Nanoscale Indentation of Polymeric Materials

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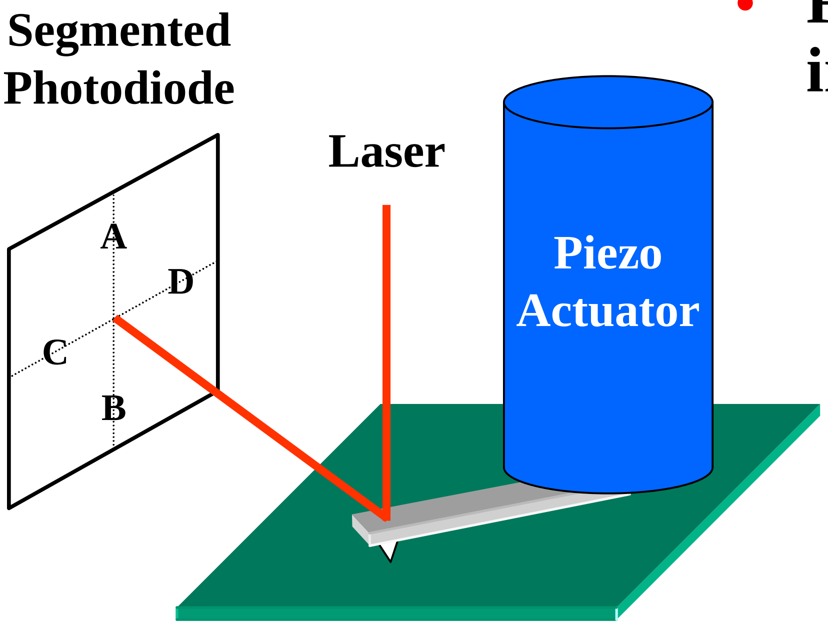
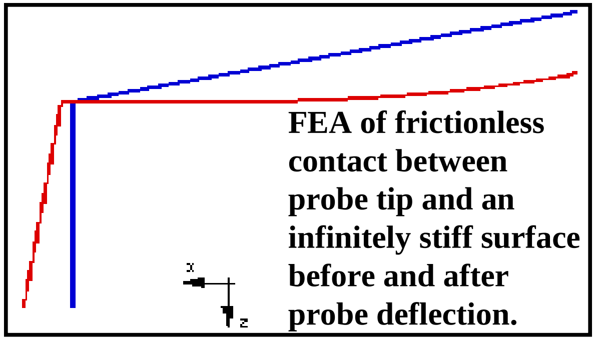
Indentation Using AFM Probes

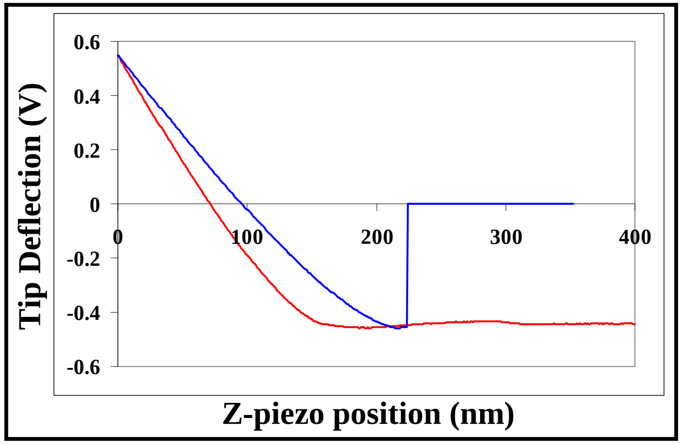




FEA of frictionless contact between probe tip and an infinitely stiff surface before and after probe deflection.

- Force Mode used to measure indentation response.
  - <u>Advantages</u>:
    - » Probe spring constant can be chosen to optimize force sensitivity.
      - – Can achieve nanoscale indentation measurements on soft materials.
    - » Combine with tapping mode/phase imaging before and after indentation measurements.
      - – Probe specific microstructural features.
  - <u>Disadvantages</u>: measurement uncertainties due to
    - » nonlinearities associated with piezo and photodiode.
    - » lateral motion of the tip caused by bending of the cantilever.
    - » non-ideal tip shapes.
    - » indentation tests are neither displacement nor load controlled.

Calculation Procedures



- Minimize instrumental uncertainties
  - use small ranges of z motion (e.g., ≤ 300 nm)
  - use middle of photodiode (e.g., ± 1 V to ± 3 V)
  - use high z scan rates (e.g., ≥ 4 Hz)
  - set up an appropriate lateral compensation
- Compliance calibration
  - Take force curve data on a stiff sample
    - before and after indenting polymer sample
- Identification of “force = 0”
  - Take force curve data with sufficient free air response
    - assume this level of tip deflection signal corresponds to zero force.
- Convert force curves to load-penetration curves
  - Use compliance calibration to subtract probe deflection from system motion to get sample penetration
  - Multiply probe deflection by spring constant to get applied force

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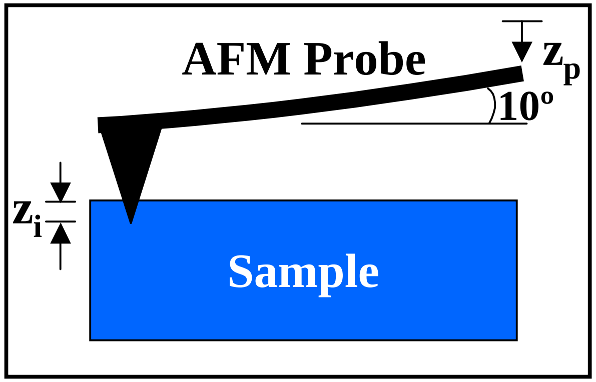
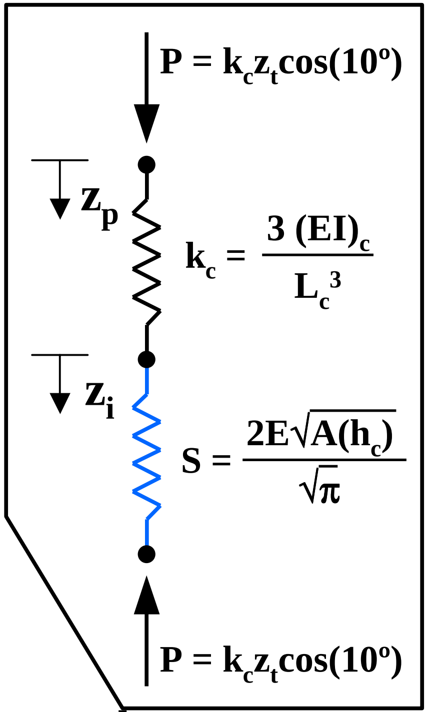
Spring Model of Probe-Sample Interaction



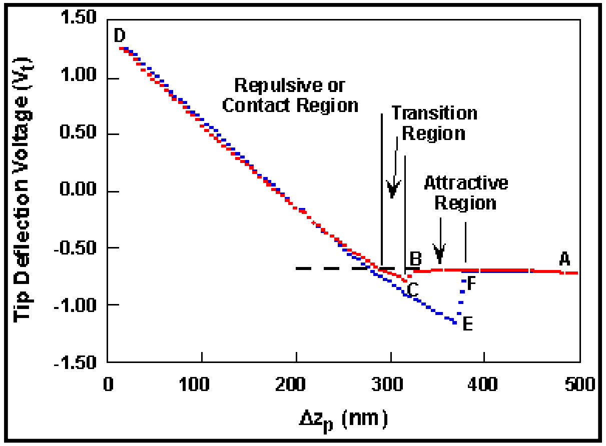


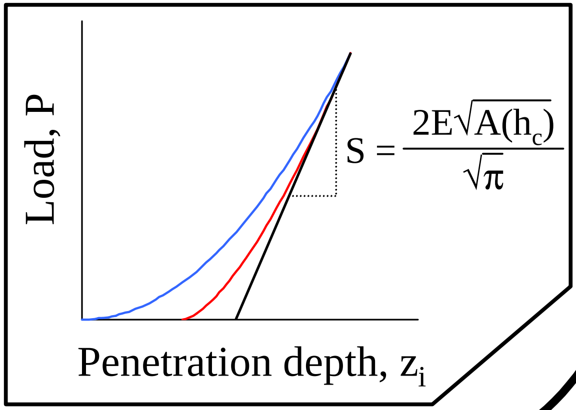
$$P = k_c z_t \cos(10^\circ)$$

$$k_c = \frac{3\,(EI)_c}{L_c^{3}}$$

$$S = \frac{2E\sqrt{A(h_c)}}{\sqrt{\pi}}$$

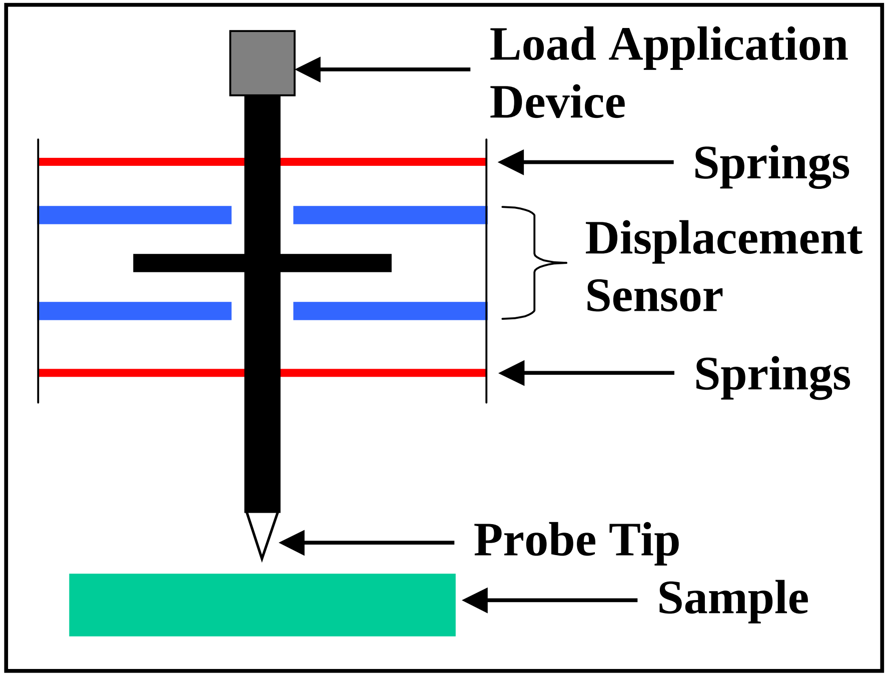
$$P = k_c z_t \cos(10^\circ)$$





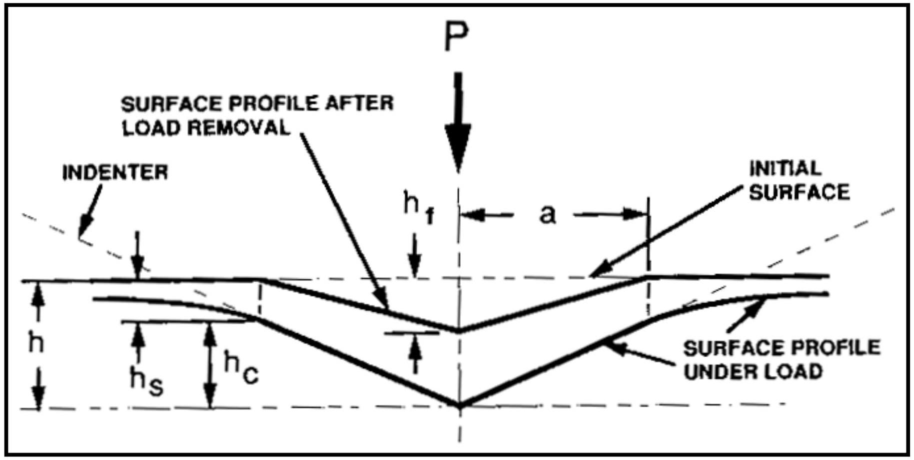
$$S = \frac{2E\sqrt{A(h_c)}}{\sqrt{\pi}}$$

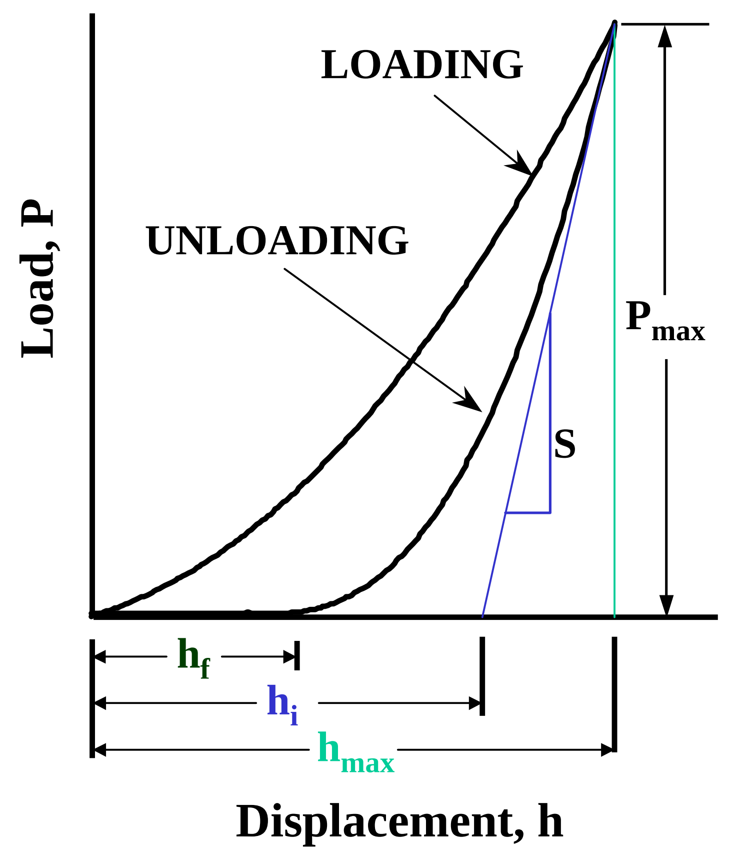
Depth-Sensing Indentation (DSI)



- Variations between different systems include:
  - How load is applied/measured
  - How displacement is applied/measured
  - Feedback control of system
  - Design for low load capabilities
- Commercial systems are available that either attach to or work with Scanning Probe Microscopes.

Oliver-Pharr Method





h_{max} = maximum displacement

h_f = final depth

h_i = intercept displacement

Calculating Elastic Modulus

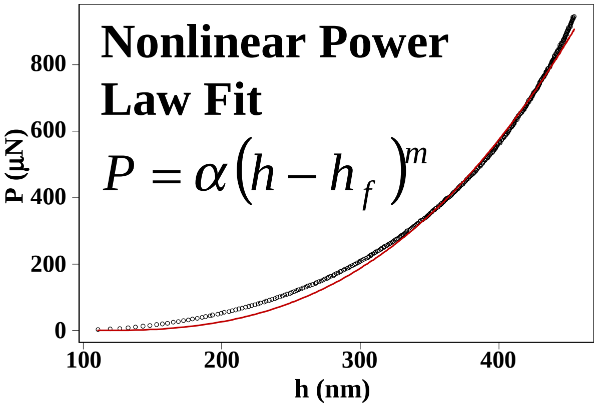
- **Load-frame compliance and tip shape calibrations performed prior to indenting samples of interest.**
  - **Indentation of reference samples.**
  - **Several different procedures used.**
- **S is typically calculated from power law fits to the unloading curve.**
  - **Type of fit and amount of data used in fit varies.**
- **Measurements on unknown samples:**
  - **Indent sample using a range of maximum loads, fit unloading data with power law expression, and calculate S.**
  - **Determine contact depth, h_c and use with $A(h_c)$ to determine contact area, A.**
  - **Calculate modulus, E_r, from stiffness, S, and contact area A.**

$$\boxed{E_r = \frac{\sqrt{\pi}}{2}\left(\frac{S}{\sqrt{A}}\right)} \qquad \boxed{\frac{1}{E_r} = \frac{\left(1-\nu_s^2\right)}{E_s} + \frac{\left(1-\nu_i^2\right)}{E_i}}$$

Reference: W.C. Oliver and G.M. Pharr, *J. Mater. Res.*, 7(6), 1564-1583 (1992)

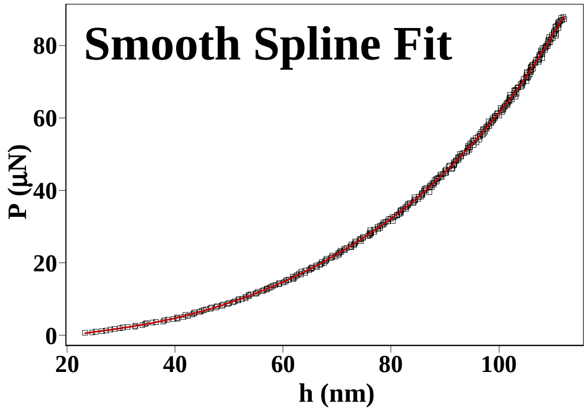
Curve Fitting

- Nonlinear power law fits are not effective for polymer unloading curves.
  - Values of contact stiffness, S, depend on choice of data region for fit.
  - Often, a convergent solution is not found.
  - Residual errors often do not meet assumptions.
- Smooth spline fits are more appropriate:
  - More representative of unloading data
  - dP/dh calculated directly from fit

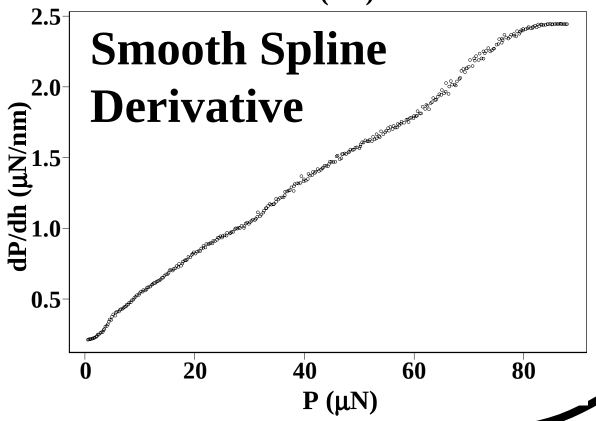


Nonlinear Power Law Fit

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

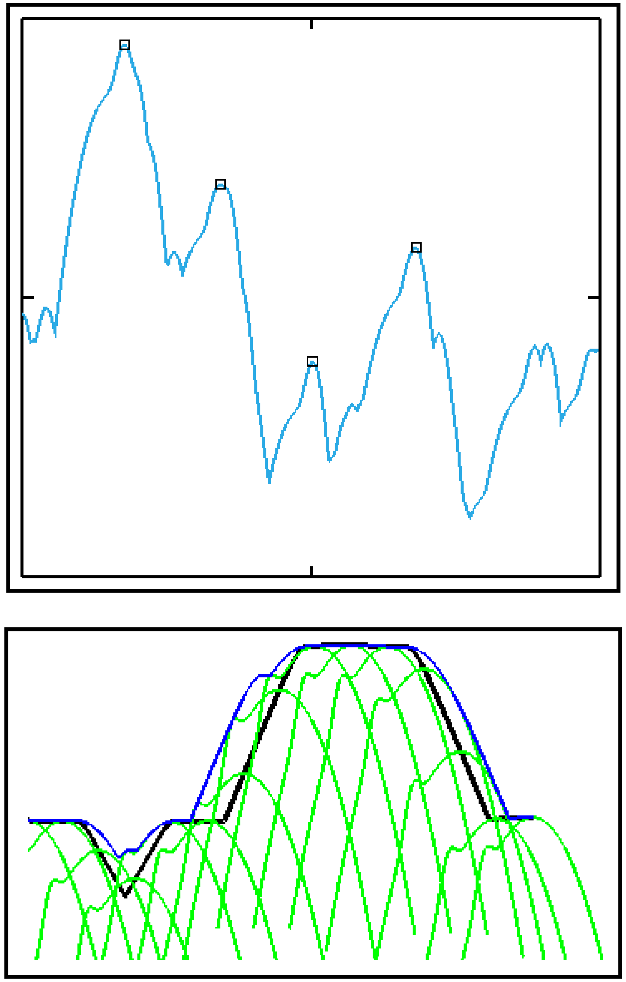


Smooth Spline Fit



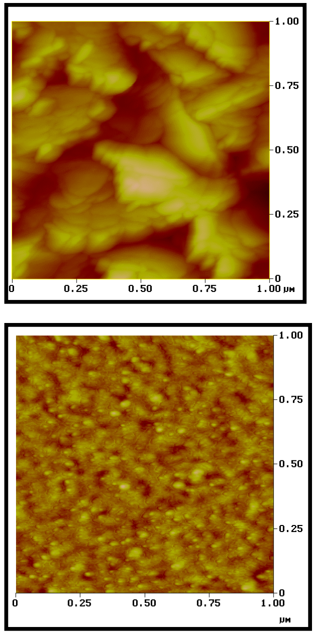
Smooth Spline Derivative

Tip Shape Measurements



- **Indentation of reference samples normally used to measure tip shape.**
  - **Appropriate polymer reference samples not available.**
  - **Not generally applicable to AFM indentation.**
- **Independent methods include:**
  - **Scanning indentation tip with AFM tip**
    - **Image will be a combination of the two tip geometries.**
  - **Blind reconstruction**
    - **Scanning a real surface yields a large number of independent tip “images”.**
  - **In both cases, the following mathematical morphology model can be used:** $\boxed{I = S \oplus P}$
    - **I represents the image**
    - **S represents the sample**
    - **P represents the probe tip**

Blind Reconstruction of AFM Tips



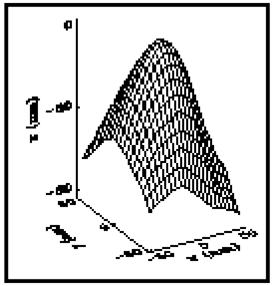
AFM images of “tip characterizer” surfaces

Tip Reconstruction

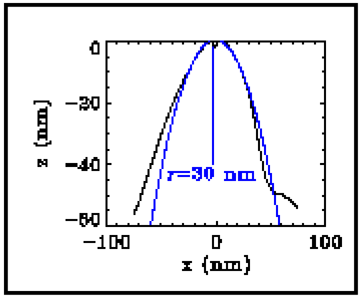
Solve: $(I \ominus P) \oplus P = I$

Result: $P_R = f(I,S,\ldots)$

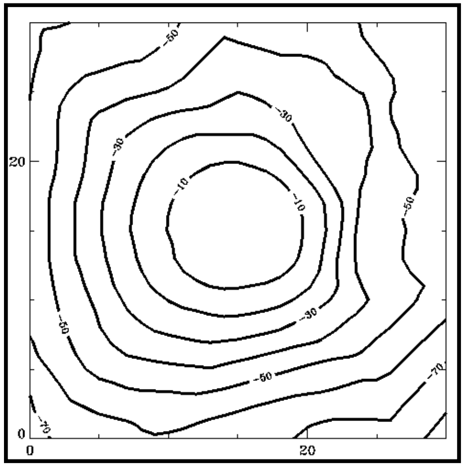
- calculated tip shape will be an outer bound
- estimate a lower bound by eroding away an assumed geometry of the sharpest surface feature



3-D tip geometry



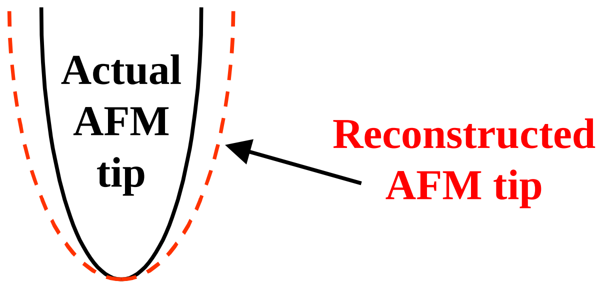
tip cross section



contour plot of tip

By using different tip characterizer surfaces, we hope to extract enough information about the tip geometry to provide an accurate representation of the change in contact area during indentation.

AFM Imaging of DSI Probe Tips



Actual AFM tip

Reconstructed AFM tip

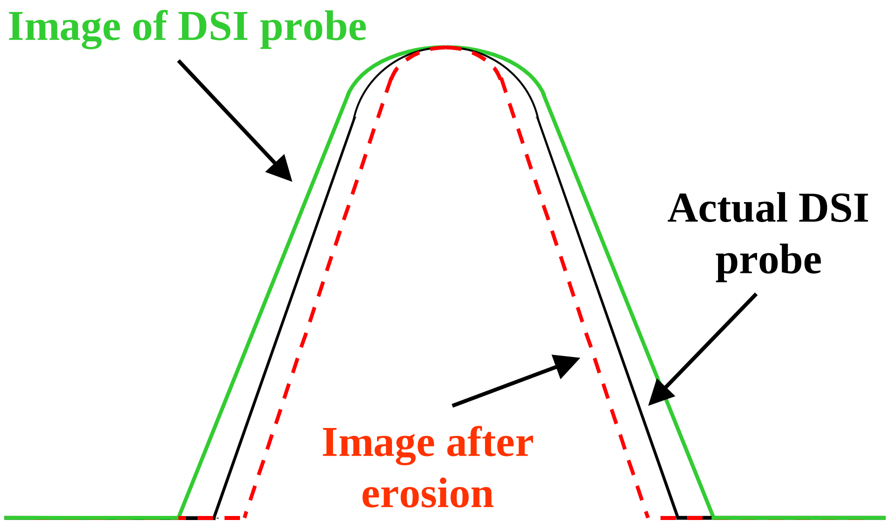


Image of DSI probe

Actual DSI probe

Image after erosion

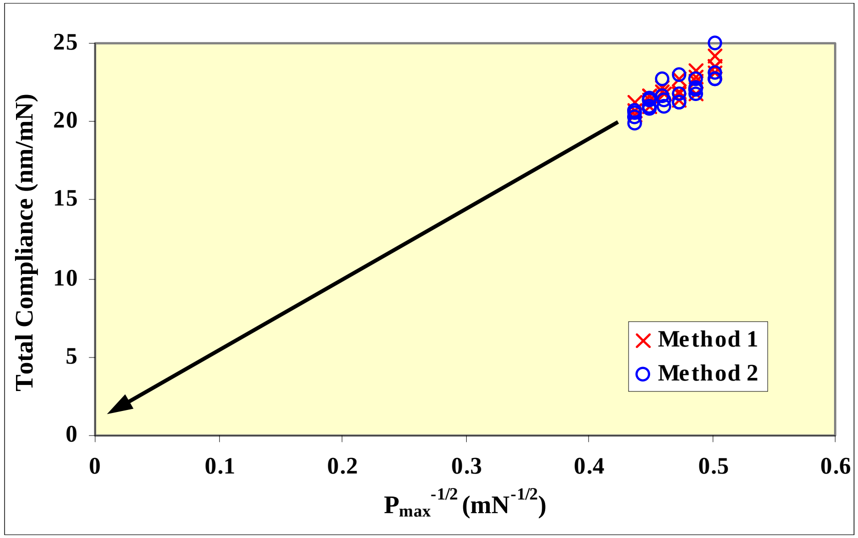
- AFM image of a DSI probe tip will be a combination of the two tip geometries:
  - Constitutes an outer bound on the true DSI probe geometry.
- Using mathematical morphology:
  - Determine an outer bound on the AFM tip shape using blind reconstruction.
  - Use erosion to produce a lower bound on the true DSI probe geometry.

$$\boxed{S = I \ominus P}$$

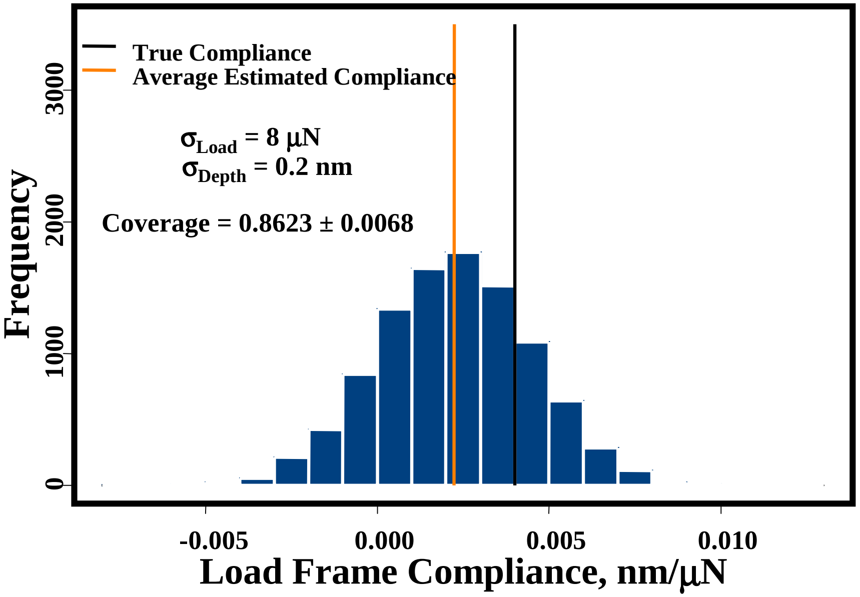
DSI Compliance Calibration

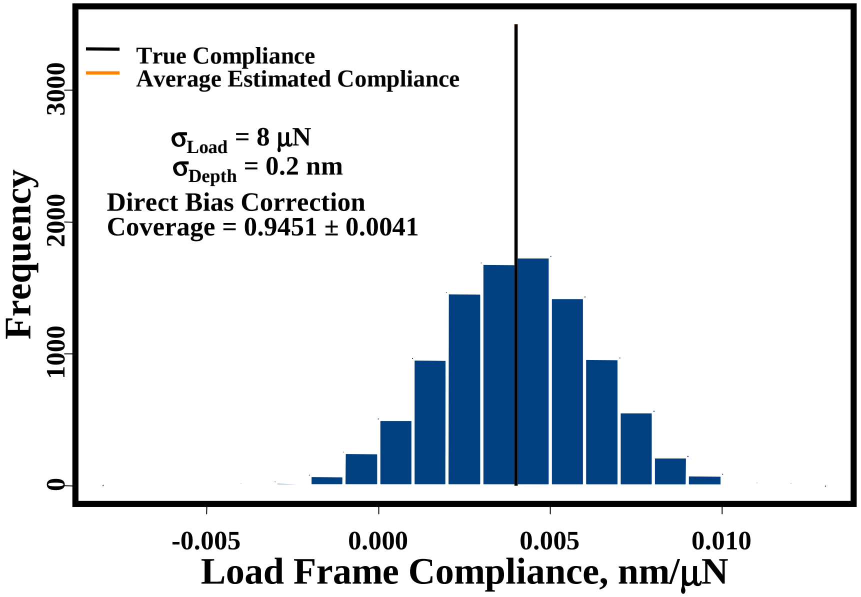
- **The total compliance is the sum of the contact compliance and machine frame compliance (everything else).**
  - **Measured displacement is due to displacements of the specimen and load frame.**
  - **Measure the compliance (C_{total} = 1/S) of several high load indents in reference material.**
  - **Frame compliance, C_f, is calculated as the y-intercept of a linear least squares fit to C_{total} vs. $1/\sqrt{A}$ or $1/\sqrt{P_{max}}$.**
    - **The latter assumes H is constant with depth.**

$$C_{total} = C_f + C_s = C_f + \frac{\sqrt{\pi}}{2E_r}\frac{1}{\sqrt{A}}$$

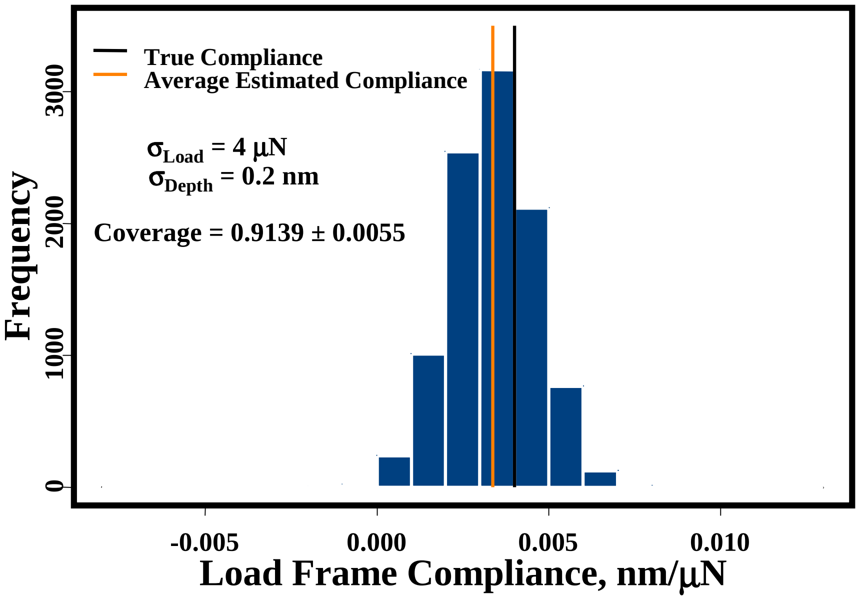


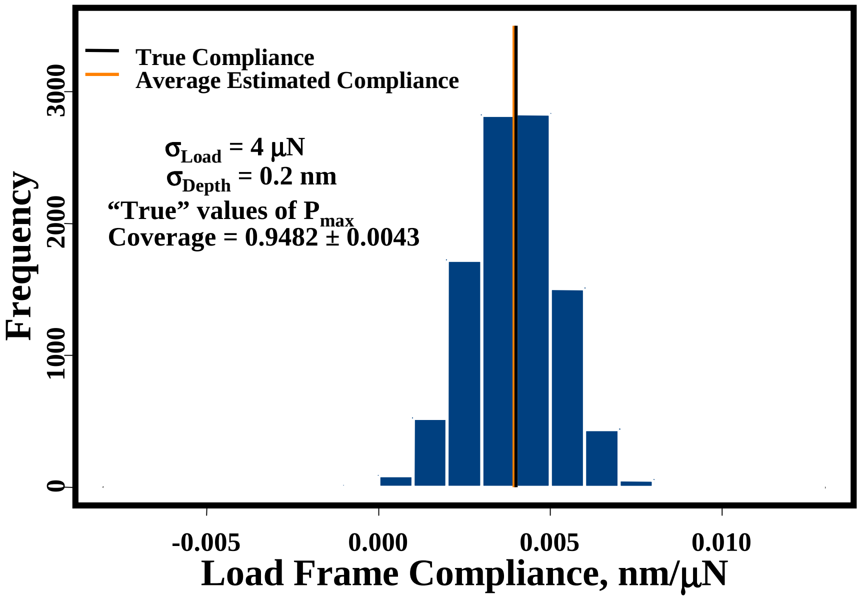
Simulations to Determine Uncertainty in C_f





Simulations (cont'd)

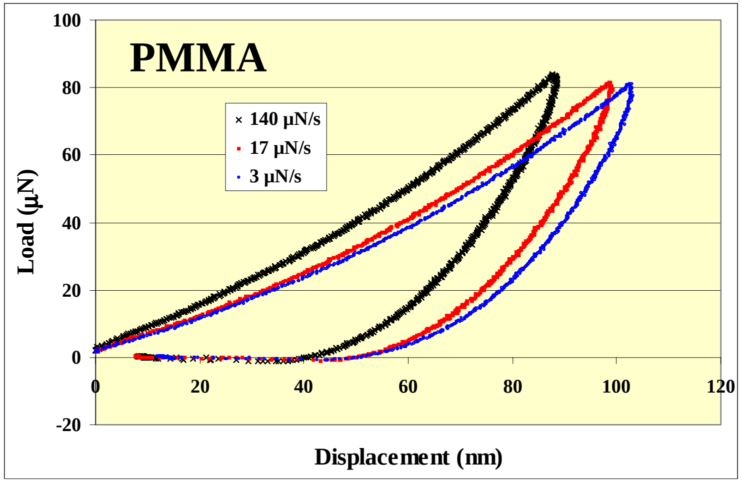


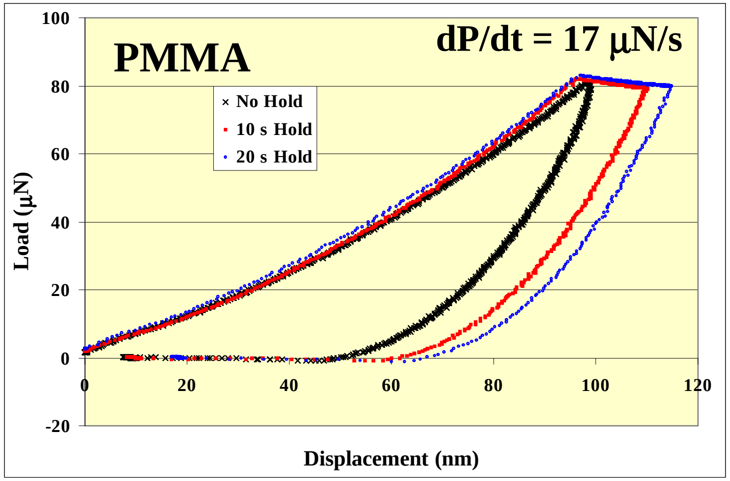


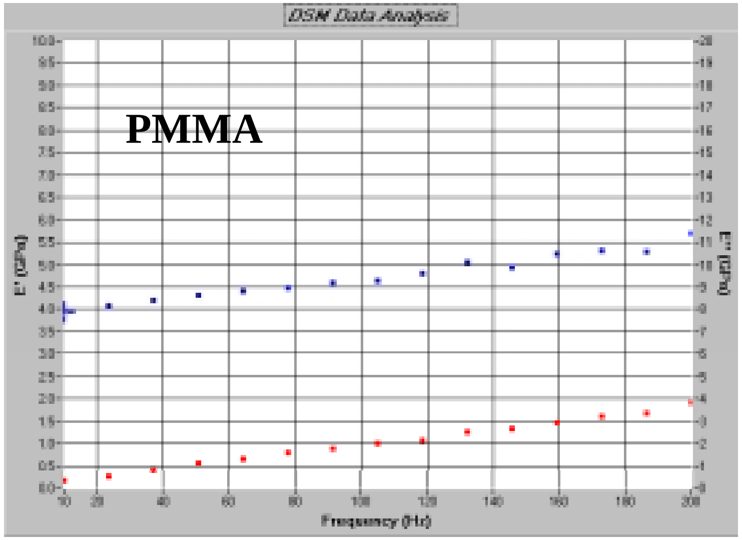
Understanding Uncertainty in C_f

- Having significant uncertainty in the x-variable is a violation of assumptions for least squares regression.
  - As a consequence of uncertainty in P_{max}, a bias is created in the least squares estimate of C_f.
    - For our simulations, this bias has always led to a value of C_f that is less than the true value.
    - Other simulation parameters will affect the magnitude of the bias.
  - Orthogonal Distance Regression may provide for a non-biased estimate of C_f and its uncertainty.
- Regardless, the uncertainty in C_f using the current approach appears to be quite large.
  - Uncertainties will propagate into uncertainties in tip shape estimates and modulus measurements.

Next Steps: Accounting for Viscoelasticity







- E varied with loading rate from 6.1 GPa to 5.0 GPa.
  - For no hold period, E = 5.3 GPa.
  - For the 10 s and 20 s hold periods, E = 4.6 GPa.
- Dynamic testing yielded an increase in E’ with frequency from 4.0 GPa to 5.7 GPa.
- AFM testing yielded E = 6.8 GPa.

Next Steps: Uncertainty Analysis

- **Investigate the effects of various parameters on the bias for the load-frame compliance calculation.**
- **Use Orthogonal Distance Regression to determine uncertainties for load-frame compliance.**
- **Determine uncertainties associated with independent tip shape methods.**
- **Explore the use of independent tip shape measurements in conjunction with load-frame compliance calculations.**
  - **Would allow compliance to be based on realistic values of contact area.**
- **Determine how uncertainties propagate into calculations of E.**
  - **Make recommendations to minimize uncertainties.**

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