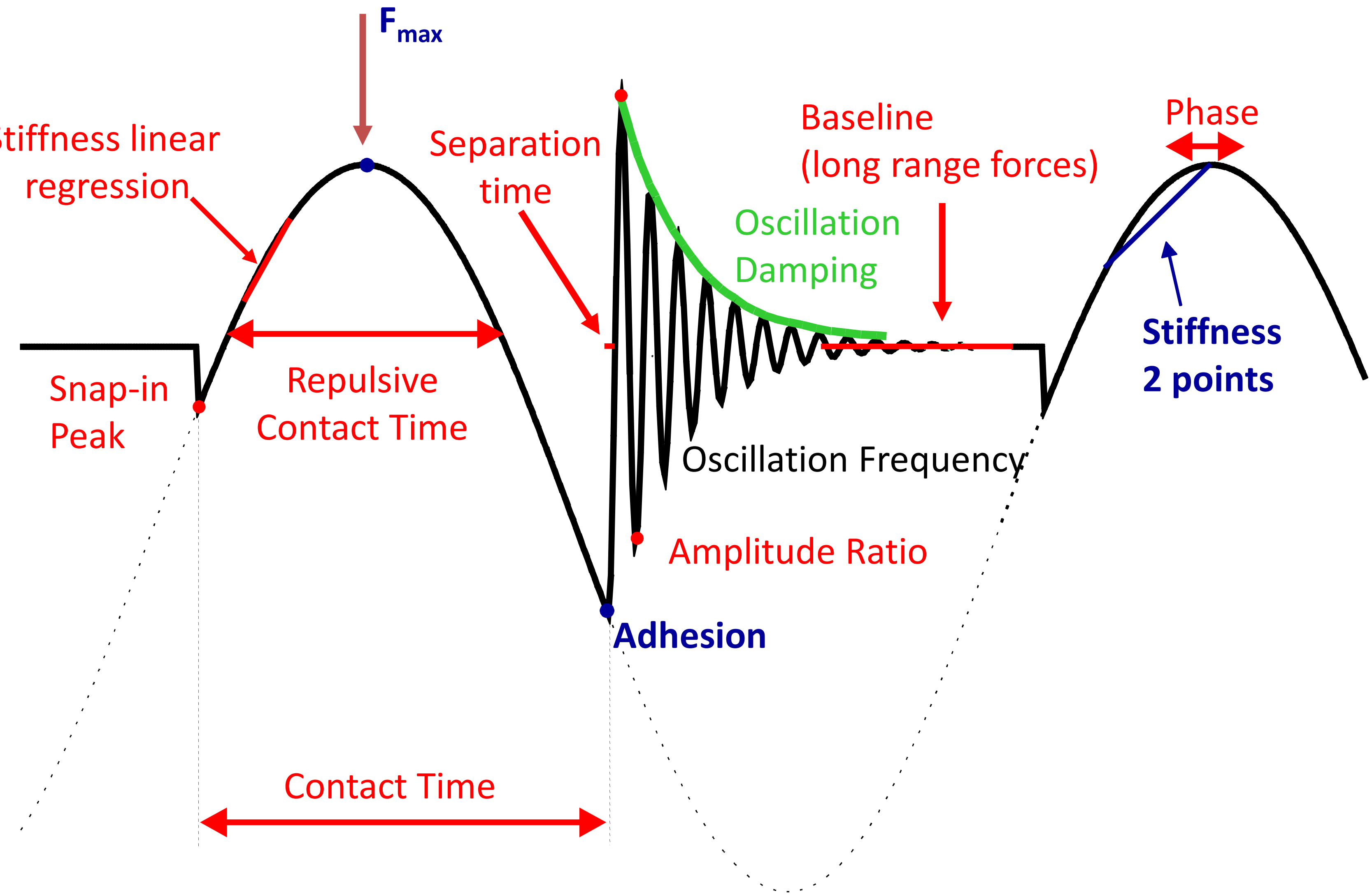
JKR is nonconservative and includes a dependency to the history of the tip-sample contact

AFM Measurements



Pulsed Force Microscopy

Information contained in a PFM Curve

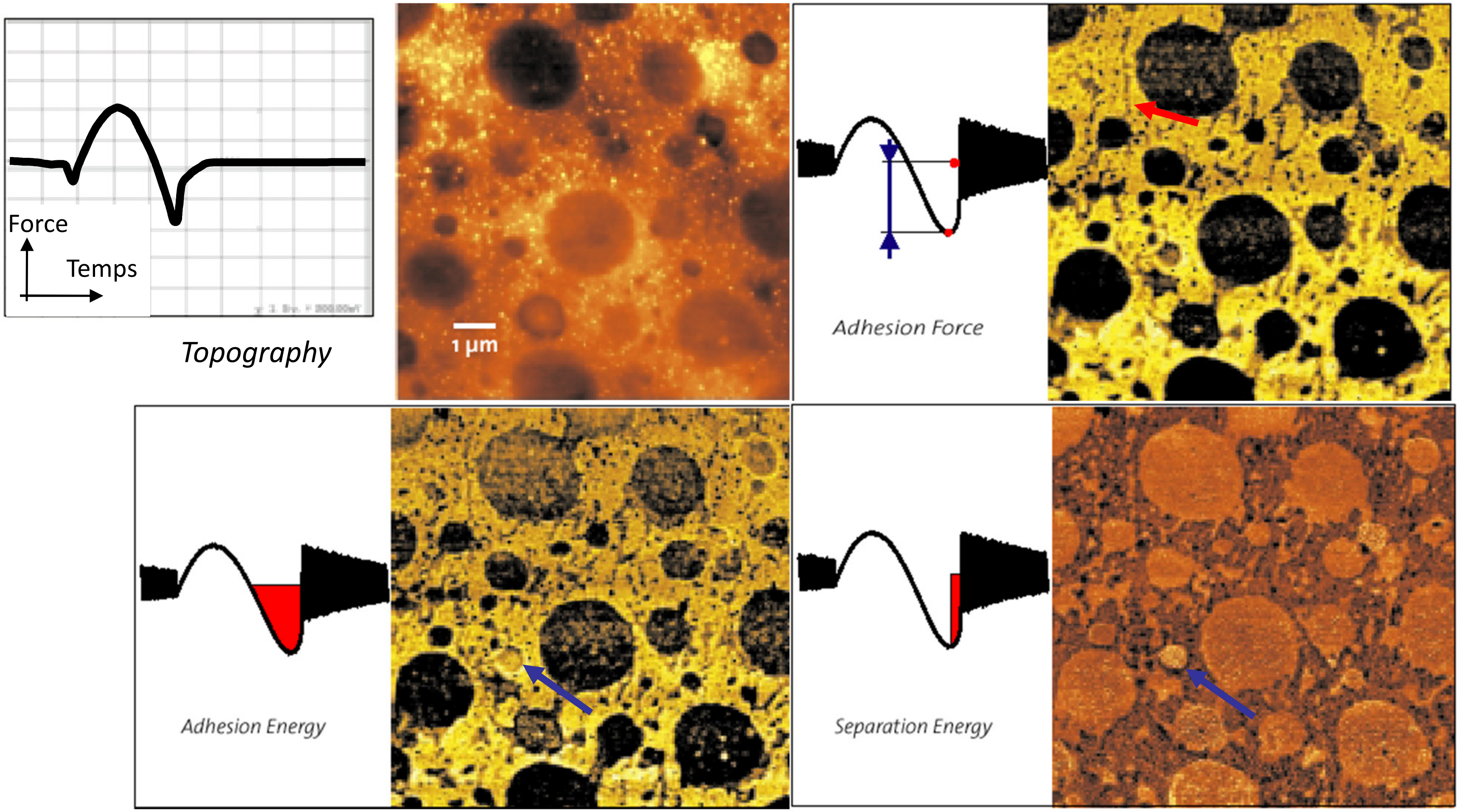


The Digital Pulsed Force Mode - DPFM

Features:

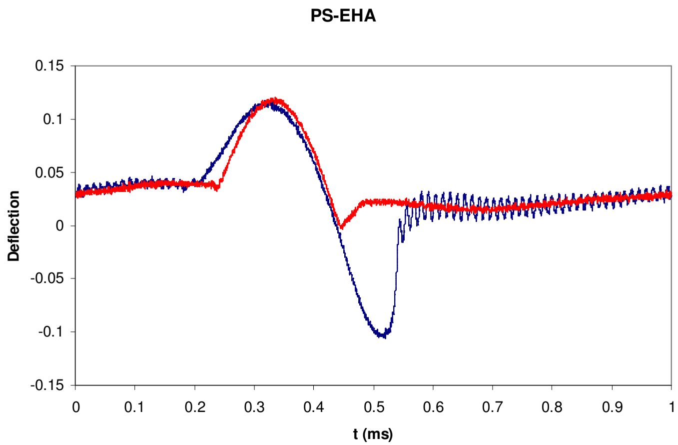
- free programmable digital function generator for cantilever excitation
- high resolution, high speed data acquisition module (5 MHz, 16 bit)
- computer controlled electronics with online data evaluation capabilities
- PC can store the complete data stream for offline data evaluation

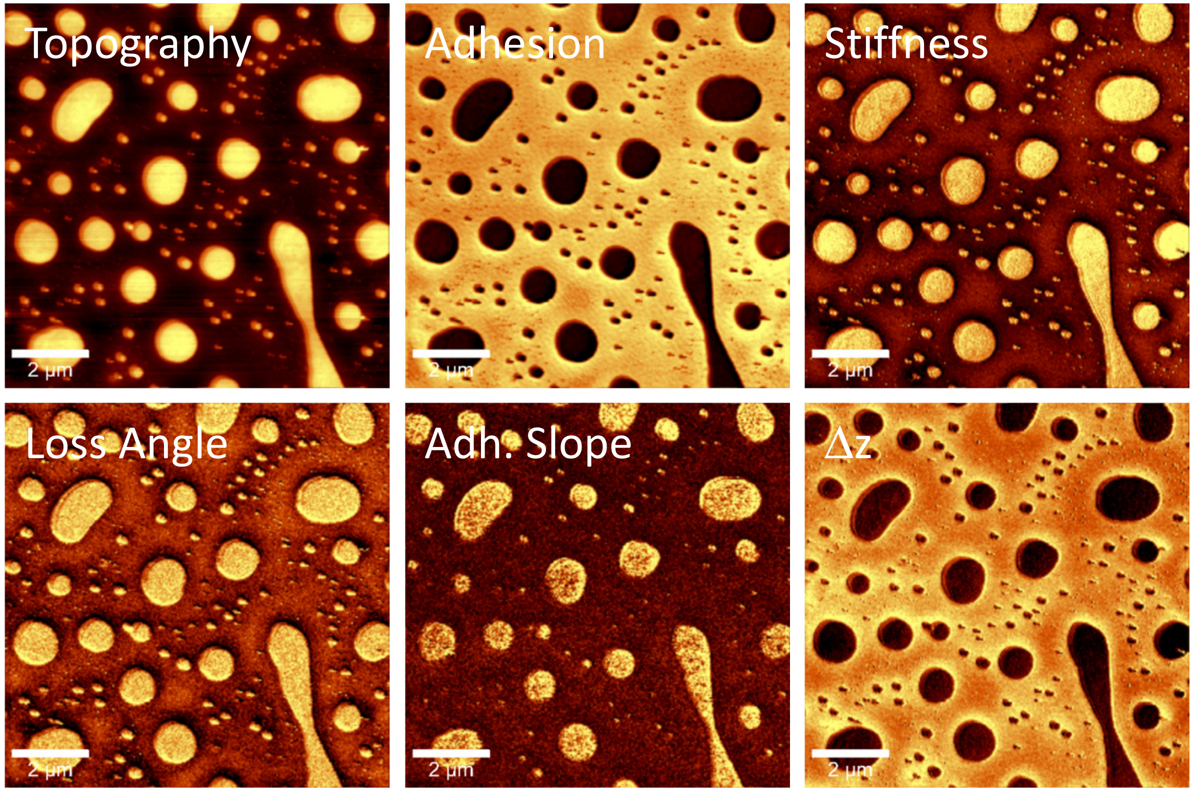
Point-by-point force curve analysis : pulsed force mode

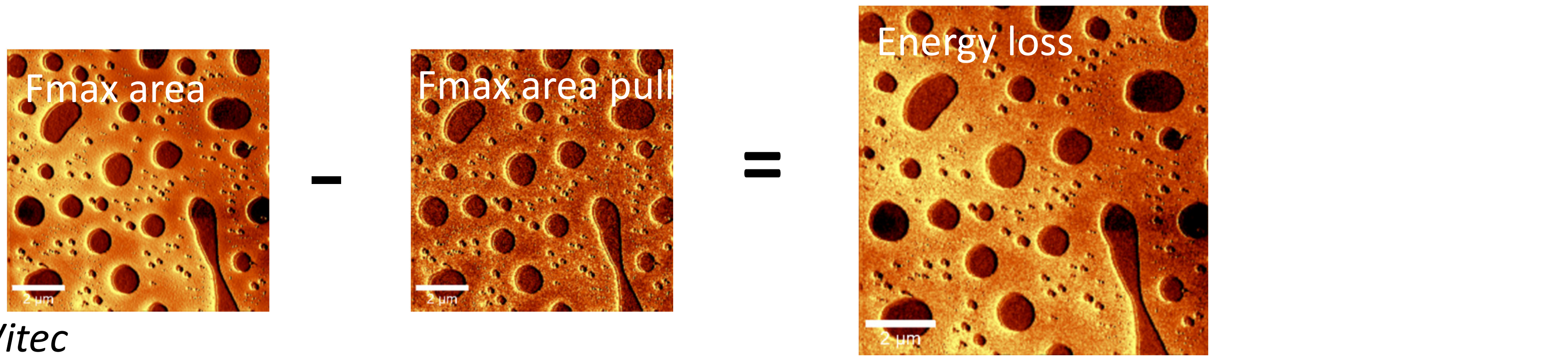


Doc. Witec

Mechanical Properties: PS-EHA



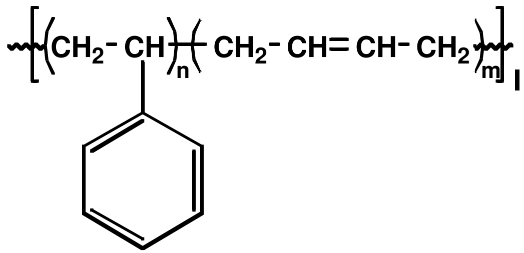




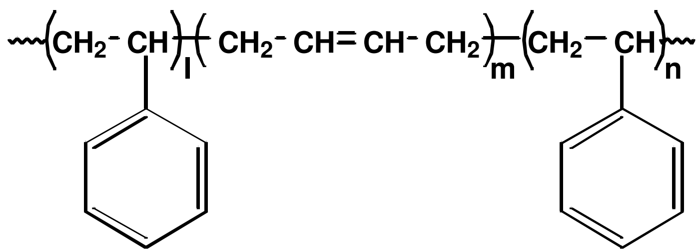
Doc. Witec

Phase Separation in Styrene Butadiene (SB) copolymers

Thin film: SBR
- statistic copolymer
- rubber
- 30% Styrene
- 70% Butadiene



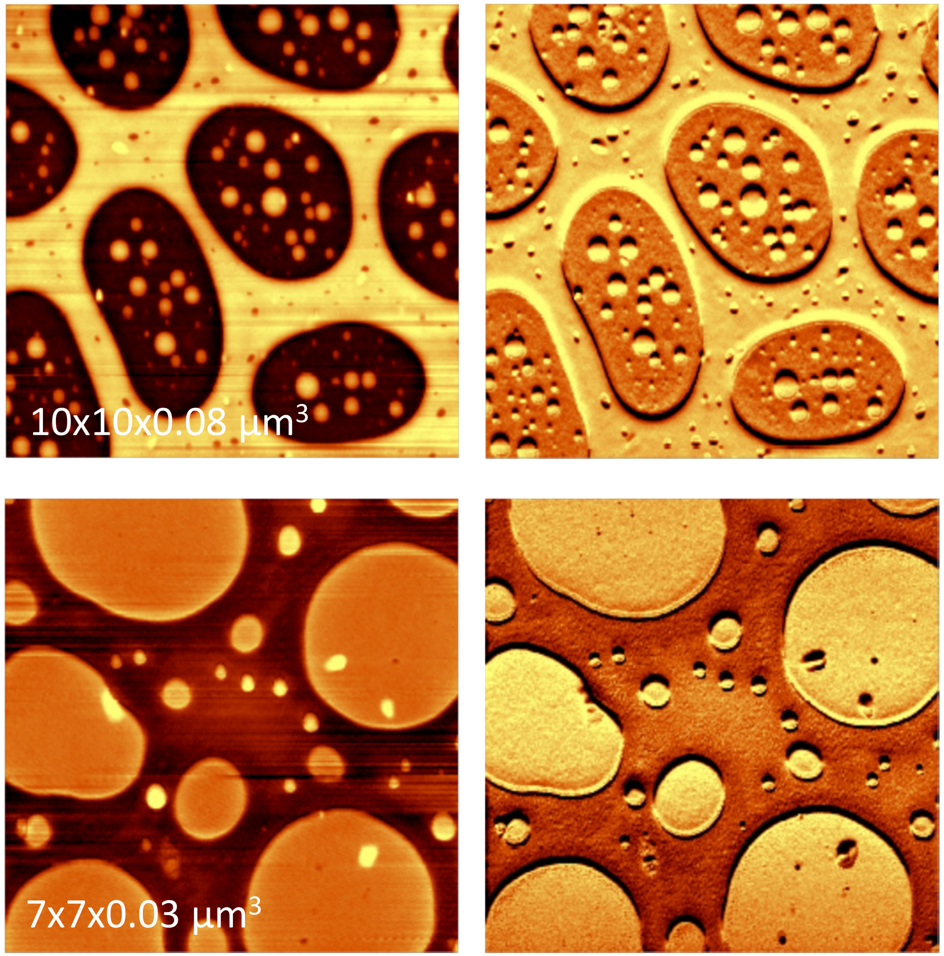
Thin Film: SBS
- block- copolymer
- thermoplastic rubber
- 30% Styrene
- 70% Butadiene

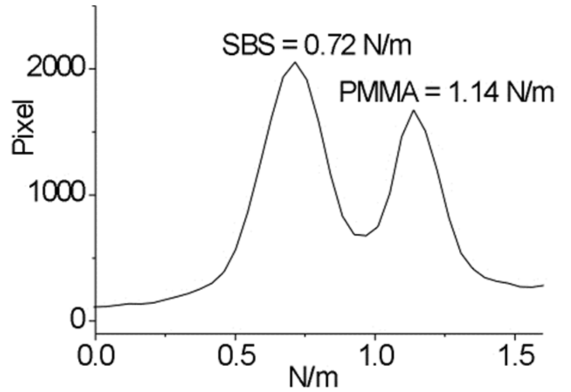


Doc. Witec

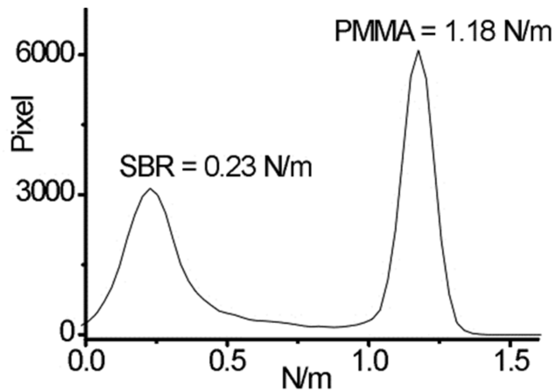
Phase Separation in Styrene Butadiene (SB) copolymers

Topography | Stiffness Map





$$\frac{\text{SBS}}{\text{PMMA}} = 0.63$$

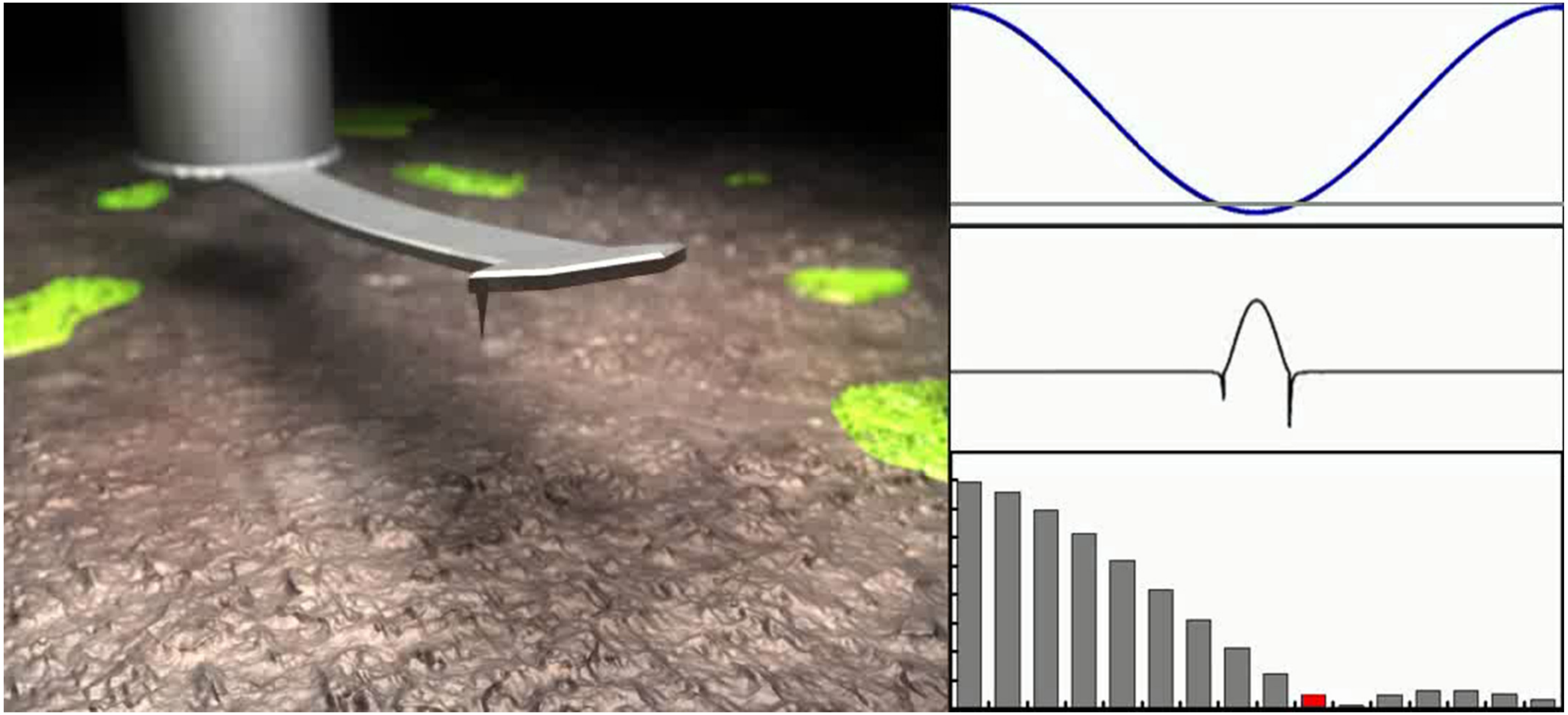


$$\frac{\text{SBR}}{\text{PMMA}} = 0.19$$

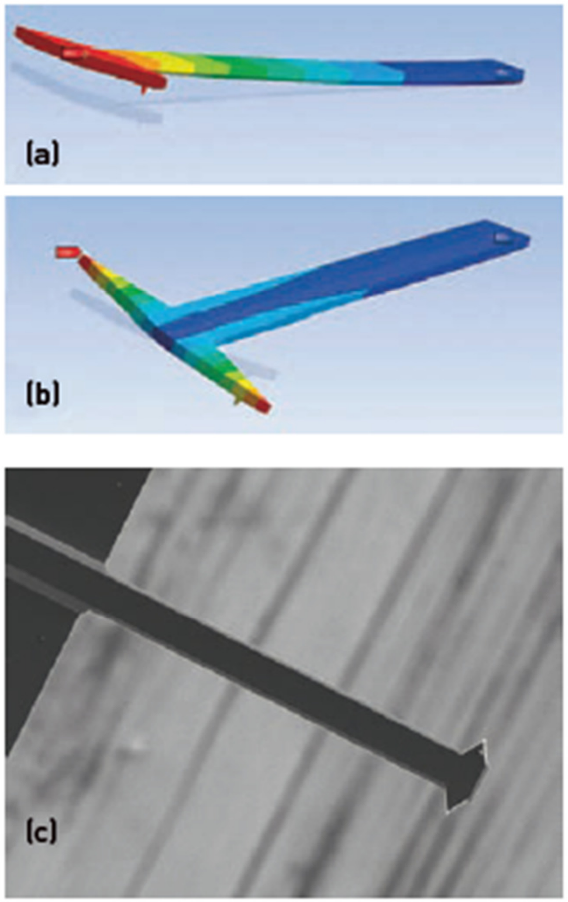
Doc. Witec

HarmoniX

Force Curves during TappingMode



HarmoniX …
Force Curves during Tapping Mode



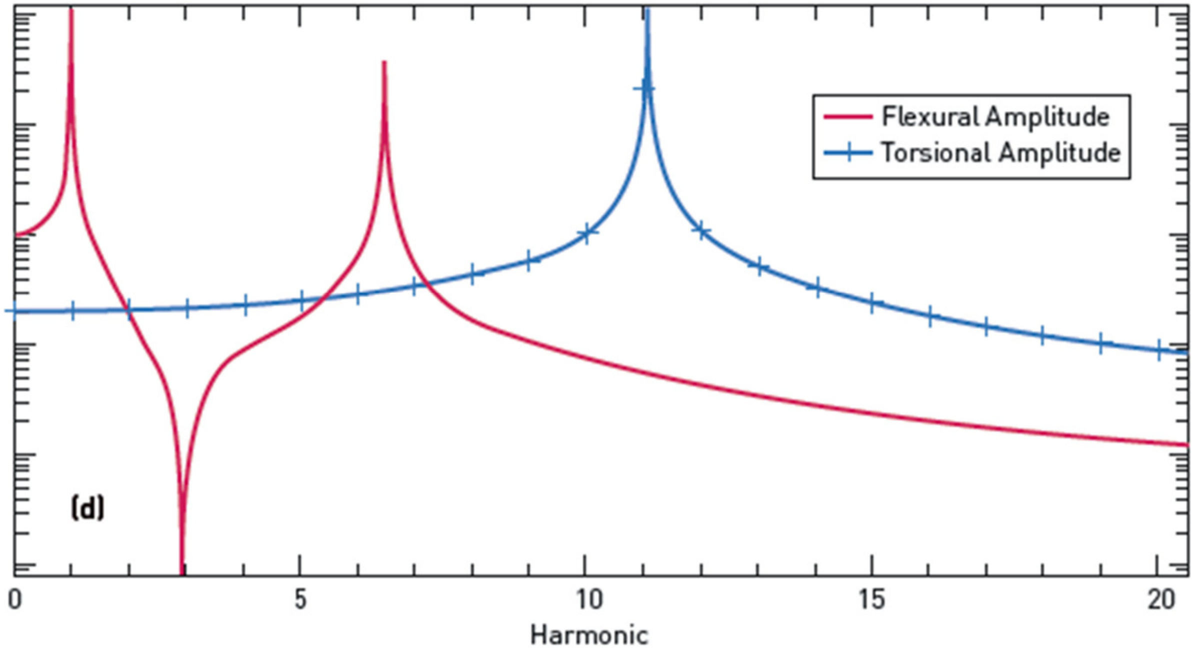
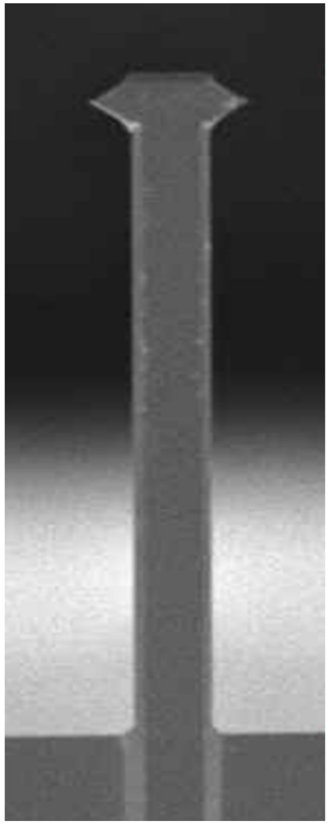


Figure 1: Torsionally coupled cantilevers: (a) flexural deflection, (b) torsional deflection, (c) Veeco Probes HarmoniX cantilever, (d) theoretical spectra of prototype flexural (red -) and torsional frequency (blue +) response.

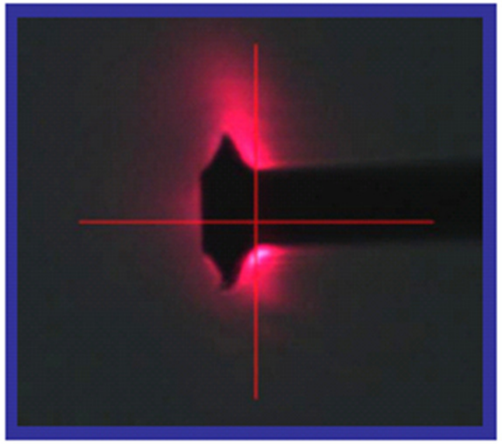
HarmoniX



- AFM mappings of:
  Elasticity/Young Modulus
  Adhesion
  And more…

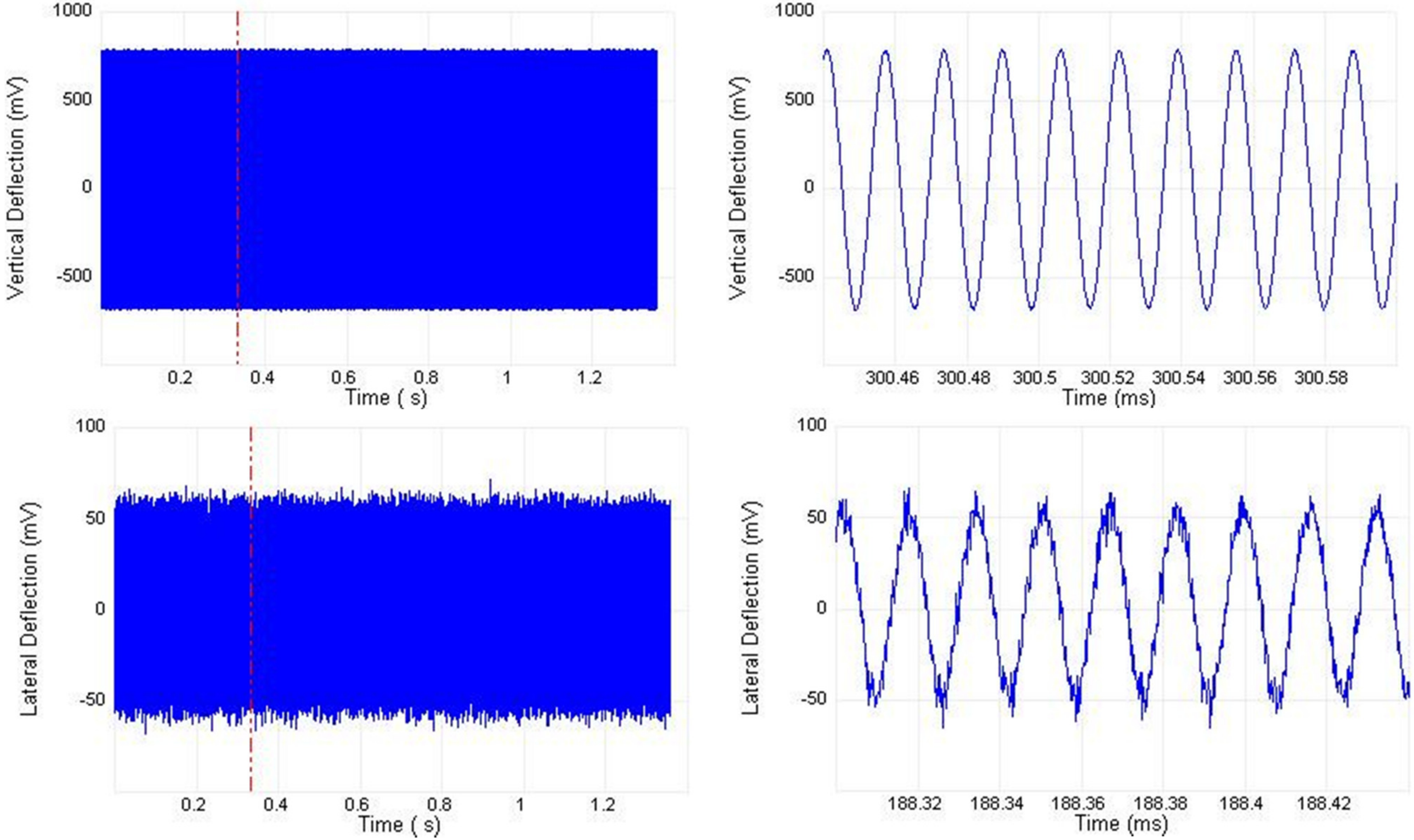
- HarmoniX is simultaneously:

  1. Quantitative
  2. Real-time
  3. High-Resolution
  4. Non-destructive

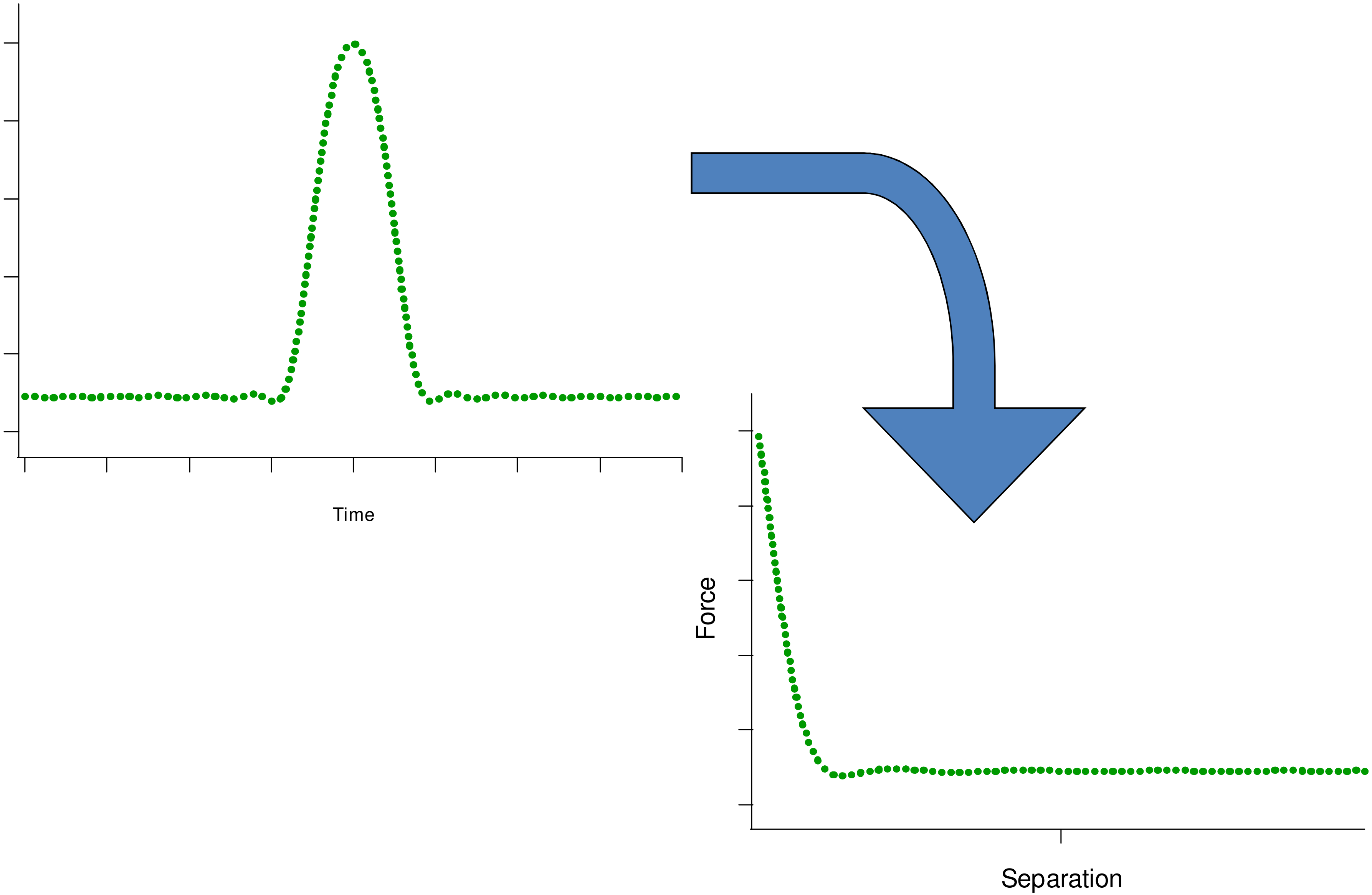


O. Sahin, C.F. Quate, O. Solgaard, and A. Atalar, *Nat. Nanotech.2007, 2, 507.*
M. Dong, S. Husale, O. Sahin, *Nat. Nanotech. 2009, 4, 514.*

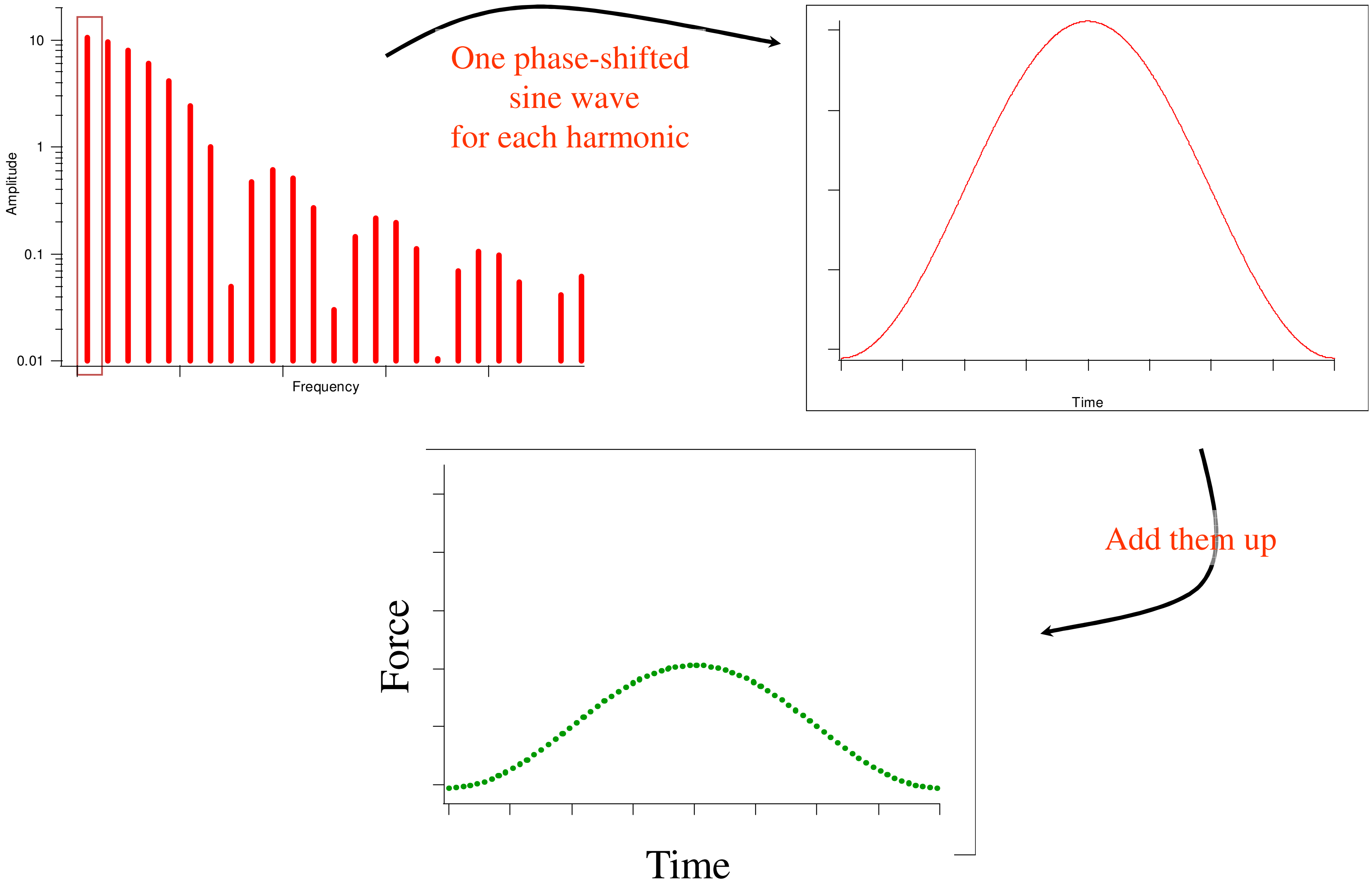
HSDC...


1000
500
0
-500
Vertical Deflection (mV)
0.2
0.4
0.6
0.8
1
1.2
Time (s)
1000
500
0
-500
Vertical Deflection (mV)
300.46
300.48
300.5
300.52
300.54
300.56
300.58
Time (ms)
100
50
0
-50
Lateral Deflection (mV)
0.2
0.4
0.6
0.8
1
1.2
Time (s)
100
50
0
-50
Lateral Deflection (mV)
188.32
188.34
188.36
188.38
188.4
188.42
Time (ms)

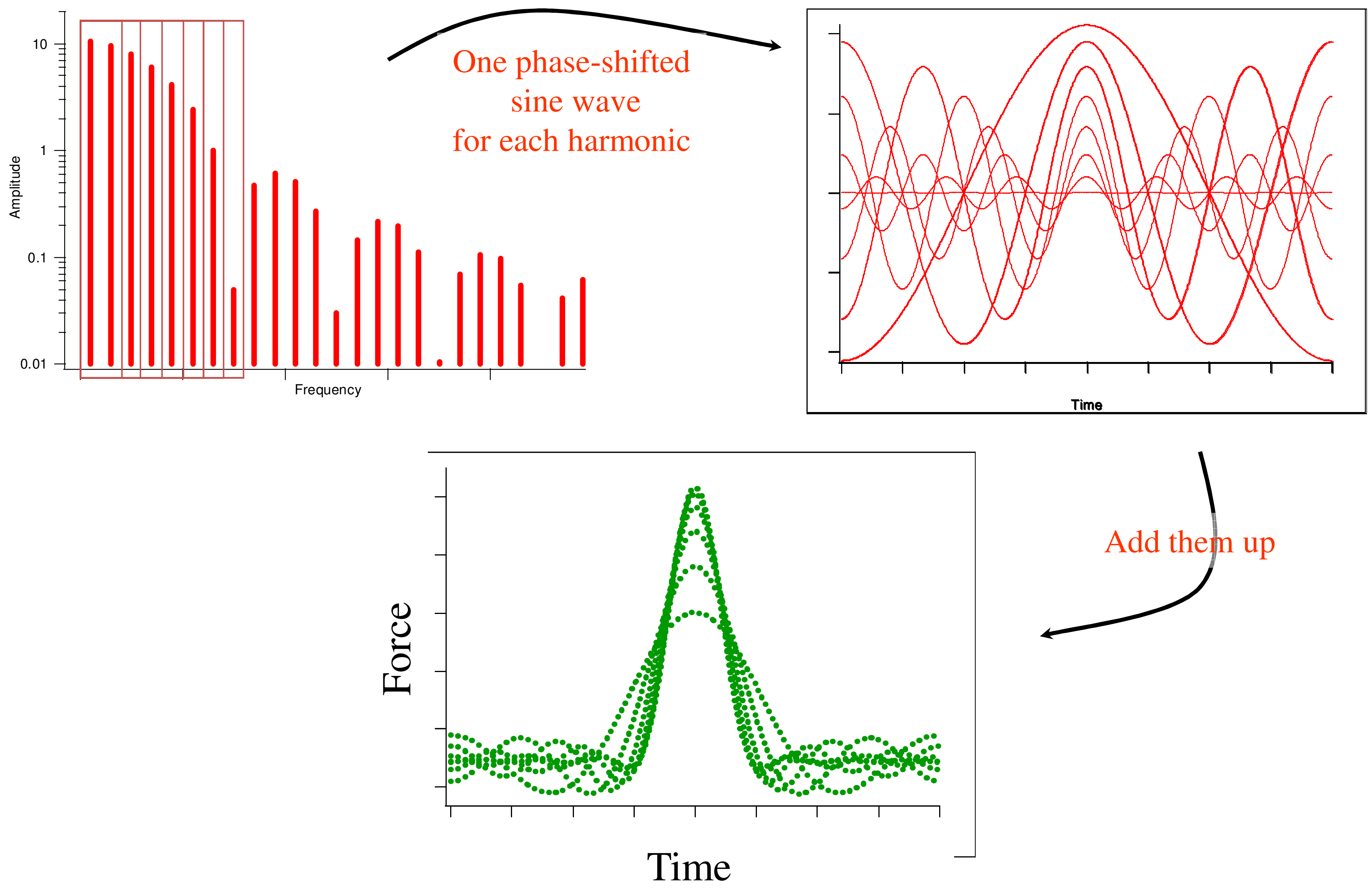
Force vs Time to Force Curve



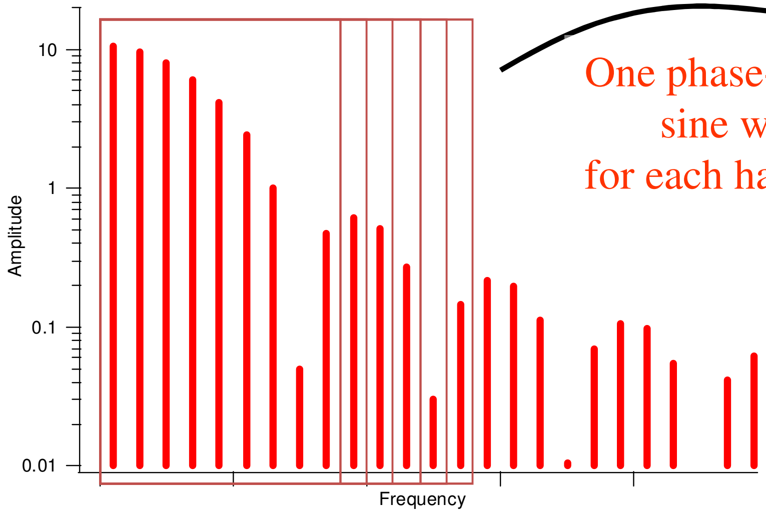
Reconstruct any Periodic Waveform from Fourier Series



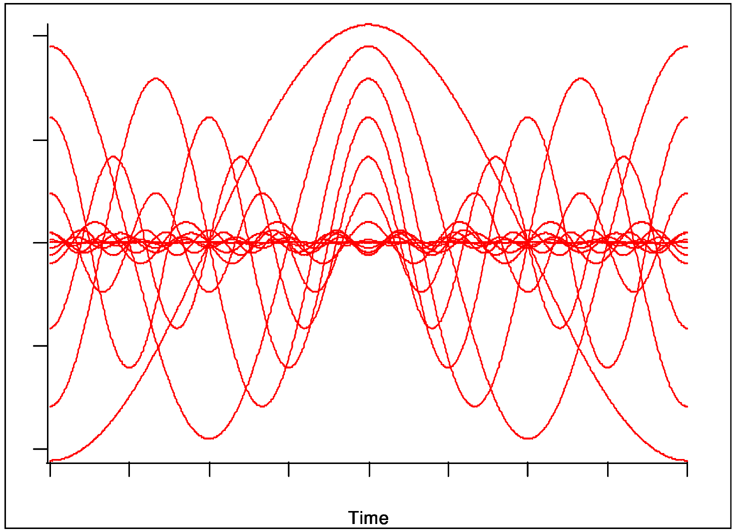
Reconstruct any Periodic Waveform from Fourier Series



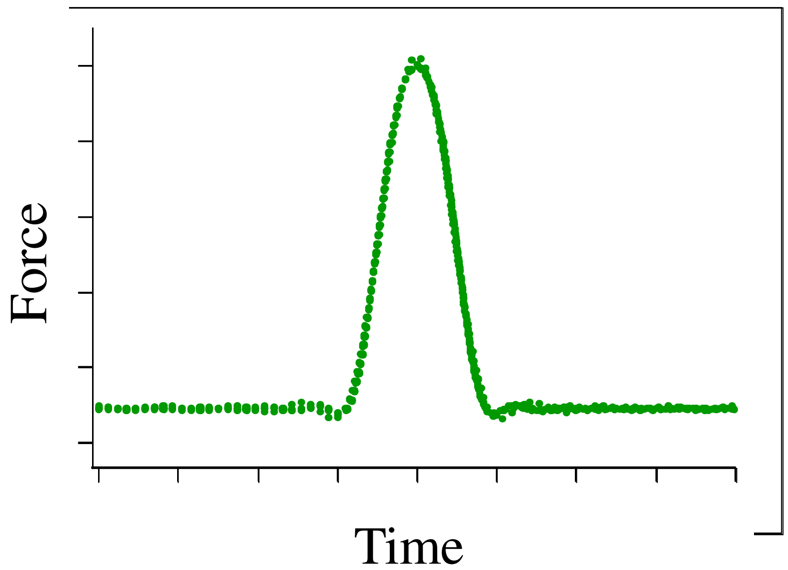
Reconstruct any Periodic Waveform from Fourier Series



One phase-shifted
sine wave
for each harmonic



Add them up



HarmoniX …
Force Curves during TappingMode

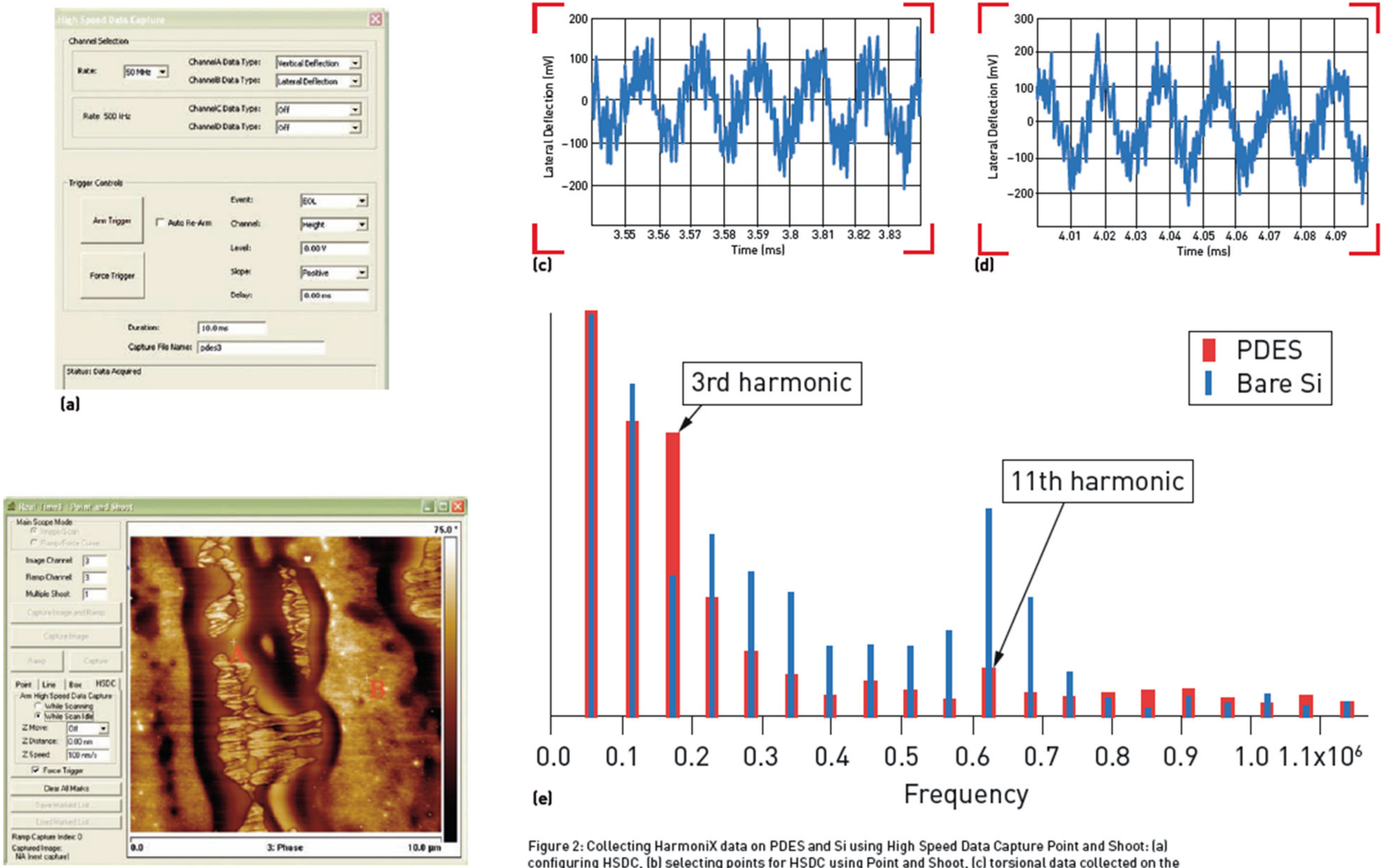
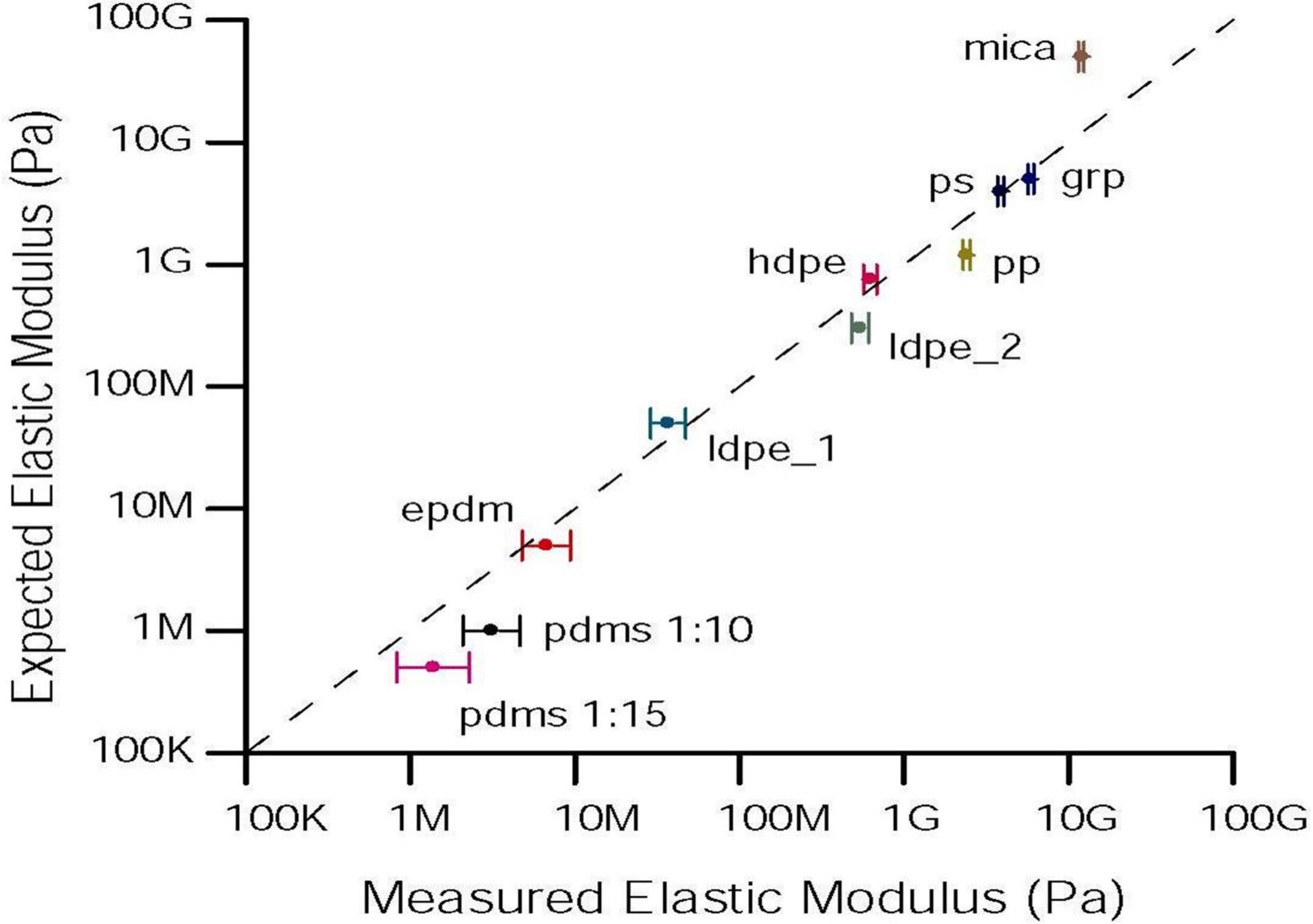


Figure 2: Collecting HarmoniX data on PDES and Si using High Speed Data Capture Point and Shoot: (a) configuring HSDC, (b) selecting points for HSDC using Point and Shoot, (c) torsional data collected on the PDES (point A), (d) torsional data collected on the Si substrate (point B), and (e) spectral analysis of the data from point A (wide red lines) and point B (narrow blue lines).

Quantitative: Comparing Modulus Results



Data courtesy O. Sahin, Rowland Institute at Harvard

Pressure-Sensitive Adhesives (PSAs)

Permanently tacky substance at room temperature that adheres spontaneously and under finger or hand pressure, and shows a good holding force on the adherend.

Removable

Semi-Permanent

Standard tapes

Labels

Permanent

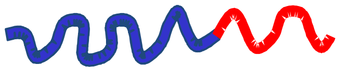
Permanent labels for cars

All renforcing tapes

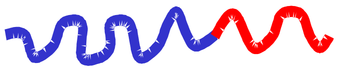
(Ex: shoes)

The Copolymer Base

Study of new block copolymer thermoplastic elastomers as bases for PSA

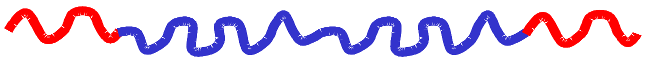
 = Two polymer segments A & B = Diblock copolymer

To compare the microscopic morphology and mechanical properties of « all-acrylate » block copolymers with different architectures.



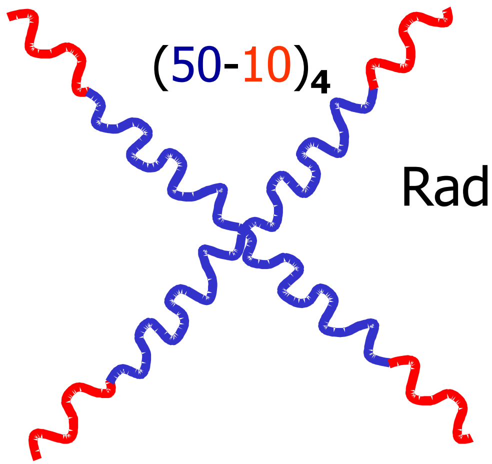
$(50\text{-}10)_1$

Diblock



$(50\text{-}10)_2$

Triblock

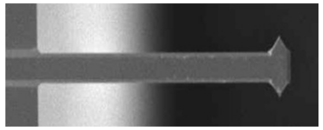


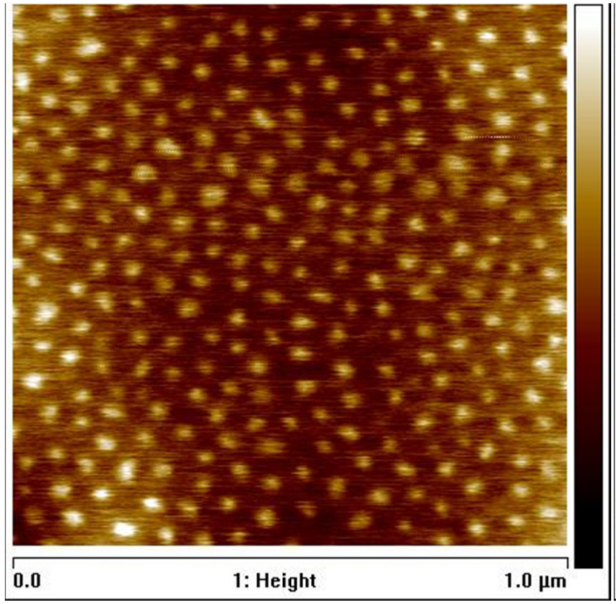
$(50\text{-}10)_4$

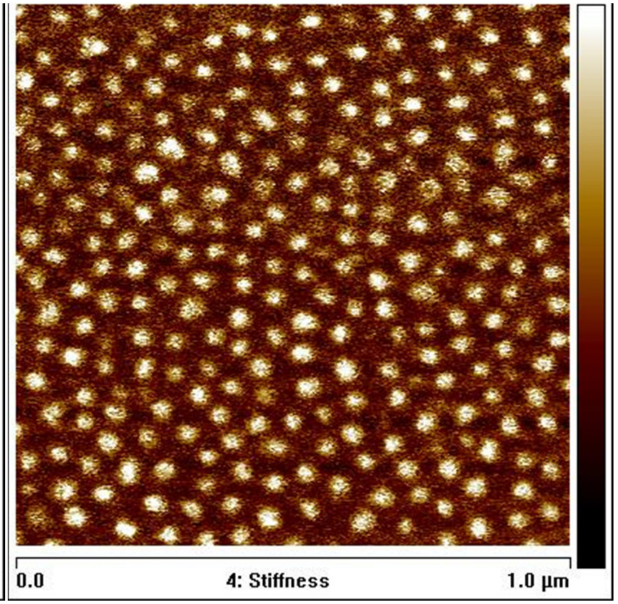
Radial

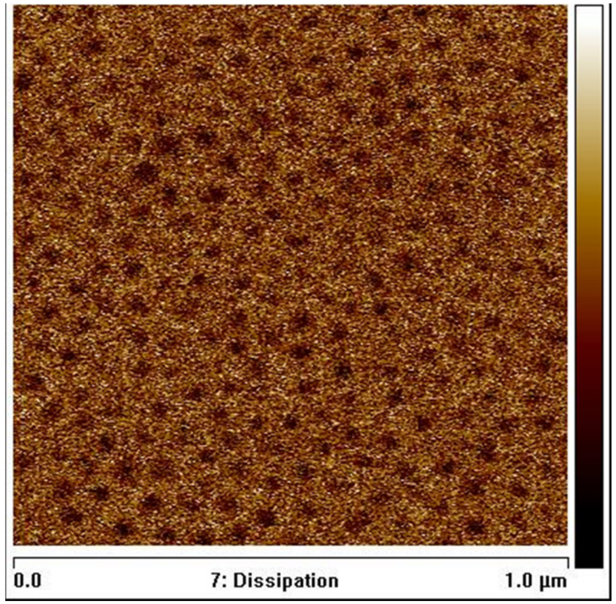
A : PMMA & B : poly(2-ethylhexyl-acrylate - co – methyl acrylate)

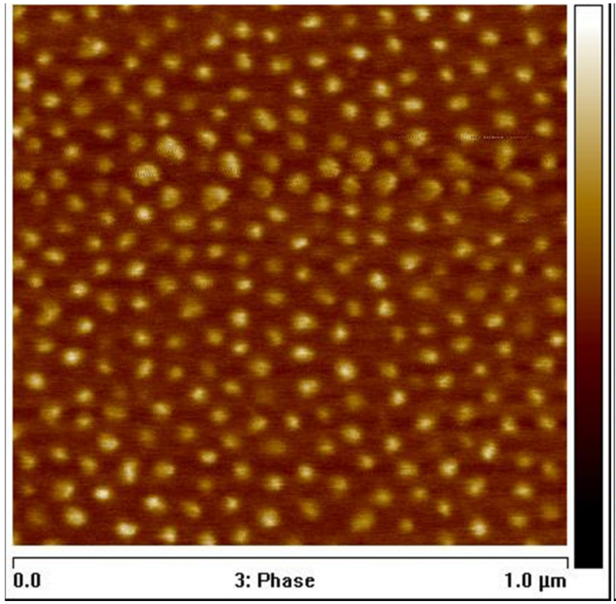
Blends with Tackifying Resins

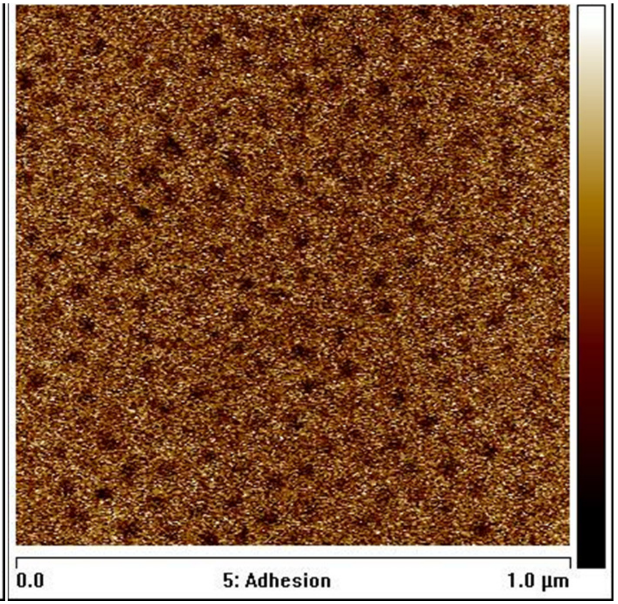












Average adhesion
135 nN

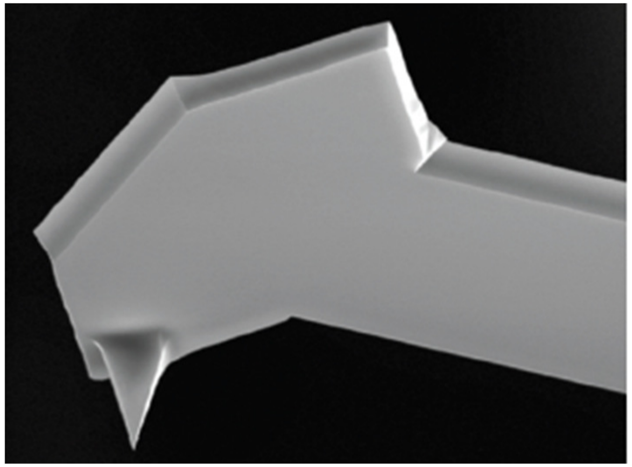
RADIAL $(50\text{-}10)_4$

HarmoniX is much faster than Force Volume

- A Force Volume image run at typical z-motion rates of 1Hz and 512 x 512 pixel resolution would take 3 days to collect
- That same acquisition with HarmoniX would take 17 minutes
- Not a few spots every micron as with a nanoindenter !

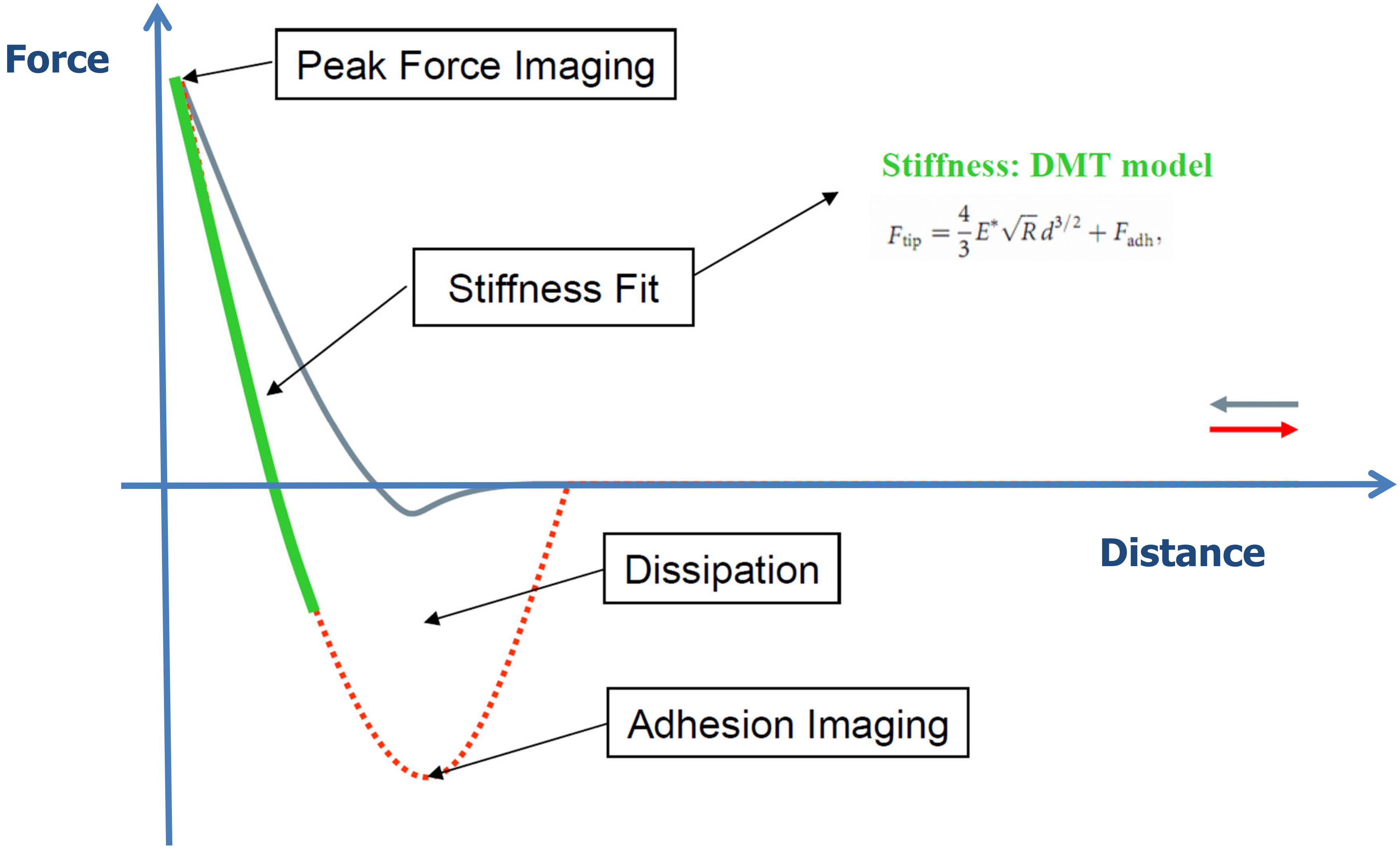
But

- It takes at least few hours for calibration !!
- Works only with special tips !!!

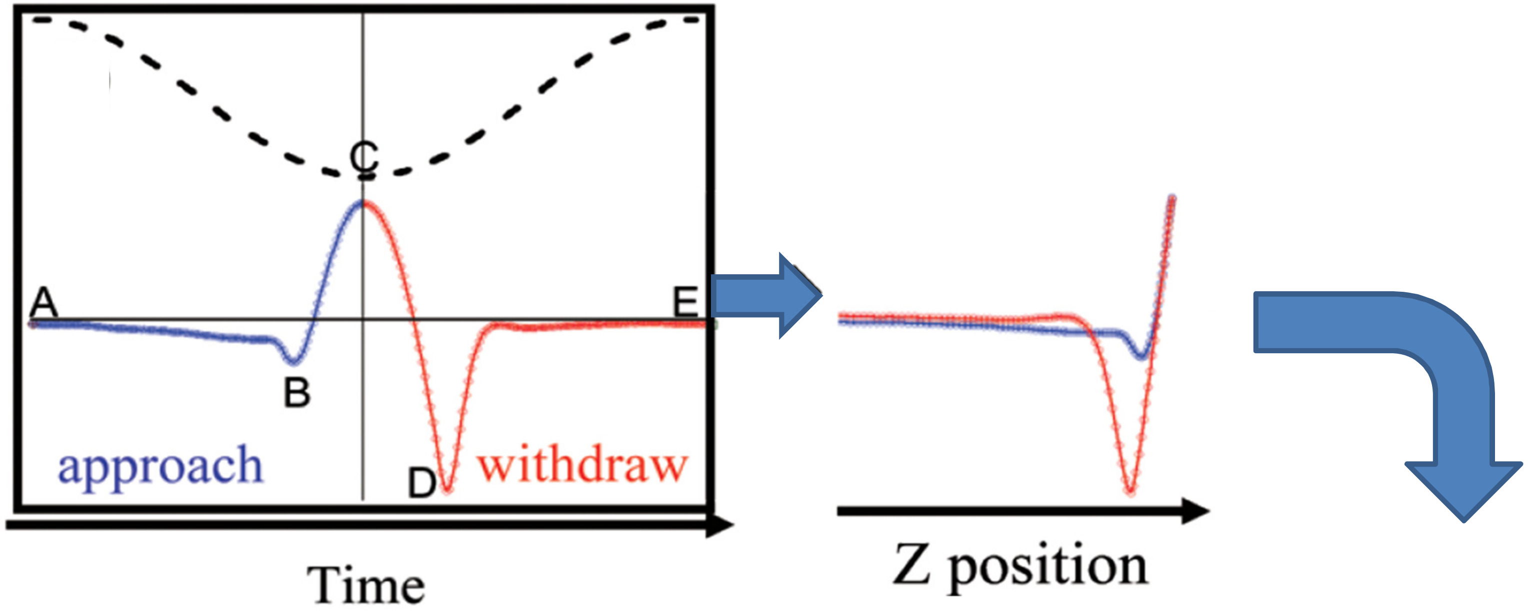


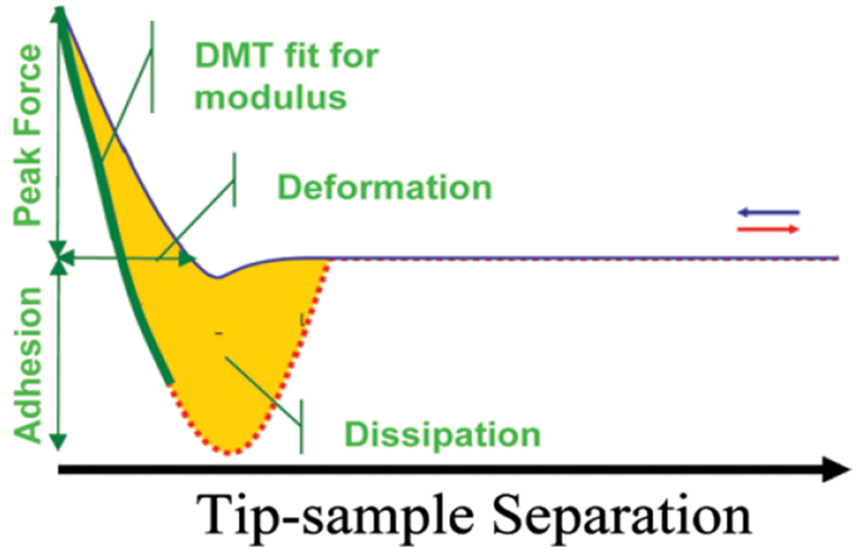
Peak Force Tapping

Force - Distance Curves



Peak Force Tapping Control (QNM)





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

How to easily make an imaging method … out of Force-Distance curves?

Force-Distance curve ramp rate:

- Standard = 1Hz
  - too slow for imaging (3 days)
- At cantilever resonance
  - too fast to measure the complete force profile & peak-force accurately (bandwidth for force detection = f_{res})
- Intermediate value (e.g. 2kHz)
  - Sufficiently fast for imaging
  - Allows one to measure the complete force profile & peak-force

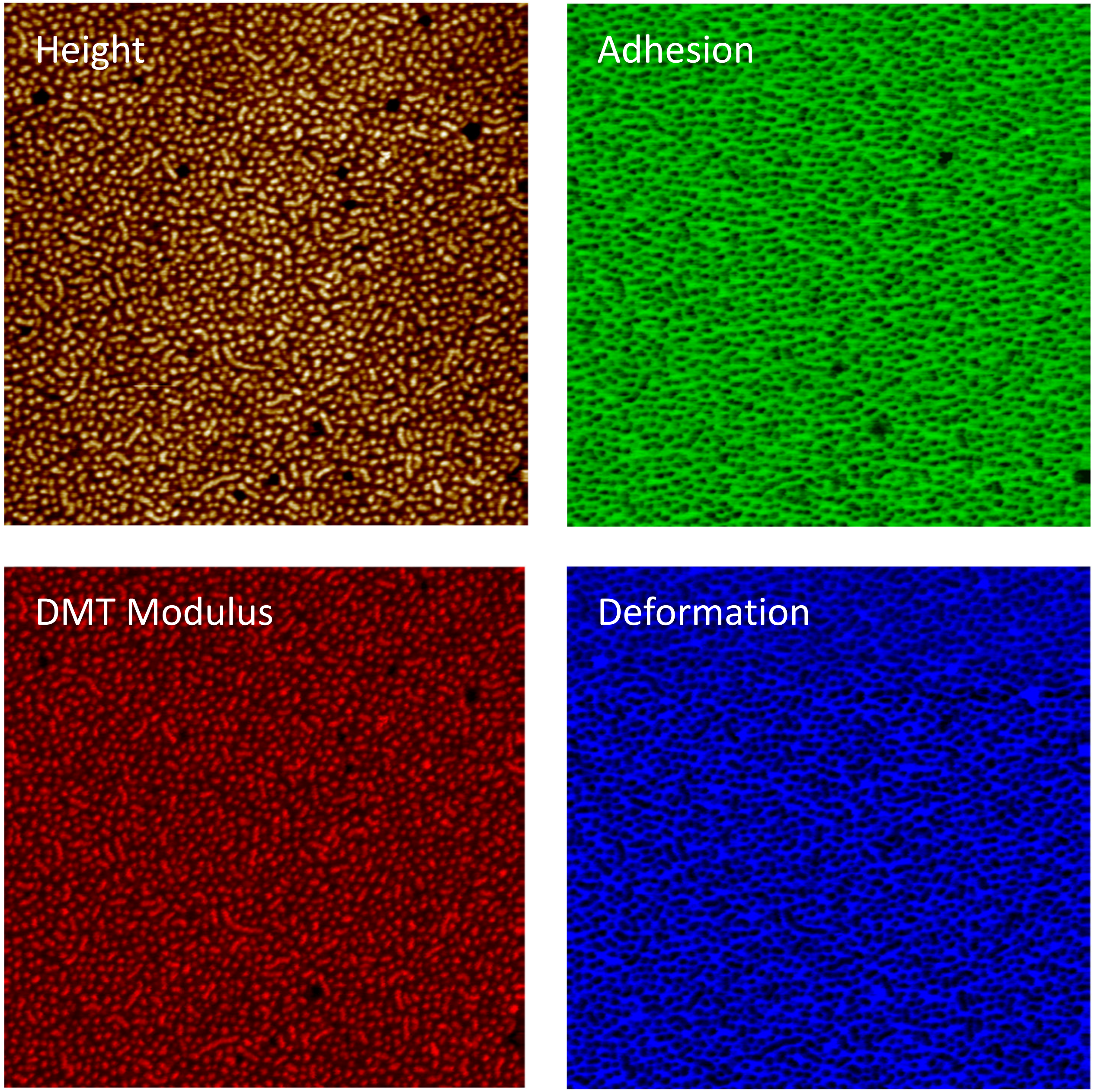
Constant ‘peak-force’: feedback setpoint = peak-force

- Constant force everywhere in the sample (unlike Tapping)

Hardware:

- “clean” & fast force-distance ramps (e.g. 2kHz)
- Collect complete force-profile and do realtime feedback on peak-force

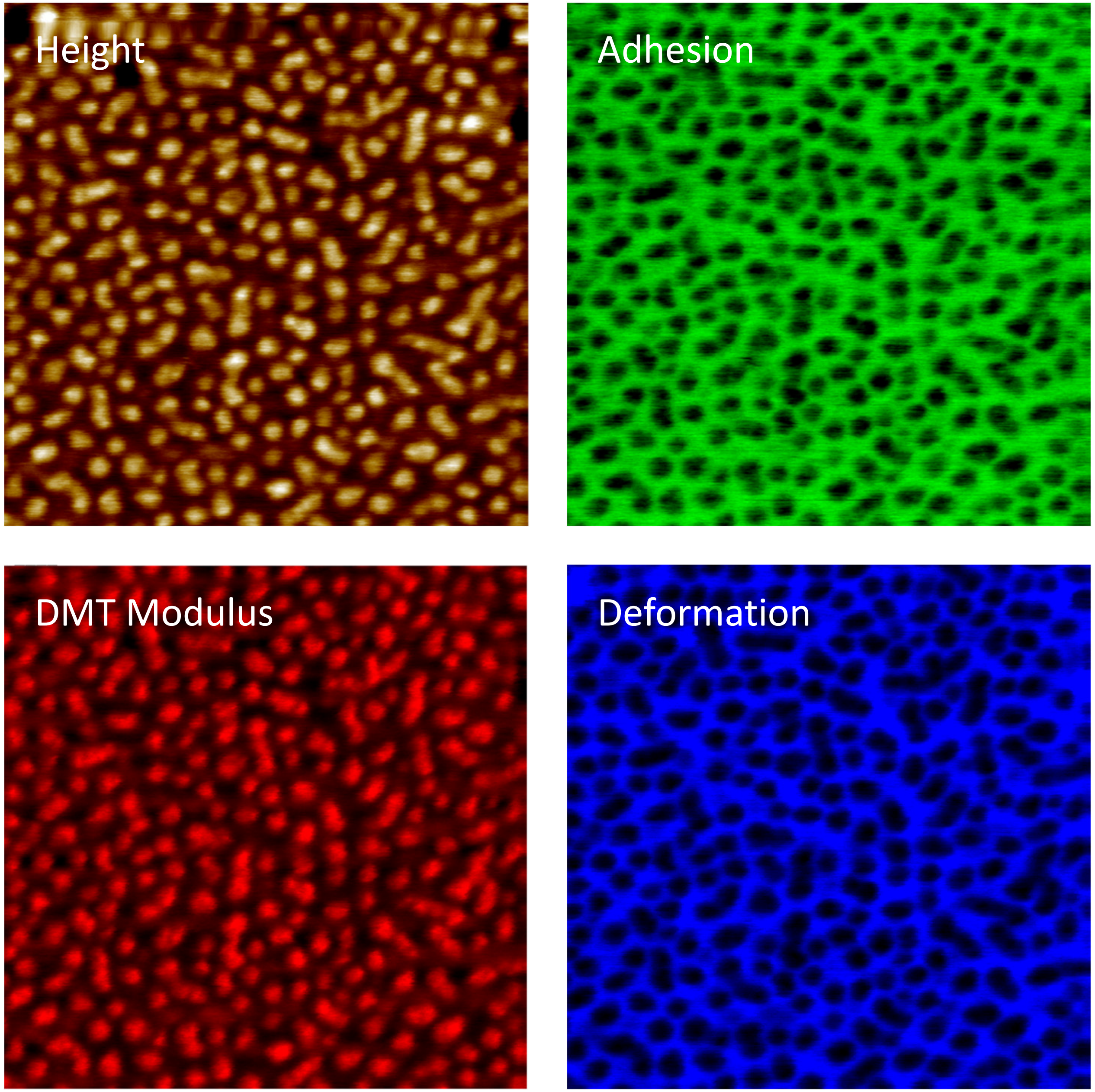
PeakForce QNM



RADIAL $(50\text{-}10)_4$

Scan size 3.0 µm

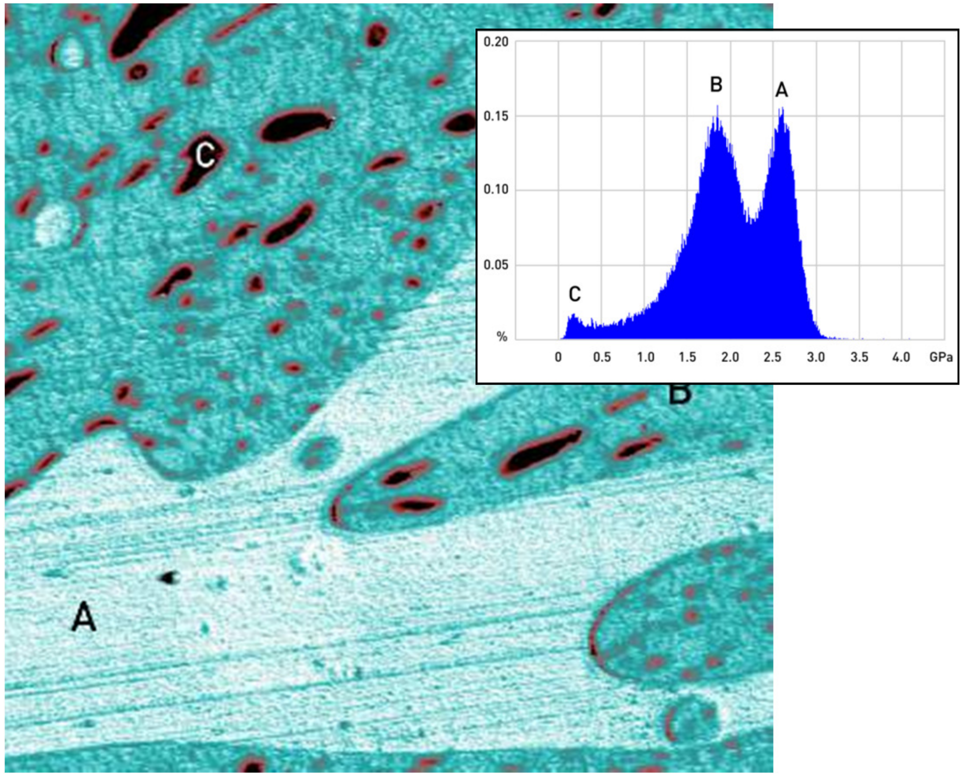
PeakForce QNM



RADIAL $(50\text{-}10)_4$

Scan size 1.0 µm

Simple solution to common questions



Multi-component polymer blend imaged on a MultiMode 8 using PeakForce QNM. A 7 µm scan of the sample modulus is shown above. There are three different components clearly present, the light blue component (A), the darker blue component (B), and the red/black component (C).

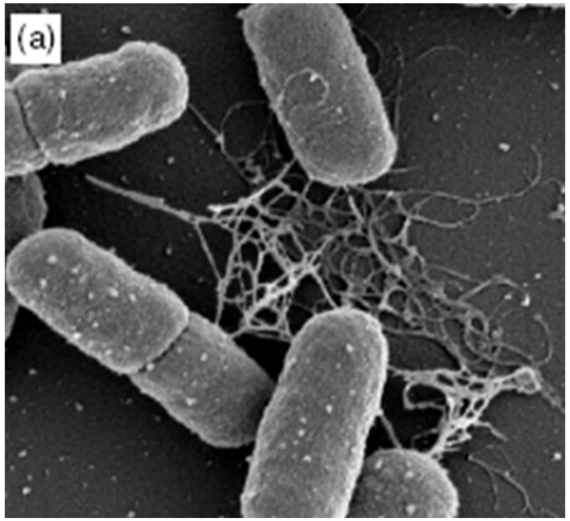
The image was then analyzed using bearing analysis to find the average modulus of each component and its proportion of the total area. This allowed the customer (undisclosed) to easily identify the exact materials in this proprietary polymer blend.

- "Phase imaging shows several different components in my material. How can I identify them and what are their proportions?"
- PeakForce QNM, unlike phase imaging, quantitatively measures sample modulus. This allows one to identify materials at the nanoscale by comparison to the bulk moduli of the materials.
- Bearing analysis yields the average modulus of each component and its proportional of the whole area

Doc. Bruker

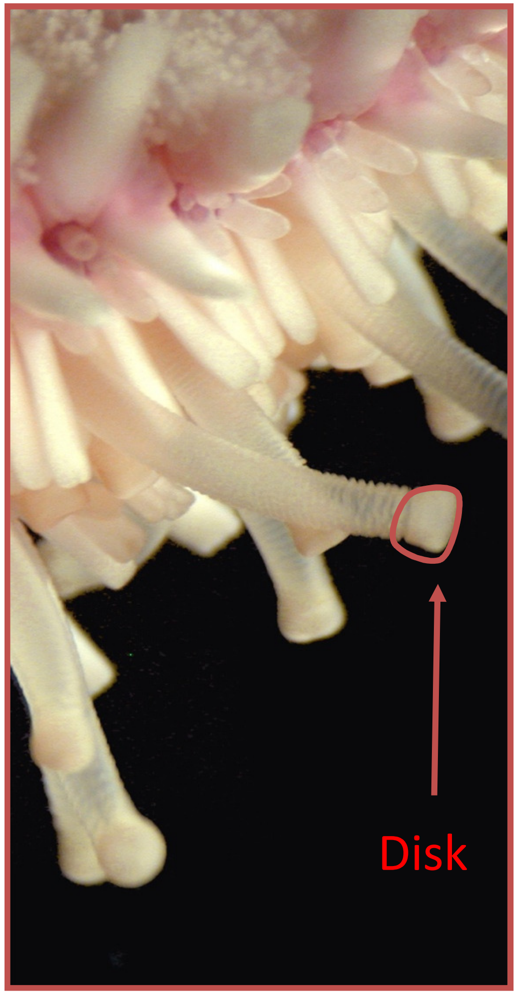
« Adhesion is a way of life in the sea »

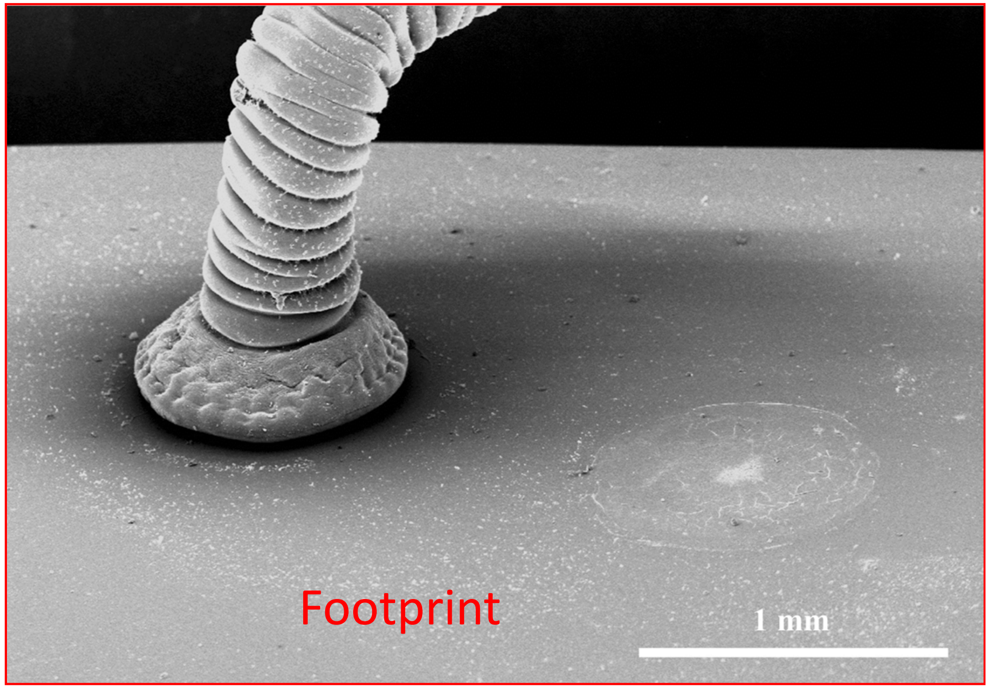
J.H.Waite (1983)



Courtesy of E. Hennebert

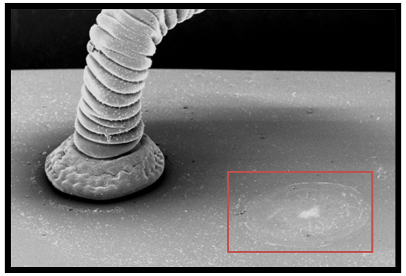
Tube foot

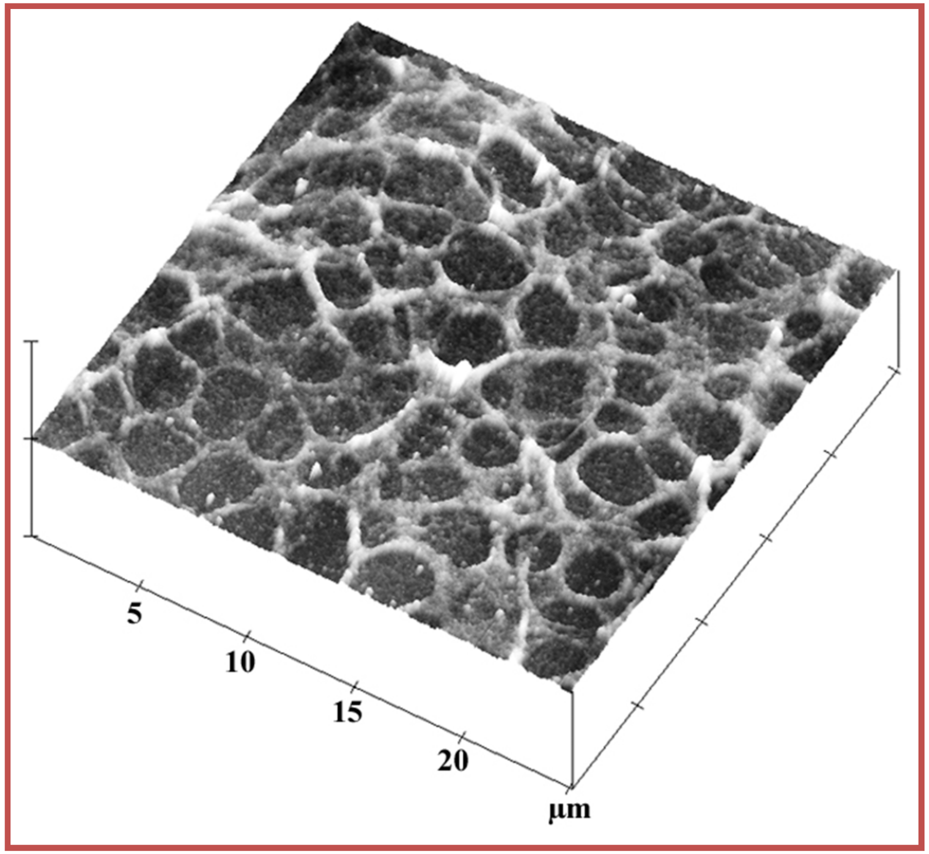




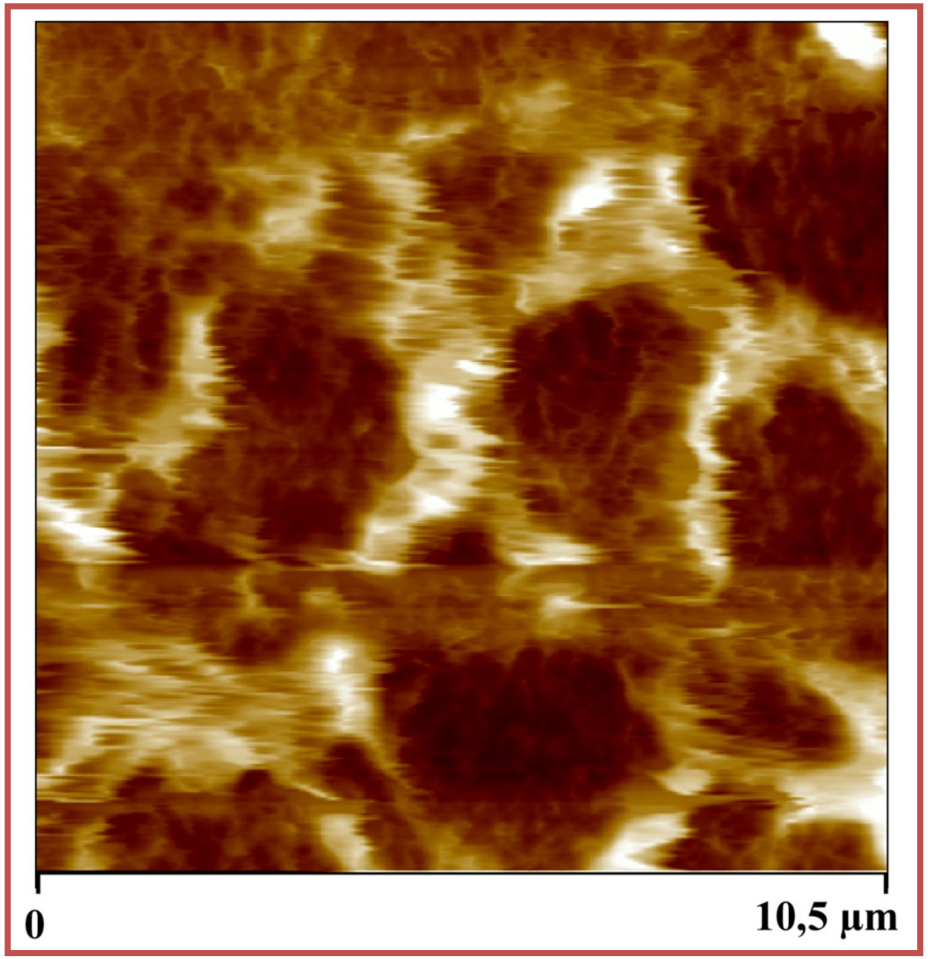
Courtesy of E. Hennebert

AFM in Fluid Cell





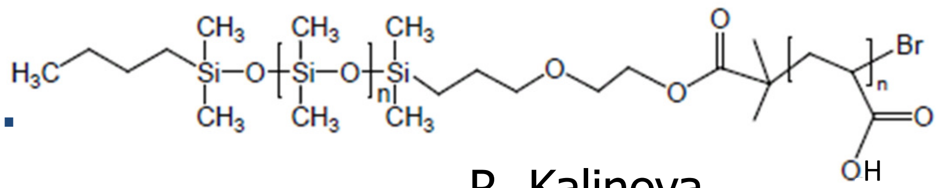
Dry sample deposited on mica, rinsed with distilled water and observed in ambient air



Fresh sample deposited on mica, observed under distilled water in fluid cell

Journal of Structural Biology **164** (2008) 108–118.

Biomimetic Polymer …

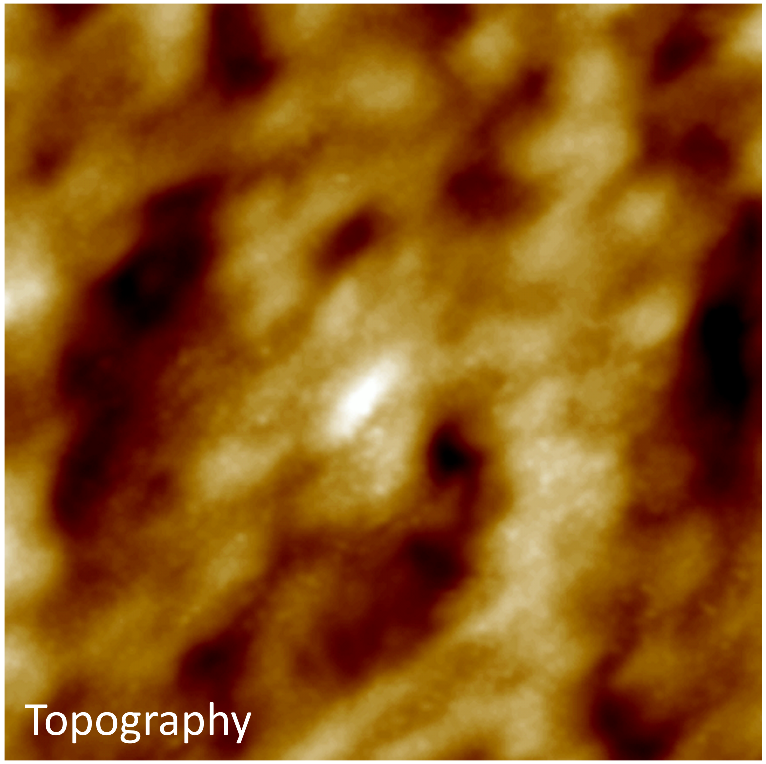


R. Kalinova

TM - AFM

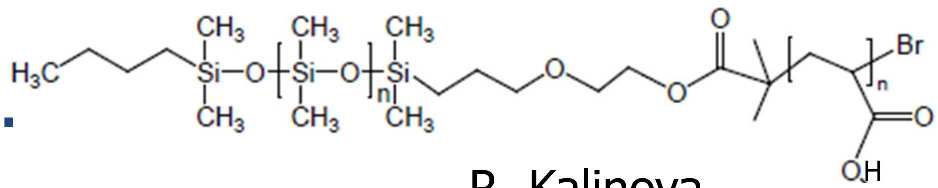
2.0 µm x 2.0 µm

PFT - AFM



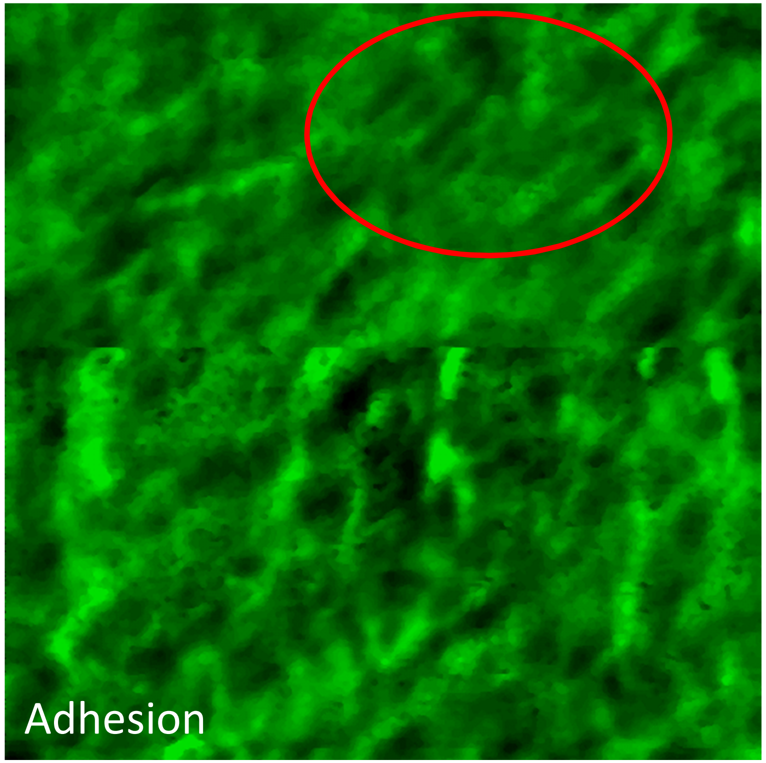
2.0 µm x 2.0 µm

Biomimetic Polymer …



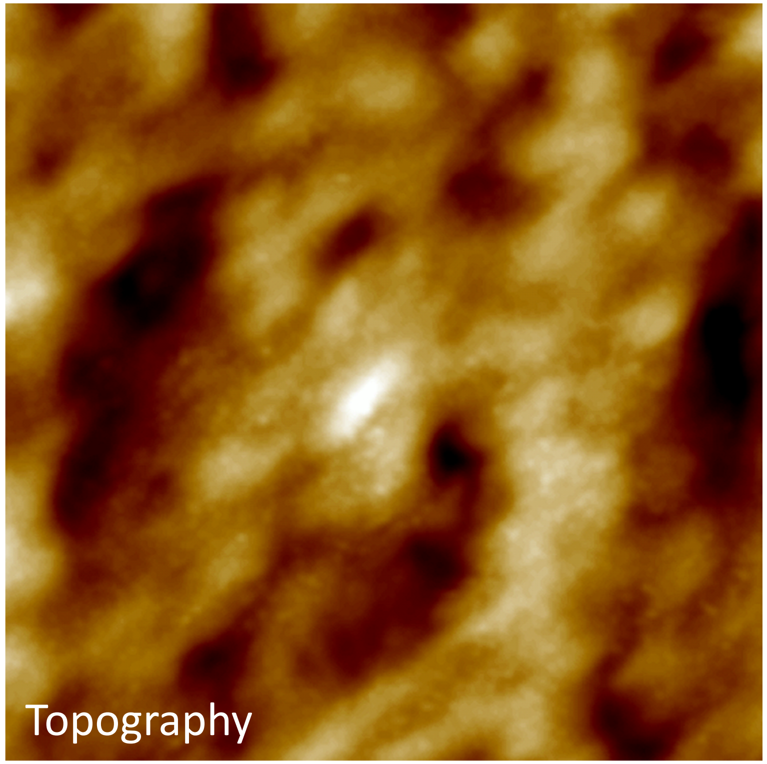
R. Kalinova

PFT - AFM



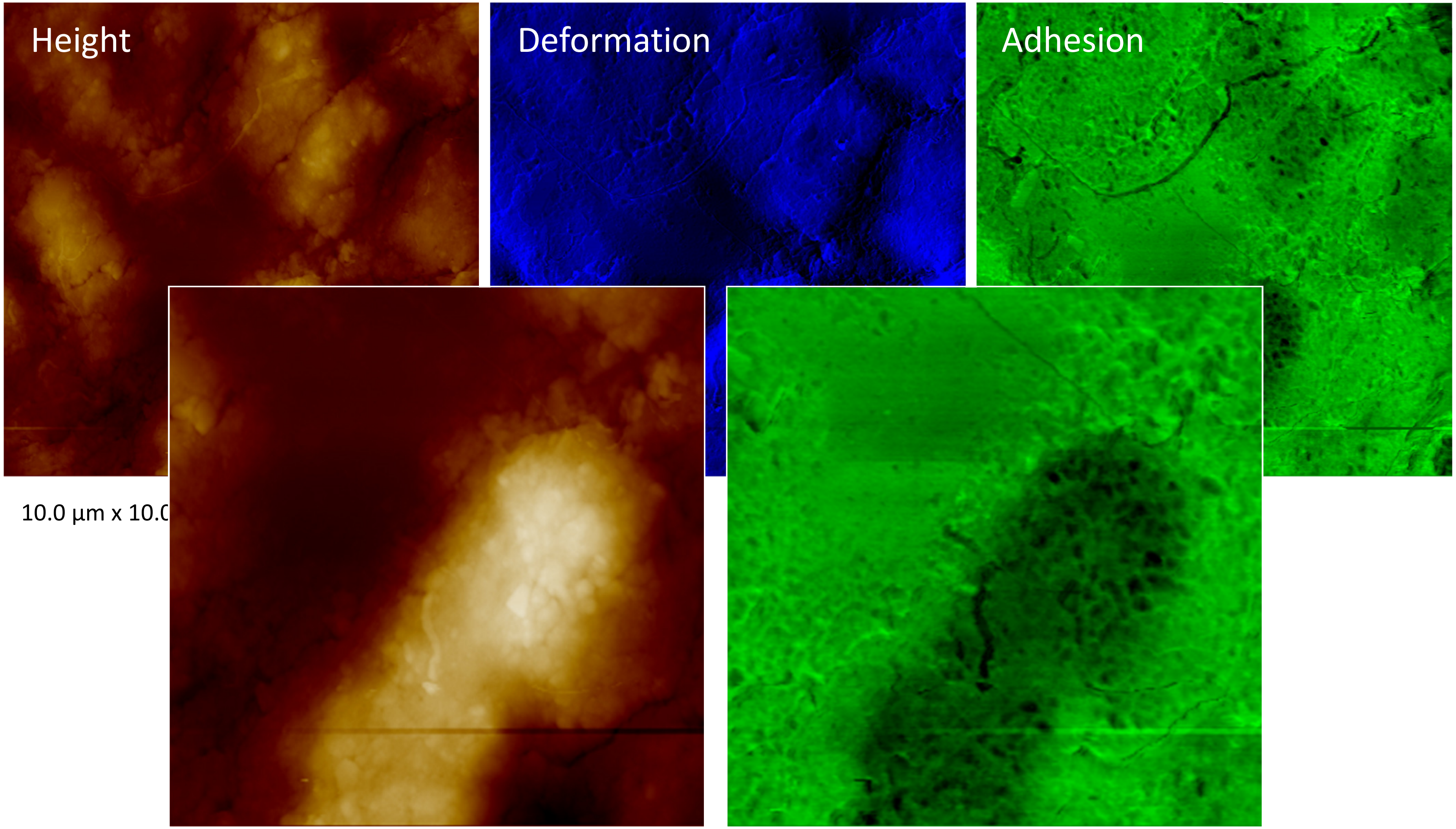
2.0 µm x 2.0 µm

PFT - AFM



2.0 µm x 2.0 µm

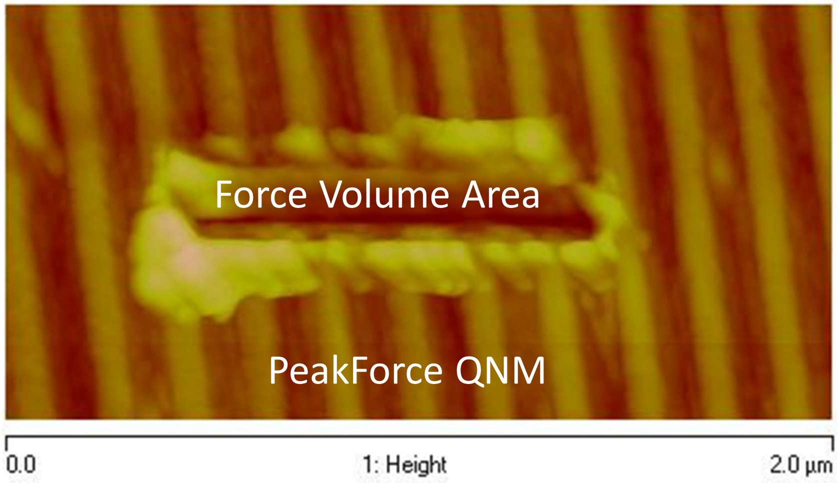
Adaptive Hydrogels…

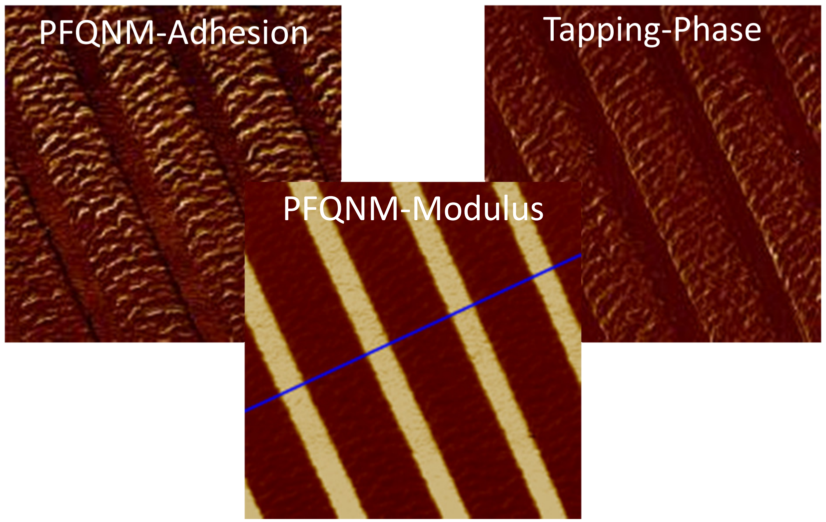


L. Mespouille

Comparison between the techniques

Multilayered polymer film (~100 to 300 MPa)





- **Current quantitative methods**
  - Nanoindentation (e.g. Hysitron and Asylum nanoindentor option)
  - Force volume (with extra analysis)

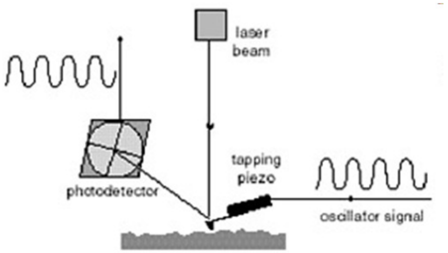
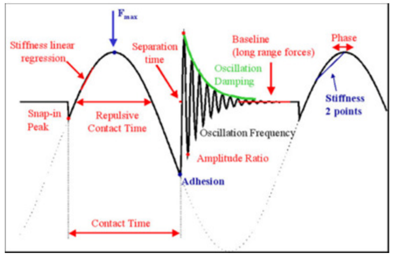
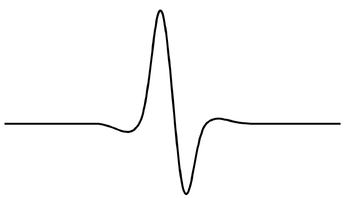
Problem: high force = low resolution

  - Large indentations limit resolution on all samples and destroy soft samples
  - Asylum's "low force" option has k=800 N/m and standard 8000 N/m
  - Compare to PeakForce QNM, where probes used 0.4 N/m < k <200 N/m

- **Current high resolution methods**
  - Phase imaging
  - Higher harmonics and Dual AC

Problem: Source of contrast unknown or unambiguous, and not quantitative even when understood

Comparison of Imaging Modes

<table>
<tr><th>Mode</th><th>How does it work?</th><th>Pros and Cons</th></tr>
<tr><td>TappingMode

</td><td>- Cantilever oscillates at its resonance frequency
- Oscillation is damped as tip begins to contact the sample
- Probe is moved up and down in a feedback loop to maintain constant oscillation amplitude.</td><td>- Gentle, vertically (1-3 nN) and laterally
- Widely applicable to many samples
- Phase imaging gives unique information
- Must “tune” resonance, difficult in fluid
- Optimum operation requires sensitive fine-tuning and is not always stable</td></tr>
<tr><td>Pulsed Force Mode (PFM)

</td><td>- Z is ramped at 100Hz - 2 kHz and deflection signal is monitored
- Let oscillation ring down and detect maximum force
- Uses maximum force for feedback</td><td>- Can derive stiffness and adhesion data from the force curves (qualitative)
- Must operate at high forces to overcome the large background signal (10’s nN)
- Large forces break tips</td></tr>
<tr><td>Peak Force Tapping
</td><td>- Z is ramped at 2 kHz and deflection signal is monitored
- Large oscillating background at 2 kHz is subtracted in real-time
- Peak force is calculated from lock-in amplifier as the feedback signal
- Not limited by background or need to let oscillations ring down</td><td>- Can operate at lower forces (~200 pN), not limited by background oscillation
- Extremely stable, not sensitive to deflection drift because force is relative
- Well-behaved feedback, not very sensitive to the exact control parameters
- Can derive stiffness and adhesion data from the force curves (quantitative)</td></tr>
</table>

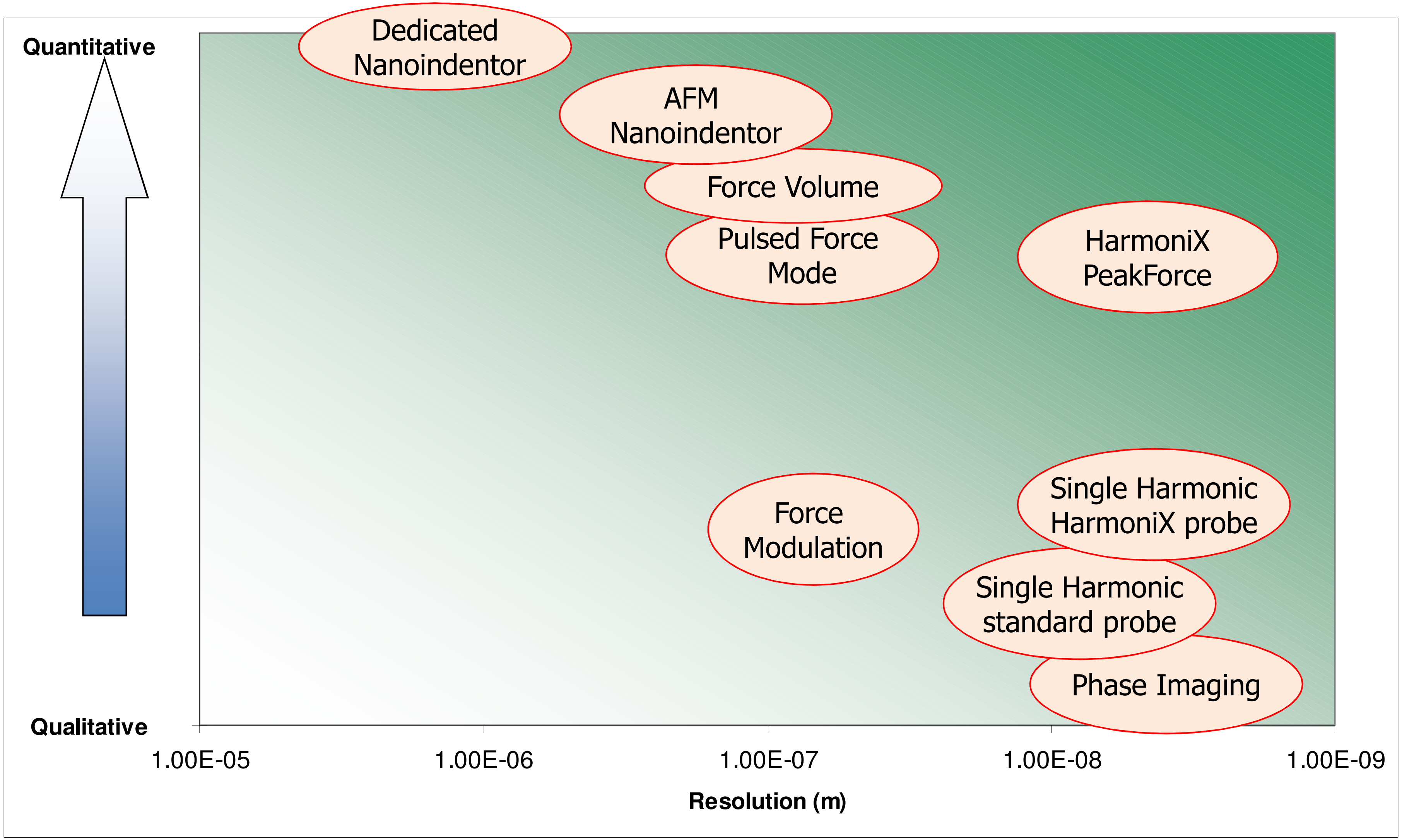
Comparison between the techniques

	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 mapping	Yes	No	No	No	No	No	Possible offline
Quantitative modulus range	0.7 MPa – 70 GPa	10 MPa – 10 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
Minimum peak force	<100 pN	<5 nN	<3 nN	<10 nN	<5 nN	<20 nN	<50 nN
Lateral resolution	<5 nm	<5 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 (1)	4 minutes	4 minutes	4 minutes	4 minutes	18 hours

(1) HMX needs a long calibration !

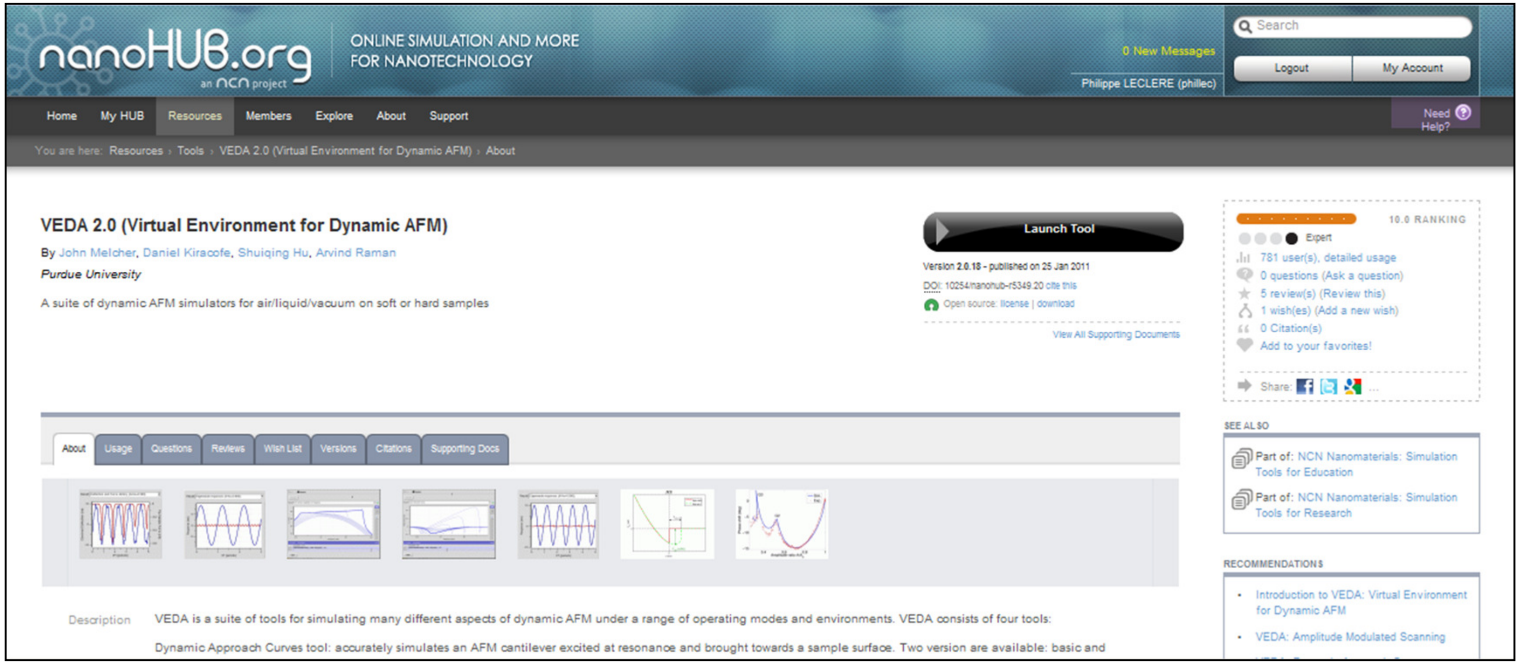
Quantitative:

Quality of Data vs. Resolution



Perspectives

- Fit of the force-distance curves by other models than DMT (for instance the ones included in VEDA 2.0)

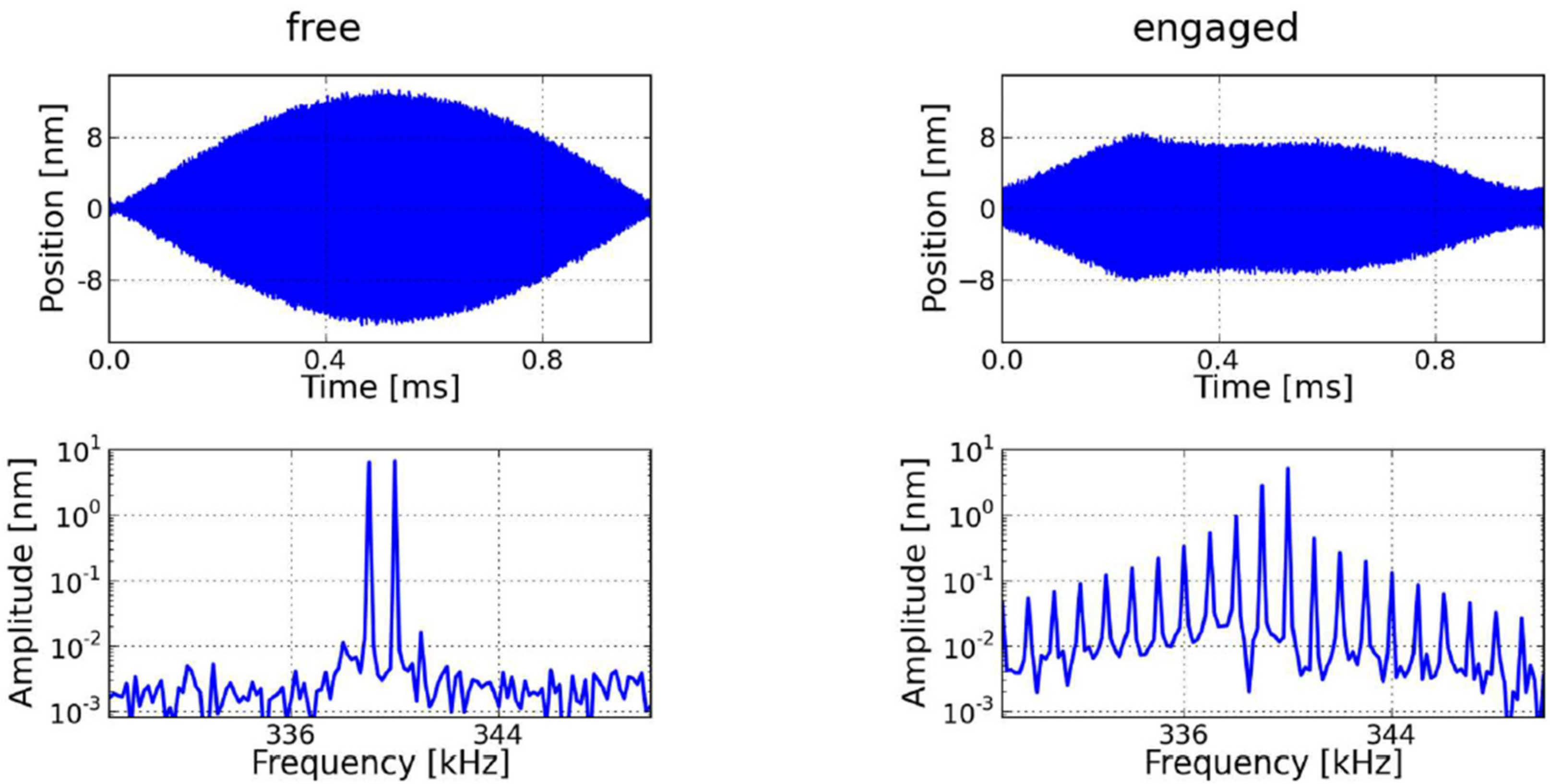


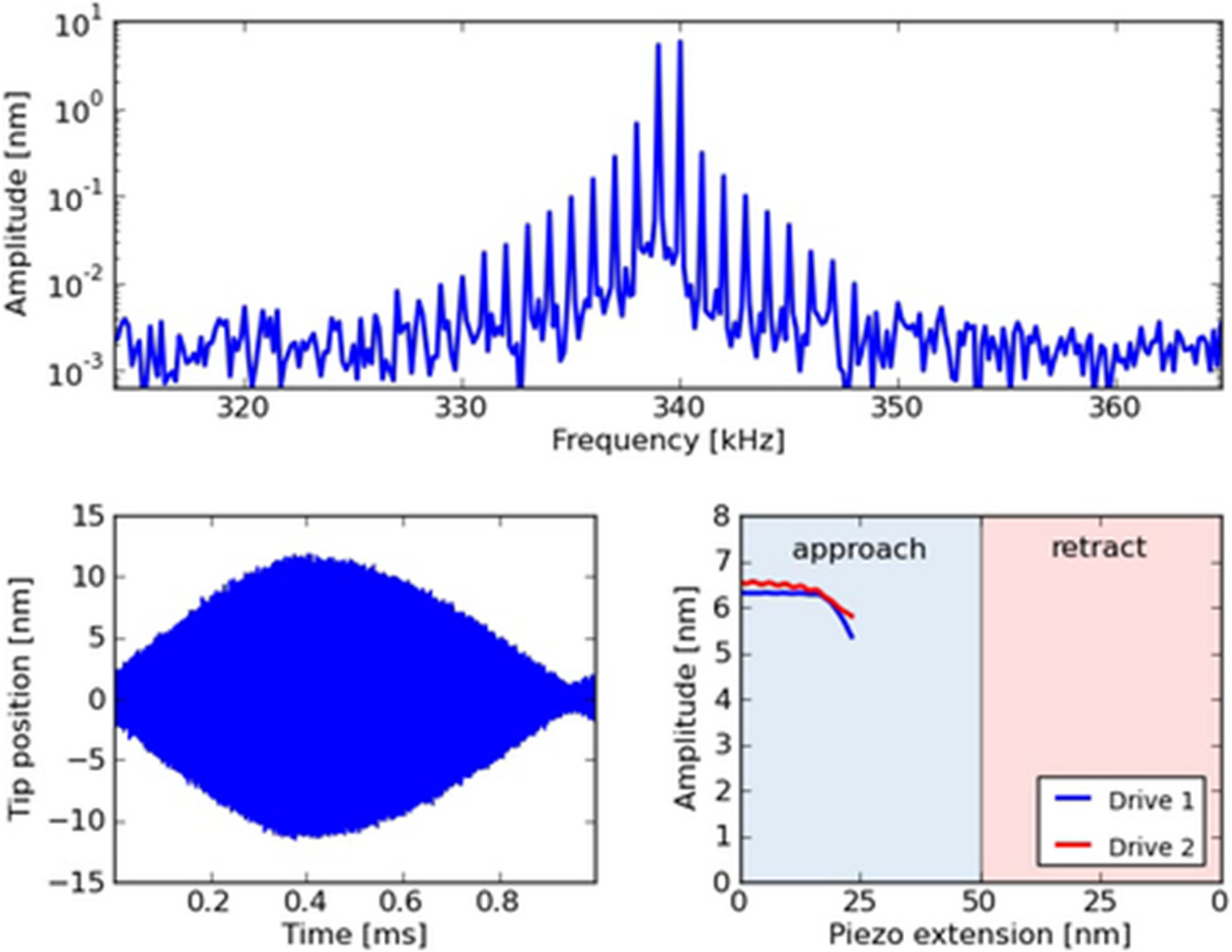
- Rheology at the nanoscale by varying the ramp rate (now at 2 kHz).
- Address the viscoelastic properties of polymeric systems.

Multifrequency Methods

Intermodulation

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

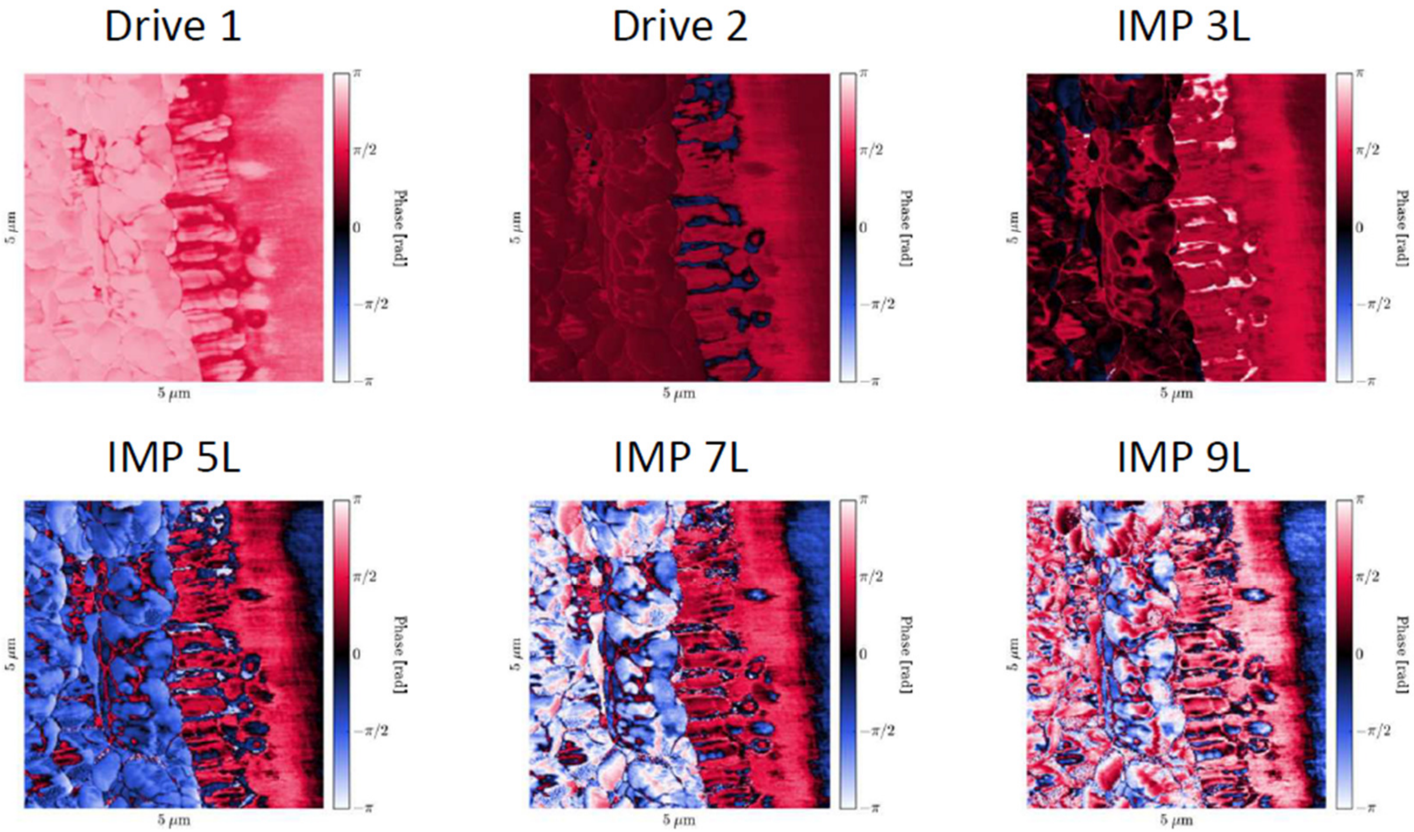




Amplitude [nm]
Frequency [kHz]
Tip position [nm]
Time [ms]
approach
retract
Amplitude [nm]
Piezo extension [nm]
Drive 1
Drive 2

Intermodulation

Each intermodulation product has amplitude and phase which can be used for imaging



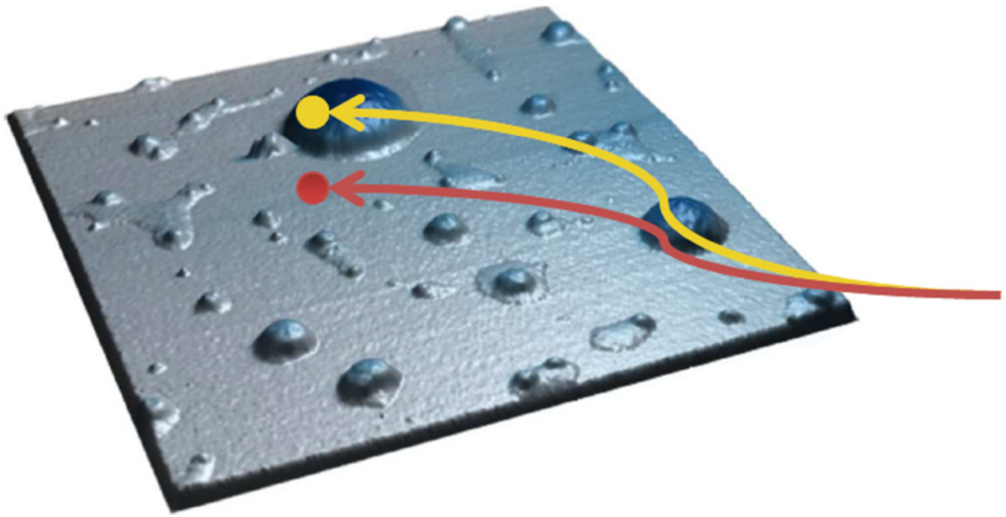
Phase images on a stack of different metals

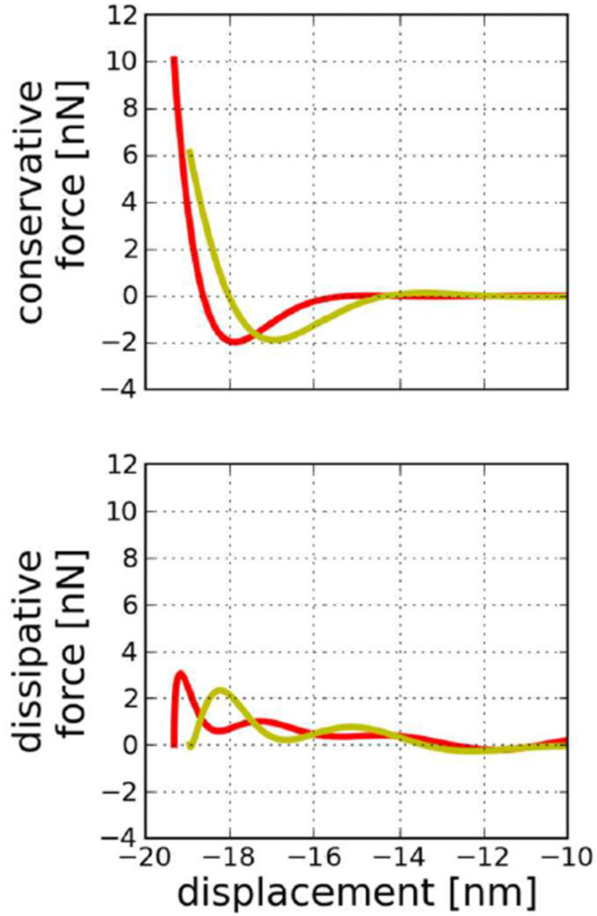
Intermodulation products

www.intermodulation-products.com

Intermodulation

Force reconstruction on two points of blend of polystyrene and poly(acrylic acid)



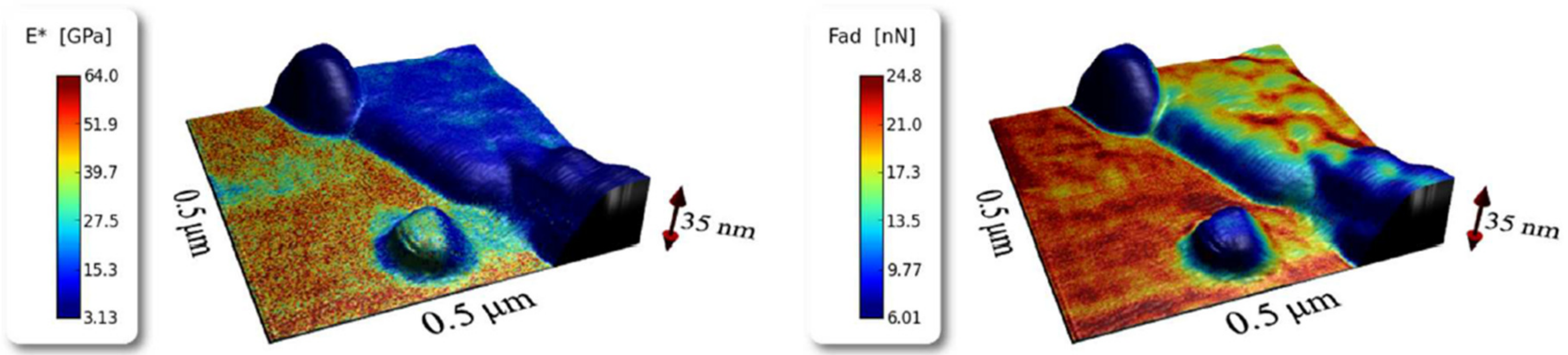


- The force is approximated as a polynomial
- Conservative forces and position dependent viscosities are reconstructed separately
- Reconstruction at fixed probe height allows force reconstruction in every pixel of an image

Intermodulation

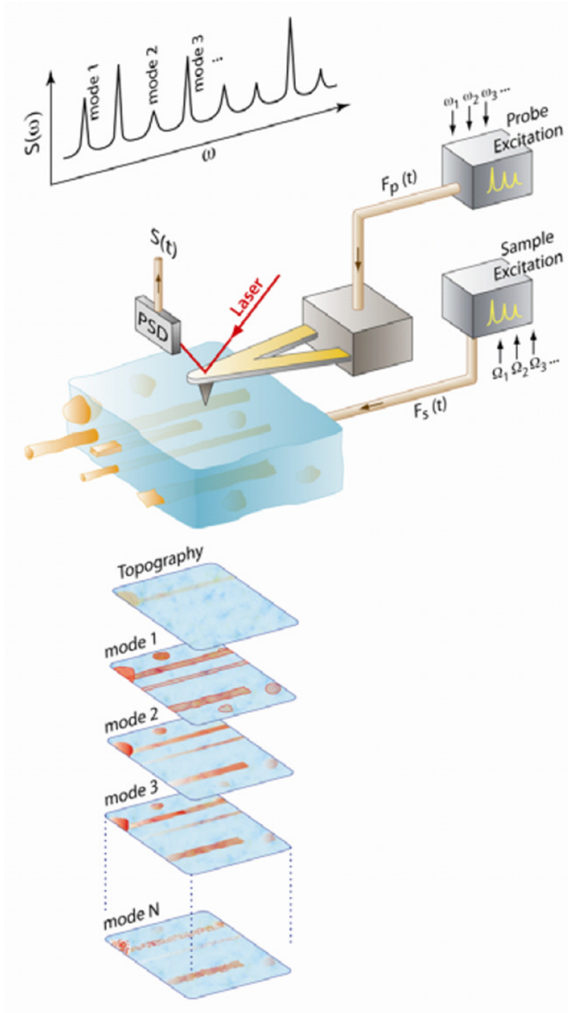
- Any force model can be assumed
- Numerical solver extracts the model parameters that fit best the measured IMPs
- Generation of high resolution surface property maps

Extracted Young's modulus and adhesive force from a van-der-Waals DMT model



Intermodulation products

Mode synthesizing AFM



L. Tetard, A. Passian, T. Thundat, *Nat. Nanotech.2009, 5, 105.*

Quelques conseils d'un Maître …

Face aux courbes de force …

« Le côté obscur de la Force, redouter tu dois. »
« À vos intuitions, vous fier, il faut. »
« Beaucoup encore il te reste à apprendre. »

Conseil aux Maîtres Jedi par rapport aux Padawans …

« Ta confiance en ton apprenti, un peu trop grande me paraît, comme l'est ta foi dans le côté obscur de la Force. »

Vis-à-vis des matériaux organiques et biologiques …

« Visqueux ? Boueux ? Ici je vis !! »