Latest Innovations in PeakForce QNM and Other Advanced Force Spectroscopy Techniques

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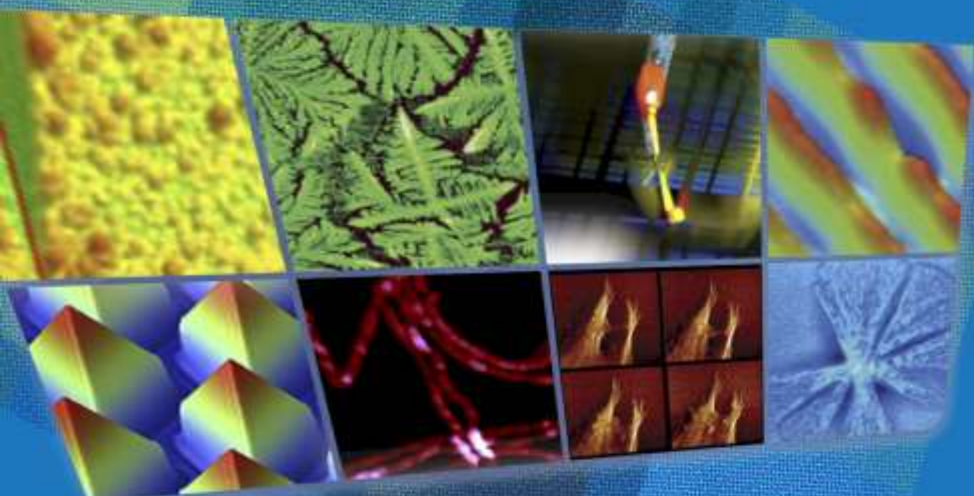


Atomic Force Microscopy
3D Optical Microscopy
Tribology
Automated AFM
Stylus Profilometry
Mechanical Testing, Nano Indentation

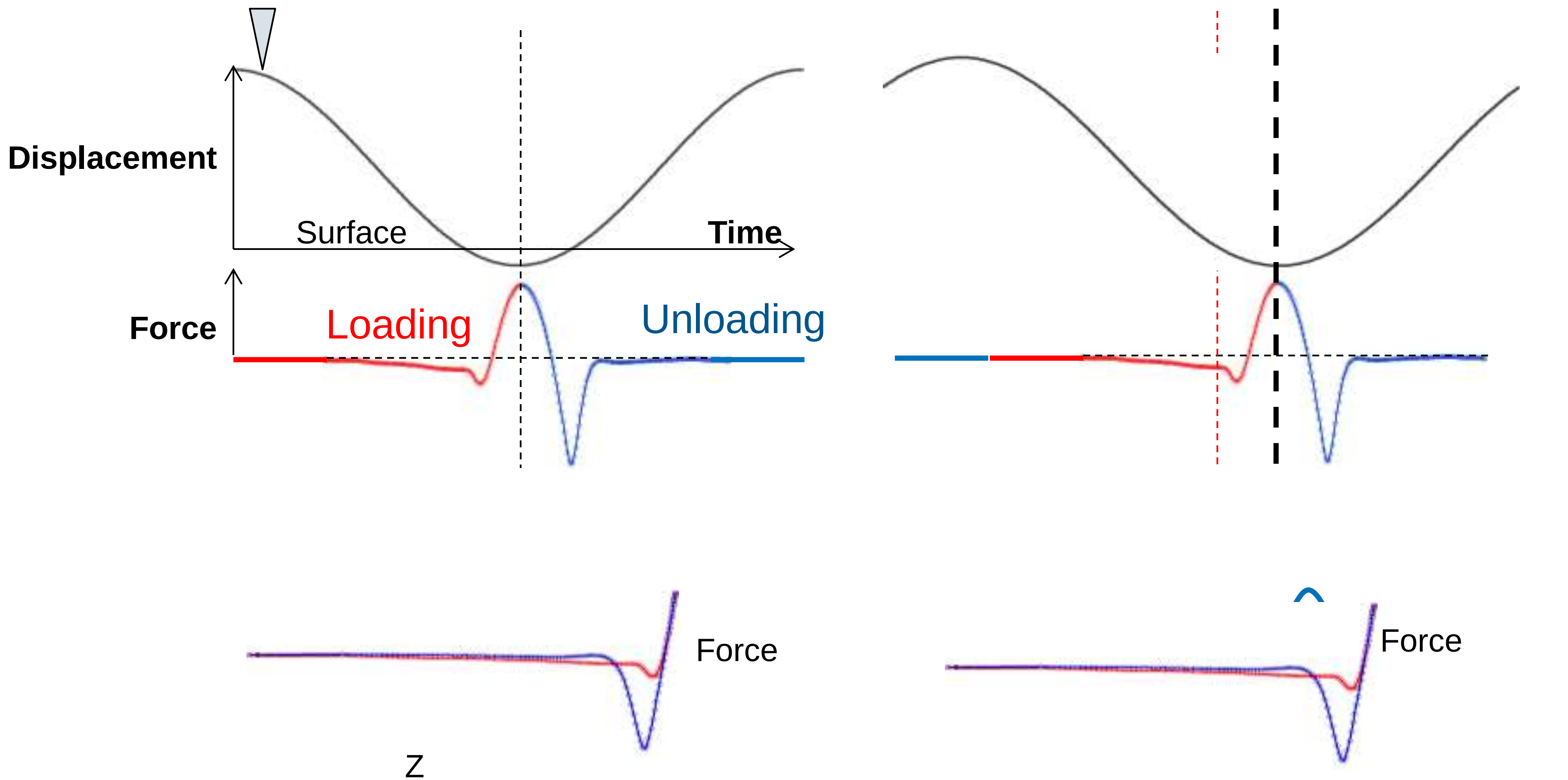
Outline

- Explain how PeakForce Tapping works
  - Getting 'Sync'hronized
  - Background subtraction
  - Calibration
  - Modeling
- Enable comparison to other modes
  - *FAST*Force Volume & Time dependence (Nanoscope v9.20)
  - Scripting, Stress & Strain Relaxation, Nano-rheology (Nanoscope v9.20)
  - Improve analysis tools (Nanoscope Analysis 1.60)
- Why is PeakForce Tapping faster than *FAST*Force Volume?
- Comparison with HarmoniX, Contact Resonance, Tapping, AM-FM, loss tangent

Explaining PeakForce Tapping

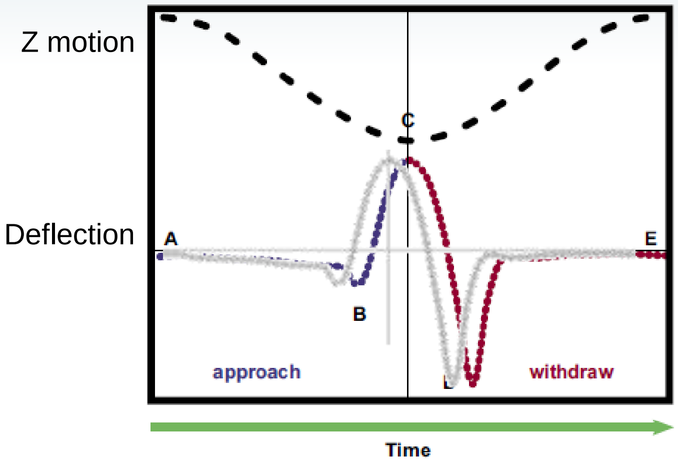
Getting Synchronized with the 'Sync Distance'

- Need to compensate for phase lag of Z motion and deflection measurement
  - Measure the phase lag on a hard sample: Lowest point of Z=Maximum Force

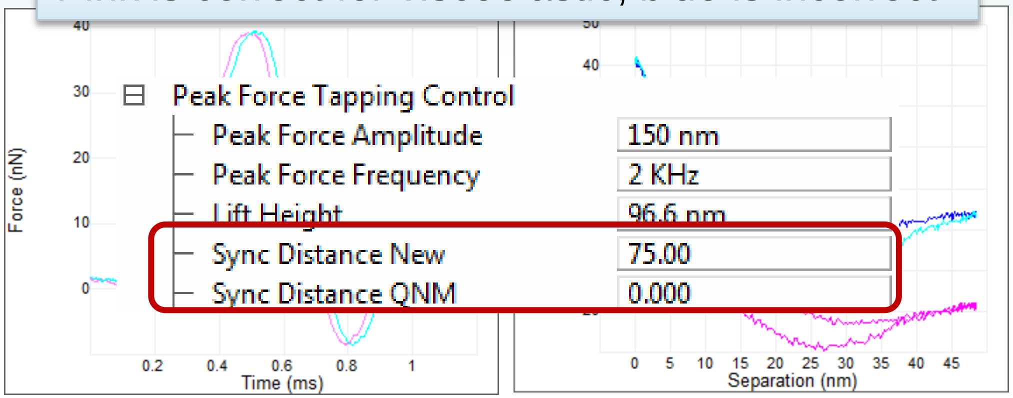


Explaining PeakForce Tapping

Addressing viscoelastic response -- separate feedback from analysis (Nanoscope v9.00)



Pink is correct for viscoelastic, blue is incorrect

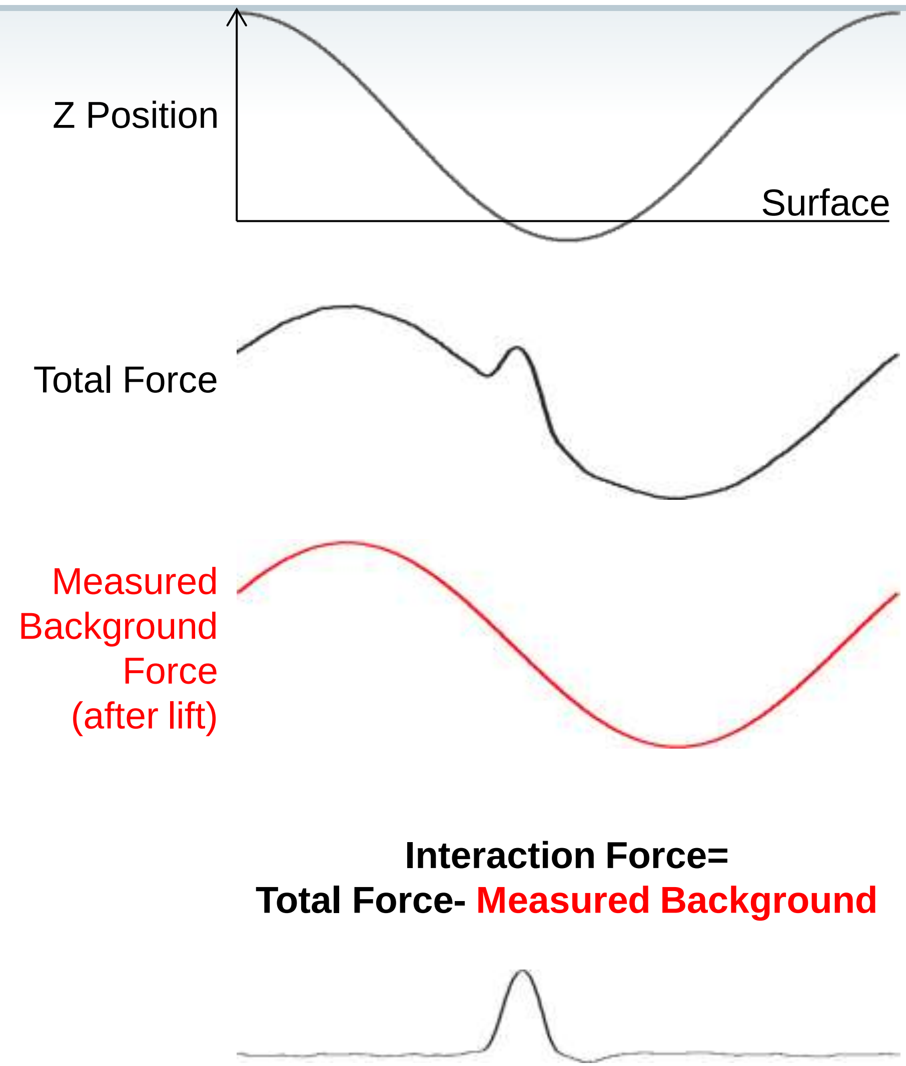


- Dilemma: when material has time dependent response, maximum force is no longer at maximum piezo extension
  - Always want to control max force: prevents damage to tip or sample
  - Want to analyze curves with turnaround always at max piezo extension
- Solution: Separate feedback from analysis
  - Feedback on “Sync distance <New>” for peak force
  - Use a separate “QNM sync distance” for force curve analysis
    - Adjust during Deflection Sensitivity calibration

Explaining PeakForce Tapping

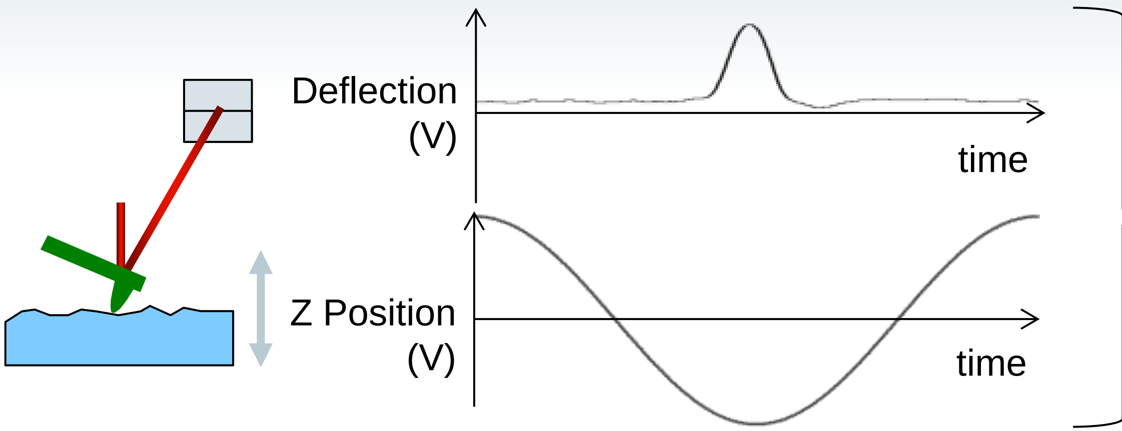
Background Subtraction: method 1 background from lift

- Background measurement triggered when user enters a new value into 'Lift Height' parameter:
  - Scanning stops
  - Z piezo is retracted by 'Lift Height'
  - Background is measured
  - Scanning resumes with new background subtracted from subsequent curves
- Some other events trigger measurement: 'Engage', 'Autoconfig', …
  - System finds lift height- note change in parameter
  - Sync Distance is typically also adjusted

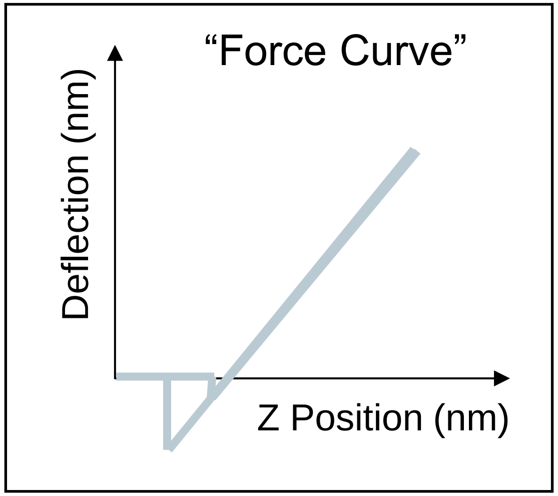


Explaining PeakForce Tapping

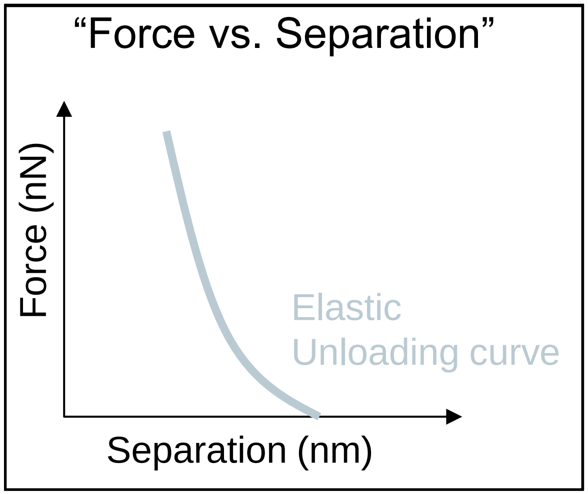
Calibration of force curves



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



4. Calculate indentation
5. Apply ‘Spring constant’



Explaining PeakForce Tapping

Calibrating Z: sensitivity and phase

- Z = A*sin(2*pi*f*t + phase)

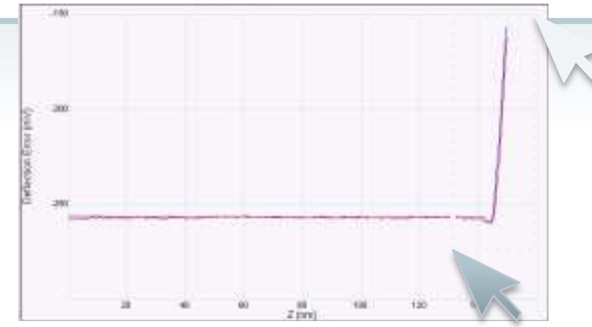
- Z amplitude can vary with frequency
  - Depends on system and precise configuration
  - Z sensor is often insufficient to calibrate it
  - Need to adjust 'Drive3 Amplitude Sensitivity'

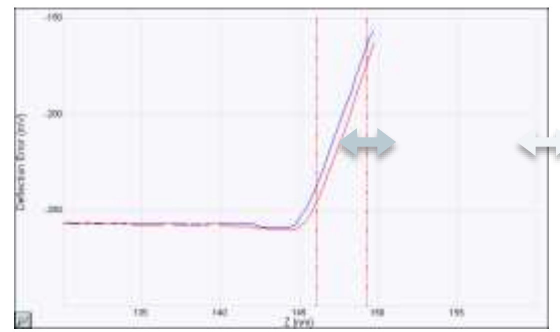
- 'QNM sync distance' is essentially the phase of the Z position and also depends on frequency

- Calibrate in three steps (with Sapphire sample)
  1. Calibrate 'Deflection sensitivity' in ramp mode
  2. Calibrate 'QNM sync distance'
  3. Calibrate Amplitude using 'Update Sensitivity'

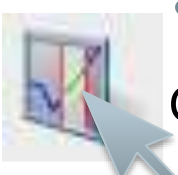
Explaining PeakForce Tapping

Calibrate Deflection Sensitivity in Ramp mode

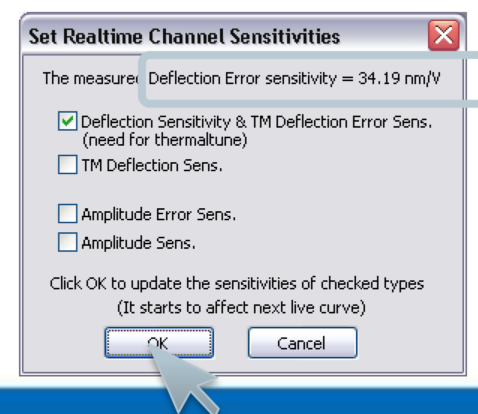




- Scan to find a 'clean' area on sapphire
- Switch to Ramp mode
- Generally need Trig Threshold 0.1-0.2V
  - Might break sharp tip
- Zoom on contact part of curve
  - Press 'Ctrl' key and drag with mouse
- Drag 2 cursors to linear part of curve
  - Drag from edge of plot

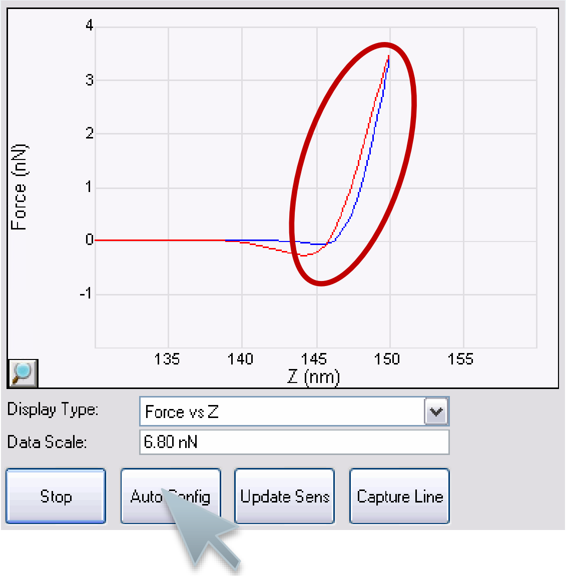


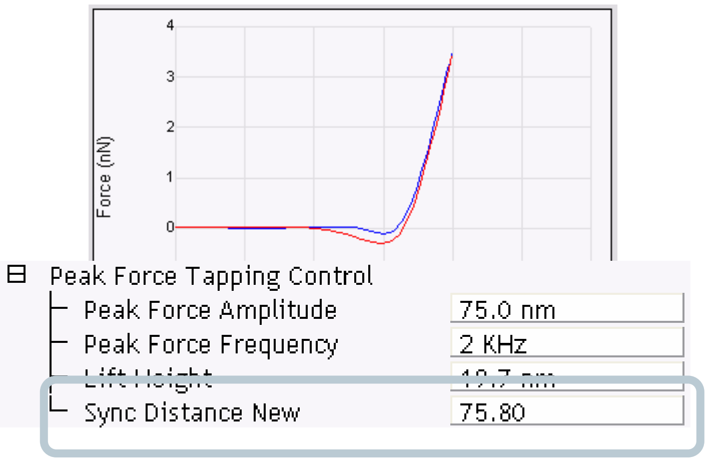
- Click 'Update Sens' and hit 'OK' in dialog
- Repeat to confirm consistency



Explaining PeakForce Tapping
Calibrate 'Sync Distance QNM' in Scan mode

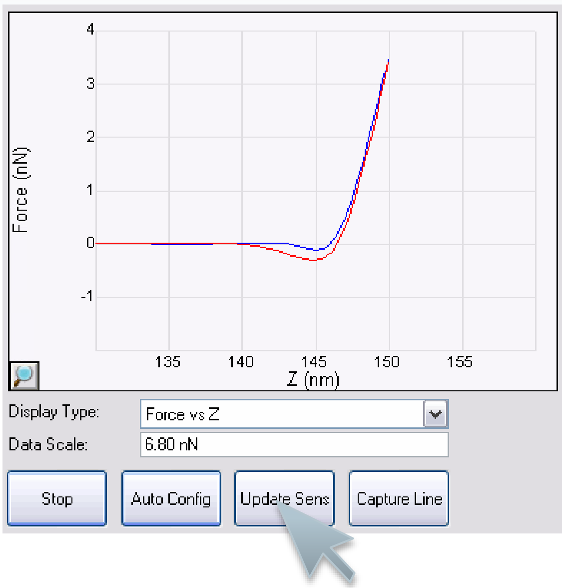
- While engaged in Scan mode on Sapphire
- Set PeakForce Setpoint to ~0.1V (type '0.1V')
- Zoom on contact part of curve in force monitor plot (use Ctrl-drag)
- If contact part of red and blue curves do not match
  - click 'Auto Config', or
  - manually adjust 'Sync Distance <New>' until they match
- Note the 'Sync Distance <New>' & 'Sync Distance QNM' (should be the same)

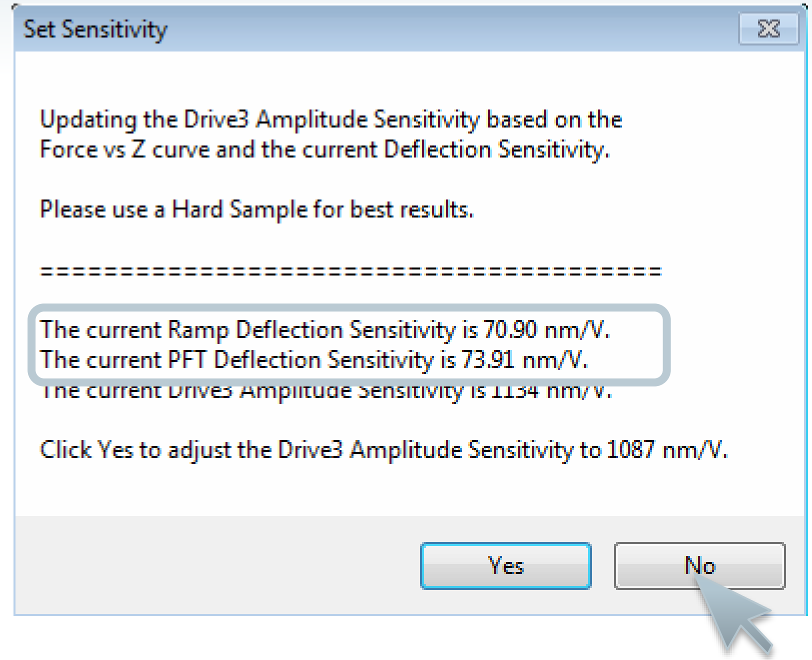




Calibrate PeakForce Tapping Amplitude

Assume Deflection Sens. is constant on Sapphire
Use this to adjust Drive3 Amplitude Sensitivity





- Be sure Sync Distance is good!
- Click 'Update Sens' on the force monitor (Nanoscope v9.10)
  - Compare Ramp Deflection Sensitivity (here 70.90 nm/V) to PFT Deflection Sensitivity (here 73.91 nm/V)
  - If they match within 10% click 'No', otherwise click 'Yes'
- Check calibration by clicking 'Update Sens' a few more times

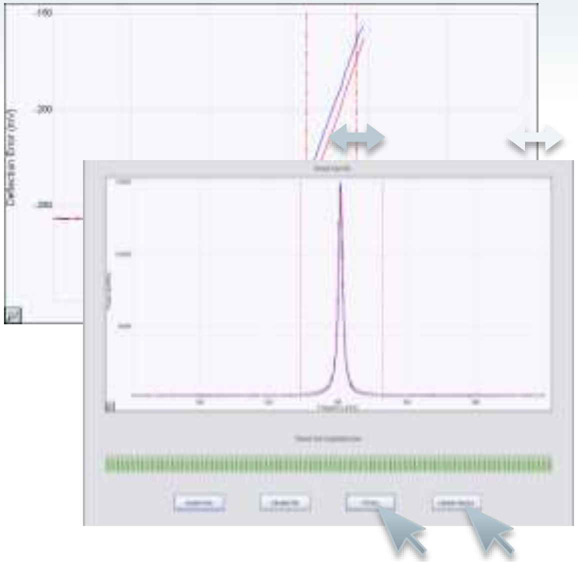
Explaining PeakForce Tapping

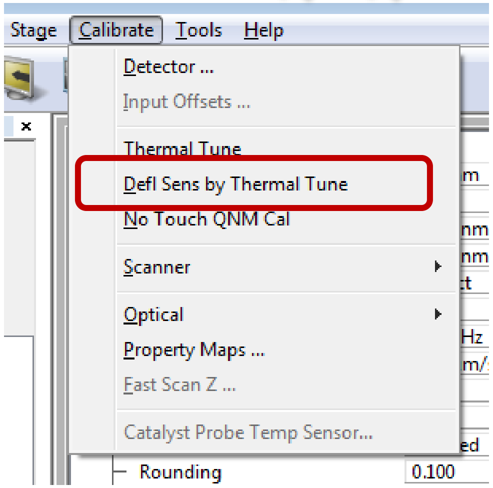
Spring Constant and Deflection Sensitivity

- Traditional way
  - Ramp on hard surface to find Deflection Sensitivity
  - Thermal Tune to find Spring constant

- Automatic calibration (Nanoscope v9.20)
  - Spring constant from LDV Pre-calibrated probes
    - Initially PFQNM-LC, SAF-HR, MLCTBio-C and E
  - Thermal Tune to find Deflection Sensitivity

- Automatic method is easier, less variable, and does not require tip to touch surface prior to measurement
  - Great for functionalized probes





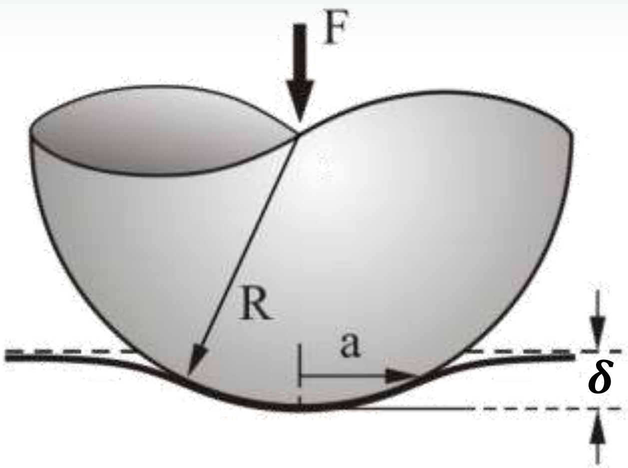
Explaining PeakForce Tapping

Modulus from Hertzian or DMT Model

$$F = \frac{4}{3}\frac{E}{(1-\nu^2)}\sqrt{R}\delta^{3/2}$$

or $$(F)^{2/3} = \left(\frac{4}{3}\frac{E}{(1-\nu^2)}\sqrt{R}\right)^{2/3}\delta$$

Linearized Equation



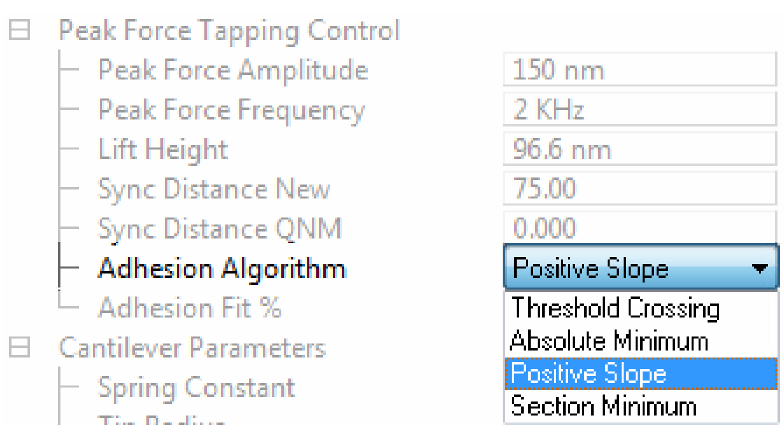
- Model is valid for a<<R
- Used for smaller sample indentation
- Real-time calculation Uses retract curve
  - DMT model adds in adhesion
  - Neglects viscoelasticity
  - Plastic deformation should be minimal in retract curve

Where
F is the force (from force curve)
E is Young's modulus (fit parameter)
ν is Poisson's ratio (typically 0.2-0.5)
R is the radius of the indenter (tip)
δ is indentation depth

Explaining PeakForce Tapping

Adhesion algorithms (Nanoscope v9.00)

- DMT model uses measured Adhesion to adjust force prior to linearization: (F-Fadh)^2/3
  - Error in Adhesion affects Modulus
  - Check by comparing force monitor and adhesion channel
  - If necessary, choose a different Adhesion algorithm
  - Online help has descriptions



Adhesion Algorithm

The ***Adhesion Algorithm*** allows you to choose among several algorithms that are used to determine the adhesion point.

Settings:

- **Threshold Crossing**: The adhesion force is a local minimum that occurs shortly after maximum indentation. "Shortly after" is defined as:
  - Draw a line (shown in red in Figure 4) between Point A, the peak force (vs. time), and a second Point B that is 30% above the global minimum. Extend this line to the global minimum force, Point C. The adhesion force is the minimum value to the left of Point C.
  - The **Threshold Crossing** algorithm sometimes fails for very soft samples.

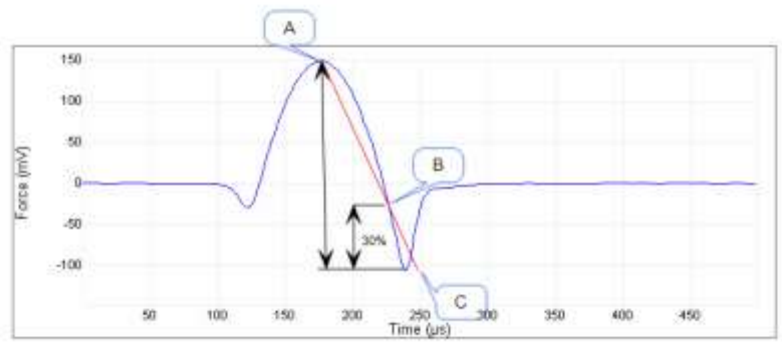


Figure 4: The Threshold Crossing adhesion algorithm

- **Absolute Minimum**: Takes the minimum point before the slope of the force versus time curve goes positive.
  - The **Absolute Minimum** algorithm sometimes fails when large optical interference exists.
- **Positive Slope**:
  - Starting at the maximum force, a straight line is least squares-fitted to the user-adjustable ***Adhesion Fit*** % of the points on the curve and its slope is calculated.
  - Another straight line is drawn with the starting point incremented by one using the above method.
  - This process is repeated and stopped when the local slope becomes positive.
  - Bruker believes that the **Positive Slope** algorithm is the most accurate of the three available Adhesion algorithms.

Explaining PeakForce Tapping

Details of PF-QNM Modulus calculation

- Acquire a period of deflection
  - Low pass filter
  - Subtract Baseline
  - Subtract first 17 points to zero baseline
- Use deflection at 'Sync Dist' for feedback
- Find Adhesion
- Linearize Force: (F-Fadh)^2/3 for DMT
- Calculate Z for each point based on Freq, Amplitude & Sync Dist QNM
- indentation d = Z – deflection + const
- Calculate slope from linear fit of (F-Fadh)^2/3 vs. indentation
- Scale floating point result in LSBs to transfer to host

DMT Model:

$$F - F_{adh} = \frac{4}{3}E^{*}\sqrt{R}d^{\frac{3}{2}}$$

So

$$E^{*} = \frac{3}{4\sqrt{R}}\left\{\frac{\partial}{\partial d}\left[(F - F_{adh})^{\frac{2}{3}}\right]\right\}^{\frac{3}{2}}$$

But the slope is calculated on the DSP in units of LSBs. Converting to LSBs

$$F - F_{adh} = \frac{S_F}{16}(F_{LSB} - F_{adhLSB}),\text{ where } S_F = \text{force sens in } \frac{N}{Arb}$$

$$d = S_D\left(\frac{4V}{2^{16}}\right)d_{LSB},\text{ where } S_D = \text{Amp sens in } \frac{m}{V}$$

So

$$E^{*} = \frac{3}{4\sqrt{R}}\frac{\frac{S_F}{16}}{\left[S_D\frac{4V}{2^{16}}\right]^{\frac{3}{2}}}(LSB\ slope)^{\frac{3}{2}}$$

But we want to give S_D, S_F, R in nm & nN

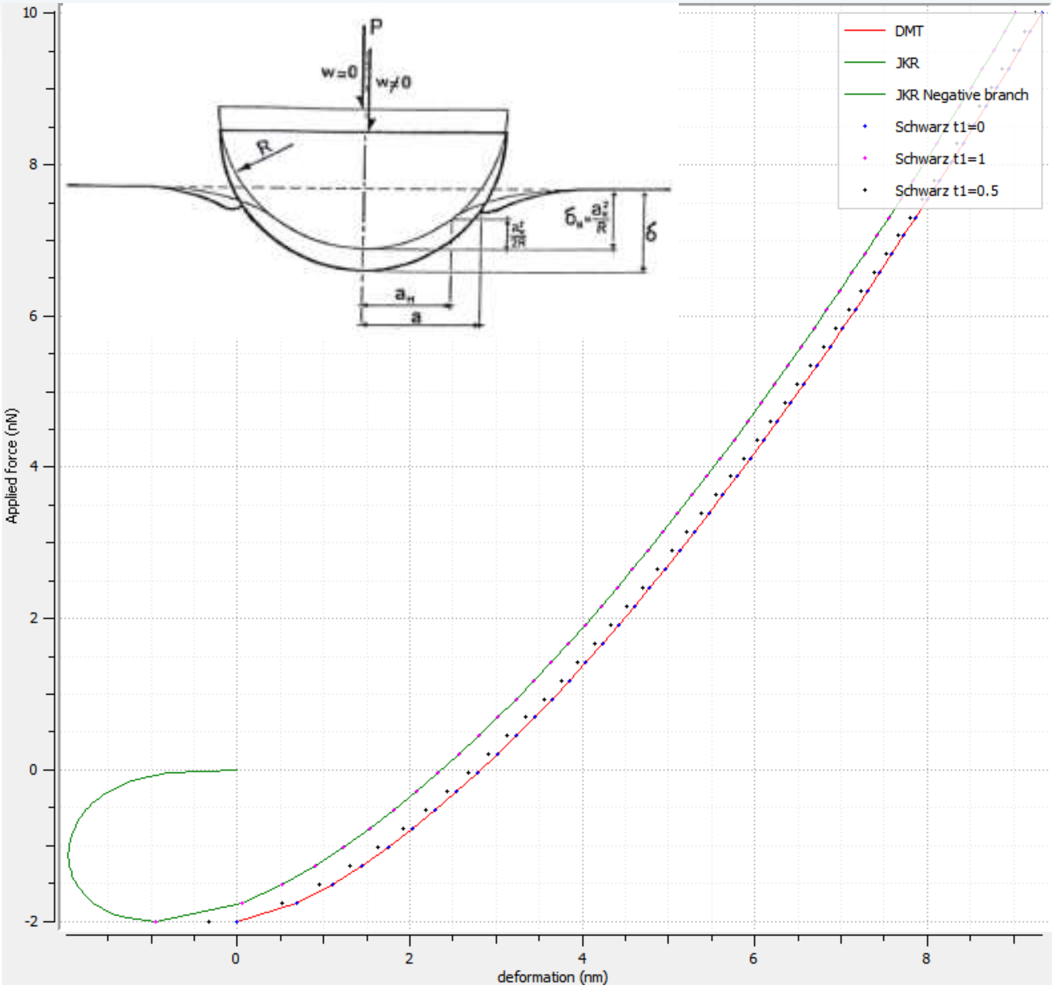
$$E^{*} = \frac{3\cdot 2^{24}S_F\cdot 10^{-9}}{4\cdot 16\cdot 8\sqrt{R\cdot 10^{-9}}(S_D\cdot 10^{-9})^{\frac{3}{2}}}(LSB\ slope)^{\frac{3}{2}}$$

$$E^{*} = 98.304\cdot 10^{12}\frac{S_F}{\sqrt{R}S_D^{\frac{3}{2}}}(LSB\ slope)^{\frac{3}{2}}$$

Explaining PeakForce Tapping

Addressing adhesion: DMT, JKR, MD, Schwarz

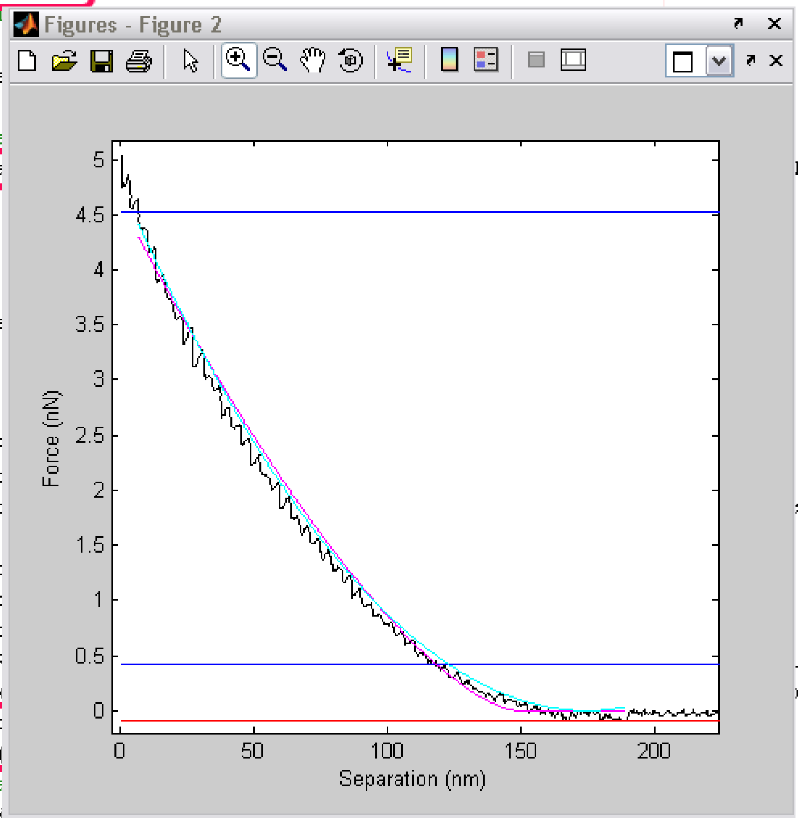
- Problem: DMT model does not fully include the effect of short range forces within the contact for soft, adhesive samples
- Maugis-Dugdale and Schwarz provide a transitional model
  - Here we have plotted DMT, JKR, Schwarz for R=10nm, Fa=2nN, E=100MPa
- If adhesion is fairly small compared to max force, differences are minimal
  - NA will support these models in the near future…



Explaining PeakForce Tapping

MATLAB Toolbox for more custom models

```
function NSMatlabExamples()
    NSMU = NSMatlabUtilities();
    %open a force curve fil
    currentFolder = pwd;
    fileName = strcat(curre
    NSMU.Open(fileName);
    %get F vs tip-sample se
    [xTrace, xRetrace, yTra
    %uncomment below lines
    %plot(xTrace, yTrace);
    %hold on;
    f2=figure(2);
    plot(xRetrace, yRetrace
    xlabel(xLabel);
    ylabel(yLabel);
    hold on;
    [contactPoint, contactP
    plot(xRetrace,contactPo
    [regionBottom, regionTo
    %mark the fit region
    plot(xRetrace,regionTop
    plot(xRetrace,regionBot
    [index1, index2] = Comp
    K = LinearizedDMTFit(xR
    K = LinearizedSnedFit(x
    PR = NSMU.GetPoissonRat
    TR = NSMU.GetTipRadius(
    TA = 0.314; %NSMU.GetHa
    E_DMT = GetDMTModulus(K
    E_Sned = GetSnedModulus(K, PR, TA)
    NSMU.Close();
end
```



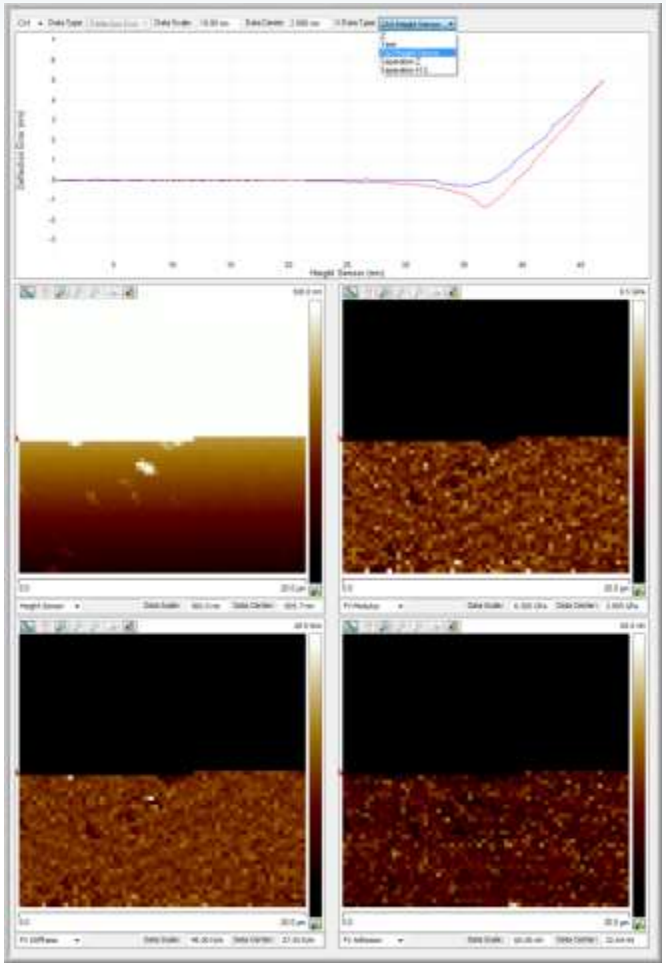
- MATLAB calls DLL to access Nanoscope data files directly
- No more concerns regarding file parsing or format changes over time
- No need to ASCII export: better automation
- Frees researchers to focus on modeling and results

Enabling comparison to other modes

What is "*FAST*Force Volume"?

(Nanoscope v9.20)

- Increased maximum 'linear' ramp rate from 10Hz to 300 Hz
- Low Force triggering
- FV Ramp channels increased from 1 to 3
  - Save Z-sensor during ramp so closed loop Z not needed
- Rectangular, bidirectional scanning
- New FV View shows selectable Ramp plot and 4 property images
  - Adhesion, force modulus, stiffness, & height
- High resolution FV = more pixels in X, Y, Z
  - (256x256)x256 increased to (256x256)x2048
  - Max pixels now (956x956)x256
- Improved analysis

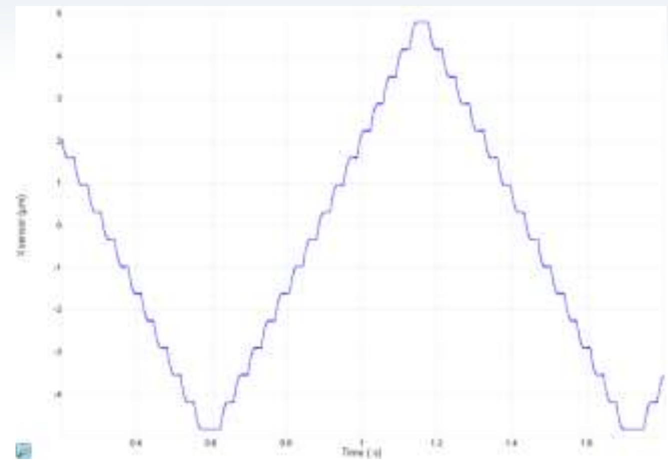


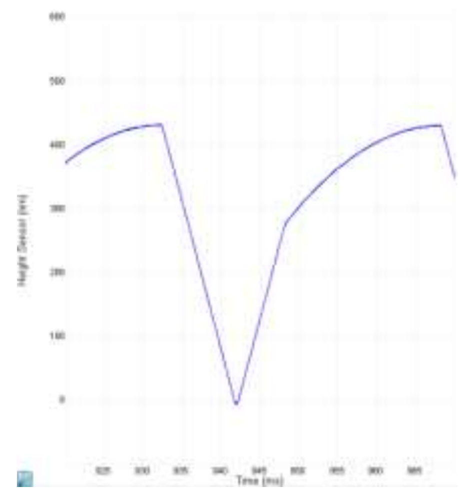
Enabling comparison to other modes

How did we make Force Volume faster?

(Nanoscope v9.20)

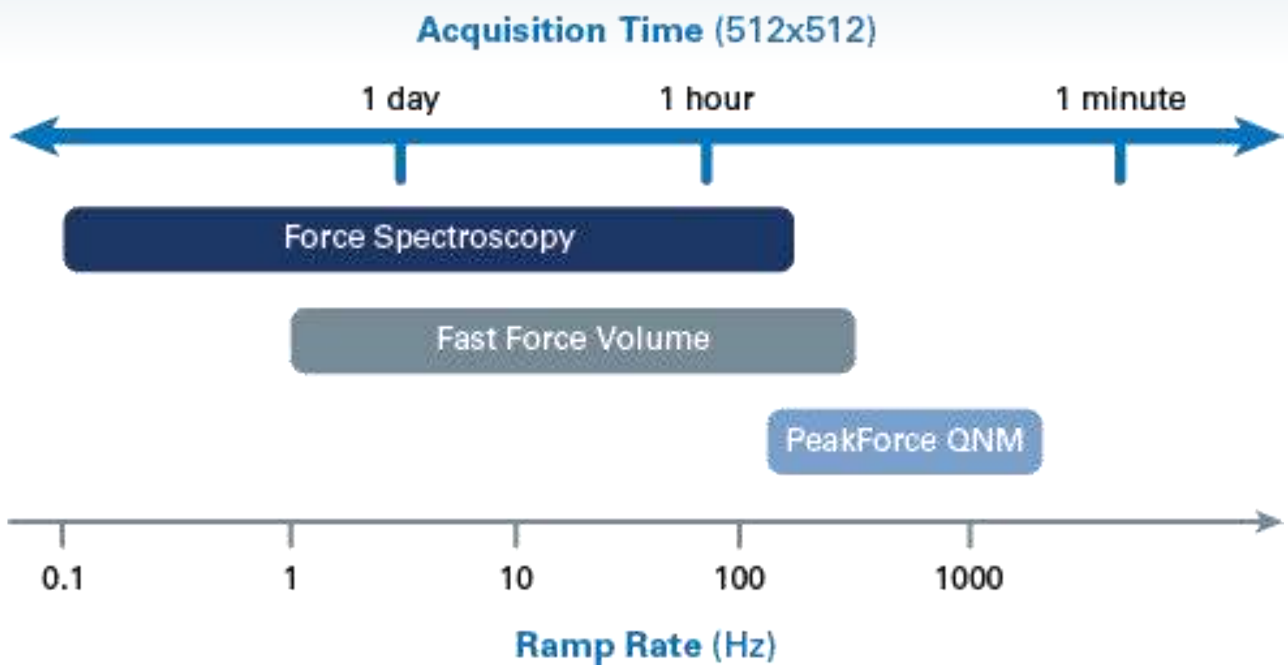
- Improved XY scanning: rectangular scan, deceleration before ramp
- 'XY Move Lift Factor': allows shorter ramps for more points & slower tip velocity in the interesting part, without crashing tip during lateral move
- 'Velocity Ramp Limit': slow down after trigger when acceleration is too great
  - Overshoot: adjust trigger
- Increased DSP sample rate to 80kHz
- Collect Height sensor during curves to avoid use of slower CLZ





Enabling comparison to other modes

Easy comparison of Force Volume & PeakForce QNM (Nanoscope v9.20)

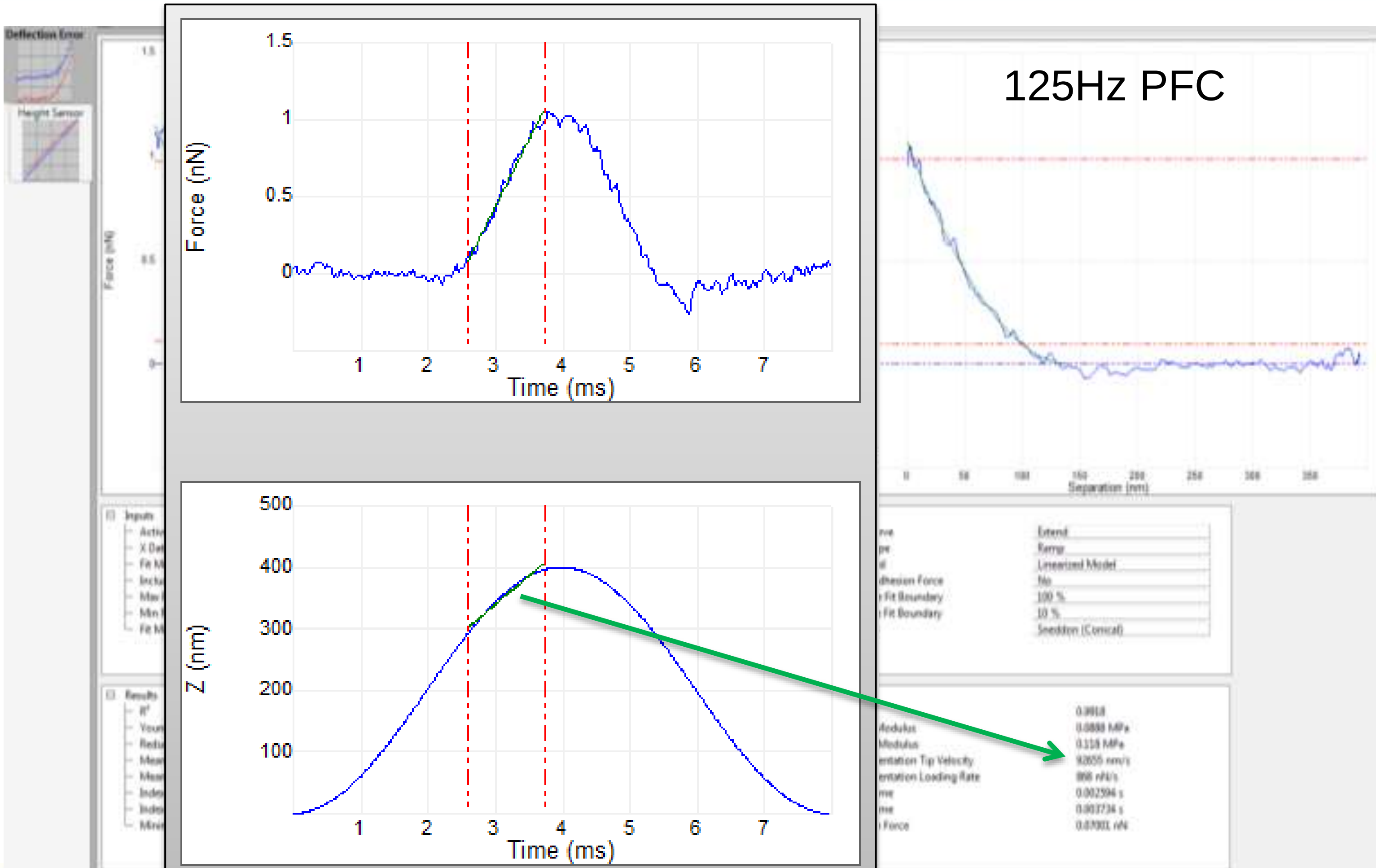


- Close the gap in frequency between Force Volume and PeakForce QNM
  - Decrease PeakForce QNM minimum frequency to 125Hz and increase FV to 300Hz
- Improves productivity and makes high-resolution FV maps practical
- Allows investigation of time dependent material property maps

Enabling comparison to other modes

Comparing Sinusoidal (PeakForce Tapping) to Linear (FV)

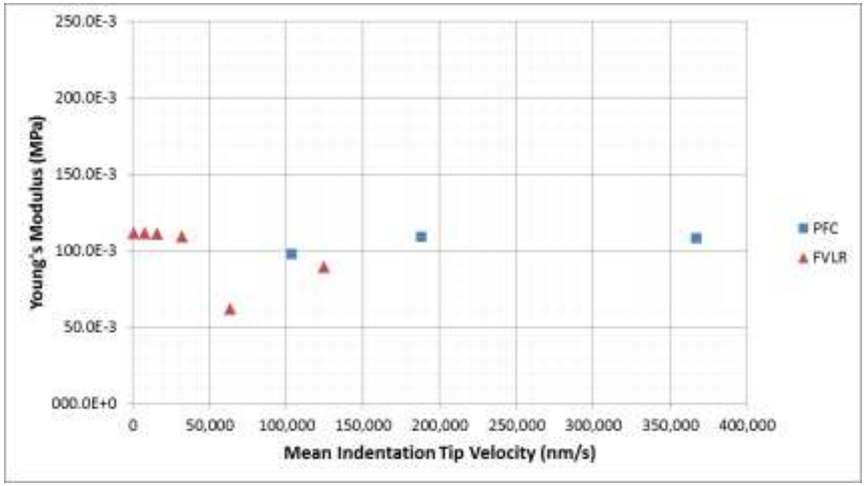
Frequency vs. Indentation tip velocity or Indentation Loading rate

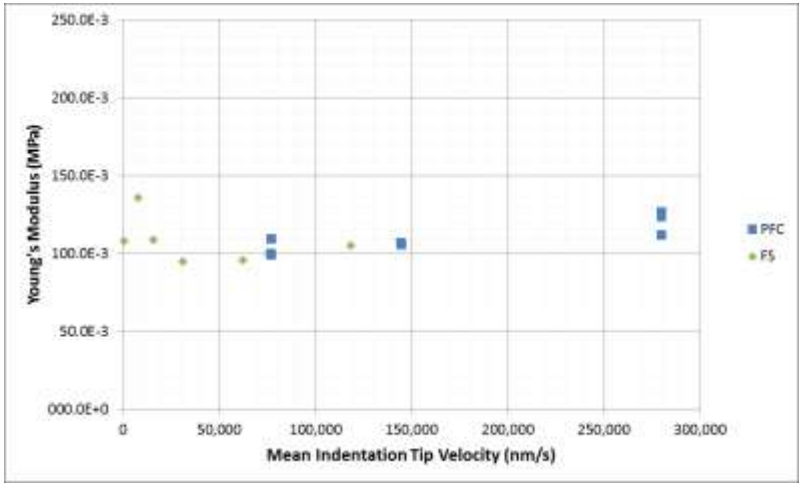


Enabling comparison to other modes

Preliminary work on Agarose gels

- Initial work on 2.5% Agarose gel with MLCT-E probe
  - Two runs on different days/probes, same system 1Hz to 500Hz
  - Good agreement between FS, FV, PFC modulus using Sneddon model



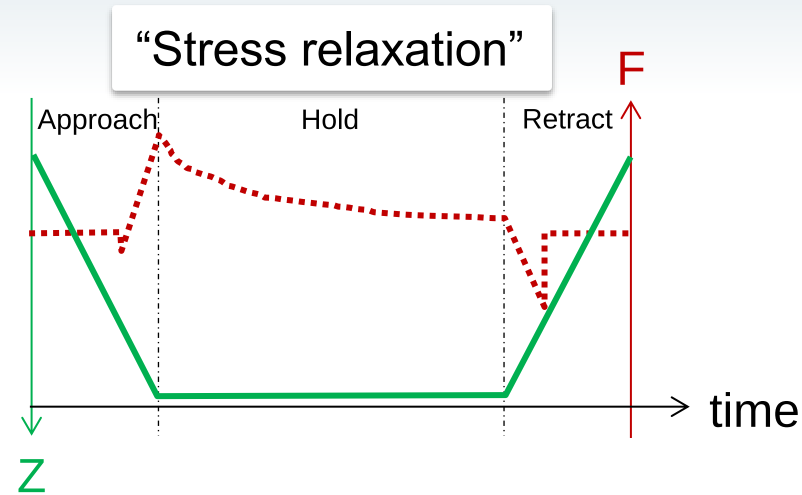


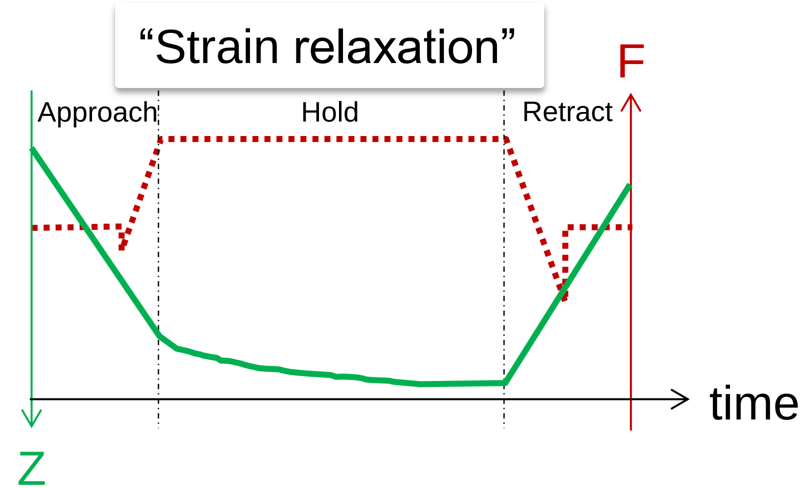
Enabling comparison to other modes

Relaxation experiments

(Nanoscope v9.20)

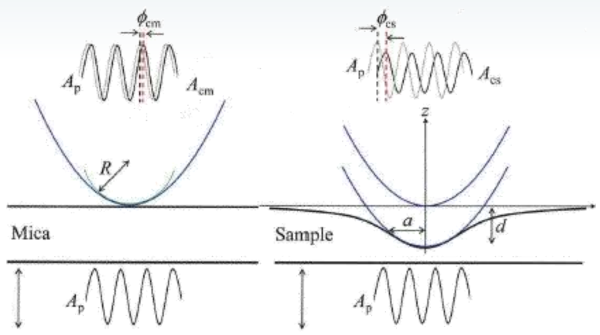
- Acquire Height Sensor and Force
- Mostly the same controls as ramp mode
  - Trigger identical to ramp mode
  - Typical approach, ret time ~0.1-10sec
- Typical Hold time ~1-5000sec.
- Sample rate during hold typically lower than approach & ret, with averaging
- For ramp+hold>a few sec
  - A plot showing force must be updated during acquisition to show ramp status
  - Ramp+hold can be cancelled
- Offline analysis
  - Support current analyses on app & ret data
  - Show app, hold, retract as a function of time with cursors & linear fitting
  - Hold analysis: plot only force or height sensor vs. time
    - Fit for exponential, indicate R^2



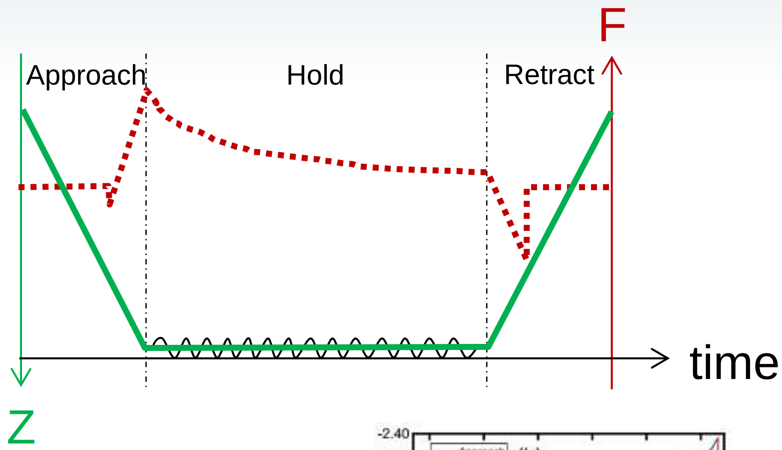


Enabling comparison to other modes

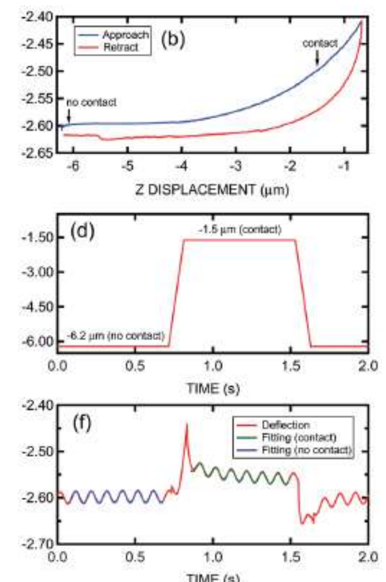
Nano-rheology



T. Igarashi, et. al, Macromolecules (2013)



- Nano-rheology requires modulation of Z during hold
  - Similar to Dynamic Mechanical Analysis (DMA)
  - Add small (~ a few nm at 5Hz-50kHz) modulation to Z position
  - Modulation off except during hold
- Record AC Force Amplitude and Phase as well as DC Force and Height Sensor
  - Need 4 channels
- Offline analysis to quantify results



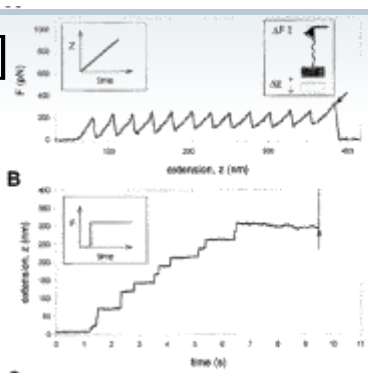
L. M. Rebêlo, et. al, Soft Matter (2014)

Enabling comparison to other modes

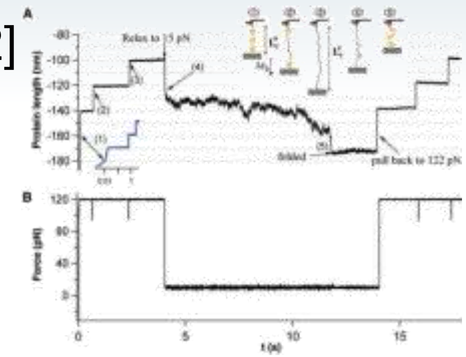
Updated Scripting for force clamp, etc.

(Nanoscope v9.20)

[1]



[2]



- Multiple steps allow preloading and molecule capture
- Step types:
  - Ramp Z to new position. Step ends early if trigger force reached
  - Ramp Force to a new Force setpoint. Step ends early if trigger Z is reached
- Step options:
  - Try script again from start if trigger is (or is not) reached
  - Apply Z modulation
  - Move in XY during step (Scratch)
  - Output TTL pulse at start of step

- Long scripts (>1 sec) display data before script is complete and can be aborted
- Save/reload predefined or user scripts
- Scripting can be automated with MIRO and ramp array
- Offline analysis
  - View entire result with synchronized cursors/zoom and indicators of step start. Read values from cursor positions, Linear fitting, R^2
  - Other analyses applied to a designated segment
  - MATLAB toolbox to import strip chart data

Enabling comparison to other modes
Improving analysis tools

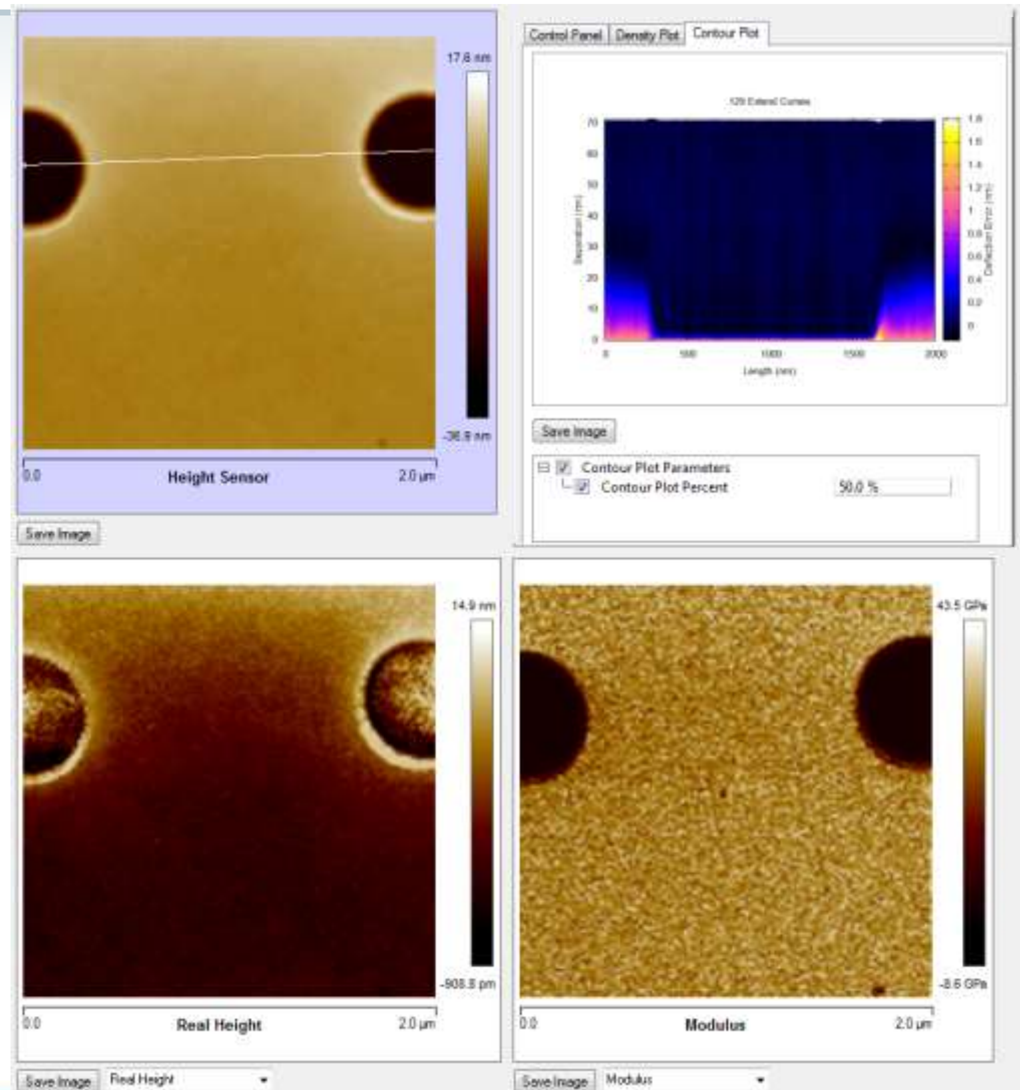
- Nanoscope Analysis v1.60 already has
  - Ramp frequency vs. Loading Rate or Tip velocity
  - Visualizing FV & PFC data cubes

- Planned for release in the near future…
  - JKR, Schwarz, Sphere-cone
  - Oliver-Pharr for plastic deformation
  - Adhesion fitting, WLC, molecular recognition with linker, etc.
  - Stress, strain relaxation analysis
  - Nanorheology analysis
  - Expand MATLAB toolbox: allow MATLAB to import new data types

Enabling comparison to other modes

Improved Force Volume & PeakForce Capture analysis

- ‘Real Height’
- ‘Density Plot’
- ‘Contour Plot’
- ‘Force Section’
- Baseline correction
- More adhesion options
- JKR model

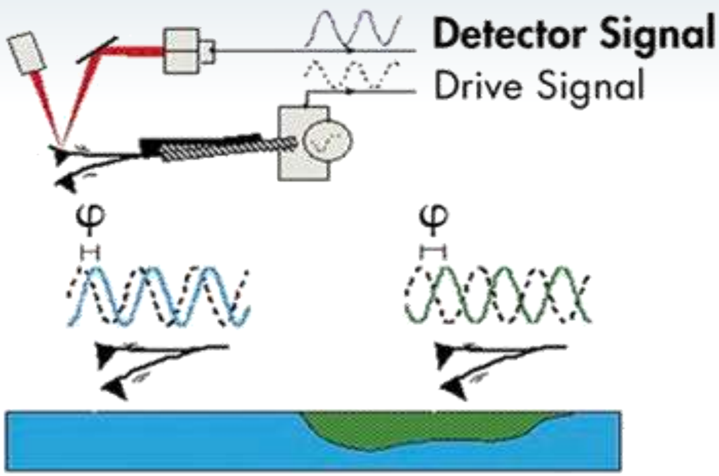


Why is PeakForce Tapping faster than *FAST*Force Volume?

- Even after adjusting Z motion to avoid resonance, Force Volume no longer works well at very high ramp rates
  - Due to method of determining turnaround point
- Force Volume waits for trigger to be reached before starting the turnaround (independent trigger for each ramp)
  - At low rates, trigger may be adjusted to compensate for overshoot
  - At high rates, overshoot becomes unacceptable: sample/experiment type determine the maximum rate
- PeakForce Tapping is much better at very high rates because triggering is not independent for each curve
  - Feedback on force at sync distance
  - System knows approximately where surface will be for the next curve & can start to slow down before reaching 'trigger'

Comparing PeakForce QNM to other mechanical mapping techniques

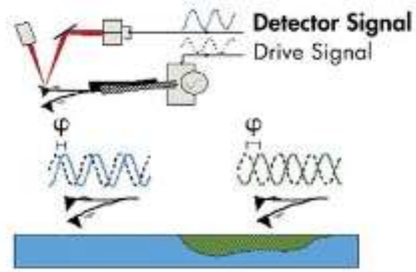
TappingMode



- TappingMode based techniques feedback on amplitude & do not use instantaneous force information
  - Amplitude variations caused by dissipation of cantilever energy (contact with surface, adhesion, damping, viscoelasticity, etc.)
  - Need to tune cantilever, gain selection is nontrivial
  - Nice because tends to reduce force on softer materials, but force is not controlled
  - May touch surface in some parts of sample, but not in others (eg. Deep trenches with squeeze film)

Comparing PeakForce QNM to other mechanical mapping techniques

TappingMode



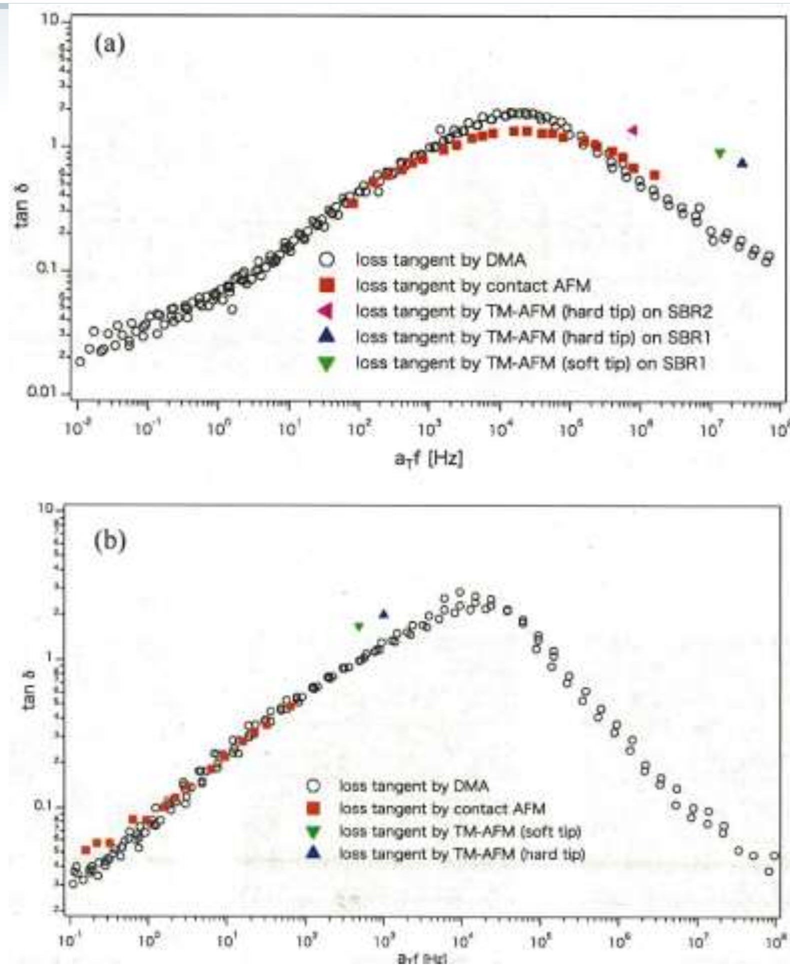
- TappingMode & Phase Imaging
  - Possibility for contrast inversion in phase image depending on spring constant, drive amplitude, amplitude setpoint

- AM-FM
  - Feedback = TappingMode, simultaneously modulate at a second cantilever eigenmode and measure frequency shift and amplitude
  - Fractional calculus allows calculation of modulus if no unexpected features in force curve
  - Adhesion is not independently measured, so no discussion of JKR vs. DMT, etc.

- HarmoniX
  - Feedback = TappingMode, uses special cantilevers to allow high bandwidth force measurement
  - Provides amplitude and phase of multiple harmonics (typically ~10)
  - Allows reconstruction of whole force curve for fitting and analysis
  - Difficult to calibrate and understand
  - Limited range, poor performance in liquid

Comparing PeakForce QNM to other mechanical mapping techniques
Loss Tangent

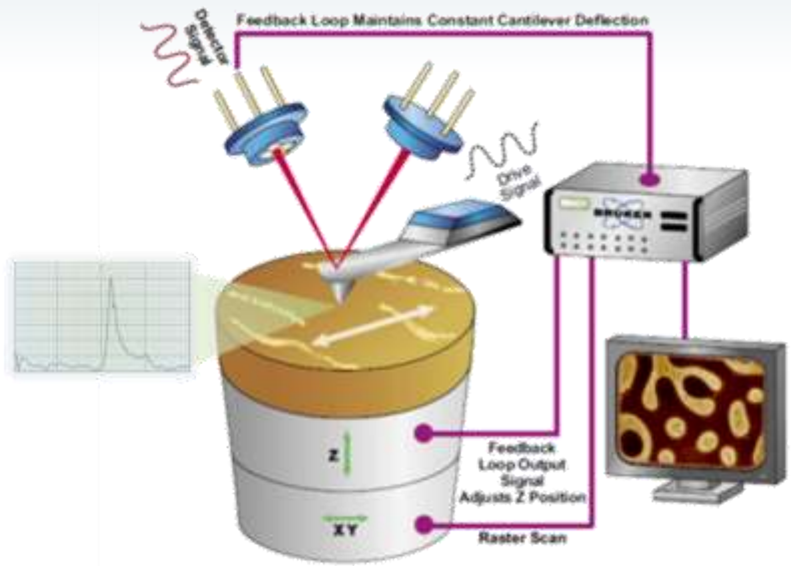
- TappingMode Phase Imaging
  - Simple calculation allows calculation of a pseudo 'loss tangent'
- "…unlike in the contact AFM, the tip in TM-AFM is not constant contact with the sample during the oscillation…some energy of the interacting system can dissipate due to the adhesion energy hysteresis…"



Nguyen, Hung K., et al. *Macromolecules* 2014

Nguyen, Hung K., et al. 2014 Macromolecules. doi:10.1021/ma501562q

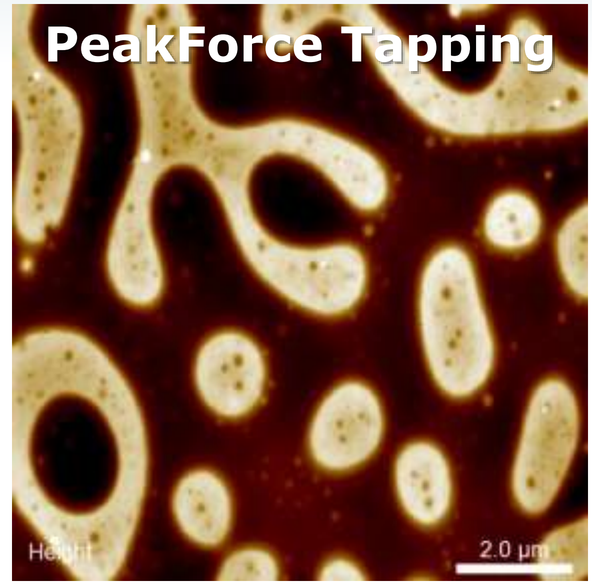
Comparing PeakForce QNM to other mechanical mapping techniques
Contact Resonance AFM



- Access higher frequencies ~100-1000kHz
- Better sensitivity for very stiff samples
- Can use multiple eigenmodes with the same probe
- Viscoelastic properties can also be measured (e.g. Yuya, Hurley, & Turner, J. Appl. Phys. 2008)

Comparing PeakForce QNM to other mechanical mapping techniques

Contact Resonance AFM on polymers



- Problem: Contact Mode
  - Sample damage: limits resolution for soft/delicate samples
  - Tip damage: Unstable property signal due to tip-sample contact area variation

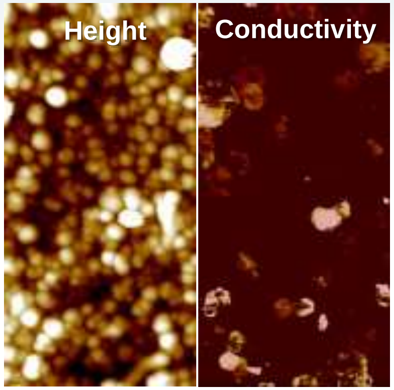
Comparing PeakForce QNM to other mechanical mapping techniques

PeakForce Tapping

- Feedback is directly on instantaneous force
  - Controls peak force on tip: preserves tip
  - Squeeze film damping is not a factor
- Off resonance modulation enables combination with other techniques & synchronization with contact part of curve
- Force distance curves contain all the details of the interaction in a single pass
  - No assumptions necessary about shape of force curve
  - Allows discovery of unexpected features in the curve
  - Allows observation of point of first contact
- No tuning to find resonance is required, but careful optimization of system, software, and probe can make a big difference in performance

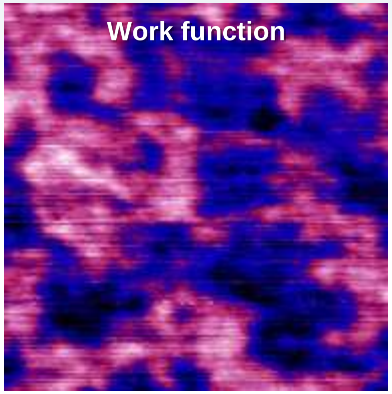
Comparing PeakForce QNM to other mechanical mapping techniques

PeakForce Tapping Mapping Breadth



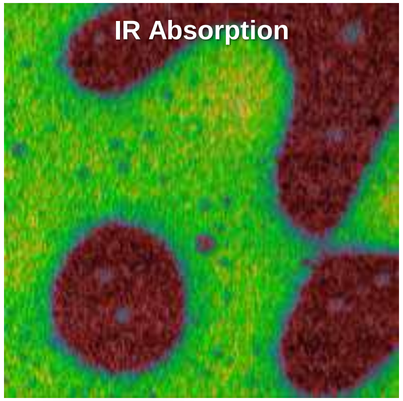
PeakForce TUNA
conductivity imaging, shown here on vertically standing carbon nanotubes. Impossible with contact mode.
1000nm image.

PeakForce KPFM
work function imaging, here shown for reduced graphene oxide. Revealing <20nm potential variations due to chemical heterogeneity.
750nm image.



PeakForce QNM
nanomechanical imaging with atomic defect resolution, shown here on calcite.
10nm image.

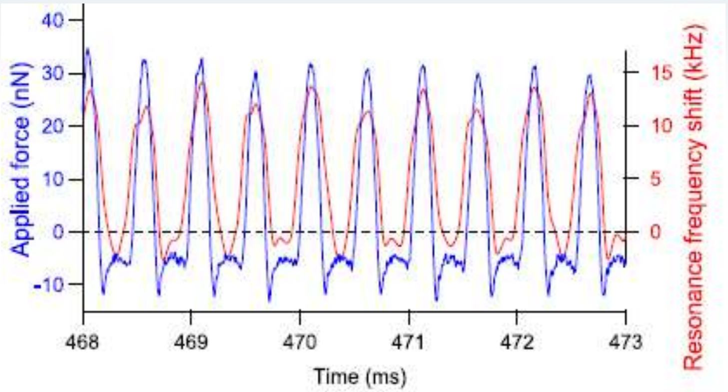
PeakForce IR:
sSNOM imaging of PS-PMMA at 1736cm-1, allowing identification of blend components based on CO stretch through either IR reflection or absorption.
4000nm image.

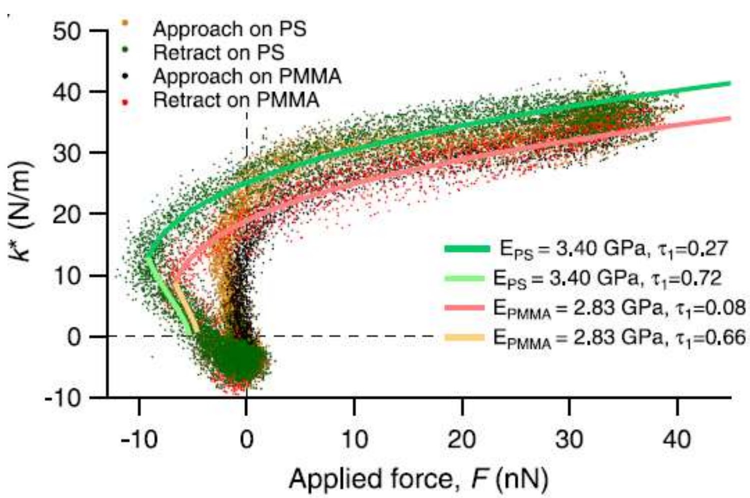


Combining CR & PeakForce Tapping for polymer research

"Intermittent contact resonance atomic force microscopy"

- Expand PeakForce Tapping Using open signal access with MultiMode and external PLL
- When PLL bandwidth is optimized for fast response, contact resonance can be observed for each tap
- "The key point in ICR-AFM is that the force– distance curves from PFT can be precisely synchronized with the resonance frequency measurements from PLL, so a contact stiffness versus force (or distance) curve can be obtained at any point in the scan."
- Provides improved sensitivity to modulus and allows investigation of variation of adhesion during contact





Stan, Gheorghe et al. 2014. Nanotechnology. doi:10.1088/0957-4484/25/24/245702

Summary

- PeakForce Tapping has many advantages over Contact Mode and TappingMode based techniques
  - Control of peak force
  - Acquisition of force curves for every tip-sample interaction
  - Off resonant modulation
- FASTForce Volume, improved Force Spectroscopy and Nano-rheology are different, slower ways of interrogating the sample
  - Wide range of properties can be mapped
  - Multiple properties can be mapped simultaneously
- Ramp rate for PFQNM >> FV
  - Allows high resolution mapping, usually with better force control
  - Enables comparison of results over wide range of indentation velocity
- The theory of PeakForce Tapping is not so complicated, but there are a few key concepts that users should understand

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