Advances in AFM Nanomechanics

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

Innovation with Integrity
AFM provides high resolution mapping of various sample properties.

- AFM - Topography
- AFM - Adhesion
- AFM - Modulus
- AFM - Deformation
- KPFM - Workfunction

[Images of various AFM and KPFM mappings are shown, labeled with sections 1 to 4.]
A brief review of AFM imaging technology

- Mapping topography -> more information
  - Contact mode (1986)
  - Tapping Mode (1992)
  - PeakForce Tapping (2009)
Bruker’s PeakForce Tapping technology

Note three essential features:

- **Sinusoidal ramping (not linear)**
  - Tip velocity approaches zero as the tip nears the sample surface
- **Real feedback loop force control**
  - Force control benefits from the results of prior force curves
- **Fast ramping**
  - Faster images, even with more pixels

**PeakForce Tapping imaging**

- Sinusoidal Z ramping
- Constant peak force feedback
- Tip intermittently “taps” sample (~1kHz)
- Best for soft samples, ultra-low forces

**The Result:**

- Best force control
- Fastest speed
- Highest resolution
- Greatest stability
Force Volume

• Force-Volume Mode
  • Linear Z ramping
  • Discrete force triggers at each ramp
  • Tip intermittently “taps” sample (\(<\sim0.01\text{kHz}\))
  • Force control is ramp speed dependent

Force-Volume potential issues:
• Linear ramping (not sinusoidal)
  • Tip hits sample at full velocity
  • Abrupt turn-around at high speed \(\rightarrow\) ringing, hysteresis
• Trigger monitored force control
  • Trigger monitors force and attempts to turn around at trigger. At high speeds, it can’t reverse fast enough, so it overshoots.

The Result, three options:
• Fast & high resolution, but poor force control, poor z accuracy
• Good force control & high resolution, but slow imaging \( (>1h)\)
• Fast & good force control, but low resolution (few pixels)
Correlated AFM and confocal Raman measurements reveal the lateral distribution of the regions of different composition.

- Regions with both polystyrene and polyisoprene present (light green) and with only polyisoprene present (dark green) are identified.
Graphene – Step By Step
Correlated Data
Unambiguously Reveals Layer Structure

• Thinnest layer is single layer as confirmed by 2D-band analysis
• Each additional layer is indeed graphene
  • AFM single layer steps exactly correspond to G-band intensity increase
• Area surrounding flake is devoid of graphene

AFM - Topography

Image size 15um

Raman - G-band

AFM step size analysis: ~300pm single layer steps

Raman 2D band analysis: characteristic single layer signature
Raman Data Points to Defect-Rich Area

- Raman D-band image suggests area of increased defect density along edge of single layer

- Can AFM yield additional insight?
Graphene shows much higher deformation, but similar modulus to SiOx substrate

- Graphene layer is initially supported on asperities...
- Layer is pushed down to SiOx surface during loading
- Layer does not fully recover during unloading
PeakForce QNM calculates sample properties directly from force curves.

The complete force curve from every interaction between tip and sample is analyzed in real-time, allowing:

- Feedback based on the peak force, protecting the tip and sample.
- Individual curves can be examined and analyzed offline (PeakForce Capture).
- Peak Force, Adhesion, Young’s Modulus, Deformation, Dissipation mapped simultaneously with topography.

\[ F - F_{adh} = \frac{4}{3} E^* \sqrt{R(d - d_0)^3} \]
Investigating the Defect Rich Area Shows Nanoscale Fragmentation

- **PeakForce QNM** shows nanoscale wrinkles in defect rich area
- Graphene wrinkles reflected strongly in mechanical properties: Softer, less adhesion
- Combined data shows that these wrinkles associated with defects impacting electronic structure
Correlated Electric Properties with PeakForce KPFM

- Measurement of workfunction dependence on number of layers
  - 80mV change from single to bilayer
  - Smaller changes for additional layers
- Workfunction known to be electric field dependent - deviation at single layer tip may be due to charges trapped in SiOx
The new Nanomechanics Package greatly expands these capabilities

- **The new Nanomechanics Package includes:**
  - New expanded PeakForce QNM capabilities for soft samples:
    - capture force curves at larger amplitudes
    - capture force curves at lower frequencies
    - addition of the Sneddon conical indenter model
  - New PeakForce Capture feature to capture full PeakForce QNM data
  - New Quantitative Force-Volume Mapping with new analysis tools
  - New comprehensive suite of force curve analysis tools

- **How do I get it?**
  - Offline tools are available to everyone at no charge – just download the latest version of Nanoscope Analysis v1.40r3
  - Users of Dimension FastScan and Icon, Bioscope Catalyst, and Multimode 8 can obtain a free upgrade to the latest version of Nanoscope v8.15r3

Expanded PeakForce QNM capabilities

- Can now choose Hertz/DMT (spherical) or Sneddon (conical) models
  - On very soft samples (e.g. cells, tissues, biomolecules), the tip often indents well past the very tip, even with the best force control, so the Sneddon model is often a better model for biological samples.

- Softer samples often require larger force curve ramp sizes
  - PeakForce QNM can now support ramp sizes up to 4µm (Catalyst only)
  - In some cases lower PeakForce QNM modulation frequencies can be useful. You can now choose among 250Hz, 500Hz, 1kHz and 2kHz (depending on system)
New, more quantitative PeakForce QNM data using the Sneddon model

- PeakForce QNM image of *E. coli* bacteria using a standard DNP-A probe in fluid with 300nm modulation amplitude at 250 Hz. The Sneddon (conical) modulus model was used with the nominal 18° tip half angle. (Scan size 5µm)
  - Note that the dividing cell on the right is significantly softer than the cell on the left (~2MPa vs ~15MPa)
  - Much of the substrate is too stiff to accurately measure under the same conditions as the bacteria, but note the presence of some softer components, including the bacterial flagella in the lower-right corner.
Sneddon model works well over the biologically relevant kPa-MPa range

- Agarose gels measured with PeakForce QNM (Sneddon model, MLCT-E probe)
PeakForce Capture
-Greater transparency and flexibility

- Capture a force curve at every pixel in PeakForce QNM images
  - QNM images still calculate and capture normally, as before
  - Additionally, force curves are captured to a separate file

- PeakForce Capture uses the Quantitative Force-Volume file format
  - Use the full Quantitative Force-Volume analysis tools on PeakForce Capture data to generate modulus and adhesion maps
  - Can import the data into custom analysis software
PeakForce Capture offline analysis
New Quantitative Force-Volume Mapping

- Force-volume has been widely used for more than 15 years for mapping sample properties
  - Important reference technique to compare to new methods
  - Allows very low ramp rates for comparison to non-AFM material property measurement techniques such as DMA

- The new Quantitative Force-Volume Mapping mode adds new real-time and offline analysis capabilities
  - Directly obtain modulus and adhesion maps from force-volume
  - Same indentation models (Sneddon & Hertz/DMT) as PFQNM
  - All force curves available for further offline processing
Force-Volume example

*E. coli* bacteria

DNP-A probe in fluid

- Quantitative Force-Volume Mapping images of *E. coli* bacteria using a 600nm ramp size and different ramp rates
  - The Sneddon (conical) modulus model was used with the nominal 18° tip half angle. (Scan size 5µm)
  - Modulus numbers vary only slightly for these ramp rates
Good agreement between PeakForce QNM and Quantitative Force-Volume Mapping

- Agarose gel series was measured with both techniques
- Many more measurements with PeakForce QNM for better statistics
  - Force volume: 256 points (16x16)
  - QNM: 16.4k points (128x128)
- PeakForce QNM provides more measurements faster
  - QNM: ~11min for 16.4k points
  - Force-volume: ~4min for 256 points
Doesn’t modulus depend on frequency?

Comprehensive force curve analysis tools

- NanoScope Analysis now includes:
  - Modify Force Parameters: Update key parameters in captured files
  - Baseline Correction: Remove force curve baseline offset and/or tilt
  - Boxcar Filter: Apply moving average smoothing filter to data
  - Indentation Analysis: Fit indentation models to obtain modulus values
  - Batch Processing: Apply multiple functions to many curves at once
  - MATLAB Toolbox: Easy loading of data directly from Nanoscope data files
Comprehensive force curve analysis tools

- These functions all work with Run History for automation!
MATLAB Toolbox

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

```matlab
function NSMatlabExamples()
    NSMU = NSMatlabUtilities();
    currentFolder = pwd;
    fileName = strcat(currentFolder, 'NSMatlabExamples_ExampleData.dat');
    NSMU.Open(fileName);
    %get F vs tip-sample separation
    [xTrace, xRetrace, yTrace] = NSMU.GetData('F', 'Tip Separation', true);
    %uncomment below line when you like to plot
    %plot(xTrace, yTrace);
    hold on;
    %plot(xTrace, yRetrace, yRetrace);
    xlabel(xLabel);
    ylabel(yLabel);
    hold on;
    [contactPoint, contactPointConfidence] = NSMU.GetContactPoint('Sample', 1);
    plot(xRetrace, contactPoint, 'o', 'MarkerSize', 8, 'MarkerFaceColor', 'r');
    hold on;
    [regionBottom, regionTop] = NSMU.GetRegion('Sample');
    hold on;
    %mark the fit region
    plot(xRetrace, regionTop, 'r--', 'LineWidth', 2);
    %plot(xRetrace, regionBottom, 'b--', 'LineWidth', 2);
    X = LinearizedDMTFit(xTrace, yTrace, 'Poisson', true);
    X = LinearizedSnedCorrelation(X, 0.314);
    PR = NSMU.GetPoissonRatio(X);
    TR = NSMU.GetTipRadius(X);
    TA = 0.314; % NSMU.GetHeleShafran()
    E_DM = GetDMTFit(X, PR, TR, TA);
    % E_Sned = GetSnedCorrelation(X, PR, TR, TA)
    NSMU.Close();
end
```
Peak Force QNM force curves: Interaction between metal-coated AFM tips & graphene

Courtesy: P. Lazar et al., ACS Nano, DOI: 10.1021/nn305608a (2013)
A powerful set of tools for Nanomechanical and co-located experimentation

- **Three techniques for QNM**
  - PFQNM for high-speed, high resolution
  - Force Volume for cases where loading rate dependence is interesting
  - Single force curves for cases where mapping is not as important

- **Complementary information from co-located techniques**
  - Topography, Raman, KPFM all reveal the graphene layers
  - Raman 2D band conclusively shows single layer
  - KPFM suggests stored charge in the wrinkled part of the layer
  - Correlation unravels nanoscale origin of observed far-field Raman spectral signatures
www.bruker.com
“On the use of peak-force tapping atomic force microscopy for quantification of the local elastic modulus in hardened cement paste”
Trtik et al, 2011

Epoxy impregnated hardened cement paste

Height (20um image) 
Adhesion 
Deformation 
Modulus 
EDS

Modulus Rendering

calcium hydroxide
unhydrated residues
other hydrates
differently oriented domains of CH
PeakForce QNM Example
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.
PeakForce QNM Example

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.