Nanoscale mechanical property measurements in AFM modes with direct force control
Part I: PeakForce Tapping and Force Volume mechanical property mapping

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A brief review of AFM imaging technology

- Mapping topography -> More information
  - Contact mode (1986)
  - Tapping Mode (1992)
  - Contact Resonance (AFAM, UAFM~1996)
  - Peak Force Tapping/PeakForce QNM (2009)
    - PeakForce TUNA (2011)
    - PeakForce KPFM (2012)
    - PeakForce IR (2014)
    - PeakForce XYZ (…)
PeakForce QNM vs. Force Volume
Mechanical property mapping modes

**PeakForce Tapping (PF-QNM)**

- Sinusoidal ramping (not linear): no piezo resonance, no overshoot
- Real feedback loop force control: benefits from prior curves
- Fast ramping (~kHz): faster images, even with more pixels

**Force Volume (FV)**

- Linear ramping: abrupt turn-around at high speed -> ringing, overshoot
- Discrete force triggers at each ramp: attempts to turn around at trigger. At high speeds, it can’t reverse fast enough, so it overshoots.
- Ramping rate is limited (<~0.01kHz for best curves)
The result combines:
- Best force control
- Fastest ramp speed
- Highest imaging resolution
- Excellent force stability

The result, three options:
1. Fast & high resolution, *but poor force control, poor z accuracy*
2. Good force control & high res., *but slow imaging (>1h)*
3. Fast & good force control, *but low resolution (few pixels)*
PFT Provides Excellent Spatial Resolution & Force Control
PF-QNM & FV calculate 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.
- Peak Force, Adhesion, Young’s Modulus, Deformation, Dissipation mapped simultaneously with topography.
- Individual curves can be examined and analyzed offline (PeakForce Capture)

\[
F - F_{adh} = \frac{4}{3} E^* \sqrt{R(d - d_0)^3}
\]
High resolution PF-QNM
New information revealed

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 – can see in averaged profile.
- Lamella are highly ordered and perpendicular to interface ~250nm into the Tie layer.
High resolution PF-QNM
New information revealed

- Tie and Sealant layers are relatively compatible = 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: more ordered region to ~1um from the interface.

Barrier layer
Nylon
Strength & gas impermeability

Tie layer
ULDPE
Preserves layer adhesion

Sealant layer
Metallocene PE/LDPE blend
Adheres to itself when heated
Variation in viscoelastic response
Visible in Dissipation map

• Dissipation in Barrier<Tie
  • Demonstrated both by images and simultaneous force curves extracted from HSDC
• Hysteresis in contact part of force curves suggests an inelastic deformation mechanism is active
Signature of viscoelasticity in force curves
VEDA simulation: ramping at different rates

- Generalized Maxwell model using Prony fit of storage & loss modulus data
- Apparent modulus changes with ramp rate
- Hysteresis in curve also changes with ramp rate

Simulated force vs. separation curves on isotactic polypropylene. Blue: sinusoidal ramps. Violet: linear ramp at 100Hz

PFQNM uncovers variation in modulus

PF-QNM extends freq. range

PS modulus roughly constant
LDPE modulus increasing with ramp rate
Contact Resonance AFM

Extending Modulus measurements to even higher frequencies

- 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)
Contact Resonance AFM

Contact Mode issues

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

- Could CR be combined with PFT?
Integrating PeakForce Tapping with TUNA (2011)

- PFTUNA is built on PF-QNM
- Additionally, PF-TUNA module has improved bandwidth:
  - PeakForce Tapping Frequency: 1 kHz - 2 kHz
  - TUNA: >10x faster
PeakForce Tapping Mapping Breadth

Stable, nondestructive imaging with simultaneous mechanical properties

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

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

PeakForce TUNA: Could you combine PFT and CR using our open signal access?
Summary

Force Volume and PeakForce QNM both allow analysis of individual force spectra
- Wide range of properties can be covered
- Multiple properties can be mapped simultaneously

Ramp rate for PFQNM >> FV
- Allows high resolution mapping
- Expands accessible range of frequency significantly

Time dependent mechanical properties can be investigated by observing modulus and dissipation at different ramp rates
- DMT, Sneddon models do not include viscoelasticity
- Further work required to make a quantitative connection between ramp observations and models
- Contact Resonance may be able to help

PeakForce Tapping is a great candidate for integration with other AFM techniques
Advanced AFM Applications Training Class

Dates: **August 25—29, 2014**
Location: Bruker AFM Headquarters, 112 Robin Hill Rd., Santa Barbara, CA 93117

Also check out Nanoscale world community and SPM Digest Forum: nanoscaleworld.bruker-axs.com/
Nanoscale mechanical property measurements in AFM modes with direct force control

Part II: Force Control in Contact-Resonance Atomic Force Microscopy

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Contact resonance AFM: cantilever dynamics

Ultasonic Atomic force microscopy (UAFM)
Yamanaka et al., Japan. J. Appl. Phys. 35, 3787, 1996

Atomic force acoustic microscopy (AFAM)

Contact resonance AFM: contact mechanics

Hertz model
(sphere on flat)

\[ k_N = \frac{\partial F_N}{\partial \delta_z} = 2rE^* \]

\[ \frac{1}{E^*} = \frac{1}{M_S} + \frac{1}{M_T} \]

\[ M = E/(1 - \nu^2) \]

\[ E_S^* = E_R^*(k_S^*/k_R^*)^n \]

\[ \frac{1}{M_S} = \left( \frac{k_R^*}{k_S^*} \right) \frac{1}{M_R} + \left[ \left( \frac{k_R^*}{k_S^*} \right)^n - 1 \right] \frac{1}{M_T} \]

\[ M_S = \frac{\left( \frac{k_{R1}^*}{k_{S1}^*} \right)^n \left( \frac{1}{M_{R2}} - \frac{1}{M_{R1}} \right) + \left( \frac{k_{R1}^*}{k_{S1}^*} \right)^n \frac{1}{M_{R1}} - \frac{1}{M_{R2}}}{\left( \frac{k_{R1}^*}{k_{S1}^*} \right)^n \left( \frac{1}{M_{R2}} - \frac{1}{M_{R1}} \right) + \left( \frac{k_{R1}^*}{k_{S1}^*} \right)^n \frac{1}{M_{R1}} - \frac{1}{M_{R2}}} \]

One reference

uncertainty 20%
U. Rabe et al., Ultrasonics 38, 430 (2000)

Two references

uncertainty 5%

A. M. Jackob et al., Nanoscale, 6, 6898, (2014): “… in accordance to, less effort in probe modeling is still sufficient for quantitative nano mechanical analysis of conventional materials as long as a multi-reference sample approach is used.
Quasi-static vs dynamic contact stiffness: measurement sensitivity

AFM spectroscopy: Force-distance curves

\[ \frac{k}{k_s} = \frac{1}{k_c} + \frac{1}{k^*}, \quad \beta = k^*/k_c \]

\[ S_{id} = \frac{1}{k_c} \frac{\partial k}{\partial \beta} = \frac{1}{(\beta + 1)^2} \]

CR-AFM spectroscopy: Resonance spectra

\[ S_n = \frac{1}{f_n} \frac{\partial f_n}{\partial \beta} = F(k_n, \beta) \]

Normalized contact stiffness, \( k^*/k_c \)

Normalized sensitivity, \( S/S(k^* = 0) \) (%)
F-d versus CR-AFM with a medium-stiff cantilever, $k_c=35.5$ N/m, on low-k dielectric films

Samples from Sean King (Intel Corp.)
CR-AFM imaging on Cu/low-\(k\) dielectric interconnects

On a Cu-low-\(k\) interconnection structure, CR-AFM provided contrast in contact stiffness and damping between the Cu lines and the surrounding dielectric material and the intervening Ta/TaN barrier layer. By varying the load applied to the probe, clear differences in the decay of damping with depth beneath the surfaces of the Cu and the dielectric were revealed.

Stan et al., Nanotechnology 23, 215703 (2012)
CR-AFM imaging on granular Au film

Both topography and contact stiffness maps were self-consistently correlated to reveal nanoscale variations of the indentation modulus at the grain level as well as across the grains.

Individual elastically-deformed asperities make a non-conforming contact with the spherical smooth end of the CR-AFM probe.

Stan and Cook, Nanotechnology 19, 235701 (2008)
Contact geometry: tip wear

Si tips, especially the sharp ones, wear when they are used in contact spectroscopy and scanning modes. Great care is required to monitor the tip wear during use. This can be done from repeated contact stiffness measurements on the same material as the contact stiffness is in direct relationship with the change in contact area, $k^* = 2rE$. Consequently, reliable contact stiffness measurements required stable tip shapes, which, most likely, will be the ones that are pre-wear.

Fresh sharp tip (NanoSensors)


Tip used in contact AFM scanning mode (Killgore, Geiss, and Hurley, Small 7, 1018 (2012))
Flattened tip used in CR-AFM measurements on low-\(k\) dielectric thin films

Credit for SEM images:
Kavuri Premsagar Purushotham (NIST)
Load-dependent CR-AFM measurements

The measurements consist of recording simultaneously both the **deflection** and **resonance frequency** of an AFM cantilever as the probe is gradually brought in and out of contact.

Real-time load-dependent CR-AFM on a 1.6 GPa low-k dielectric

Flat-punch approximation:

\[ k^* = 2r_c E^* = 2r_c \left(\frac{1}{M_T} + 1/M_S\right)^{-1} \]
Intermittent Contact Resonance AFM (ICR-AFM)

The measurements consist of recording simultaneously the deflection, resonance frequency, and amplitude of the AFM cantilever as the probe is gradually brought in and out of contact at any point in the scan.

Key points for quantitative nanoscale mechanical property characterization by 3D ICR-AFM:

- force control during intermittent contacts (Force Volume, Peak Force Tapping)
- adhesive force measurement
- force-resonance frequency correlation during contacts
- imaging at a non-eigenmode frequency (lower than $f^1$)
Intermittent Contact Resonance AFM (ICR-AFM) in Force-Volume AFM

ICR-AFM on PS-PP blend: 128x128 ramps over 2 µm x 2 µm area; 1 s per ramp.

Approach

Resonance frequency  |  Resonance amplitude
---|---
660 | 0.50 | δ = - 5.0 nm
662 | 0.45
668 | 0.40
665 | 0.30 | δ = - 2.5 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = - 1.0 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = - 0.5 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = 0.0 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = 0.5 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = 1.0 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = 2.5 nm
665 | 0.20
660 | 0.15
660 | 0.10 | δ = 5.0 nm

Retract

Resonance frequency  |  Resonance amplitude
---|---
670 | 0.40 | δ = - 5.0 nm
665 | 0.35
660 | 0.30 | δ = - 2.5 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = - 1.0 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = - 0.5 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = 0.0 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = 0.5 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = 1.0 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = 2.5 nm
660 | 0.20
660 | 0.15
660 | 0.10 | δ = 5.0 nm

$f_1^{\text{air}} = 104.9$ kHz, $f_2^{\text{air}} = 657.6$ kHz; $k_c = 9.5 \pm 0.5$ N/m
Tomographic ICR-AFM

Fast dynamic indentation on elastomers

In the case of a fast dynamic indentation of an elastomer (Wahl et al., *J. Colloid Interface Sci.*, 2006, 296, 178), due to viscoelastic effects, the contact area remains approximately constant during oscillations and the contact geometry resembles that of a “flat punch” configuration, with \( \frac{k^*}{r_c} \) rather than \( \frac{k^*}{\partial F / \partial \delta} \).

With Schwarz contact model (U. D. Schwarz, *J. Colloid Interface Sci.*, 2003, 261, 99), a transition model between DMT and JKR models, the depth-dependence of the contact stiffness in the “dynamic flat-punch” limit is given by:

\[
\delta = \frac{k^{*2}}{4R_iE^{*2}} - \frac{\tau_1}{\sqrt{4 - \tau_1^2}} \sqrt{2k^*F_a/(R_iE^{*2})}
\]

\( \tau_1 = 0, \) DMT -long-range attractive force outside the contact area.

\( \tau_1 = 1, \) JKR -short-range attractive force inside the contact area.
Intermittent Contact Resonance AFM (ICR-AFM)

Indentation modulus, $E^*$

Transition parameter, $\tau_1$
ICR-AFM: Frequency, amplitude, and dissipated energy

Resonance frequency (kHz) vs. Indentation depth, δ (nm)

Resonance amplitude (nm) vs. Indentation depth, δ (nm)

Dissipated power (fW) vs. Distance (nm)

Legend:
- PS: Approach, Retract
- PP: Approach, Retract

Indentation depth, δ (nm)
- 60
- 40
- 20
- 0

Dissipated power (fW)
- 60
- 40
- 20
- 0
Intermittent Contact Resonance AFM (ICR-AFM) in Peak Force Tapping

- force control during intermittent contacts (Force Volume, Peak Force Tapping)
- adhesive force measurement
- force-resonance frequency correlation during contacts
- imaging at a non-eigenmode frequency (lower than $f_1$)

$\begin{align*}
    f_1^\text{air} &= 107.3 \text{ kHz}, \\
    f_2^\text{air} &= 670.5 \text{ kHz}, \\
    f_3^\text{air} &= 1,865.5 \text{ kHz}; \\
    k_c &= 9.12 \pm 0.07 \text{ N/m}
\end{align*}$

ICR-AFM as Amplitude Modulation – Frequency Modulation of Peak Force Tapping

(a) Topography (PFT)
(b) Adhesion (PFT)
(c) Dissipation (PFT)
(d) DMT Elastic Modulus (PFT)

Resonance frequency shift $f_3$ (ICR) slow PLL - 100 µs time constant
Resonance frequency shift $f_3$ (ICR) fast PLL - 1 µs PLL time constant
ICR-AFM: Individual oscillations

With a slow detection, the changes in the contact resonance frequency are *averaged* over the entire period of an oscillation including out-of-contact intervals.

With a fast detection, the averaging time is reduced, so the changes in the contact resonance frequency during individual oscillations are *momentarily tracked*.
Positive – slope region:

\[ E_{PS} = 3.40 \pm 0.10 \text{ GPa}, \quad \tau_{1} = 0.27 \pm 0.04 \]
\[ E_{PMMA} = 2.83 \pm 0.09 \text{ GPa}, \quad \tau_{1} = 0.08 \pm 0.04 \]

Negative – slope region:

\[ E_{PS} = 3.40 \pm 0.10 \text{ GPa}, \quad \tau_{1} = 0.72 \pm 0.01 \]
\[ E_{PS} = 2.83 \pm 0.09 \text{ GPa}, \quad \tau_{1} = 0.66 \pm 0.03 \]
Conclusions

- Depth-dependence of contact stiffness in force-controlled CR-AFM.


- ICR-AFM (in force volume and peak-force tapping) is a new 3D high-speed nanomechanical property measurement AFM technique.

- Improved quantitative elastic modulus measurements were demonstrated by using ICR-AFM on PS/PP and PS/PMMA blends.

- Transition contact models (e.g. Schwarz model) provide a self-adaptive analysis for the heterogeneous mechanical properties of elastomeric surfaces at the nanoscale.
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Also check out Nanoscale world community and SPM Digest Forum:
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