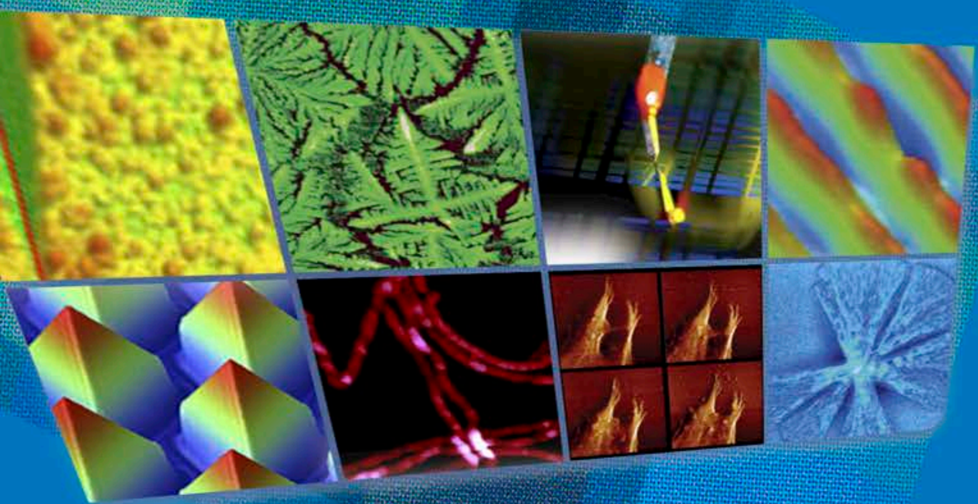
Recent Developments in Nanomechanical Characterization Techniques in AFM

John Thornton, Sr. Applications Engineer, john.thornton@bruker.com



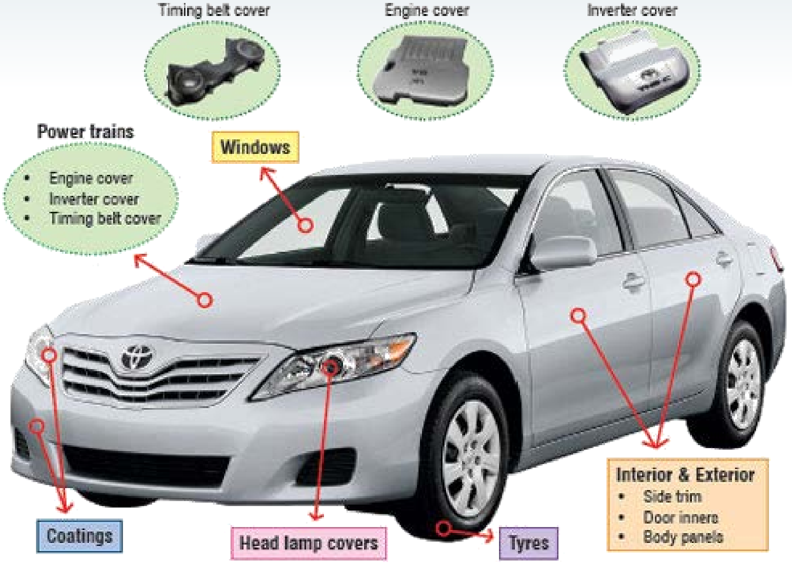
Atomic Force Microscopy
3D Optical Microscopy
Tribology
Automated AFM
Stylus Profilometry
Mechanical Testing, Nano Indentation

Bruker Nano Surfaces Division

Innovation with Integrity

Why Study Nanomechanics by AFM?

- Influence of nanoscale mechanical properties on macroscale behavior
  - Distribution of domains in heterogeneous material
  - Mechanical properties of those domains
- Bulk methods require large amount of material
- Nanoscale methods allow access to components in-situ
  - Small amount of material
  - Domains confined within matrix or adjacent to filler

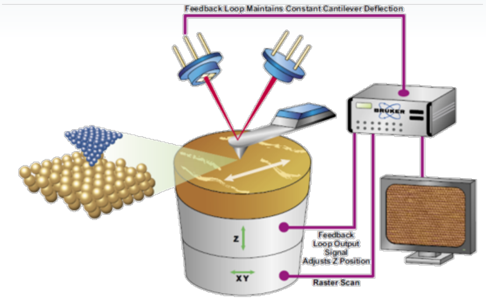


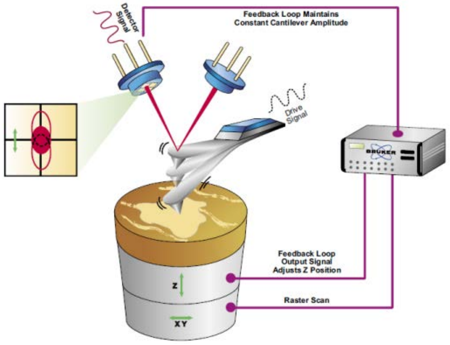
Epitaxial lamellae at barrier-tie interface: heat sealed food packaging

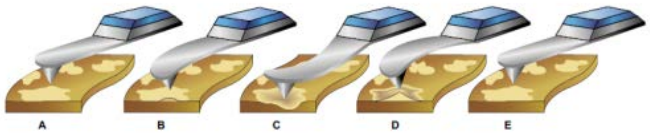
AFM Imaging Technology

- Mapping topography -> More information
  - Contact mode & force spectroscopy (1986)
  - TappingMode & phase imaging (1992)
  - Force-Volume Mapping (~1992)
  - Contact Resonance (AFAM, UAFM~1996)
  - HarmoniX (2008)
  - PeakForce Tapping/QNM (2010)
    - PeakForce TUNA (2011)
    - PeakForce KPFM (2012)
    - PeakForce sMIM (2015)
    - PeakForce SECM (2016)
  - Fast Force Volume (2014)
  - FFV – Nanomechanics/CR (2016)
  - FFV – Nanoelectrical (2018)
  - AFM-nDMA

More to come …

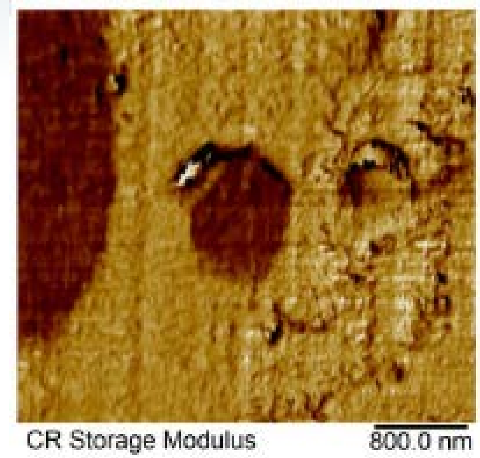




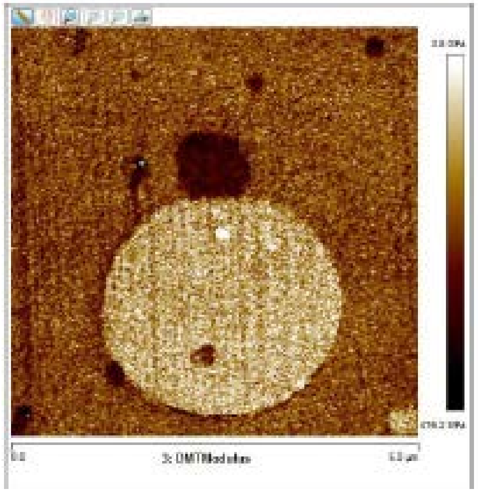


Nanomechancial Measurement Techniques with AFM

- **Force Spectroscopy** (Elastic Modulus)
- **Phase Imaging** (Convolution of elastic and viscoelastic properties)
- **Contact Resonance** (Viscoelastic Properties at high frequency)
- **PeakForce QNM** (Elastic Modulus)
- **AFM-nDMA** (viscoelastic moduli)

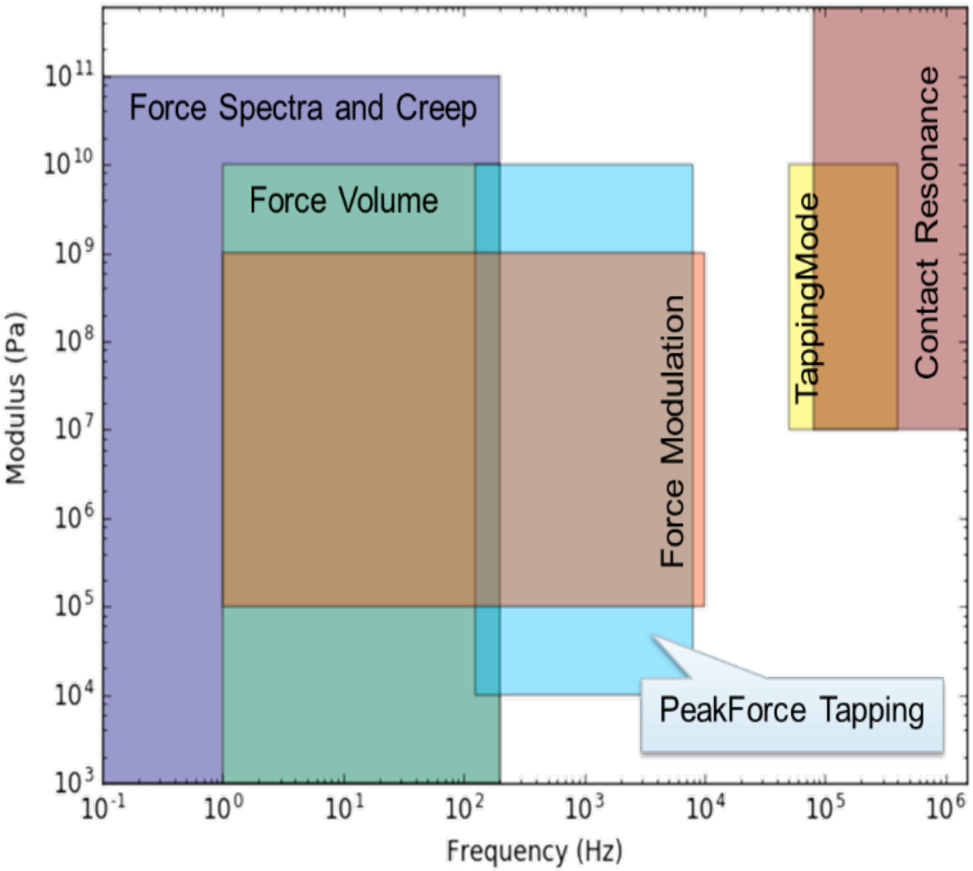


CR Storage Modulus

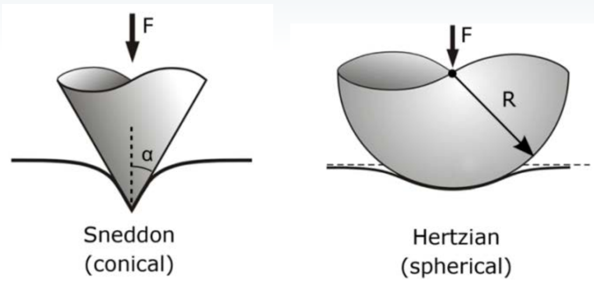


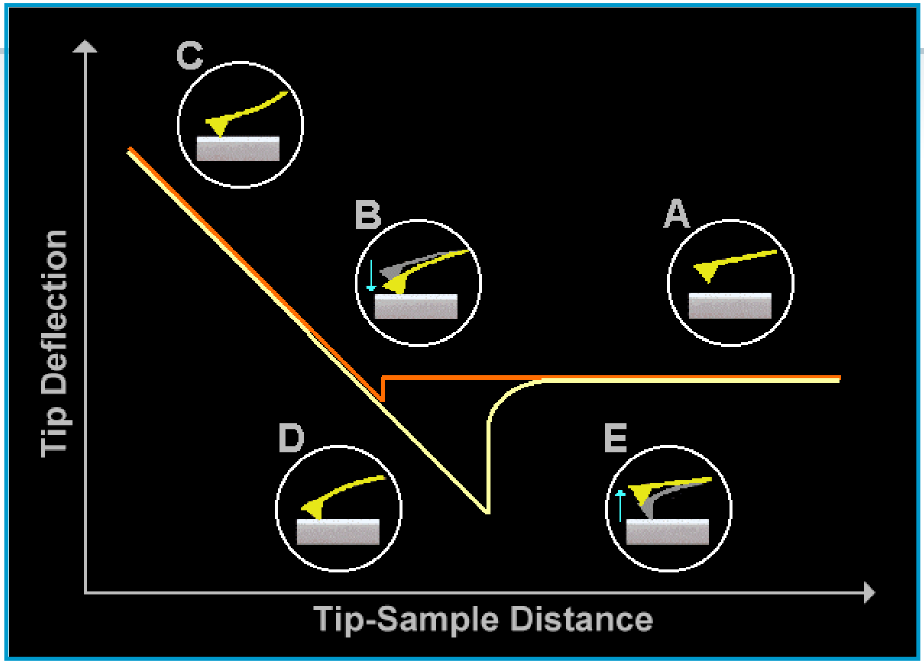
Different AFM modes & cantilevers cover wide range of modulus and measurement frequency

- At first glance, covers range of frequencies and moduli
- For sure AFM offers attractive spatial resolution
- Repeatable measurements possible with good system calibration

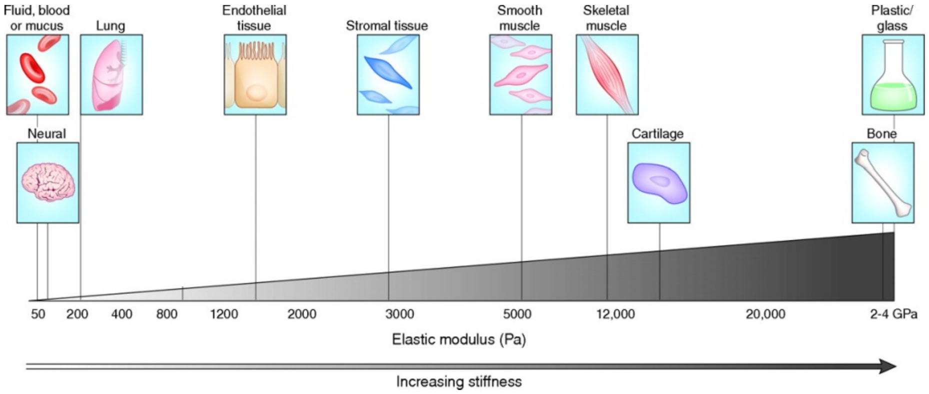


Force Spectroscopy for Nanomechanical Measurements





- Force-Distance curves collected and fit with models to measure
  - Elasticity/Stiffness
  - Adhesion
  - Attraction

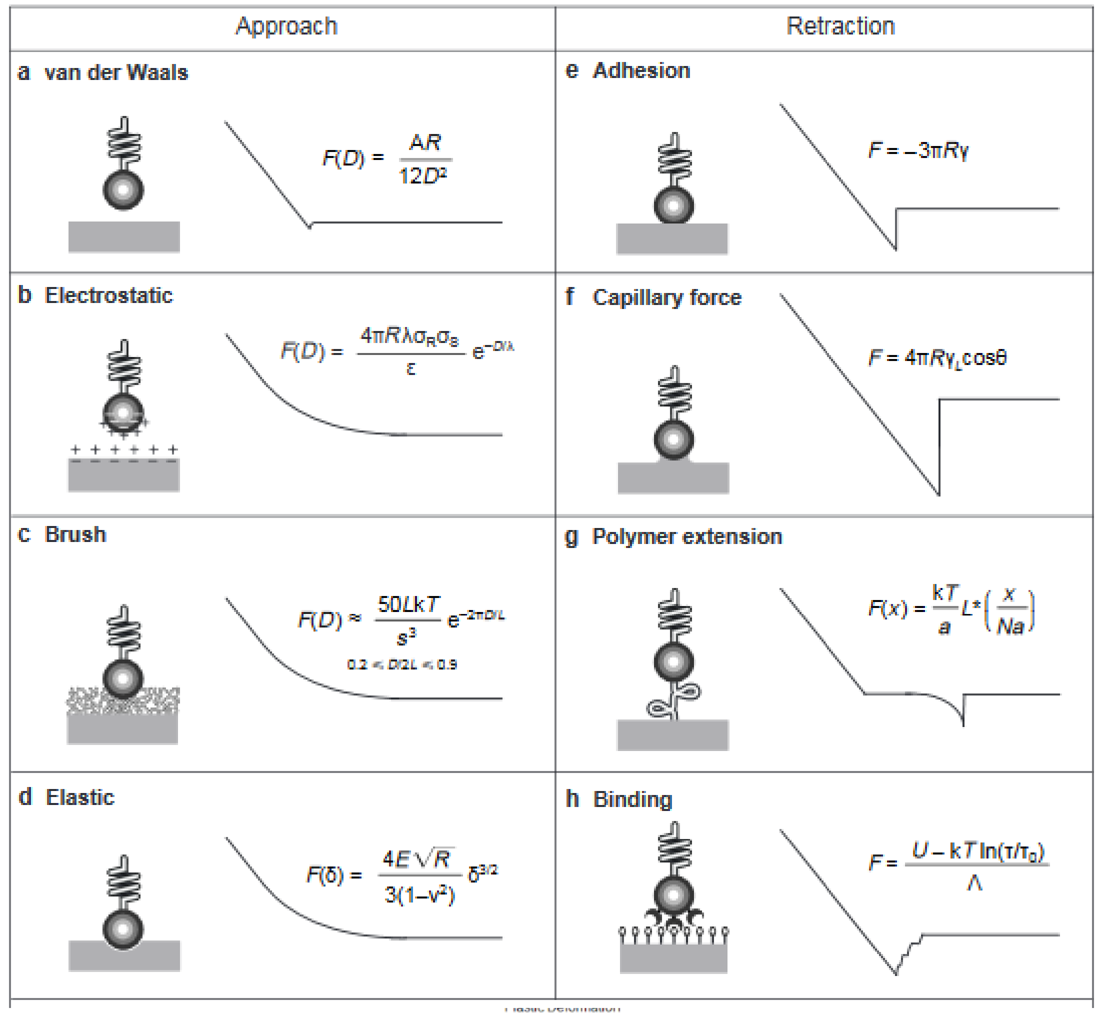


Modified from Cox and Erler. Dis. Model. Mech. (2011) 4:165-178.

Interpreting Force Curves

- Measures
  - attractive,
  - repulsive, and
  - adhesive forces between tip and sample

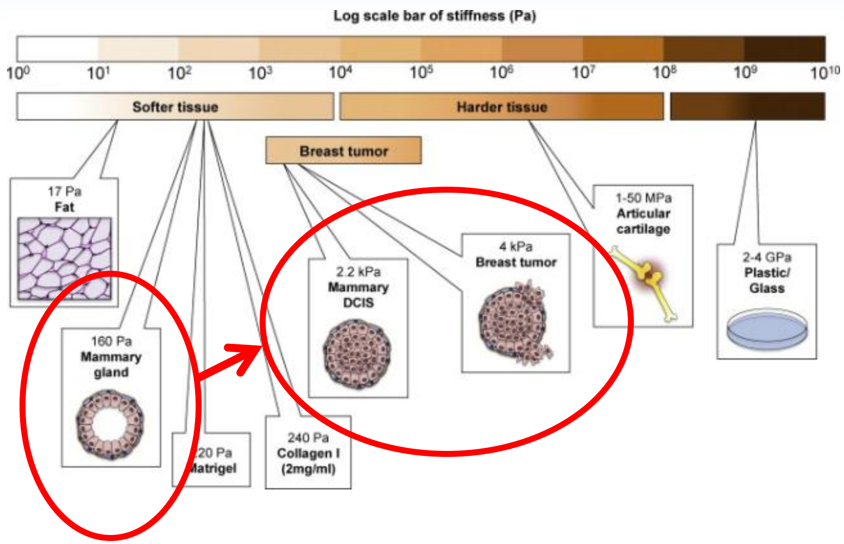
- Applications
  - investigating fundamental force interactions
  - nano-scale adhesive and elastic response
  - binding forces
  - collodial studies
  - chemical sensing

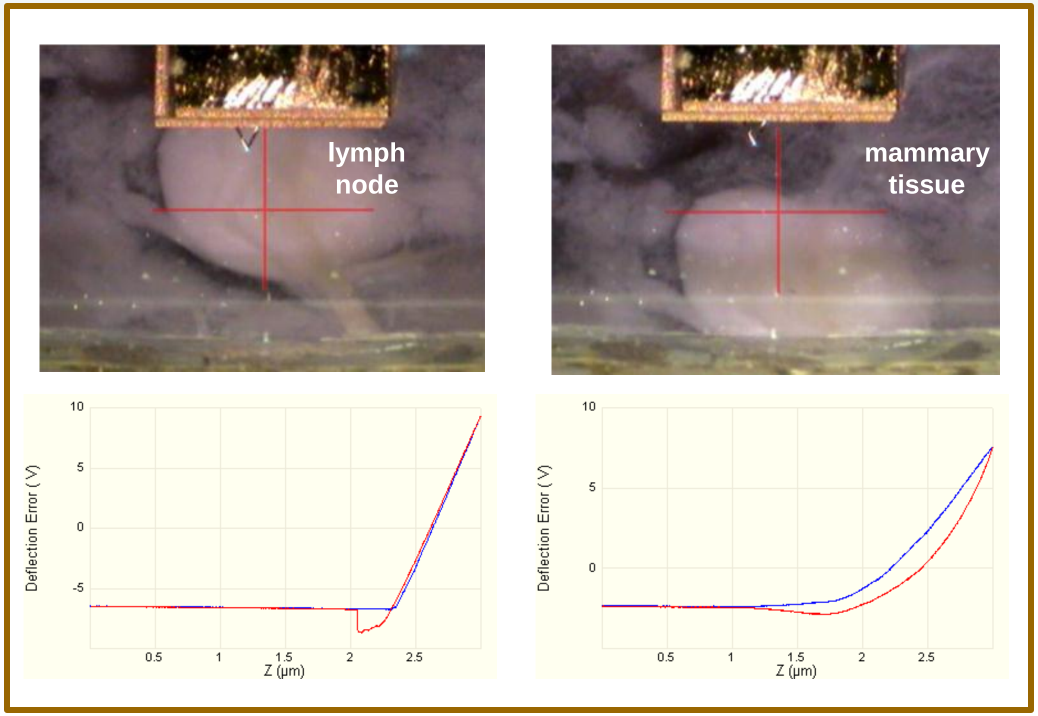


WF Heinz, JH Hoh - Trends in biotechnology, 1999

Nanomechanical Properties of Tissues

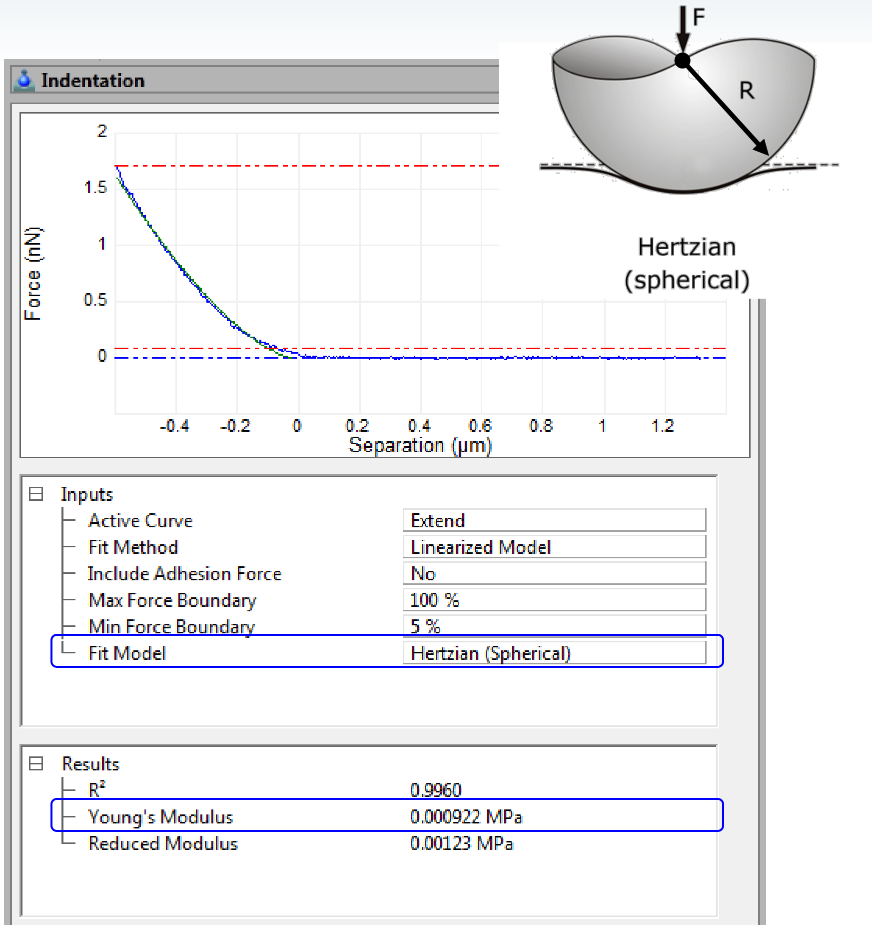
Mammary Gland



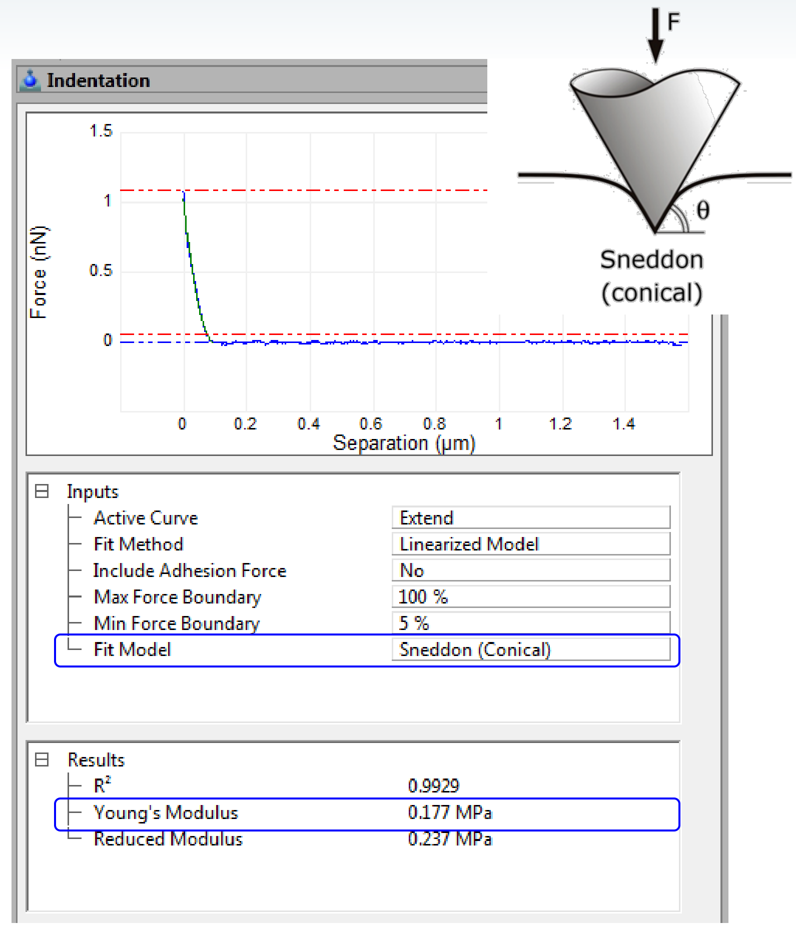


- Role of forces in disease states (eg. breast cancer).
- Mammary gland becomes increasingly stiffer with tumor progression.
- Force curves show lymph node stiffness > mammary tissue stiffness.

Example: Indentation Analysis -Choosing an indentation model



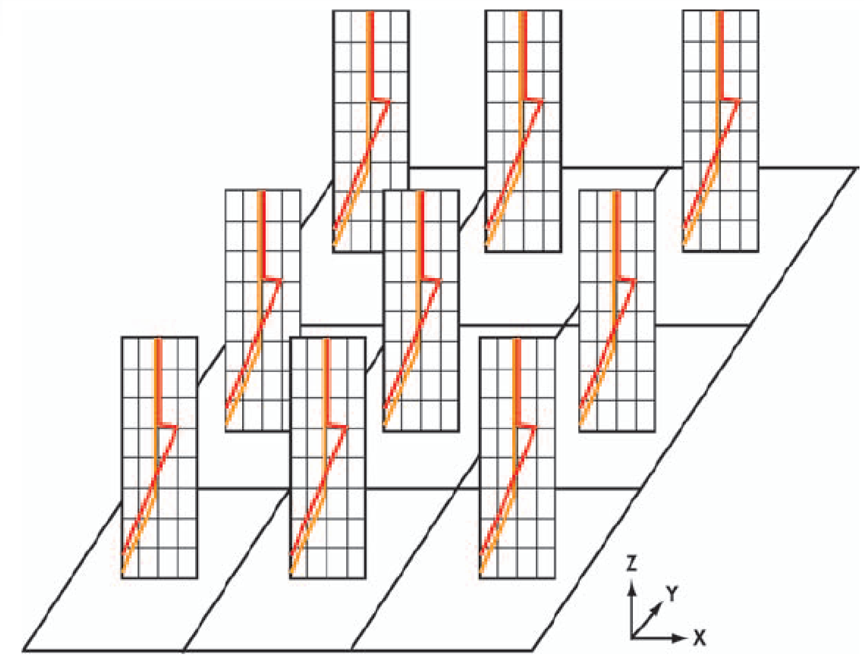
Force curve taken on a live HEC1A cell with a 5µm radius colloid probe cantilever



Force curve taken on a live HeLa cell with an unmodified MLCT probe

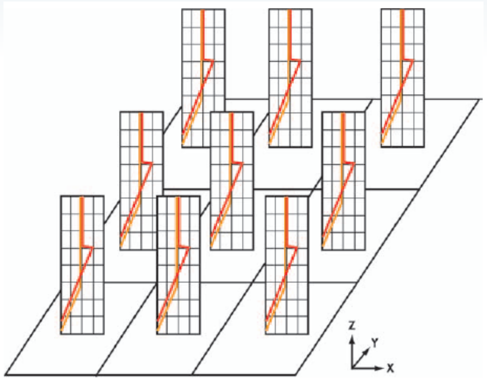
Force Volume Imaging: Principle

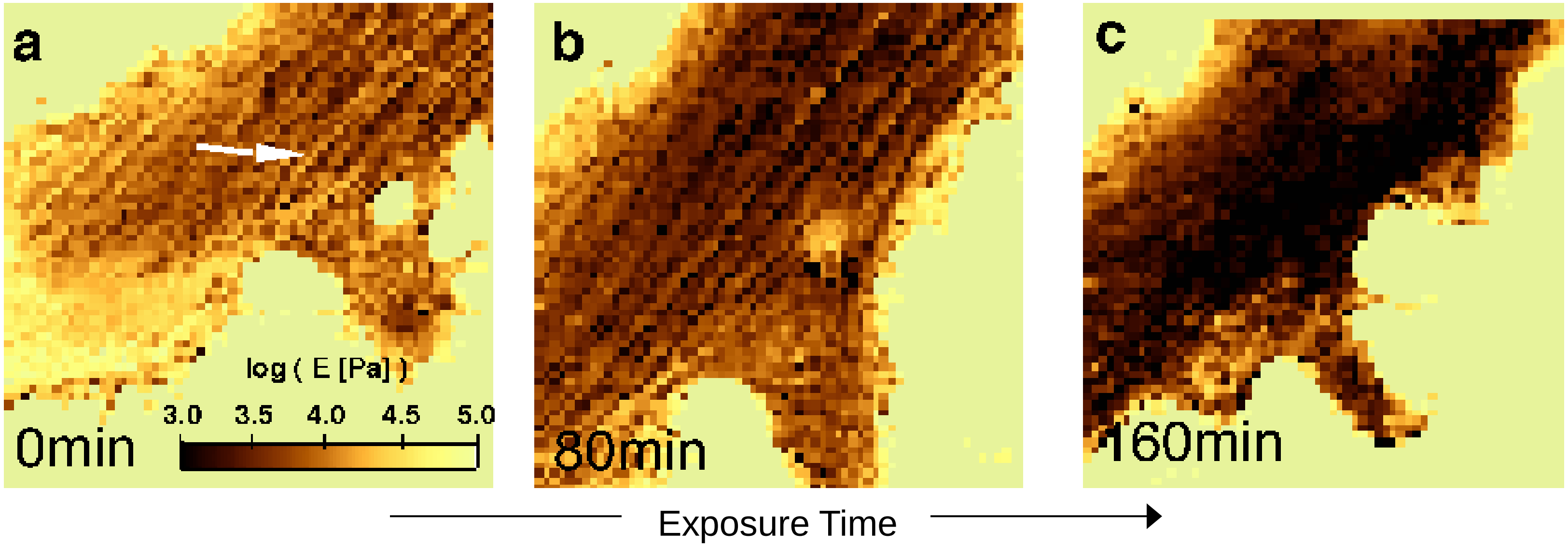
- A force-distance curve in each pixel of the image
- The force-distance curve is ‘triggered’: the Z movement stops when a user-defined force (trigger) is reached. The Z position at this force is used to construct the Height image
- All force distance curves are sued to create ‘force slice’ images.



Force mapping in mechanobiology – conventional approach

- 2-Dimensional array of force curves conducted over a defined scan area.
- Disassembly of actin filaments after treatment of living 3T3 fibroblast cells with the drug Cytochalasin B.
- Slow acquisition speeds and low resolution have hindered wide adoption.

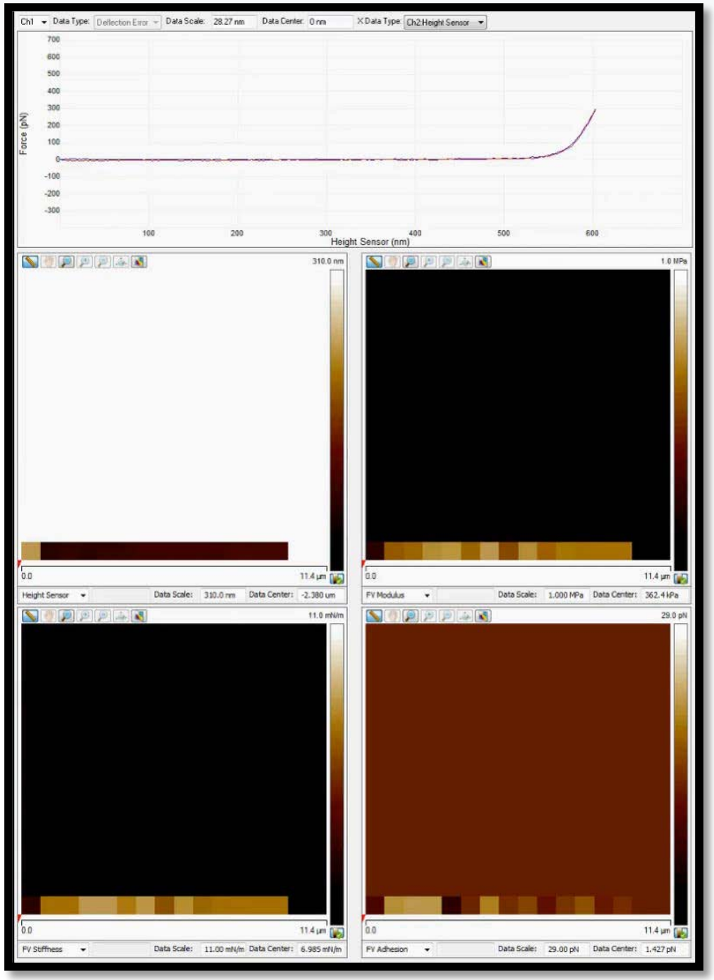




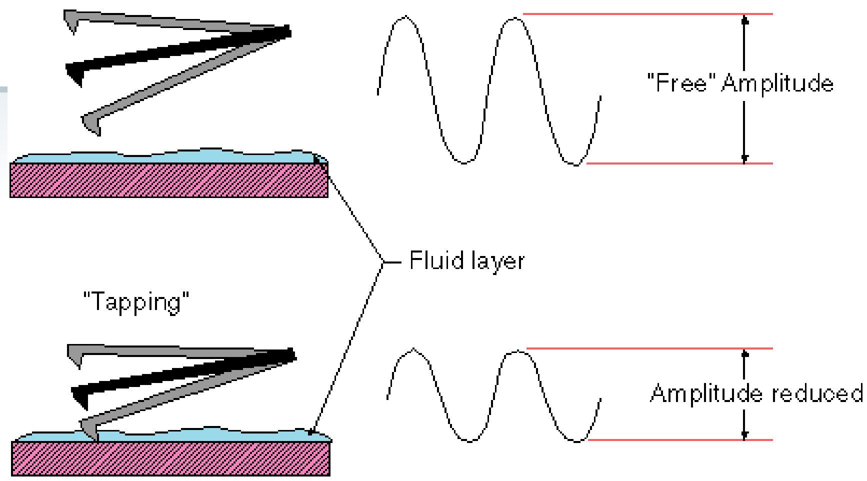
Radmacher et al. (2000) Biophys. J., vol 78: 520-35.

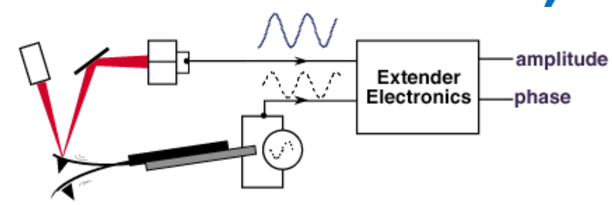
Widest Range – High Speed Quantitative Data with FASTForceVolume

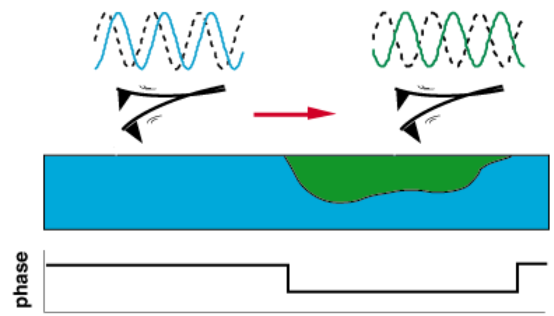
- Highest speed linear ramping, to 300Hz
- All the data: pixel resolution up to 256x256x2048 or 956x956x256
- Real-time analysis: Instant property channels incl adhesion and modulus
- Force control with <50pN low force trigger
- Study time dependence – closes gap between traditional slow ramps and PeakForce Tapping



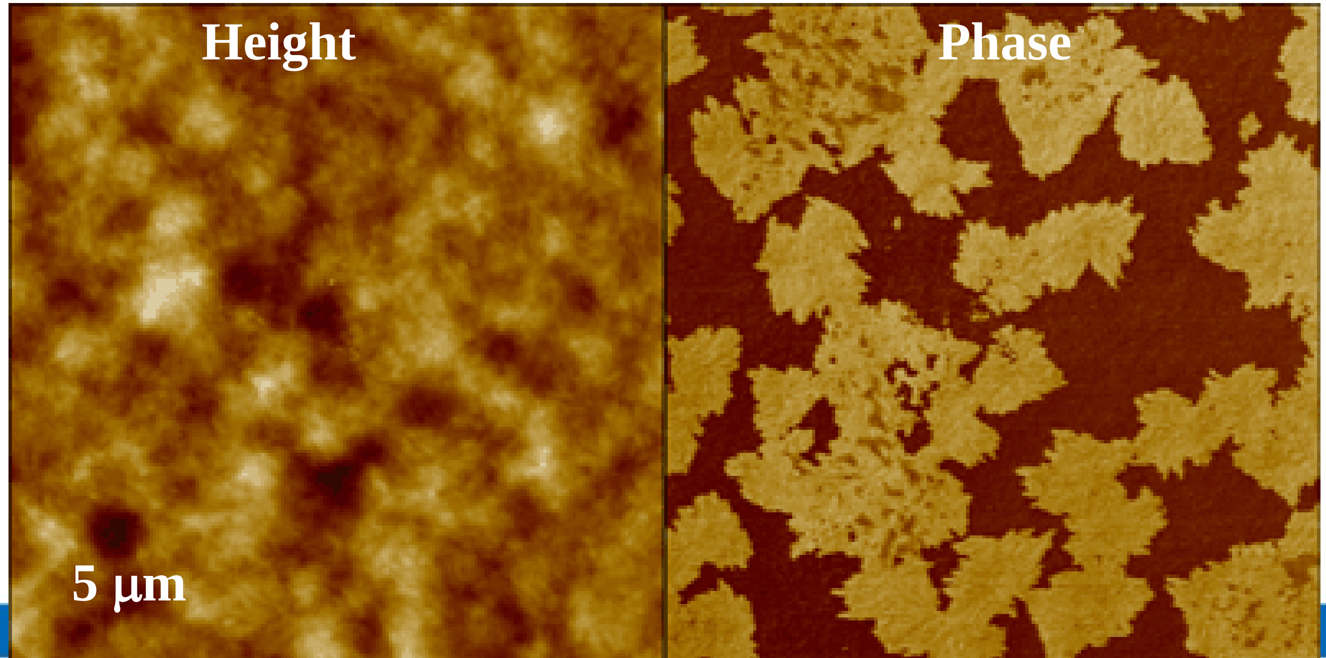
Phase Imaging for mechanical contrast





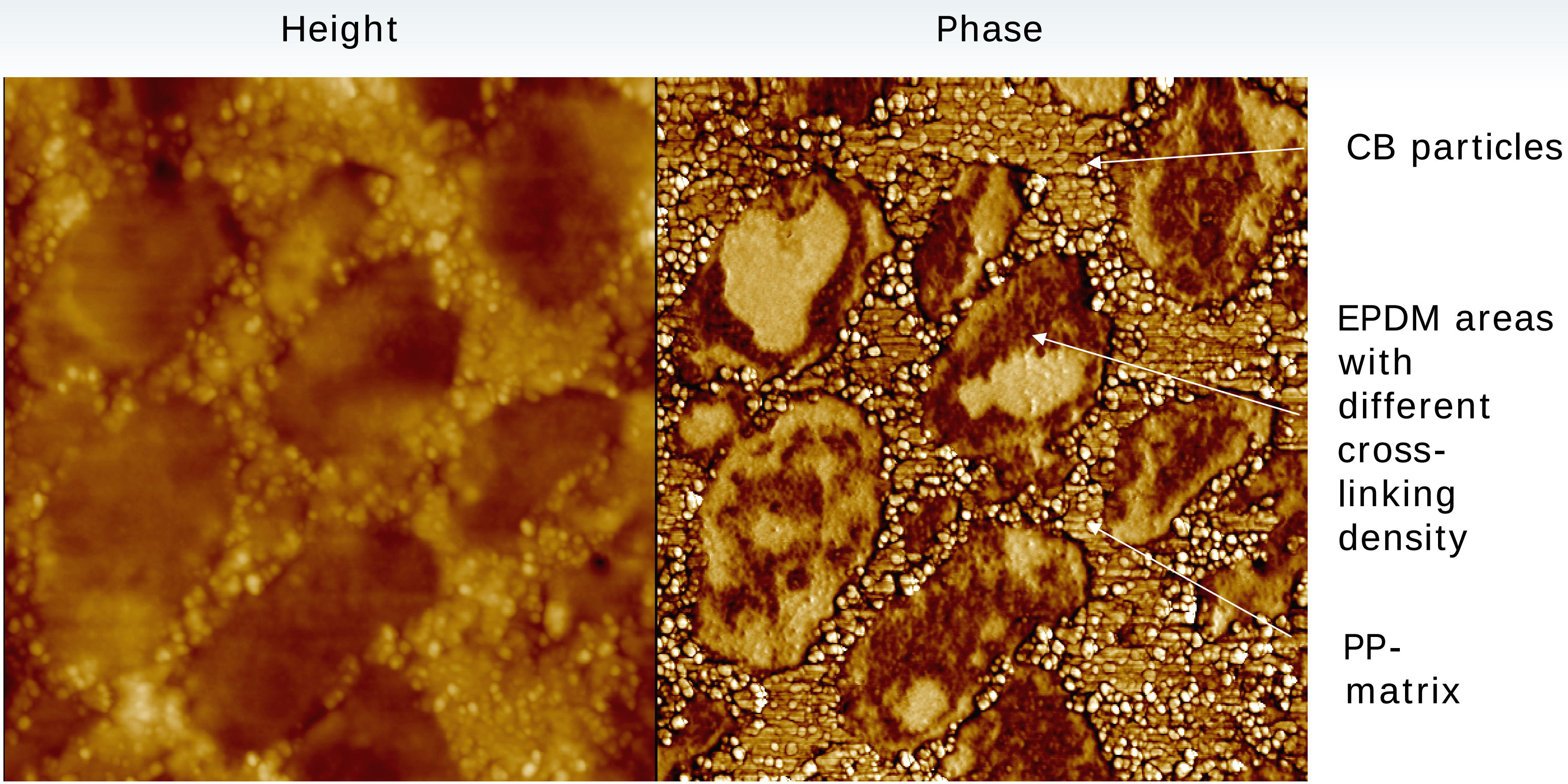


Polyurethane material



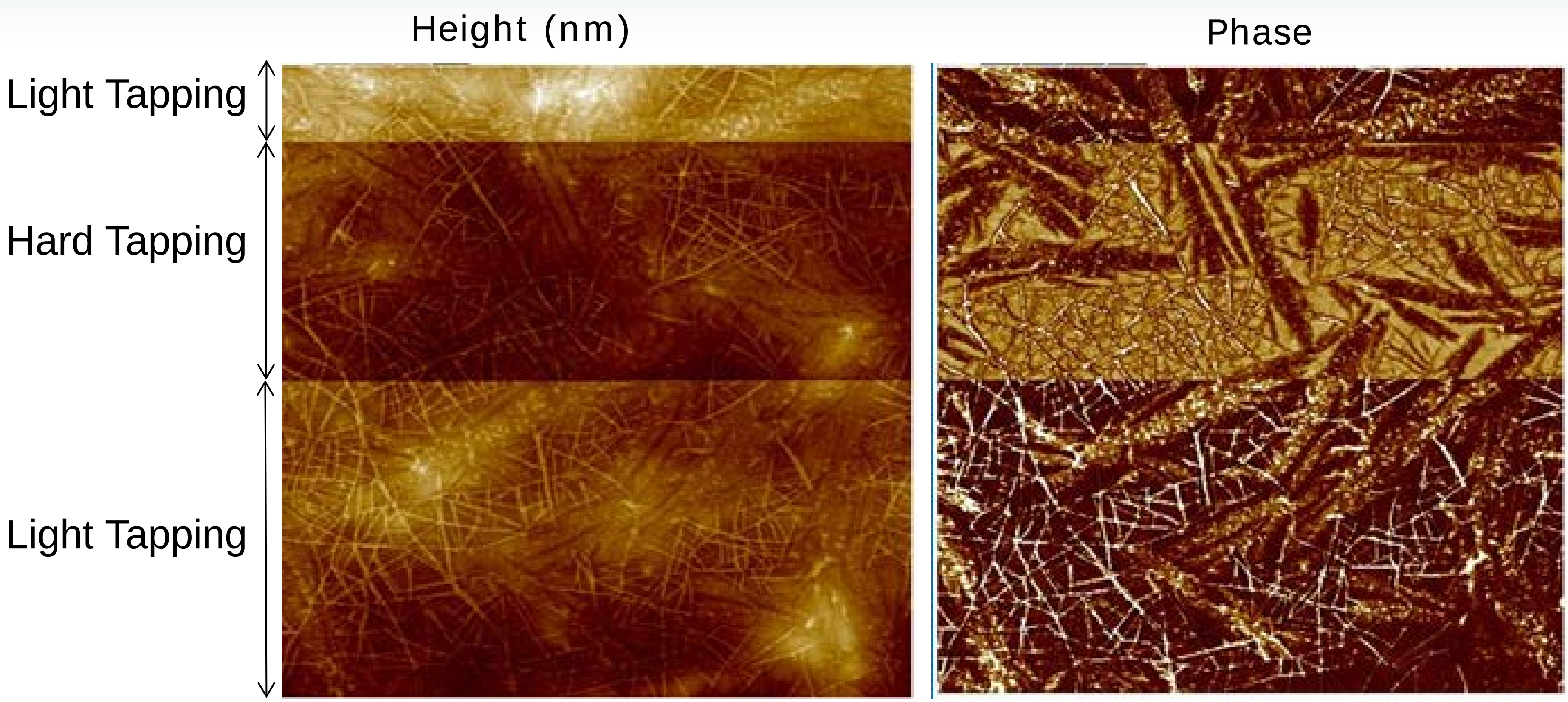
Sample courtesy
Y.Tang, U.of Toronto

Phase Imaging:
Component maps, more complex
- Rubber Material (EPDM+iPP+CB), 5um scan



Phase imaging shows high sensitivity, allowing one to differentiate different components

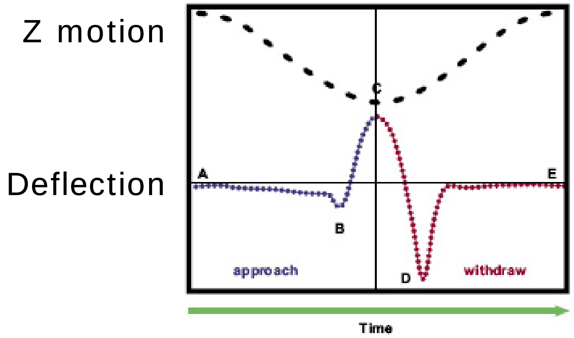
Phase contrast highly variable
- Polypropylene-Rubber blend, 5um scan

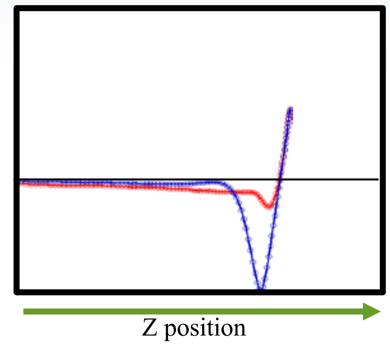


Limitation: Phase images strongly depend on parameter settings (drive amplitude & amplitude setpoint) and can even reverse contrast

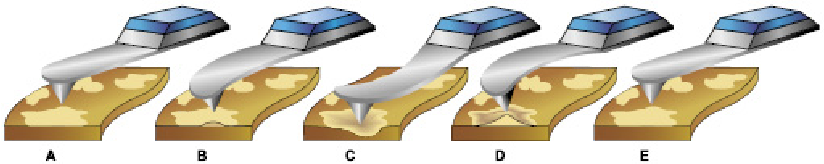
PeakForce Technology

Controls and measures force as feedback





Resembles a typical force curve…

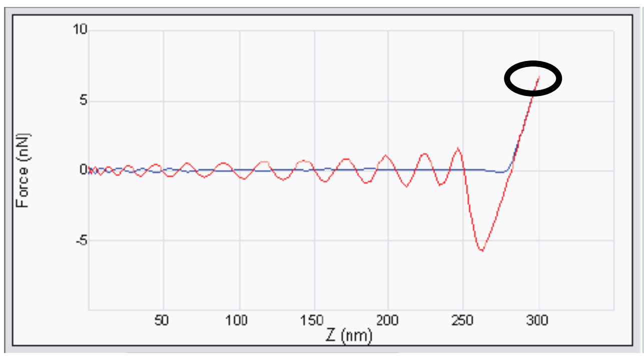


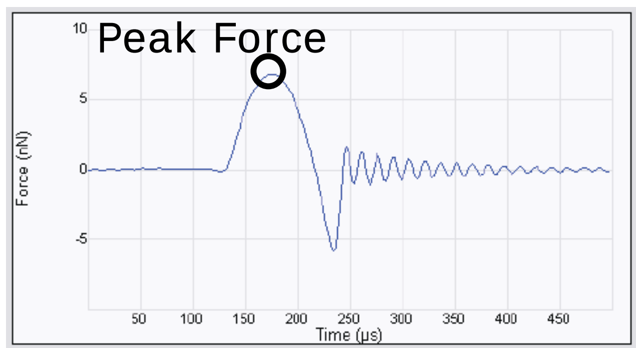
PeakForce Mode:

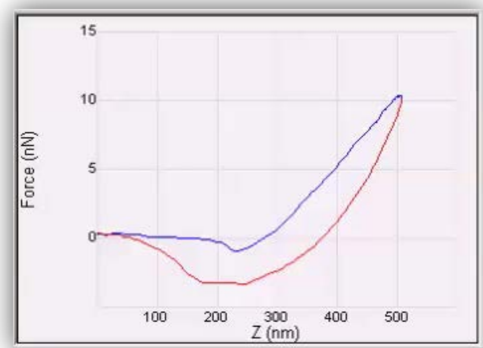
- Probe modulated at small amplitudes at low frequency (1-2kHz).
- Feedback signal is peak force between tip and sample.
- Direct control of imaging forces with ultra-low setpoints (<100pN).
- Images acquired at typical scan rates (1000's force curves/sec).

PeakForce Mode

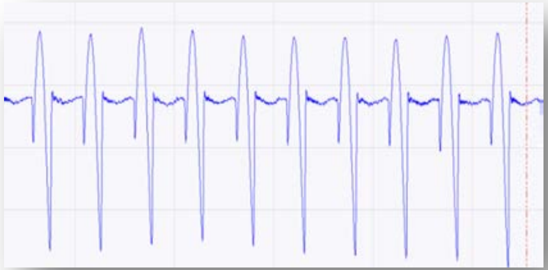
- When the linear motion is replaced with a sinusoidal motion, we can ramp much faster: for example 2kHz *– this is unique*
- Instead of ‘force trigger’, we will use true feedback on the maximum or ‘peak force’ = much *better force control*





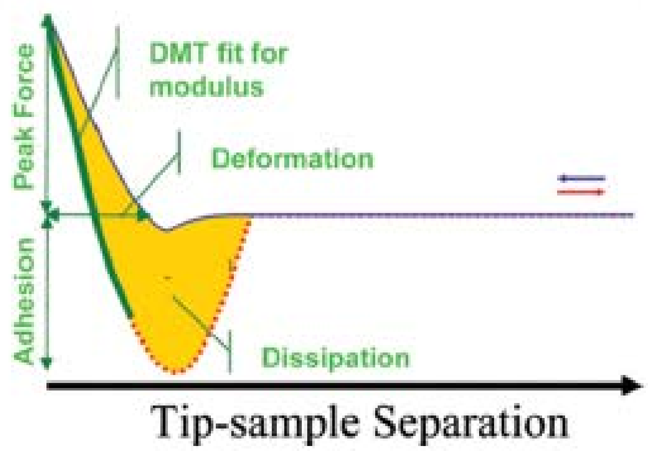


- Result:
  - Standard imaging speed
  - Full force mapping
  - Extreme good force control (down to < 20 pN)

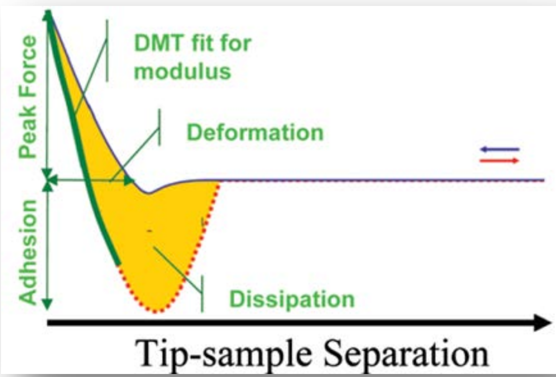


PeakForce QNM

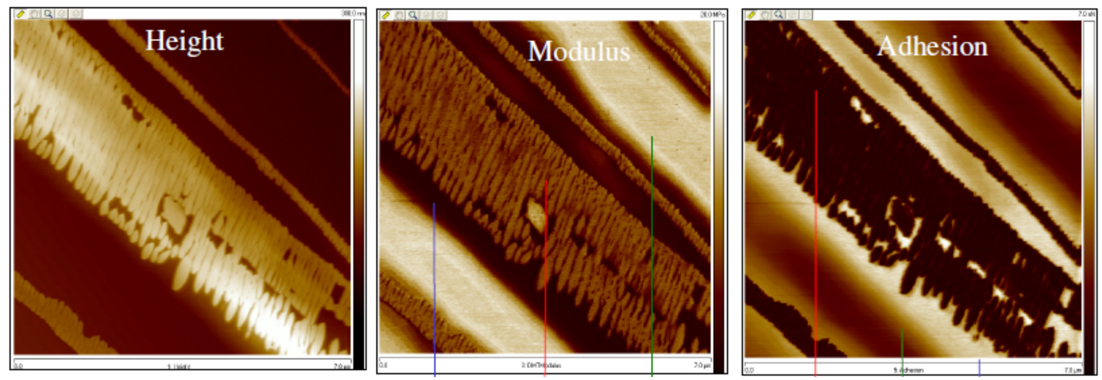
Topography and material property channels collected simultaneously in a single scan

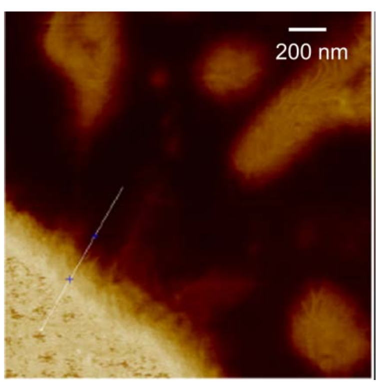


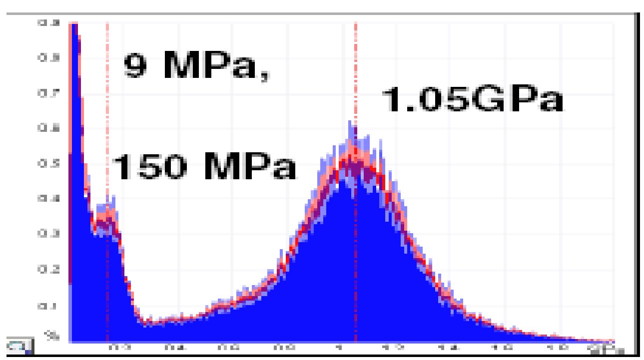
Quantifying PeakForce QNM data



Height, Modulus & Adhesion maps of Polydiethylsiloxane (PDES) on Si showing the 3 different materials with high resolution and in normal imaging time (9 min for 512x512 image)



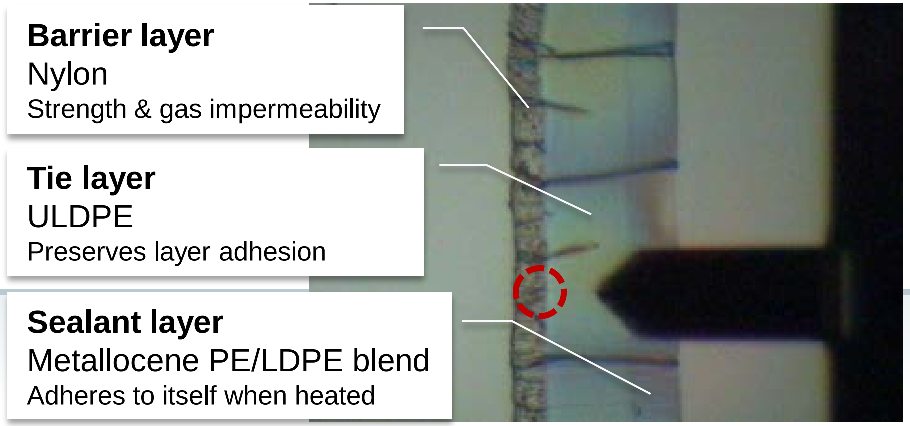


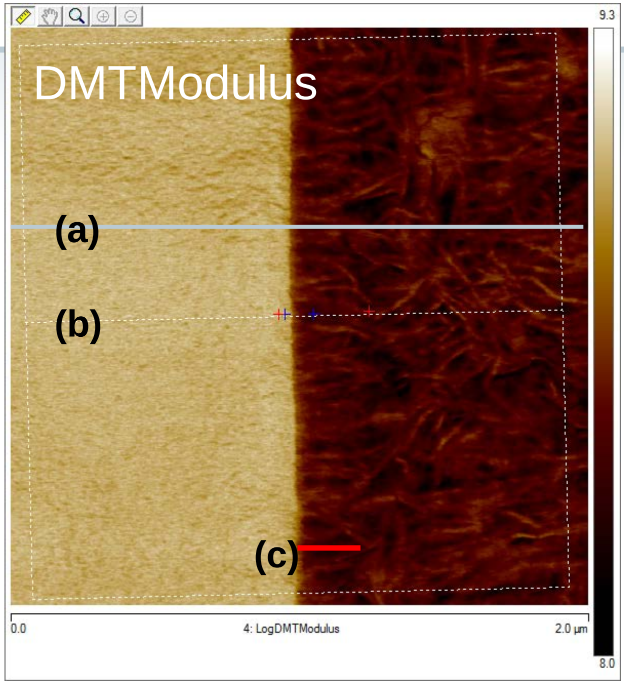


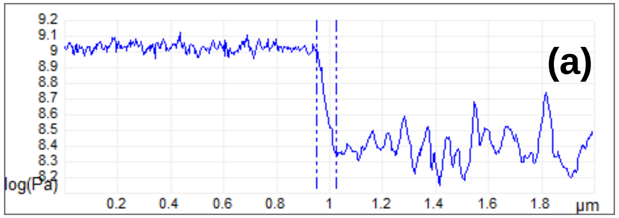
3-compound polymer: hard matrix with rubbery inclusions & semi-crystalline phases. The modulus image & histogram show the 3 materials with high resolution.

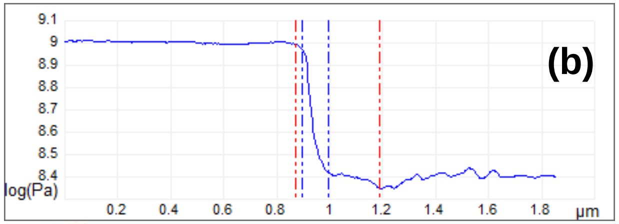
Polymer composites

Heat-sealed bag







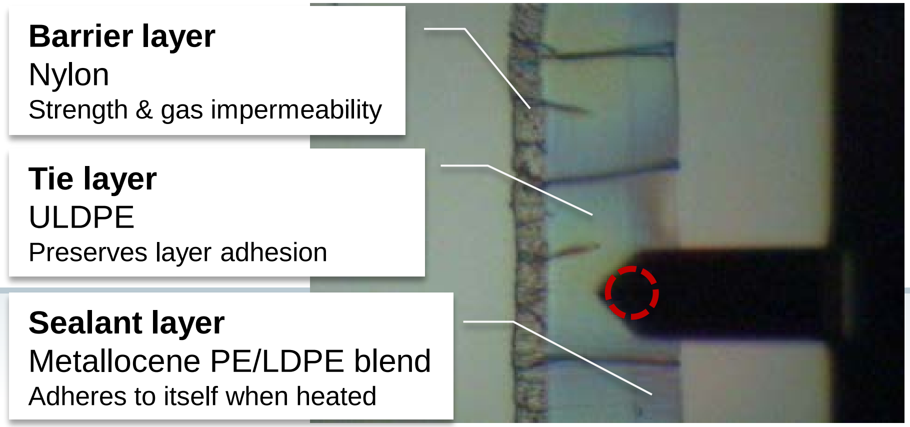


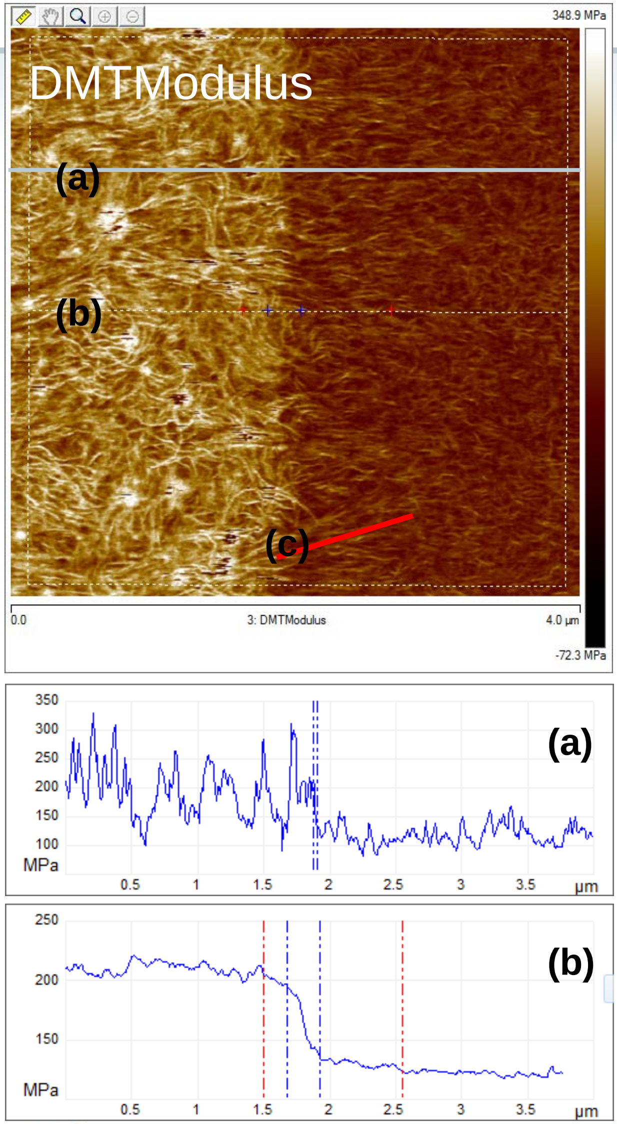
Barrier and Tie layers are incompatible, so we expect a relatively abrupt interphase.

- Single scan line has a clear step in modulus over a distance of ~75nm.
- Lamella do not cross the interface, but grow epitaxially from the Barrier layer ~250nm into the Tie layer.

Polymer composites

Heat-sealed bag



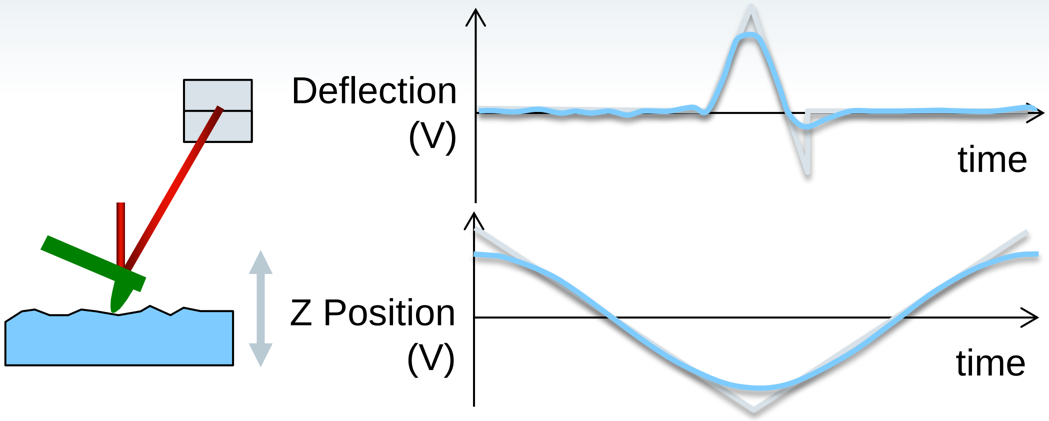


Tie and Sealant layers are more compatible, so we expect a wider interphase.

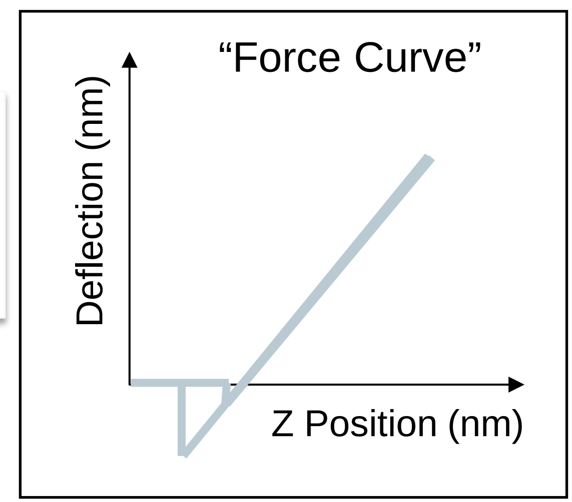
- Single scan line: the variation in modulus is dominated by individual lamella.
- Collectively: modulus varies over a much wider range ~250nm to ~1um.
- Lamella from Tie layer act as nucleation sites or penetrate into the Sealant layer resulting in a more ordered region up to ~1um from the interface.

Analyzing Force Curves: FV & PFT

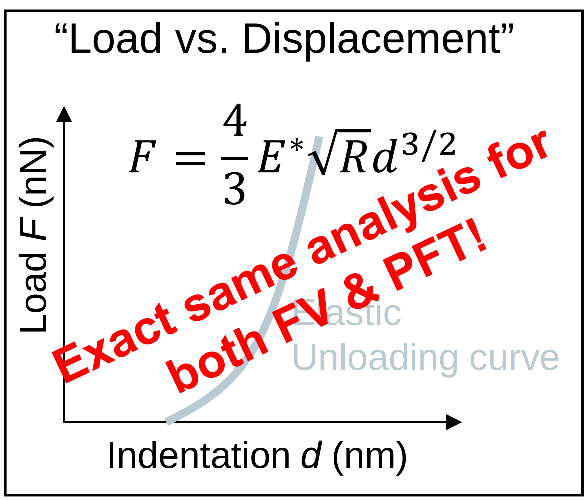
From Deflection and Z to modulus



1. Eliminate time
2. Apply 'Deflection sensitivity'
3. Apply 'Z sensitivity'

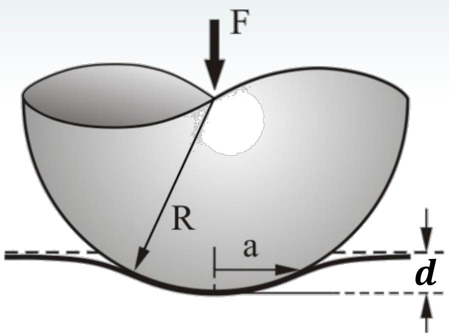


4. Calculate indentation
5. Apply 'Spring constant'
6. Fit data with contact mechanics model

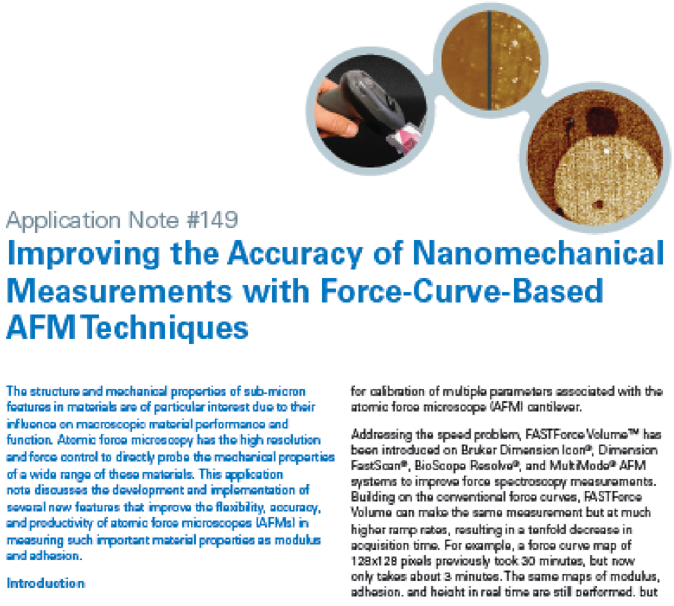


Force Volume Error Analysis

- Potential sources of error include:
  - Tip radius (*R*) ~ 15%
  - Spring constant (*Kc*) ~ 6-16%
  - Deflection sensitivity (*Sd*) ~ 5%
  - Deflection voltage (*V*) ~ 1%
  - *Z* position ~1%



- Conclusion
  - Low modulus limit is dominated by error in R and Kc
  - High modulus limit dominated by error in Z and Deflection Sensitivity



Application Note #149

Improving the Accuracy of Nanomechanical Measurements with Force-Curve-Based AFM Techniques

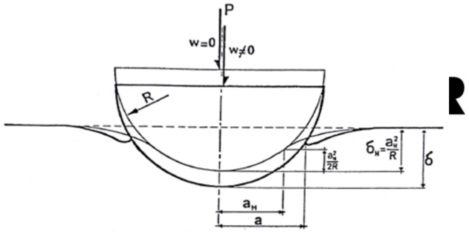
The structure and mechanical properties of sub-micron features in materials are of particular interest due to their influence on macroscopic material performance and function. Atomic force microscopy has the high resolution and force control to directly probe the mechanical properties of a wide range of these materials. This application note discusses the development and implementation of several new features that improve the flexibility, accuracy, and productivity of atomic force microscopes (AFMs) in measuring such important material properties as modulus and adhesion.

Introduction

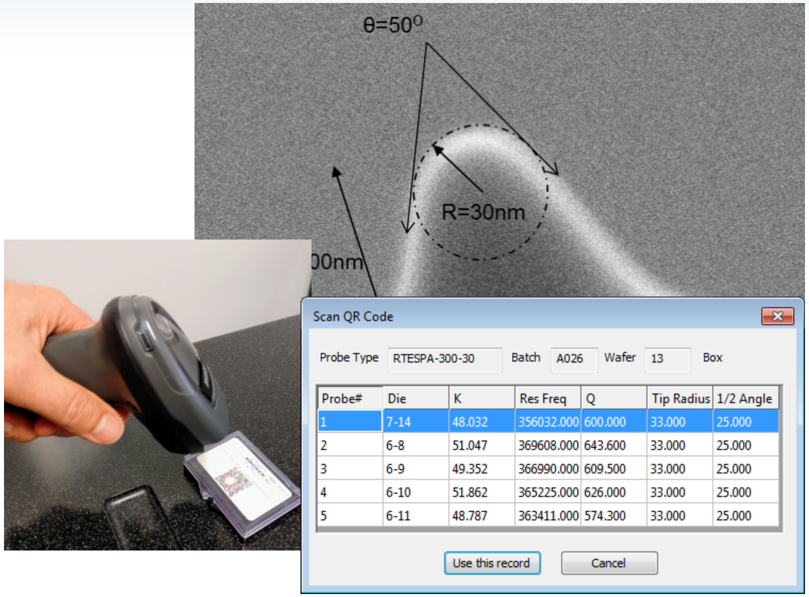
for calibration of multiple parameters associated with the atomic force microscope (AFM) cantilever.

Addressing the speed problem, FASTForce Volume™ has been introduced on Bruker Dimension Icon®, Dimension FastScan®, BioScope Resolve®, and MultiMode® AFM systems to improve force spectroscopy measurements. Building on the conventional force curves, FASTForce Volume can make the same measurement but at much higher ramp rates, resulting in a tenfold decrease in acquisition time. For example, a force curve map of 128x128 pixels previously took 30 minutes, but now only takes about 3 minutes. The same maps of modulus, adhesion, and height in real time are still performed, but

How did we improve the accuracy of Force Volume & PeakForce Tapping?



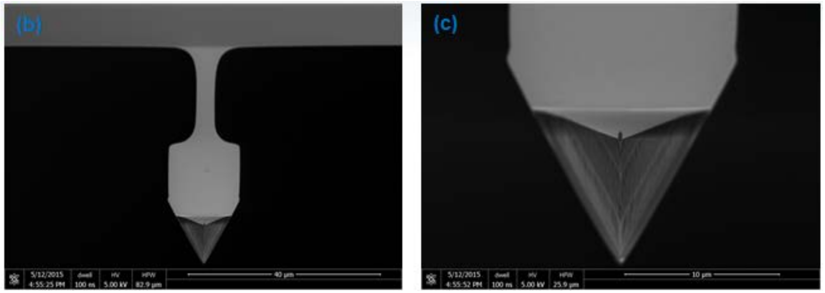
- New probes for materials
  - LDV calibrated spring constants
  - Controlled tip radius =33nm
  - Selection of spring constants to cover range of moduli
    - 0.25, 5, 40, 200 N/m



- New probes for cellular work
  - Calibrated spring constant <0.1N/m
  - Controlled tip radius =65nm
  - Tip Height – 17um

- Guided calibration software for deflection sensitivity

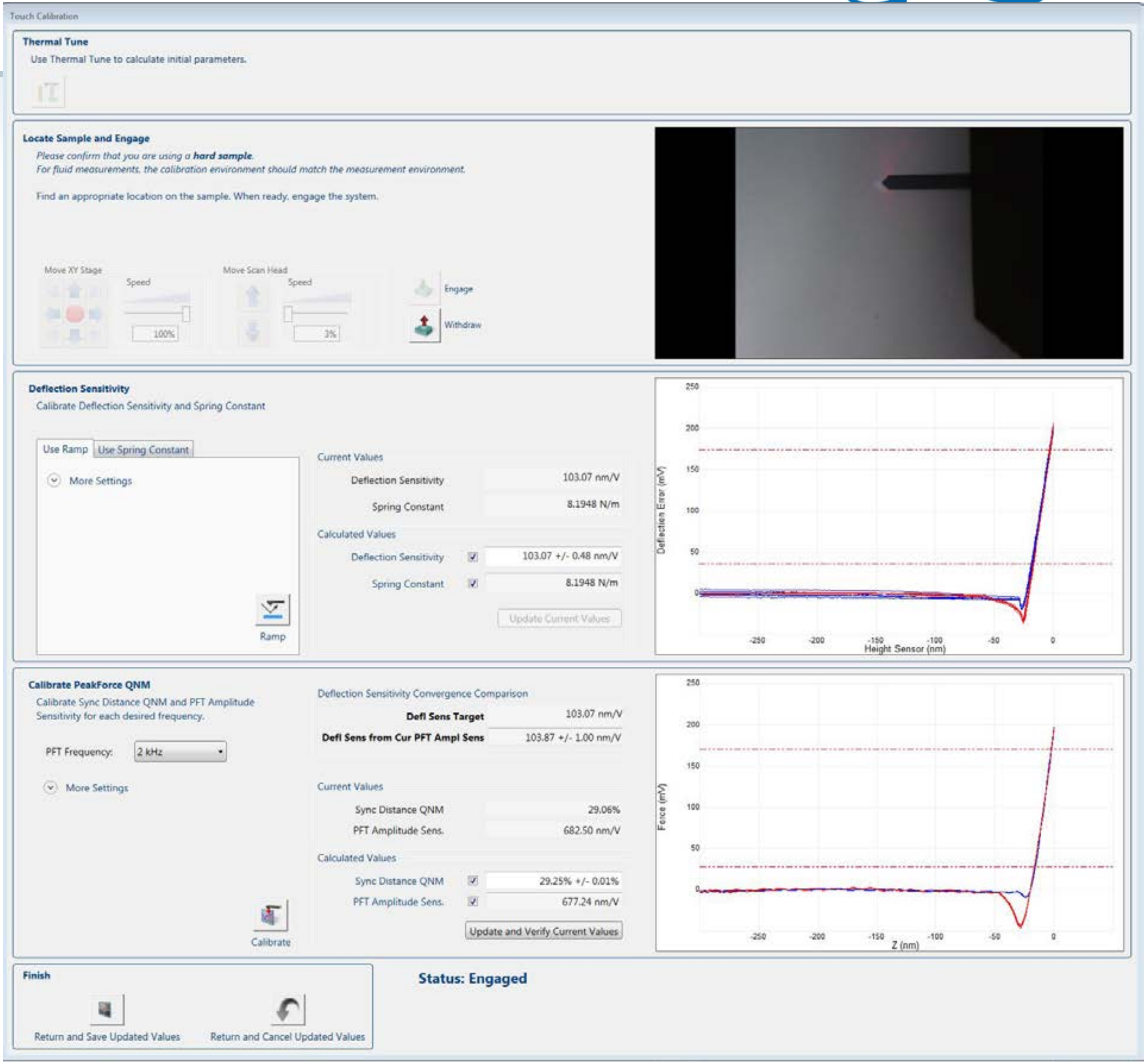
- Better contact modeling



PeakForce QNM – Guided calibration

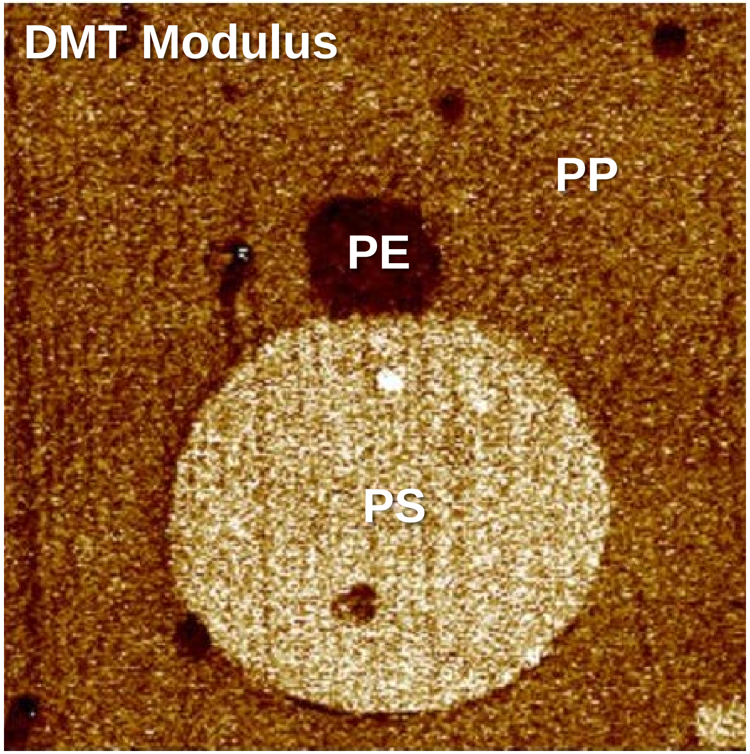
Touch Calibration

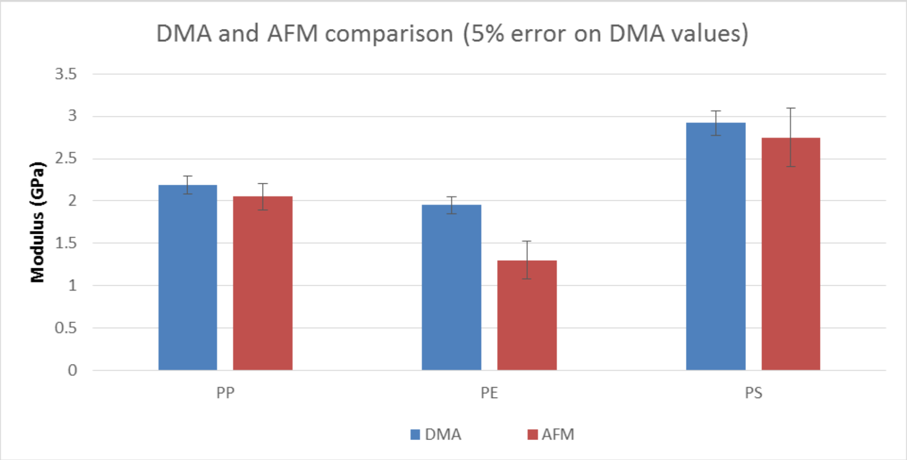
- High accuracy, guided calibration of key parameters for force spectroscopy and PF-QNM
  - Calibrates Deflection Sensitivity, Spring Constant, QNM Sync Distance, PFT Amplitude Sens
- **No-Touch calibration also available**
- Spring constant calibration by Thermal Tune or Sader Method



Accuracy of PF-QNM (vs. DMA)

Ternary polymer blend

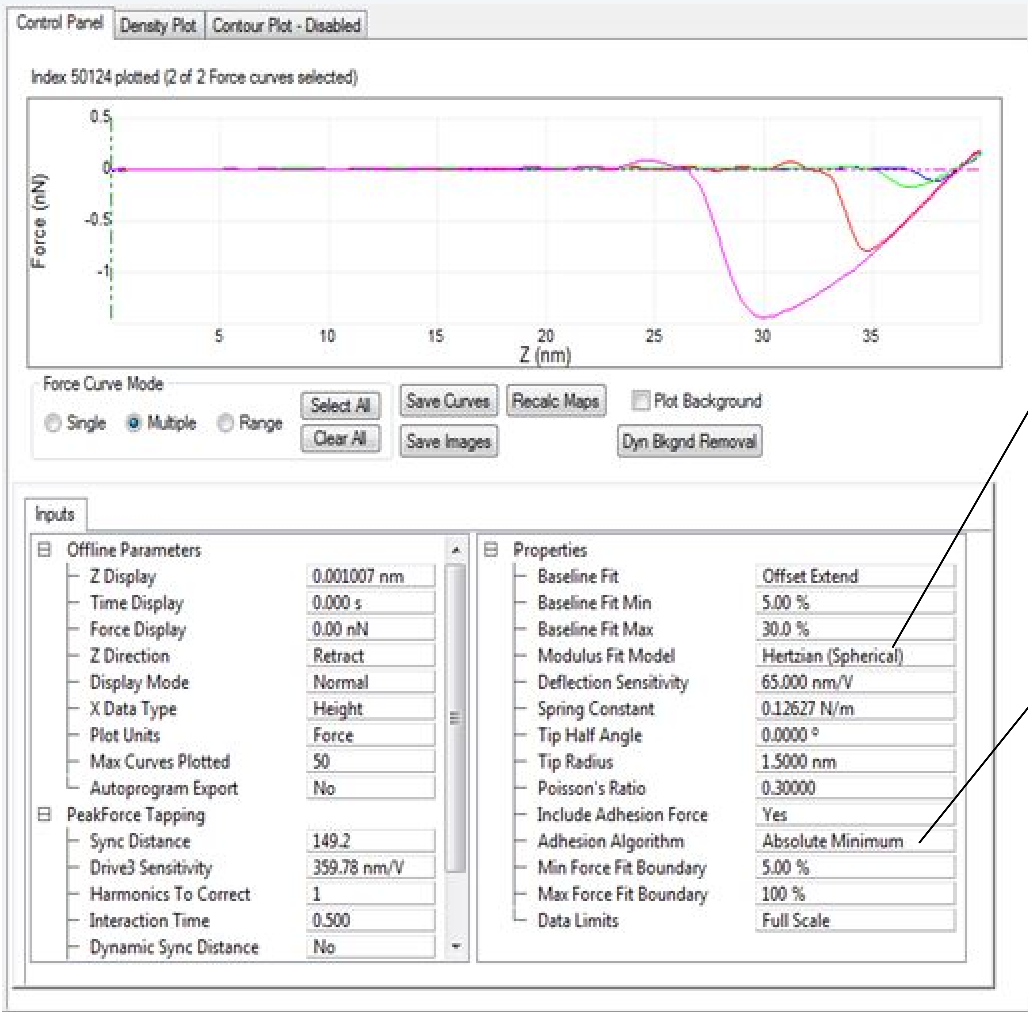




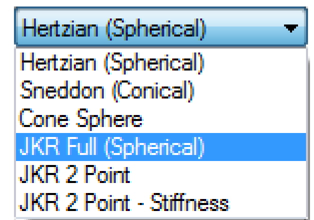
	PP	PE	PS	PE:PP	PS:PP
DMA	2.19	1.95	2.92	0.89	1.33
avg AFM	1.98	1.24	2.63	0.62	1.32
stdev	0.16	0.22	0.35	0.08	0.10
stdev/avg	8%	18%	13%	12%	8%
DMA-AFM	10%	45%	10%	36%	1%

Force spectroscopy maps can be collected using PeakForce Capture during PeakForce QNM imaging, or FastForce Volume

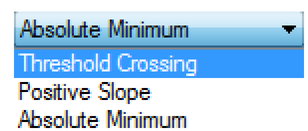
Recalculation of saved data with different models for modulus and adhesion



PeakForce Capture provides the force curve at each pixel up to 256x256



Modulus models



Adhesion models

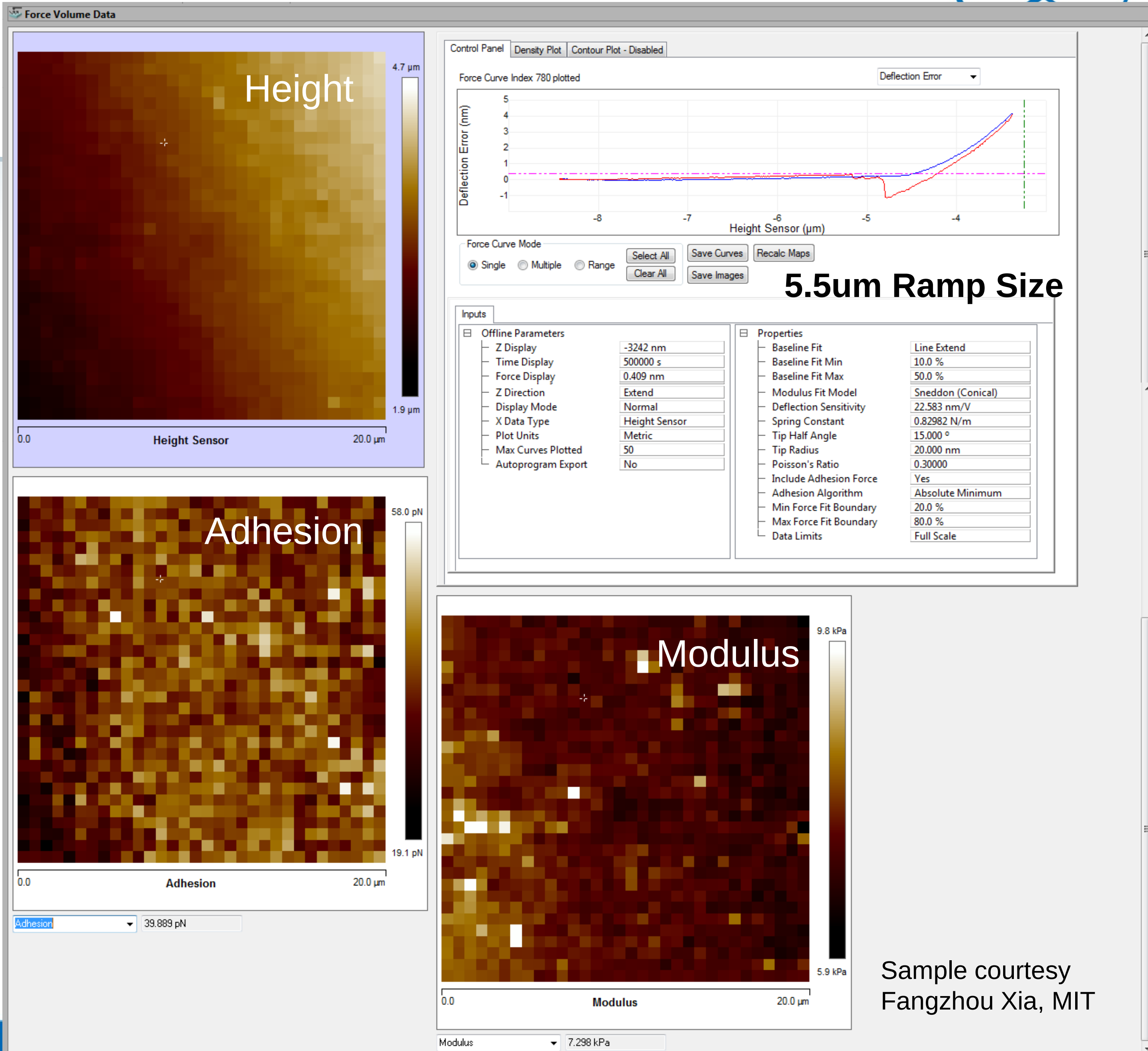
Individual force curves can be accessed and analyzed at each pixel.

Modulus, Adhesion, and Stiffness maps can be recreated using different models or acquisition parameters, such as spring constant or deflection sensitivity

Hydrogel in fluid - FastForce Volume map 20um area

Each image of force data can be saved and analyzed individually

Often use Live Cell pre-calibrated probes for this measurement on Hydrogels

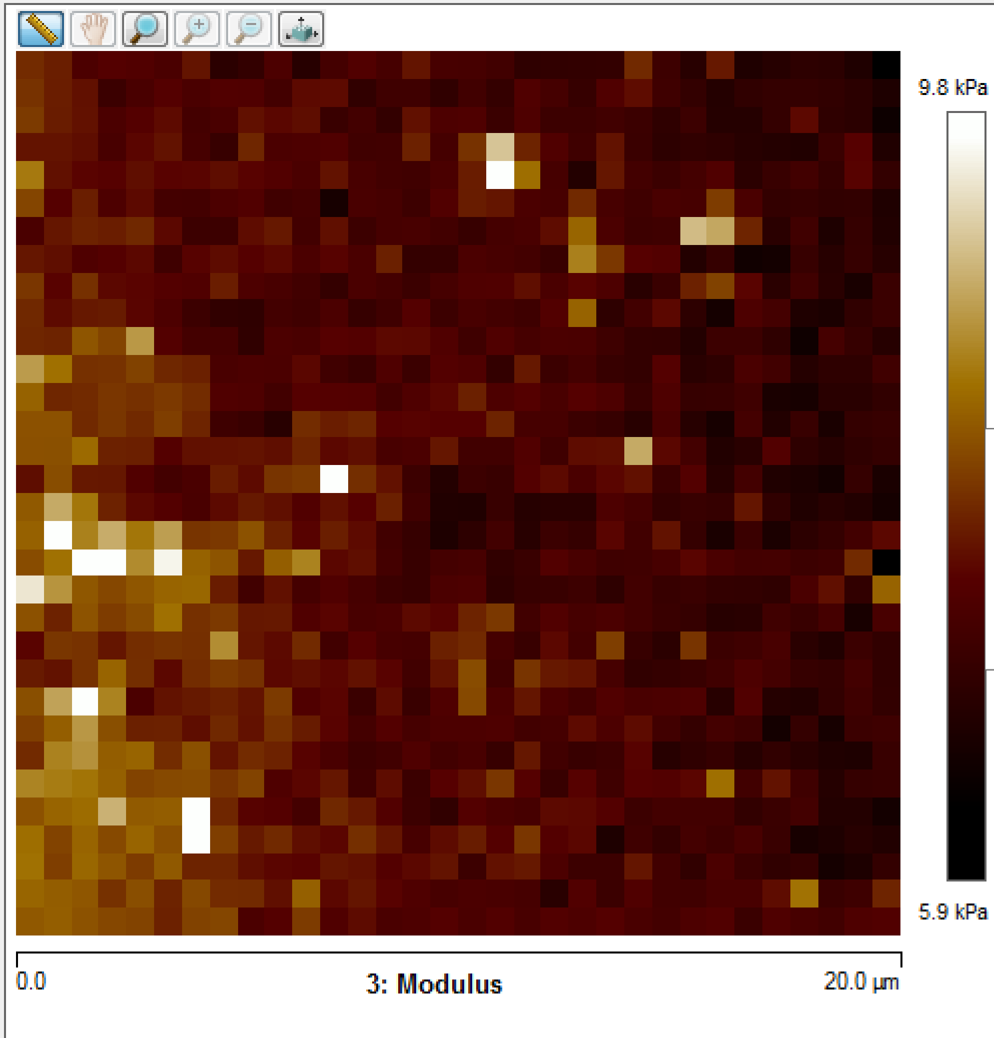


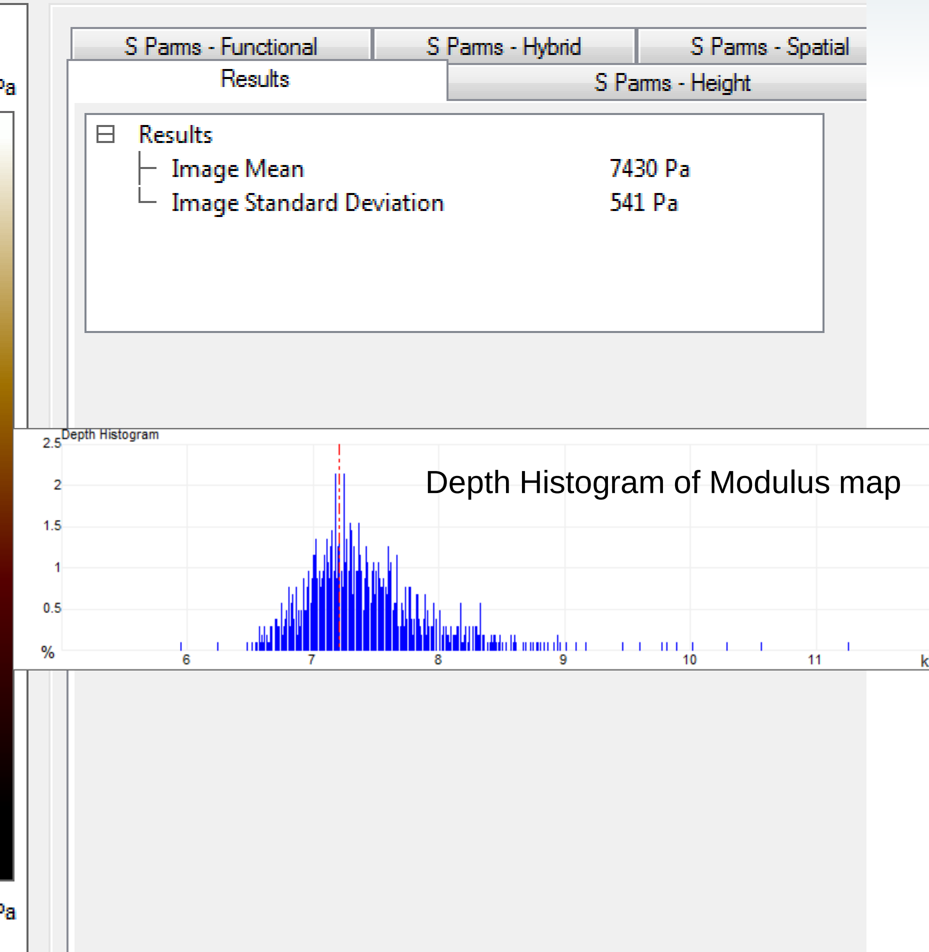
Sample courtesy Fangzhou Xia, MIT

Modulus map – 20um area

Using Sneddon model for modulus calculation

Mean value = 7.4kPa, Std Dev 0.541kPa



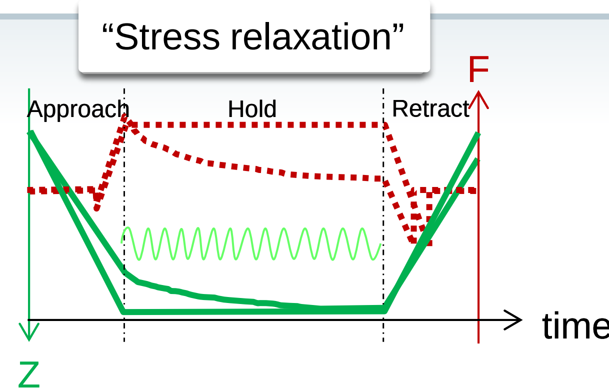


Sample courtesy Fangzhou Xia, MIT

Ramp & Force Volume Expansion

Ramp&Hold based measurements

- **Relaxation: best for very soft samples with long relaxation times**
  - Hold Force or Z sensor
  - Measure Z sensor or Force
  - Fit hold data to calc. viscoelastic props
- **Force Modulation: best for moderate stiffness samples**
  - Add modulation: single frequency or sweep during hold
  - Measure amplitude and phase at frequencies far below contact resonance
  - Calculate storage & loss modulus from hold data
- **Contact Resonance: best for stiff samples**
  - Add modulation: sweep frequency while holding force
    - Range chosen to cover contact resonance
  - Fit CR peak to find f, Q
  - Calc. storage & loss modulus from f, Q



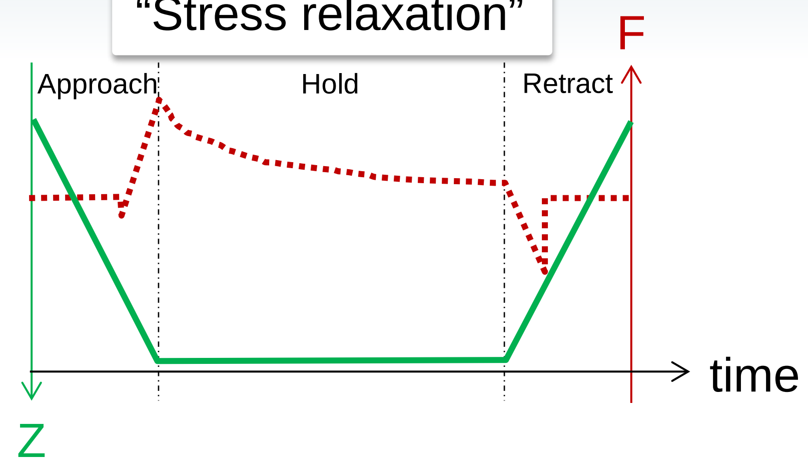
Trigger	
Trigger Mode	Relative
Data Type	Deflection Error
Trig Threshold	300.0 nN
Trig Safety	3.624 uN
Baseline Fit	0.00 %
Baseline Extrapolation	30.0 %
Surface Controls	
Hold Time	100 ms
Hold Samples	520
Hold Type	Trigger Force
Modulation Type	High Freq 2 to External
Modulate Amplitude	100 mV
Drive2 Frequency	400.0000 kHz
Lock-In2 Phase	0 °
Lock-In2 BW	1.000 kHz
Sweep Type	Drive2 Frequency
Sweep Start	400.0000 kHz
Sweep End	700.0000 kHz

Ramp&Hold Z or Force

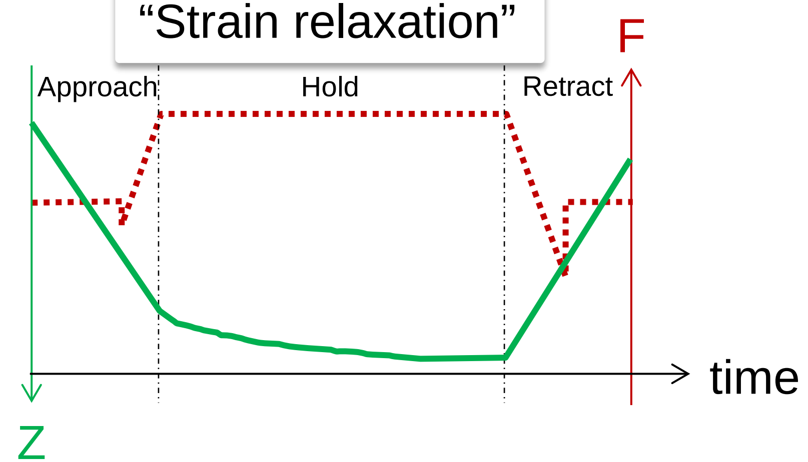
Stress or Strain Relaxation

- Hold Z, hold trigger force, or hold user defined force
- Integrated with Force Volume
- Easy: similar to ramp mode
  - Typical ramp time~0.1-10sec
  - Typical Hold time ~1-5000sec.
  - User definable sample rates
- For Ramp&Hold>a few sec, the plot is updated during acquisition and can be cancelled
- Offline analysis

“Stress relaxation”

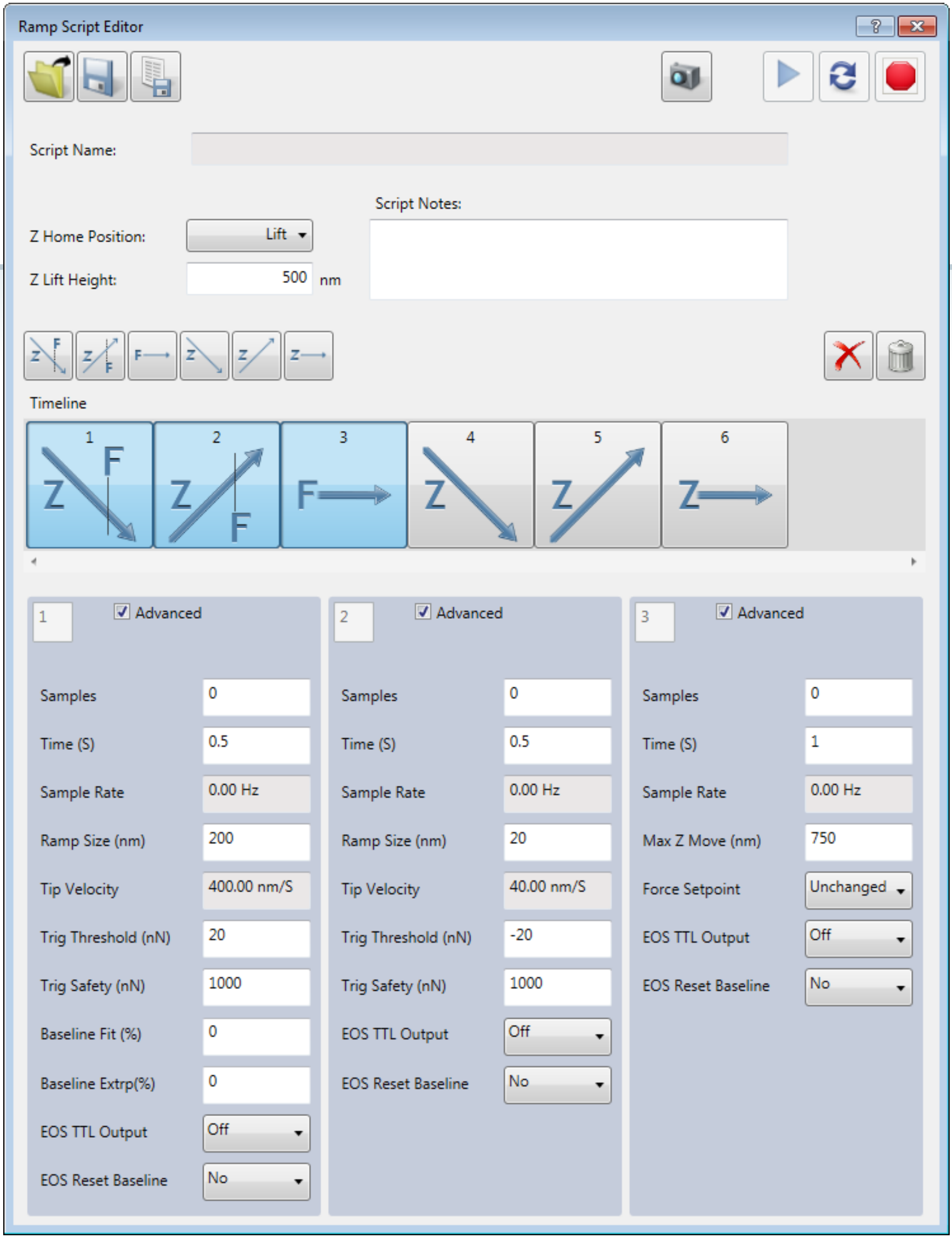


“Strain relaxation”



RampScript Editor

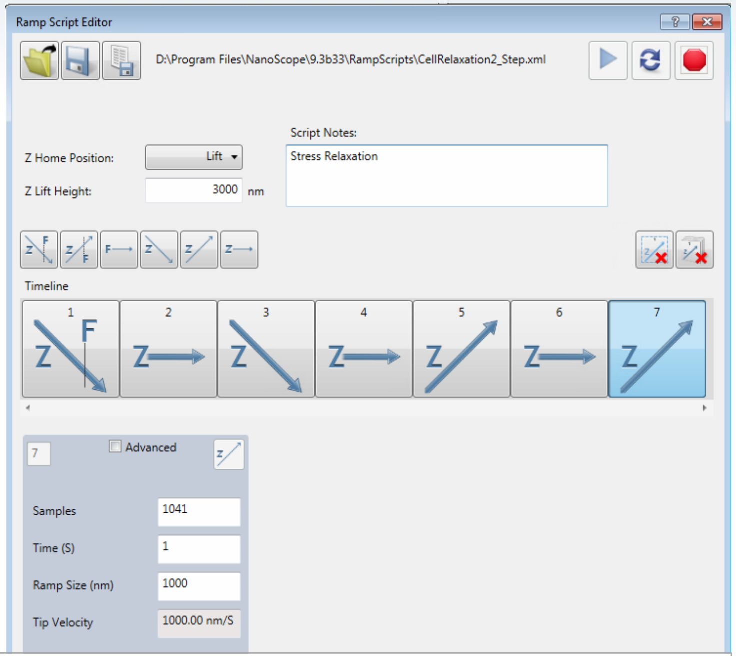
- Multi-segment types and control in a single script.
- Force Ramps and Frequency Sweeps.

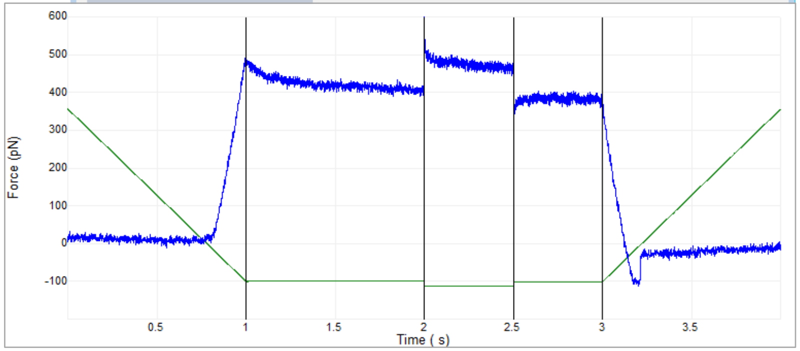


Viscoelastic Properties of Cells

Studying Time-Dependent Mechanical Properties

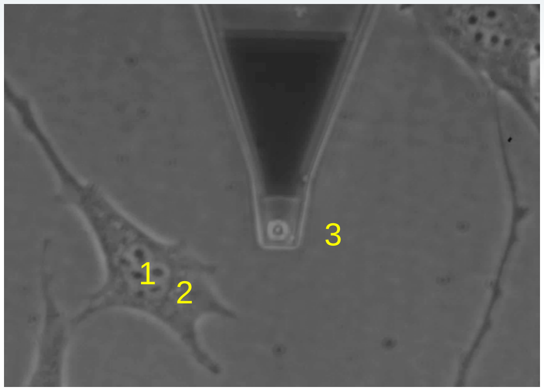
- To fully understand cell mechanics need to consider viscoelastic properties (time-dependent)
- Ramp Scripting on ICON and Resolve
  - Easy to use software interface for designing customized, advanced force measurement studies
  - Scripts can be conducted at single point positions or as an array for mapping viscoelastic properties



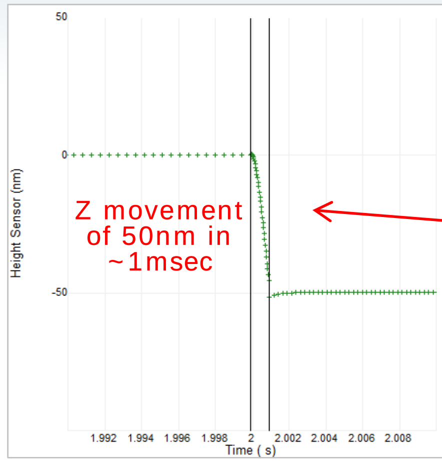


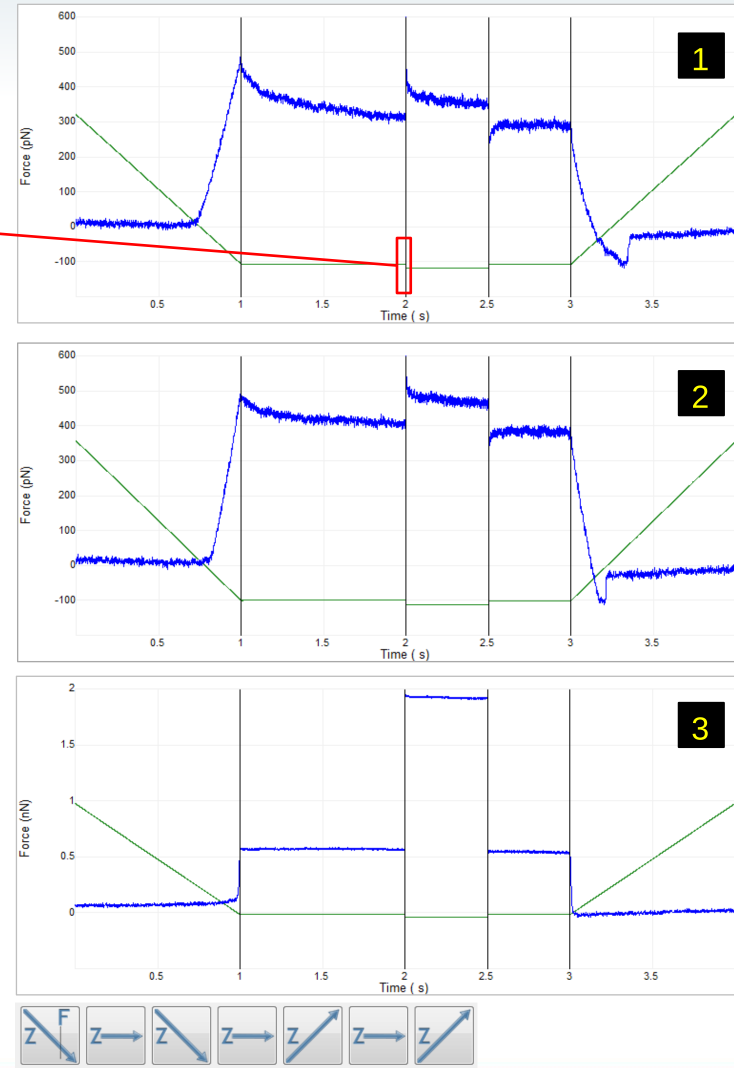
Ramp Scripting for Mechanobiology

Viscoelastic Creep Response of Living Fibroblast Cells



MIROView was used to target the:
(1) cell nucleus, (2) cell extension, (3) petri dish.
MLCT-Bio-DC probes (k~0.011N/m).



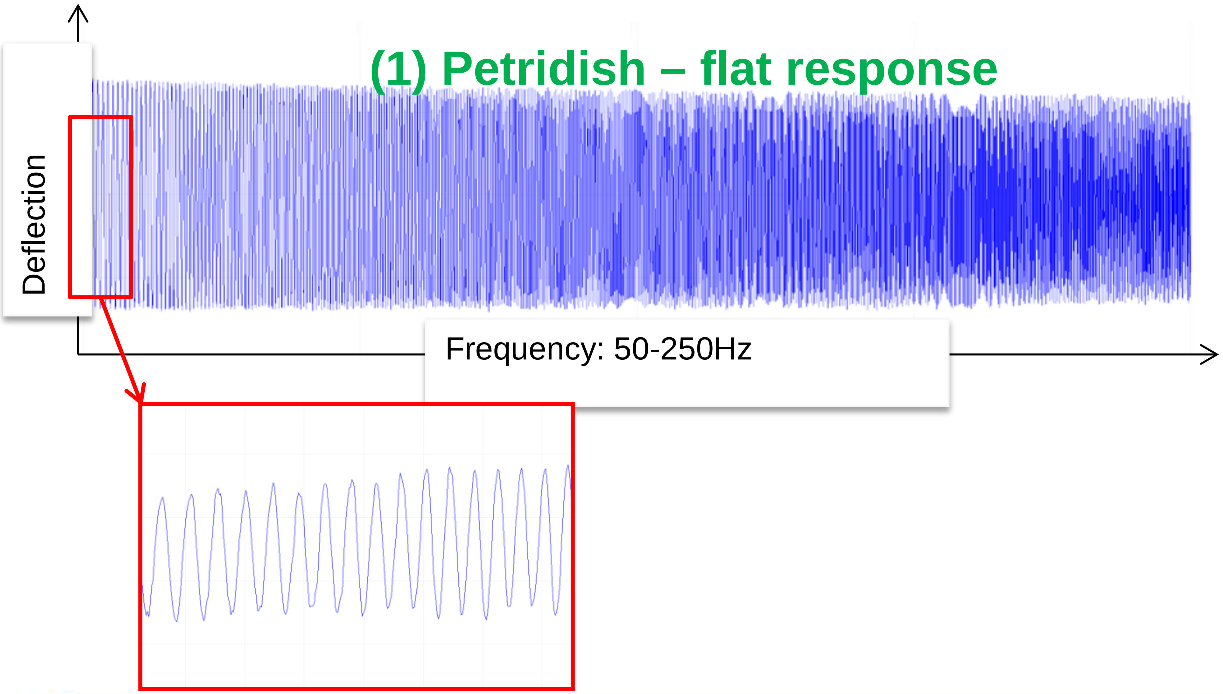


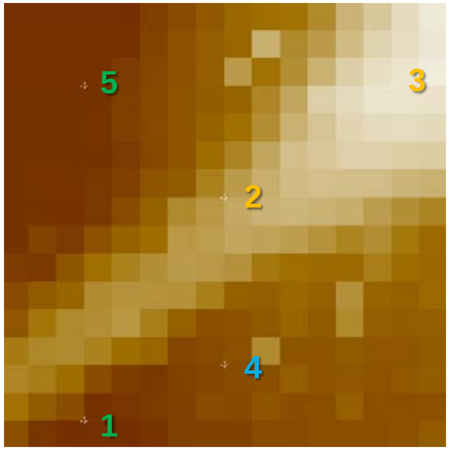
- Advantages of Ramp Scripting on Icon:
  - Fast feedback (z movement <10msec)
  - High stability (holds over several seconds)
  - Most sensitive force control (~10pN)
  - Per segment TTL for synchronization

In collaboration with Prof. Manfred Radmacher, Universität Bremen, Germany

New Force Hold with Frequency Sweep for Dynamic Mechanical Analysis

- New integrated frequency sweep during hold enables dynamic mechanical analysis (DMA).
- DMA provides frequency domain response spectrum. Amplitude and phase, can be converted to storage and loss modulus as function of frequency.

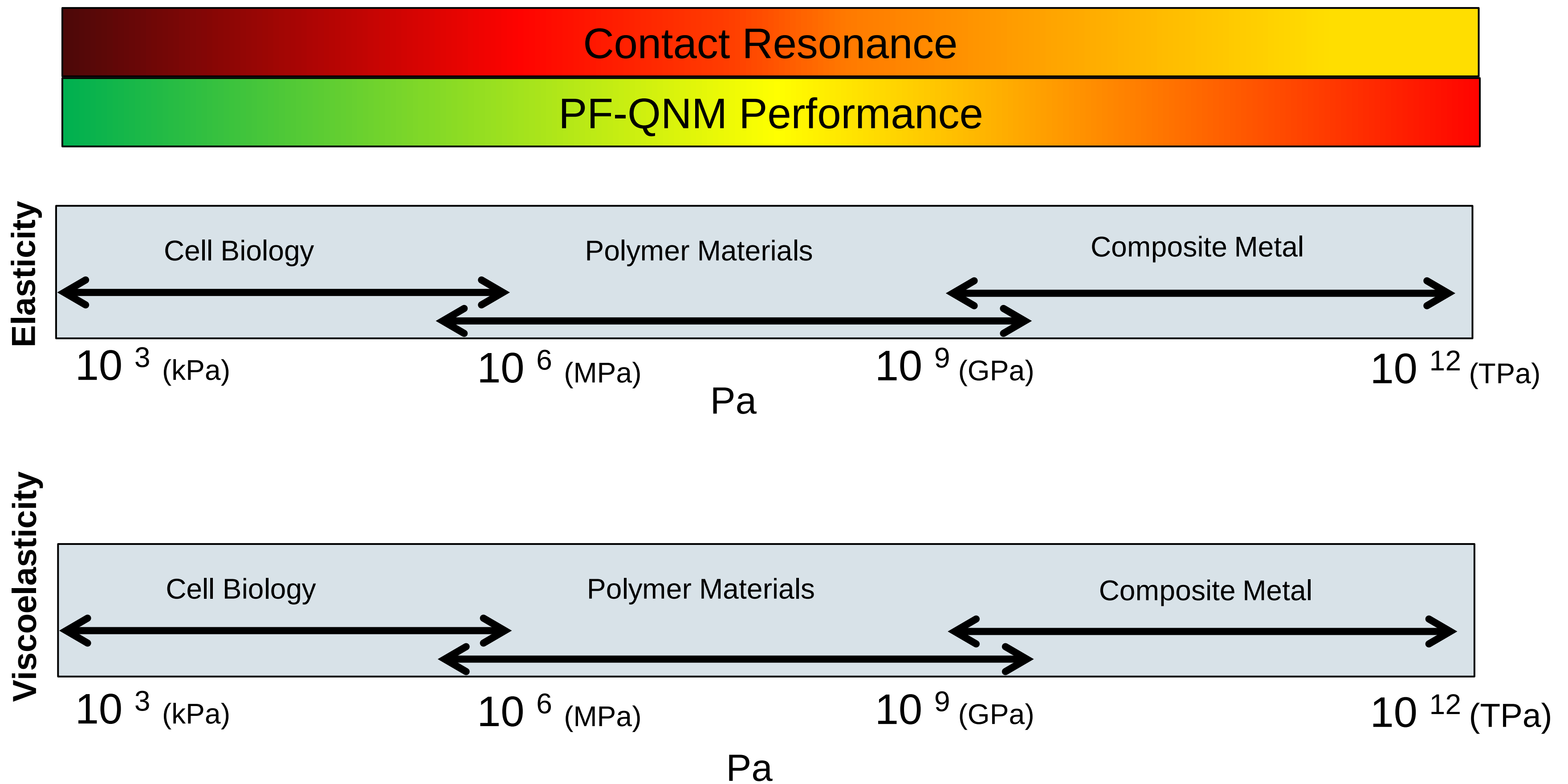




Elasticity and Viscoelasticity Characterization

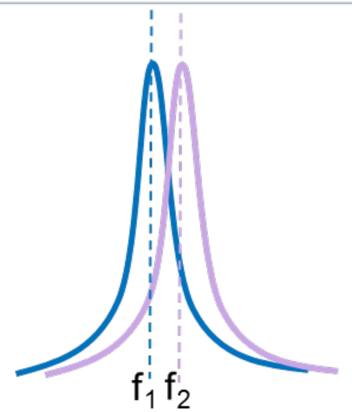
Accurate Measurements of Materials 1kPa to 300+ GPa

Complete Solution for Nanomechanical Characterization

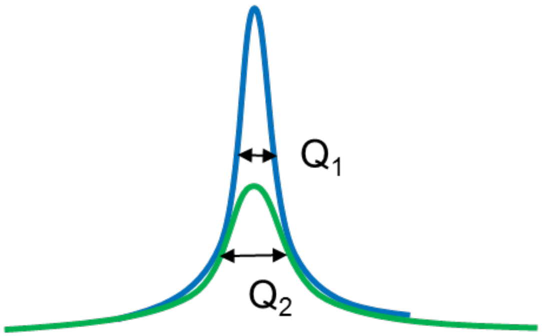


Contact Resonance Mode Principle

- Developed in the 1990s
- Tip is in contact with the sample
- Sample is placed on an actuator which oscillates the sample at fixed amplitude over a frequency range
- Cantilever (contact) resonance spectra are measured in each pixel and provide storage & loss modulus at a discrete (high) frequency
  - Dissipation is proportional to Quality factor Q
  - Stiffness is proportional to frequency



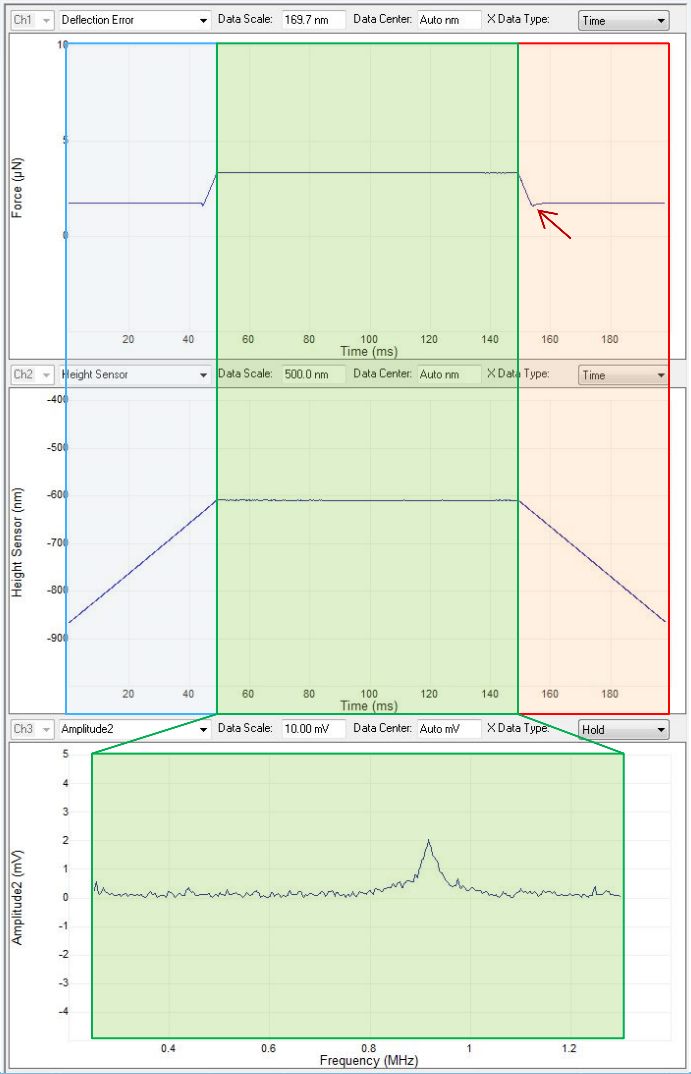
Material 2 has higher stiffness than material 1



Material 1 has higher dissipation than material 2

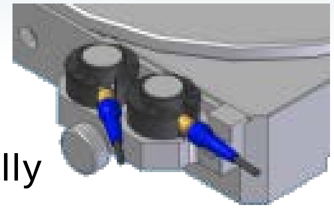
Contact Resonance Mapping Principle

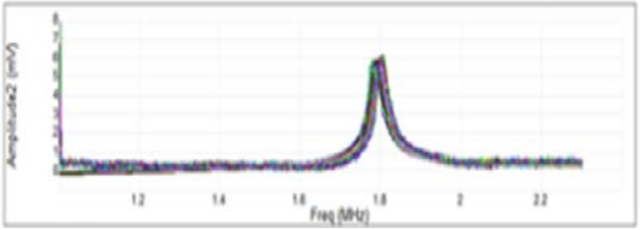
- In every pixel, a standard force curve + contact resonance spectrum is acquired
  - Approach
  - Hold Force and sweep frequency
  - Retract
- Compared to contact mode: More repeatable & longer tip lifetime (lateral force on tip is minimized)
- Allows measurement of Adhesion force for each pixel = better contact mechanics modeling
- Real-time maps of both raw data and mechanical properties (E’, E’’, loss tan)

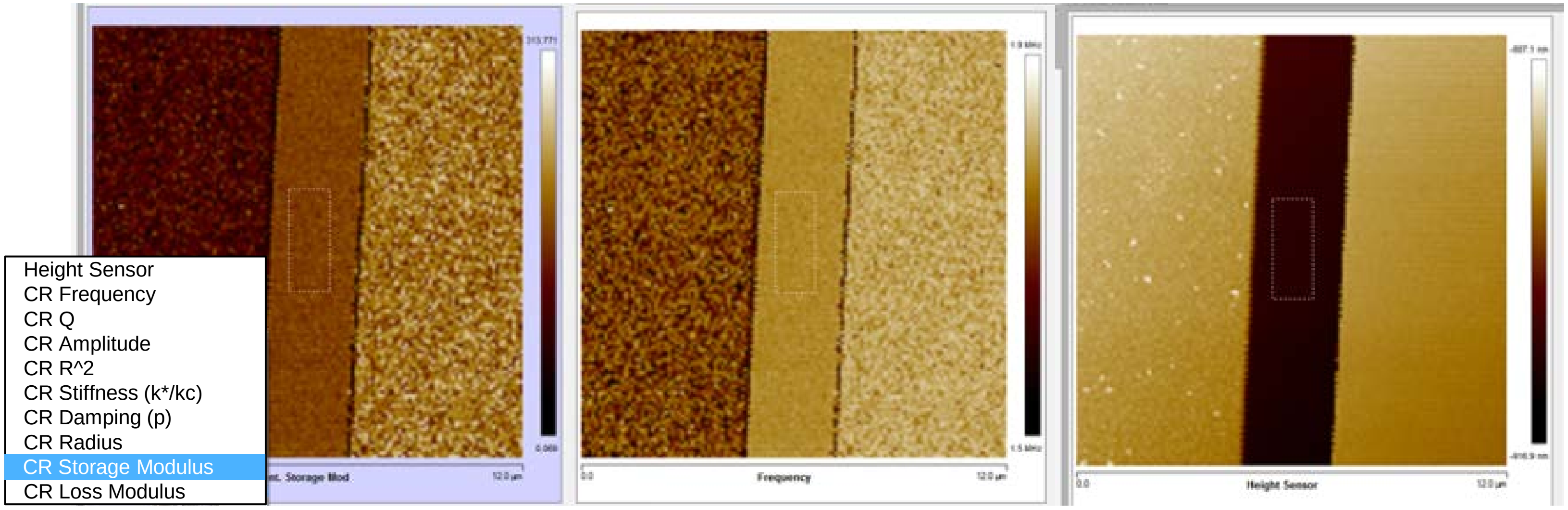


Contact resonance for hard materials
- Al & Cr film on Si, 10um scan

- Principle:
  - Tip is in contact with the sample
  - Using a transducer, the sample is excited mechanically at & around contact resonance frequency
  - Measure f_{CR} & Q_{CR} at the contact resonance
  - f_{CR} & Q_{CR} can be translated into storage & loss modulus
- Good sensitivity for stiff samples (10-300GPa)



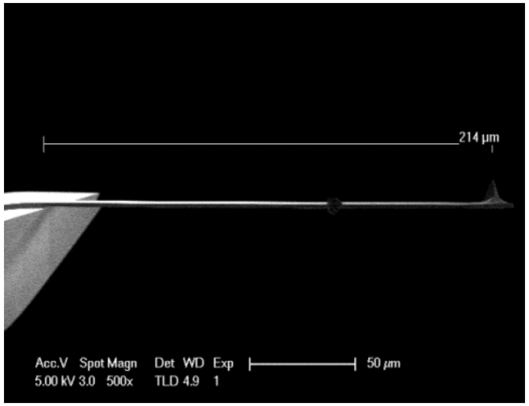


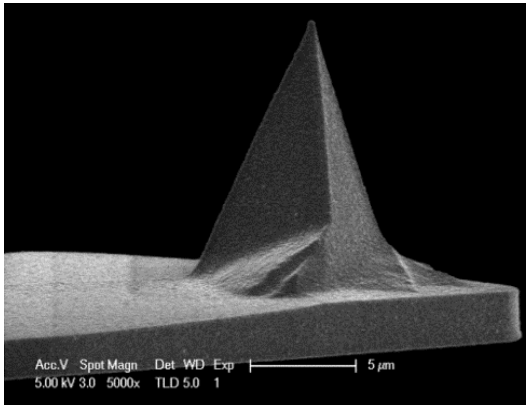


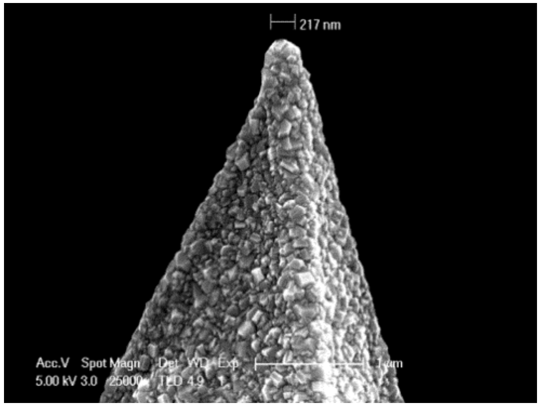
Contact Resonance Mapping
Probes & Samples

- 3 probe types
  - Diamond coated
  - Various spring constant cover modulus range from 1 GPa to 300+ Gpa
  - Note: During development, our engineering team used 6 probes to collect over 2.7 million CR spectra and lasted 257 hours of CR operation

- 7 reference samples
  - HOPG, Mica, Fused Silica, Al (50nm film), Si, Cr (50nm film), and Sapphire

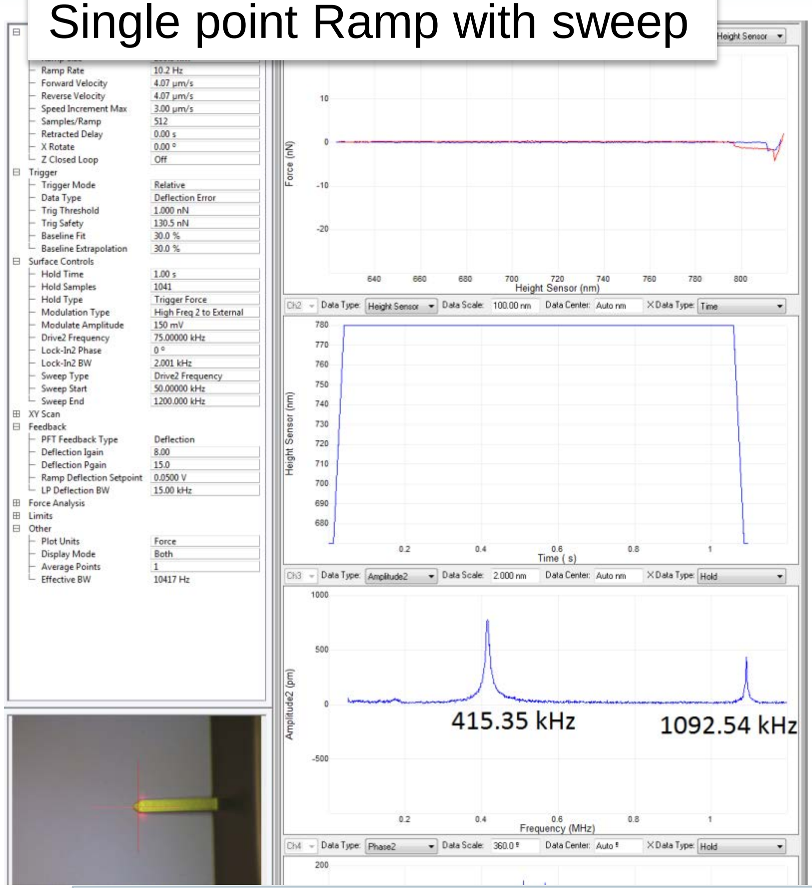




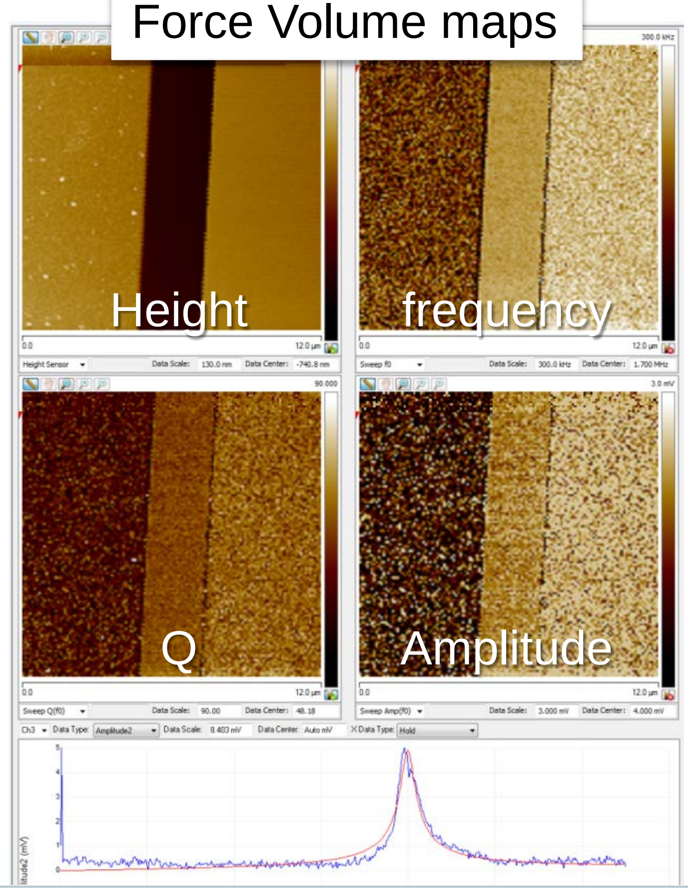


Contact Resonance Mapping
‘Raw data’ Example

Single point Ramp with sweep



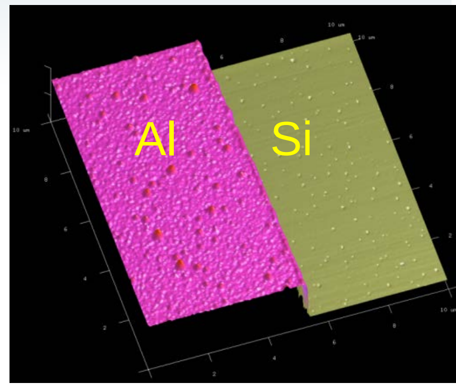
Force Volume maps



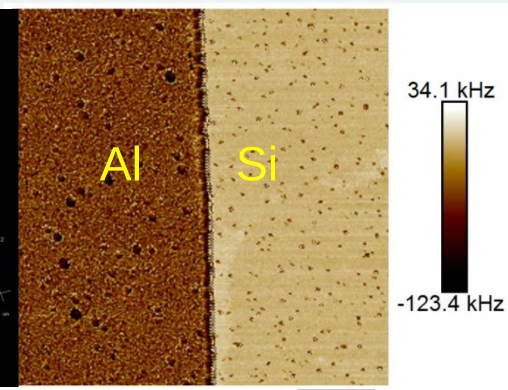
In Force Volume: Ramp and hold trigger force, then sweep at each pixel.

Contact Resonance Mapping
Sample: Al film on Si

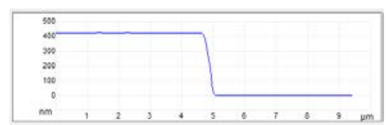
- 10x10 µm scan
- Large amount of data:
  - Every force curve includes 4 channels
  - 256x256 pixels (2048 spectra points)
  - Maximum 956x956 pixels (256 spectra points)
- More than 15 data types can be selected:
  - Frequency, Amplitude & Q
  - Loss Modulus & Storage Modulus
  - Tan delta
  - Adhesion
  - ..

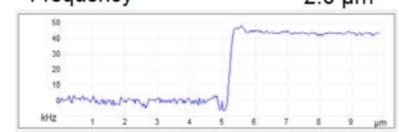


Topography

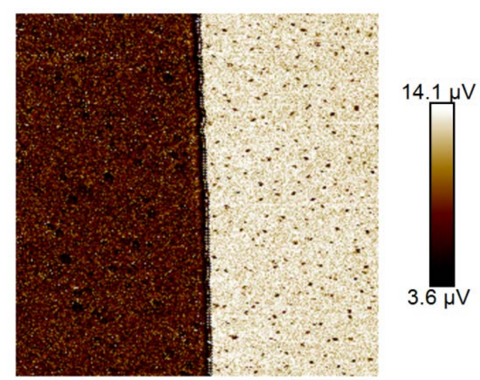


Frequency 2.0 µm





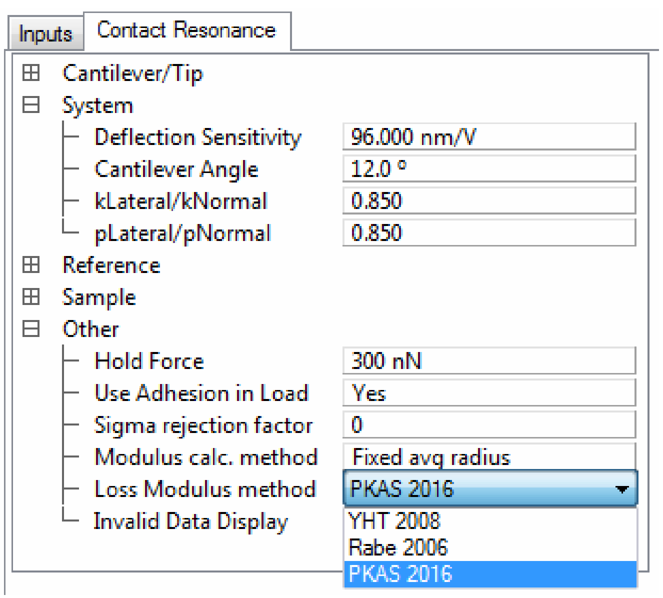
Slice
Modulus
Log Modulus
Stiffness
Adhesion
Force Section
Real Height
Height Sensor
CR Frequency
CR Q
CR Amplitude
CR R^2
CR Stiffness (k*/kc)
CR Damping (p)
CR Radius
CR Storage Modulus
CR Loss Modulus



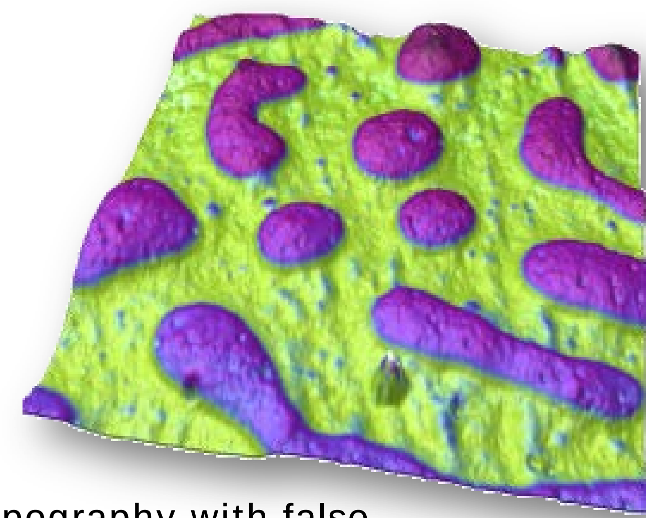
Amplitude 2.0 µm

Contact Resonance Mapping
Loss Modulus & Loss Tangent

- Loss modulus can be calculated from the Q of the CR peak
- Research community lacks consensus about the best way to do this, so we implemented three algorithms
  - YHT 2008 and Rabe 2006 are very similar and both require the reference sample to have a known loss modulus
  - PKAS 2016 does not require a reference sample with known loss modulus



$$\tan\delta = \frac{E''}{E'}$$

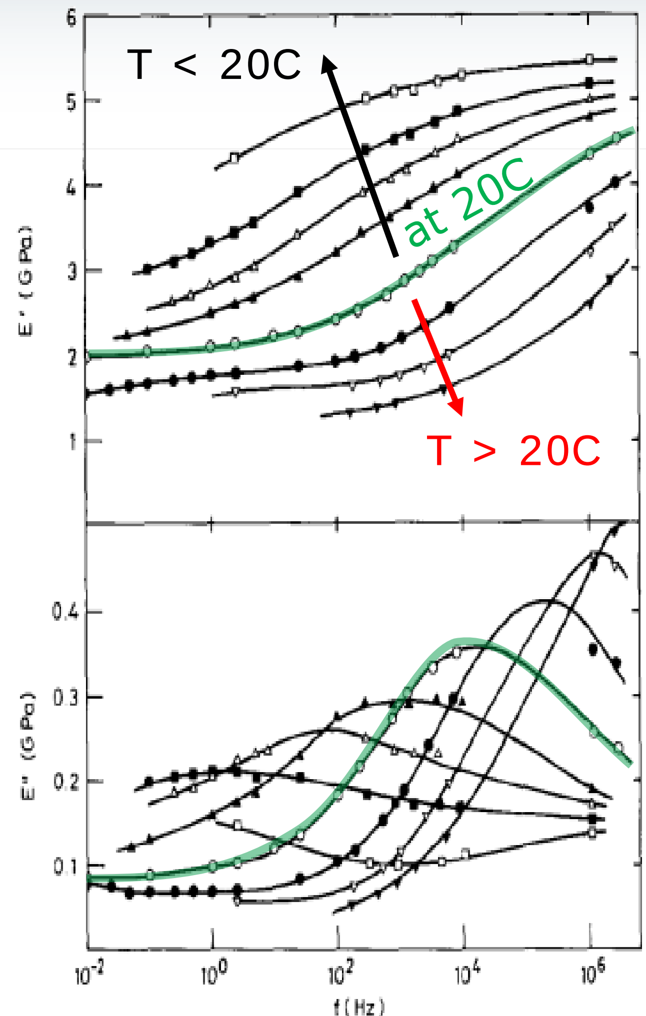


PS-PMMA topography with false coloring by loss modulus.

What about frequency dependence? AFM-nDMA

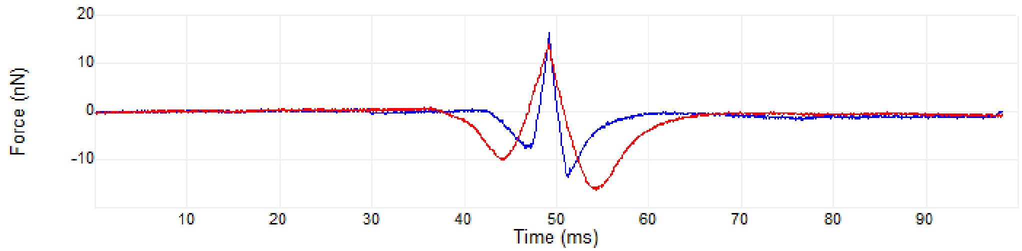
- *E'* and *E''* (or *tan delta=E''/E'*) vary with frequency & temperature
  - *E'* of amorphous polymers increase with loading rate or decrease with temperature
  - Variation can be quite significant!

- Rheologists need measurements at multiple frequencies and temperatures for a complete analysis



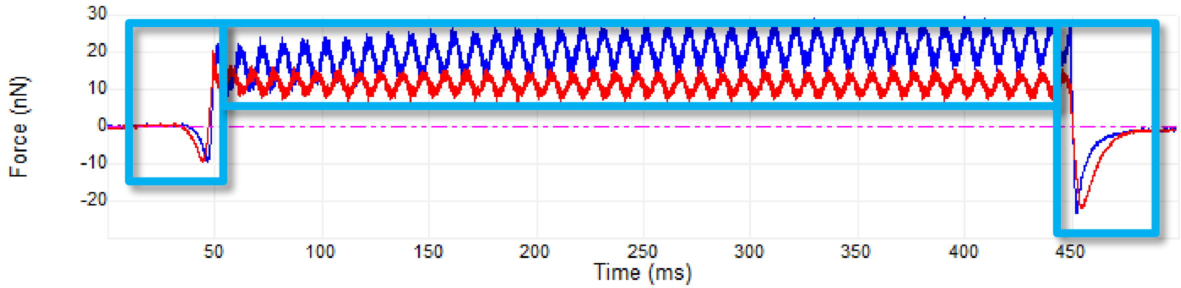
Bulk dynamic modulus of Isotactic polypropylene (Read, B.E 1989)

Imaging focused modes - not suited for quantifying viscoelasticity



- Probing sample impulsively
  - Plunge-in and rip-out in each cycle, make-and-break contact
  - Not a linear measurement
  - Since it's not linear, the nominal frequency is not the only frequency
  - Cannot really quantify frequency dependence
- Tapping based methods introduce added constraints
  - Frequencies fixed and 100,000x too high
  - Challenge in quantifying load and adhesion

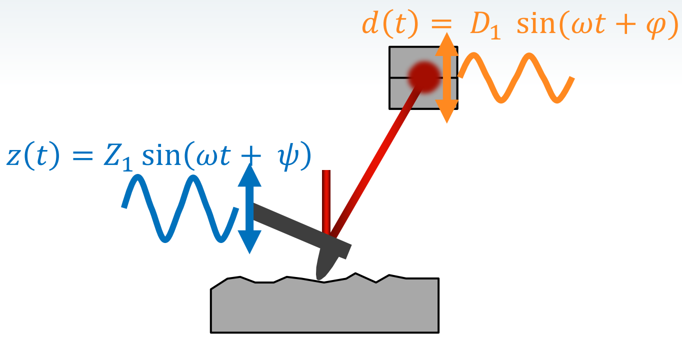
Start with time dependence
Basic idea of AFM mode for rheology

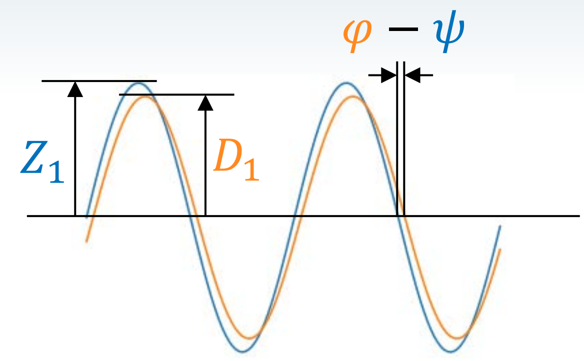


- Approach: Preload the sample at known force
- In contact: Modulate at well-defined, rheological freq, low amp
  - Low amplitude provides small perturbation in force: linear regime
  - Cover 0.1Hz to 300Hz: single frequency or spectrum
- Retract: fit with contact mechanics model that includes adhesion (e.g. JKR) to obtain contact radius (ac)
  - Need contact radius to extract moduli (E’, E”) from raw data

T. Igarashi, S. Fujinami, T. Nishi, N. Asao, and K. Nakajima, Macromolecules (2013)

AFM-nDMA theory





- Need to extract amplitude ratio (D_1/Z_1) and phase shift ($\varphi - \psi$) and do a little complex algebra to get

  stiffness = force/deformation

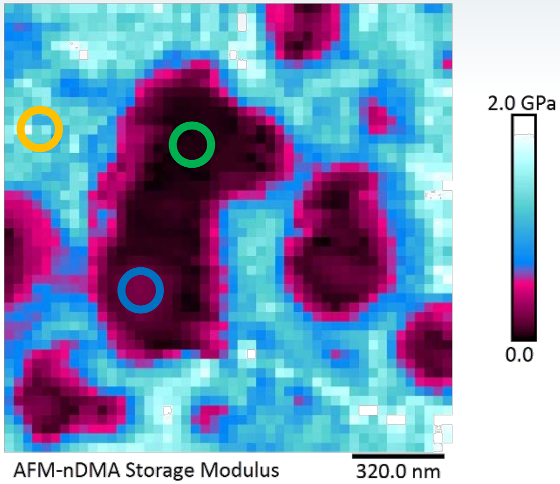
  - $S^* = S' + iS" = K_c D_1 e^{i\varphi} / [Z_1 e^{i\psi} - D_1 e^{i\varphi}]$
  - $S' = \frac{K_c D_1}{Z_1} \frac{\cos(\varphi-\psi) - D_1/Z_1}{(\cos(\varphi-\psi) - D_1/Z_1)^2 + (\sin(\varphi-\psi))^2}$ *Elastic component, in phase*
  - $S" = \frac{K_c D_1}{Z_1} \frac{\sin(\varphi-\psi)}{(\cos(\varphi-\psi) - D_1/Z_1)^2 + (\sin(\varphi-\psi))^2}$ *Viscous component, out of phase*
  - Loss tangent is then: $\tan\delta = S"/S' = \frac{\sin(\varphi-\psi)}{\cos(\varphi-\psi) - (D_1/Z_1)}$

Two modes quantify viscoelasticity
E', *E''*, *tan δ* at bulk DMA frequencies

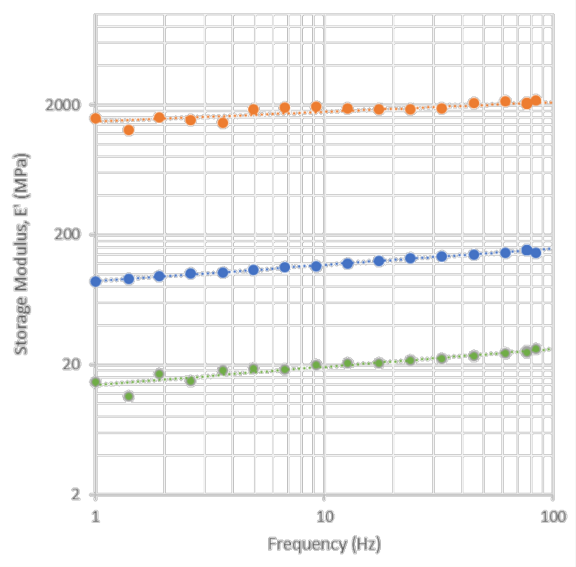
- Mapping with Fast Force Volume
  - Simple, single modulation segment embedded in force curve

AFM-nDMA storage modulus map of polymer blend (100Hz)

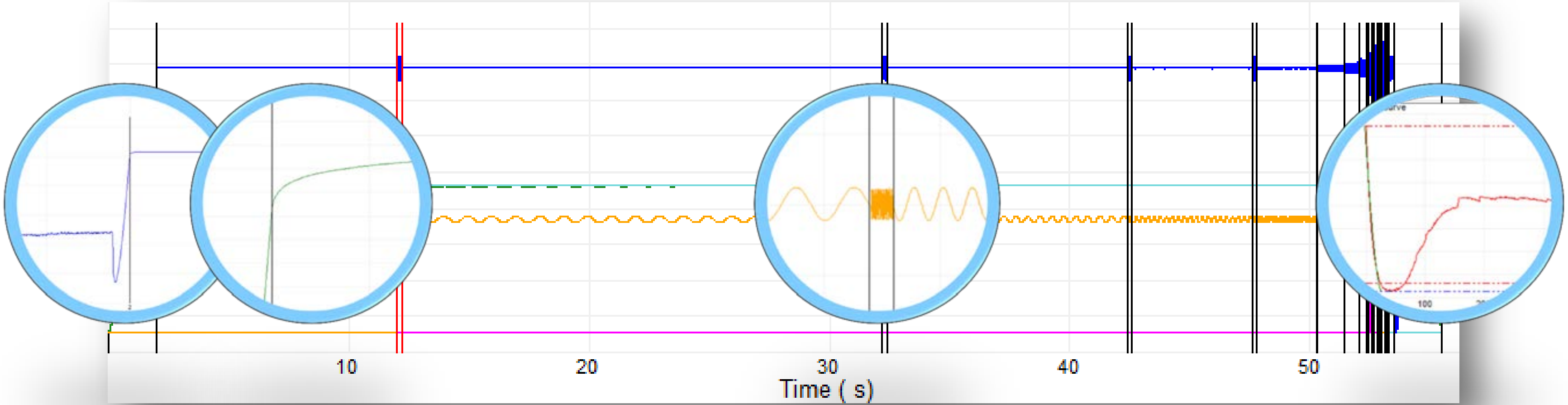
With correlated, frequency spectra at selected locations



- Spectroscopy with RampScripting
  - measurements at multiple frequencies at a single point

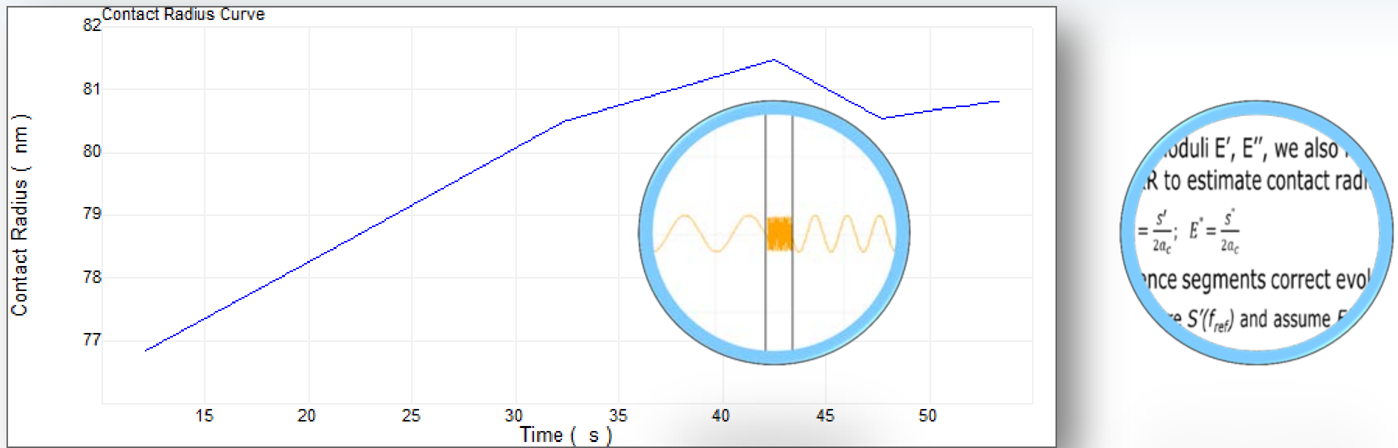


How are these spectra collected?



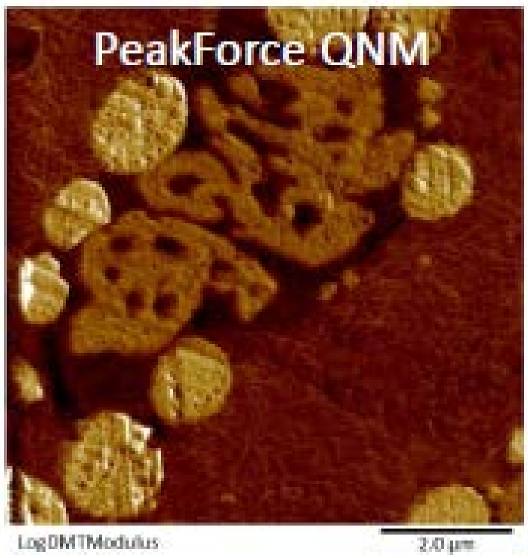
- An AFM-nDMA "RampScript" has segments that allow for control of preload, relaxation, modulation, and calculation of contact radius
- Low frequency segments use raw deflection for better filtering, while higher frequencies use lock-in based demodulation

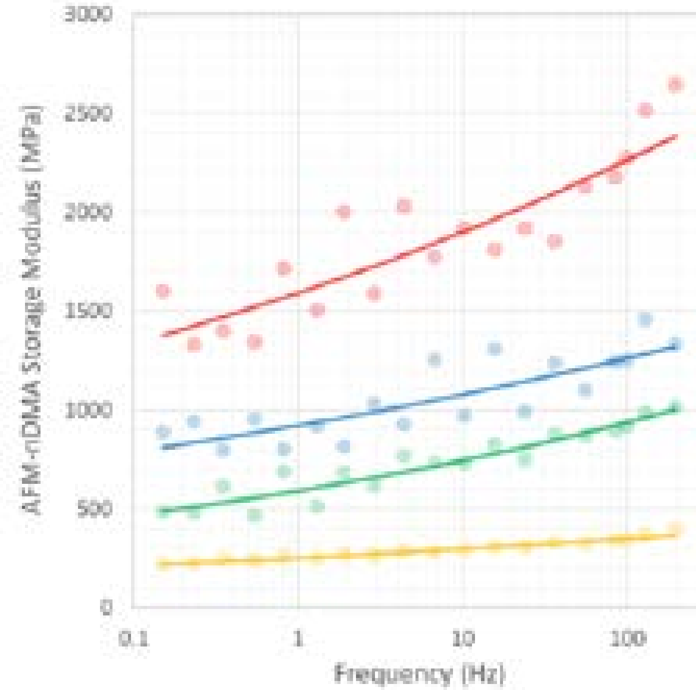
Managing changes in contact radius



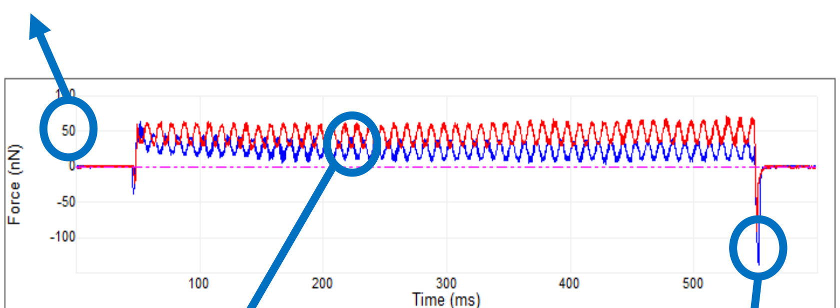
- To get moduli E', E'', we also need a contact mechanics model like JKR to estimate contact radius (ac)
  - $E' = \frac{S'}{2a_c}; \quad E'' = \frac{S''}{2a_c}$
- Reference segments correct evolution of contact radius over time
  - Measure $S'(f_{ref})$ and assume $E'(f_{ref})$ is constant during script

nDMA Mapping & Spectroscopy, and PeakForce QNM in same analysis session



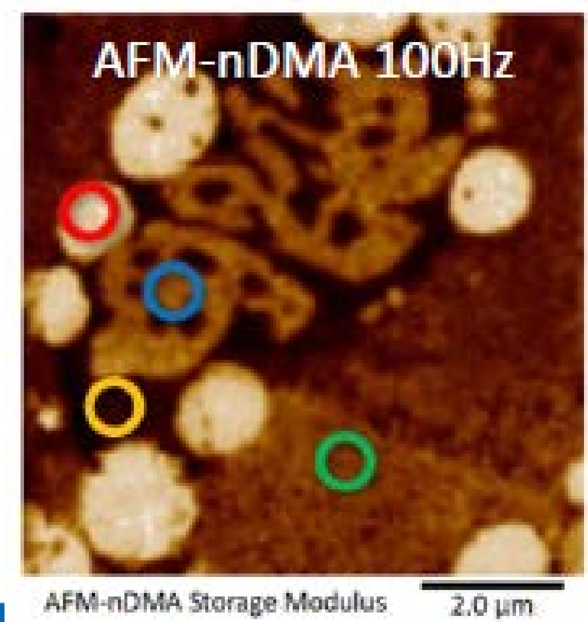


Preload control



Low-frequency, in-contact

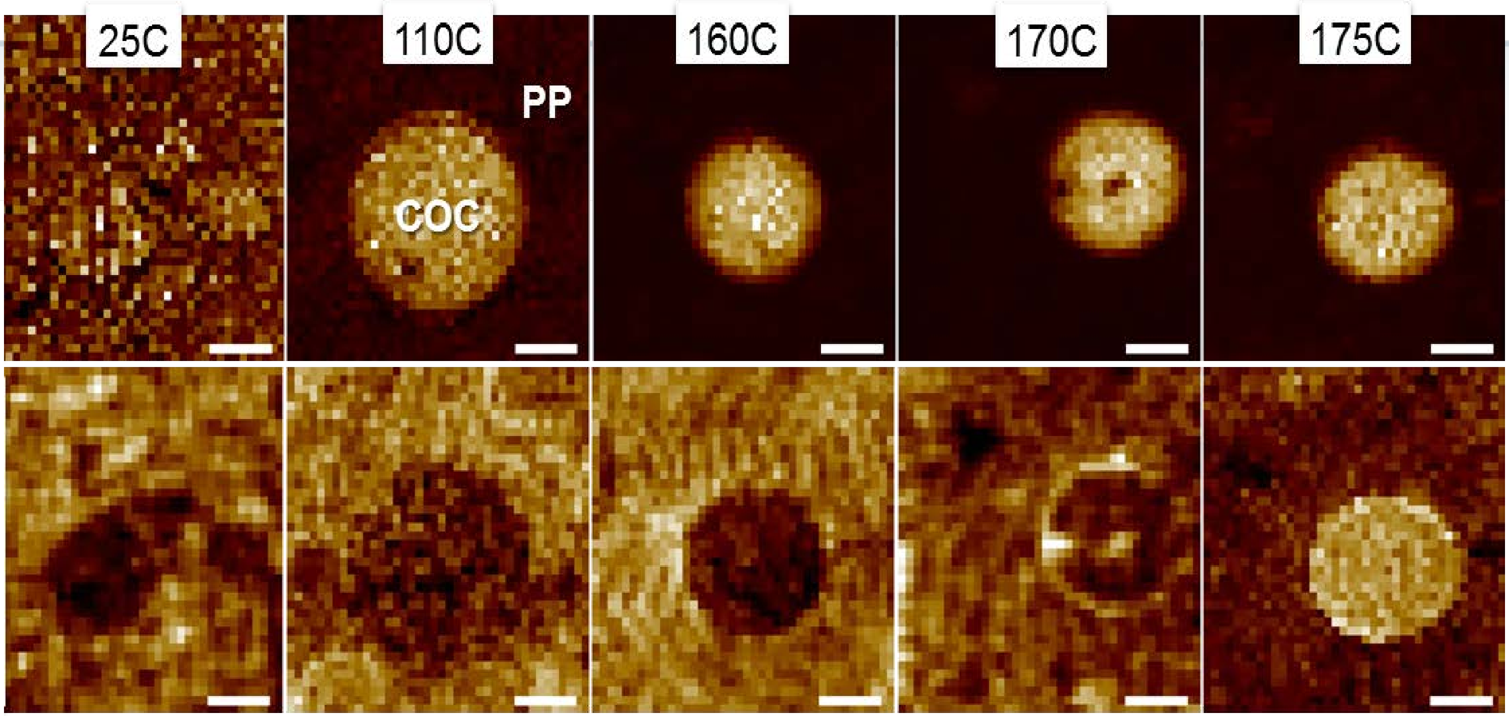
Adhesion quantified

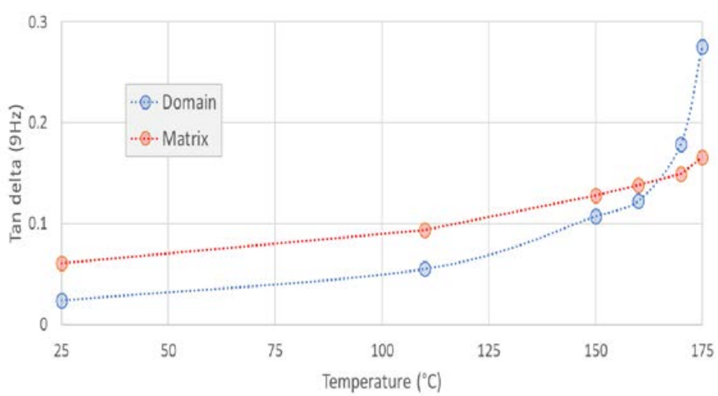


AFM-nDMA Temperature Study
Cyclic olefin copolymer / PP

Storage Modulus

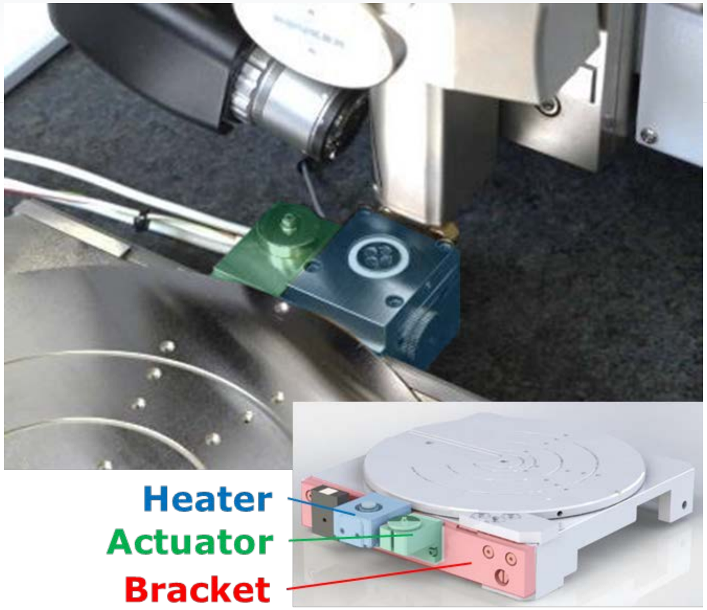
Loss Tangent

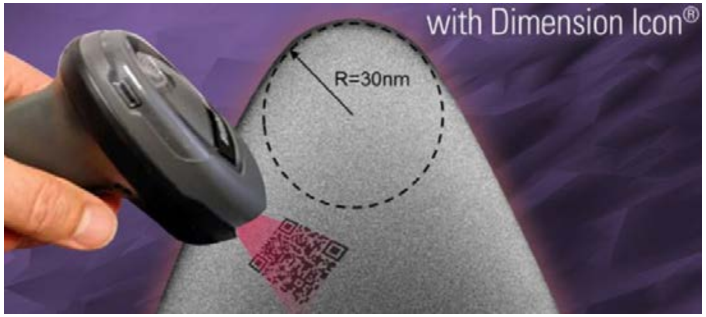




What is AFM-nDMA – Hardware

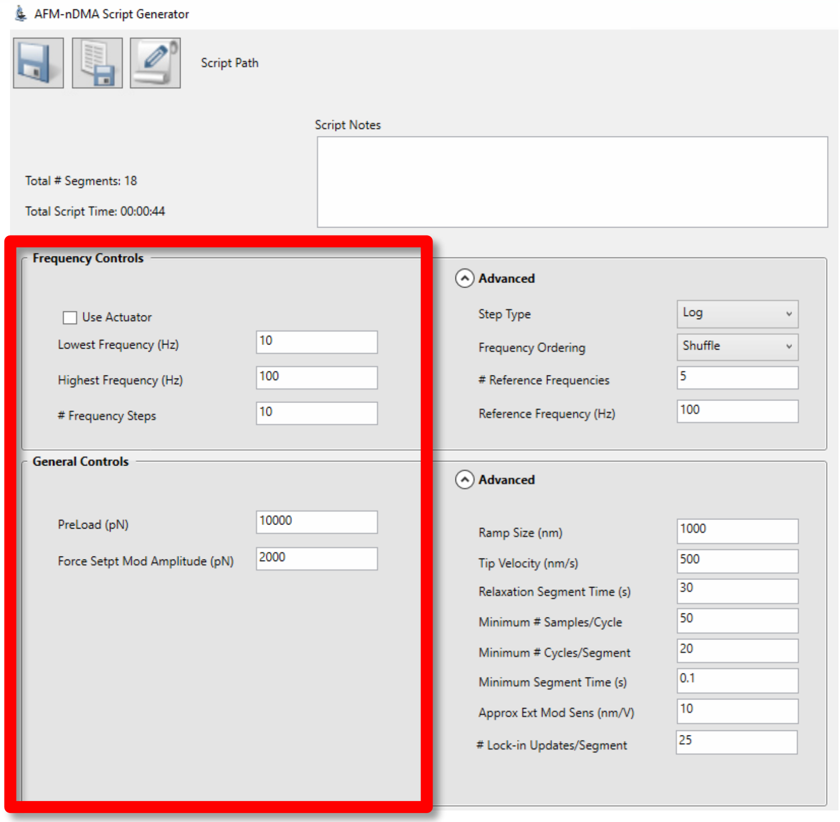
- **nDMA heater**
  - Ramps and stabilizes 5x faster than standard heater-cooler
  - RT-250C, 0.1Hz-300Hz
- **High frequency sample actuator**
  - For 300Hz to 20kHz range at room temp
  - Produces total range of 0.1Hz to 20kHz
- **Precalibrated probes solution**
  - 2 end radii – 30nm and 125nm
  - 3 spring constants ~ 0.4, 5, 40N/m
  - QR reader for probe parameter reading
- **Test & training samples**
  - Validation (PDMS, FEP) and imaging (PPE, PC-ABS)





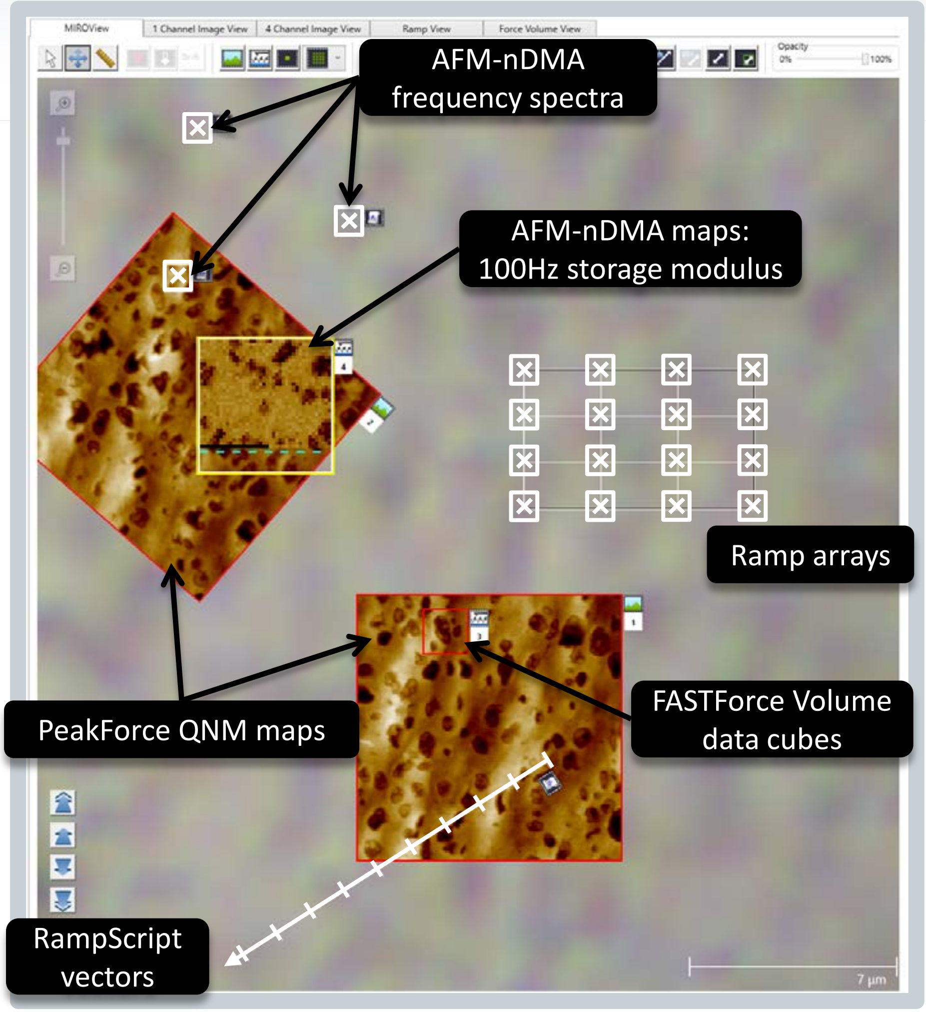
Setting up AFM-nDMA spectroscopy
Efficient generation of scripts

- Quick set up with DMA focus
  - Frequencies, preload, modulation amplitude
- Advanced parameters if wanted
  - Log vs linear frequency distribution
  - Frequency shuffle avoids artifacts
  - Modify reference segments
  - Change length of relaxation segment
  - Adjust any ramp parameter
- Or edit segment-by-segment in general ramp scripting interface
  - Maximum flexibility

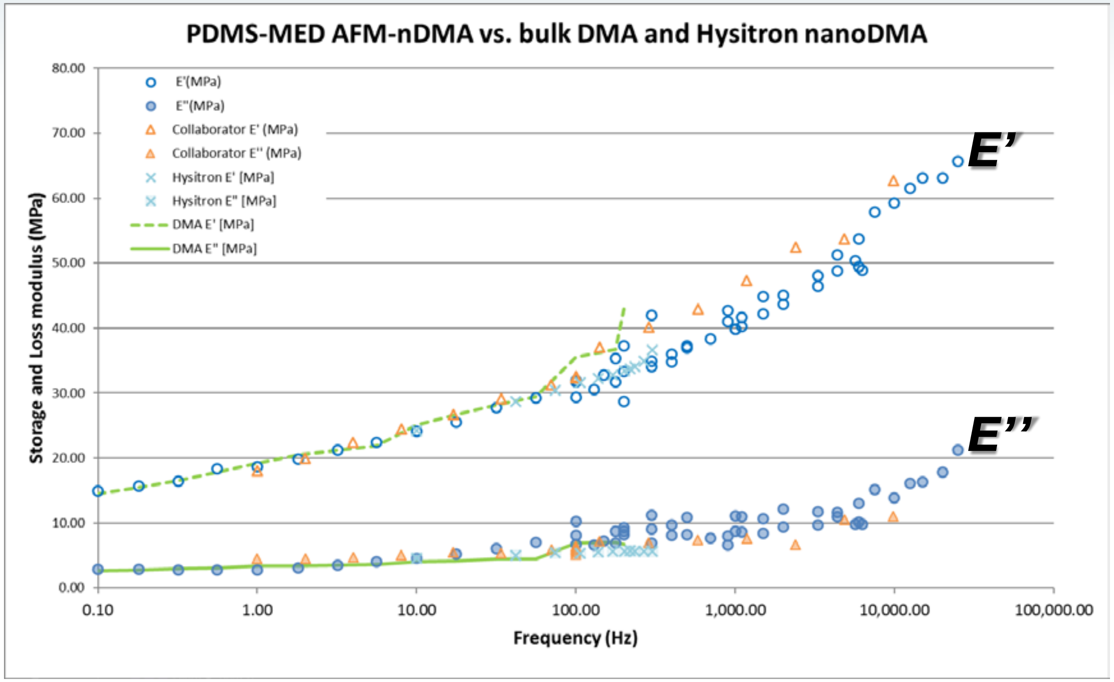


Addressing the smallest nanoscale domains with the highest AFM resolution on polymers

- PeakForce QNM achieves the highest resolution – allows targeting the smallest domains
- MiroView integrates AFM-nDMA with PeakForce QNM – use same probe, allows full automation
- Use AFM-nDMA maps for added quantitative information and to distinguish multiple phases
- Use AFM-nDMA frequency spectra for most complete information at targeted points



Can a nanoscale measurement tie directly to bulk DMA?

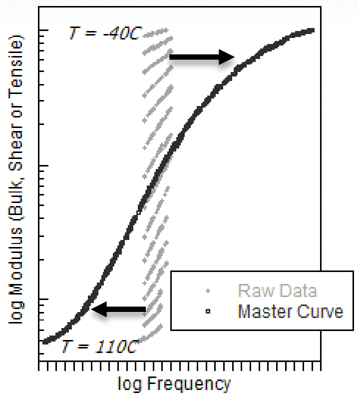


- Nanoscale AFM-nDMA results show excellent agreement with
  - micrometer scale Hysitron Nanoindenter
  - millimeter scale Bulk DMA
- Consistent results across labs and operators (no reference samples)
- Directly cover bulk frequencies and extend to 20kHz with external actuator

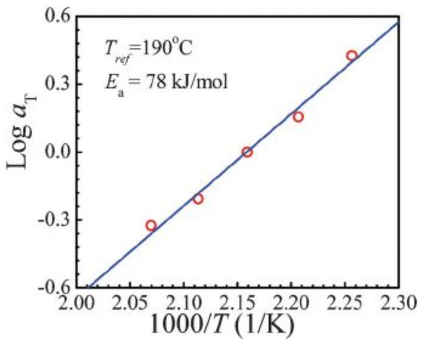
Time Temperature Superposition

- Collecting frequency spectra at several temperatures enables a more complete analysis
- TTS principle: near glass transition, raised temperature is equivalent to lowered frequency and vice versa
- Master curve: single curve resulting from shifting data measured at different temperatures
- Shift factors: can be parameterized via either WLF or Arrhenius model.
  - Arrhenius equation gives activation energy from temperature dependence of a rate – energy needed to kick off a mechanical relaxation process

TTS master curve construction



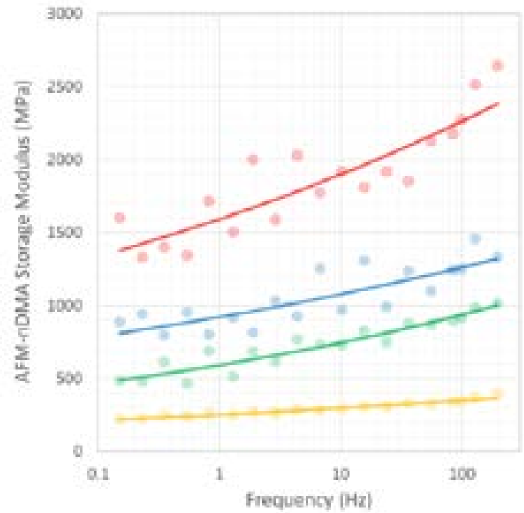
Activation energy analysis for a polymer
Arrhenius: ln(aT) = - Ea/R (1/T – 1/To)

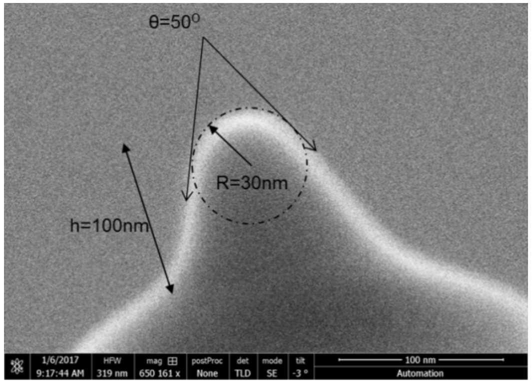


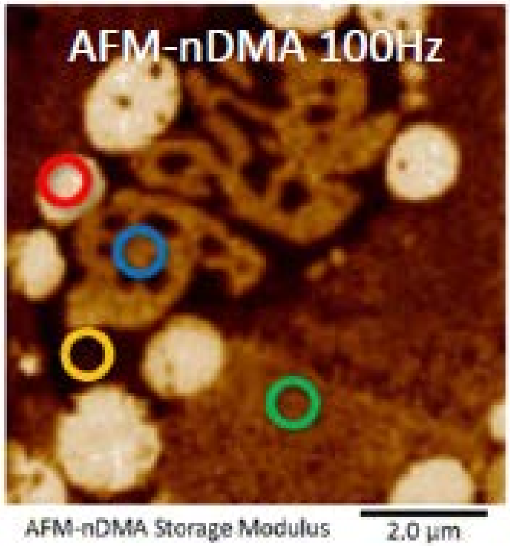
Summary

Recent Development in Nanomechanical Measurements by AFM

- Force-based and Nanomechanical Techniques:
  - Force Spectroscopy
  - FastForce Volume
  - Peakforce Tapping/PeakForce QNM
  - Ramp Scripting and Ramp and Hold
  - AFM-nDMA (released Nov 2018)
  - Contact Resonance based on FastForce Volume
  - PeakForce QNM-High Accuracy (PFQNM-HA)
  - MIROView
  - Probes







www.bruker.com

Questions?
john.thornton@bruker.com