Experimental uncertainties in extracting material properties from F-Z curves

10/6/10 – Lecture 12
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AFM Force Displacement (F-Z) Curve Experiment

Nomenclature:
- \( Z_V \) – Voltage input to the Z-piezo
- \( \delta_V \) – Voltage output of the Photodiode
- \( Z_{nm} \) – Z-piezo (Sample) Displacement in nm
- \( \delta_{nm} \) – Cantilever deflection in nm
- \( d \) – Tip-sample distance
AFM F-Z Curve Analysis

F-Z Curve Analysis includes two steps:

1. Approach: The tip moves towards the sample, increasing the force.
2. Retraction: The tip moves away from the sample, decreasing the force.

**Nomenclature:**
- F – Tip-sample force
- \( Z_{nm} \) – Z-piezo Displacement
- d – Tip-sample distance

**Elastic modulus (E)** is estimated by fitting a model for tip-sample interaction to the F-d Curve:

\[
d = Z_{nm} - \delta_{nm}
\]
F-Z curve calibration

• 3 calibration parameters needed:
  – nm to V conversion for Z-piezo input signal ($C_Z$)
  – nm to V conversion for photodiode output signal ($C_L$)
  – nm to nN conversion for cantilever deflection ($k_L$)
Z-Piezo calibration

• If we assume a linear relationship between voltage input into the Z-Piezo and displacement output

\[ Z_{nm} = C_Z Z_V \]

• One method:
  – Scan a sample of “known” height
Good Assumption?
Photodiode calibration

\[ \partial_{nm} = C_L \partial_V = mC_Z \partial_V \]

- One method:
  - Assume that the cantilever and Z-piezo move with a one to one ratio when the sample is “stiff”
Cantilever Stiffness calibration

\[ F = k_L \partial_{nm} \]

- Large body of literature regarding stiffness calibration (> 100 papers).

- A few common methods include:
  - Sader’s method, Thermal Methods, and Cleveland's Method

Thermal Method:

\[ k_L = 0.97k_B \frac{T}{\langle \delta_{nm} \rangle^2} \]
Calibration “Paths”

• Recap:
  – Measure a sample of known height.
    \[ C_Z = f(\partial_V, Z_V) \]
  – Measure a F-Z curve on a stiff sample.
    \[ C_L = f(\partial_V, Z_V, C_Z) \]
  – Measure the thermal oscillations of the cantilever:
    \[ k_L = f(\partial_V, C_L, T) \]

• This is not the only method.
Cantilever tilt correction

\[ F = \frac{k_L \delta_{nm}}{\cos^2(\alpha)} \]

Hutter, Comment on Tilt of Atomic Force Microscope Cantilevers: Effect on Spring Constant and Adhesion Measurements, Langmuir V 21, 2005
Force-Distance (F-d) Curves

- Need to convert F-Z curve into F-d curve because the tip sample interaction models are given in terms of F versus d

\[ d = Z_{nm} - \partial_{nm} \]
\[ = C_Z Z_V - C_L \partial_V \]
\[ = C_Z (Z_V - m \partial_V) \]

\[ F = \frac{k_L C_L \partial_V}{\cos^2(\alpha)} \]
Tip-Sample interaction models

- Many ways to model the interaction of the AFM tip with the sample.

- One example is the Derjaguin Muller Toporov (DMT) model

$$F = S d^{3/2} + F_0$$

$$F = f (d, \text{material properties, surface geometry})$$

- One example is the Derjaguin Muller Toporov (DMT) model
DMT contact mechanics

• Modification of Hertz model to include adhesive forces:

\[ F = S(d - a_0)^{3/2} - F_0 \]

Intermolecular distance

Constant related in tip and sample properties and geometry

• \( F_0 \) is related to work of adhesion between tip and sample as:

\[ F_0 = 4\pi \frac{W}{\hat{R}} \]
Effect of surface geometry on DMT model
Effect of surface geometry on DMT model

- For the geometry of a sphere interacting with a cylinder $S$ can be related to $E$ via the equations*:

$$S = \frac{2\pi (\tilde{E}(k_p))^{1/2}}{3\sqrt{1-k_p^2 (\tilde{K}(k_p))^{3/2} (\hat{R})^{1/2} \hat{E}}}$$

where

$$\tilde{K}(k_p) \equiv \int_0^{\pi/2} \frac{d\theta}{\sqrt{1-k_p^2 \sin^2(\theta)}}$$
$$\tilde{E}(k_p) \equiv \int_0^{\pi/2} \sqrt{1-k_p^2 \sin^2(\theta)}d\theta$$
$$\hat{E} \equiv \left(1-v^2 + \frac{1-v_{tip}^2}{E/E_{tip}} \right)$$

$k_p$ is found by solving

$$\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{1/(1-k_p^2) \ast \tilde{E}(k_p) - \tilde{K}(k_p)}{\tilde{K}(k_p) - \tilde{E}(k_p)}$$

- $E$ is directly proportional to $S$ if $E >> E_{tip}$

Effect of surface geometry on DMT model

• Common geometry in AFM

  – Sphere-Sphere:

  \[
  S = \frac{4}{3} \sqrt[3]{\frac{1}{E}} \left( \frac{1}{R_{\text{tip}}} + \frac{1}{R_{\text{surf}}} \right)^{-1/2}
  \]

  – Sphere-Plane:

  \[
  S = \frac{4}{3} \sqrt{\frac{R_{\text{tip}}}{E}}
  \]
Curve fitting procedure for DMT model

• The DMT model can be linearized by defining a parameter $d^*$ such that:

$$d^* = (d - a_0)^{3/2}$$

The linearized model is then given as:

$$F = Sd^* - F_0$$

• $S$ and $F_0$ can then be found from the $n$ data pairs $(F_i, d^*_i)$ as:

$$S = \frac{n \sum_{i=1}^{n} d_i^* F_i - \sum_{i=1}^{n} d_i^* \sum_{i=1}^{n} F_i}{n \sum_{i=1}^{n} (d_i^*)^2 - \left( \sum_{i=1}^{n} d_i^* \right)^2}$$

$$F_0 = \frac{\sum_{i=1}^{n} (d_i^*)^2 \sum_{i=1}^{n} F_i - \sum_{i=1}^{n} d_i^* \sum_{i=1}^{n} d_i^* F_i}{n \sum_{i=1}^{n} (d_i^*)^2 - \left( \sum_{i=1}^{n} d_i^* \right)^2}$$

• One additional complications arises as $Z_V$ is a relative measurement hence the $d$ value resulting from this procedure can be offset by a constant value. This constant is found by maximizing the $R^2_{gof}$ value of the curve fit.
Summary

• We can consider the above process as inputting $2n+11$ or $2n+8$ ($n$ is number of data points in F-Z curve) parameters into a “Data Reduction Equation” and outputting elastic modulus or work of adhesion

\[
E = f_1(Z_{V_1}^*, ..., Z_{V_n}^*, \delta_{V_1}^*, ..., \delta_{V_n}^*, Z_{V,shift}, \delta_{V,shift}, C_Z, m, k_L, \alpha, R_V, R_{tip}, E_{tip}, \nu_{tip}, \nu)
\]

\[
W = f_2(Z_{V_1}^*, ..., Z_{V_n}^*, \delta_{V_1}^*, ..., \delta_{V_n}^*, Z_{V,shift}, \delta_{V,shift}, C_Z, m, k_L, \alpha, R_V, R_{tip})
\]
Case study: Cellulose Nanocrystals

$E = 10.3 \text{ GPa}$

$W = 120 \text{ mJ/m}^2$
Uncertainty in measurement

- Lab A and B are given a sample, say X.
  - Lab A \(\rightarrow\) flux capacitance = 7
  - Lab B \(\rightarrow\) flux capacitance = 30
  - Are these measurements in agreement?
Classifications of uncertainty

• 3 classification systems
  – Random and systematic
    • Random – Varies over the course of the experiment
    • Systematic – Does not vary over the course of the experiment
  – Aleatory and Epistemic
    • Aleatory – Uncertainty associated with parameters within a model
    • Epistemic – Uncertainty associated with the form of the model
  – Type A and type B
    • Type A – Evaluated by statistical means
    • Type B – Evaluated by other means
Uncertainty Propagation

Let r be a measured variable then

\[ b_r \] – systematic standard uncertainty associated with r
\[ s_r \] – random standard uncertainty associated with r
\[ u_r \] – standard combined uncertainty associated with r

\[ u_r = \left( s_r^2 + \sum b_r^2 \right)^{1/2} \]

\[ U_{x,r} \] – expanded uncertainty estimate associated with r:

\[ U_{x,r} = k_x u_r \]

\[ U_{x,r} \] corresponds to the range that we are x percent confident that the true value of r falls within \( r_{\text{best}} \pm U_{x,r} \)

If we have \( f(r_1, \ldots, r_n) \) then the uncertainty in f propagates as:

\[ u_f = \left( \sum_{i=1}^{n} \left( \frac{df}{dr_i} u_{r_i} \right)^2 \right)^{1/2} \]

Taylor Series uncertainty propagation formula
Uncertainty Propagation

1. Identify Input Parameters and uncertainties
2. Propagate input uncertainties to output uncertainty
3. Identify Dominant Contribution to Output Uncertainty
4. Try to improve experiment based on uncertainty analysis
Summary

• Applying the Taylor series uncertainty propagation formula to the data reduction equations results in:

\[ u_E = \left( \frac{df_1}{dZ_{V_1}} u_{V_1} \right)^2 + \cdots + \left( \frac{df_1}{dZ_{V_n}} u_{Z_{V_n}} \right)^2 + \left( \frac{df_1}{d\delta_{V_1}} u_{\delta_{V_1}} \right)^2 + \cdots + \left( \frac{df_1}{d\delta_{V_n}} u_{\delta_{V_n}} \right)^2 + \left( \frac{df_1}{dZ_{V_{shift}}} u_{Z_{V_{shift}}} \right)^2 + \left( \frac{df_1}{d\delta_{V_{shift}}} u_{\delta_{V_{shift}}} \right)^2 + \left( \frac{df_1}{dC_Z} u_{C_Z} \right)^2 + \left( \frac{df_1}{dm} u_m \right)^2 + \left( \frac{df_1}{dk_L} u_{k_L} \right)^2 + \left( \frac{df_1}{d\alpha} u_{\alpha} \right)^2 + \left( \frac{df_1}{dR_V} u_{R_V} \right)^2 + \left( \frac{df_1}{dR_{tip}} u_{R_{tip}} \right)^2 + \left( \frac{df_1}{dE_{tip}} u_{E_{tip}} \right)^2 + \left( \frac{df_1}{d\nu_{tip}} u_{\nu_{tip}} \right)^2 + \left( \frac{df_1}{d\nu} u_{\nu} \right)^2 \right)^{1/2}

(\text{Result for } W \text{ is similar})
Case Study Cellulose Nanocrystals

A) 744.19 mV

B) Thermal Tuning Spectra

C) Force-Displacement Curves on a Stiff Sample

D) 100 nm
Case Study: Cellulose Nanocrystals

<table>
<thead>
<tr>
<th>Value</th>
<th>Mean</th>
<th>95% CI</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_t$</td>
<td>7.9</td>
<td>[2.9, 22.0]</td>
<td>GPa</td>
</tr>
<tr>
<td>$W$</td>
<td>116</td>
<td>[77, 180]</td>
<td>mJ/m$^2$</td>
</tr>
</tbody>
</table>

## Sensitivity Analysis

### Sample Uncertainty Table for Elastic Modulus Analysis

<table>
<thead>
<tr>
<th>Variable ($x$)</th>
<th>Description</th>
<th>Value</th>
<th>Standard Uncertainty ($u_x$)</th>
<th>Sensitivity ($dE/dx$)</th>
<th>Contribution to Elastic Modulus Variance ($dE/dx \cdot u_x^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calibration Parameters:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_z$</td>
<td>Z-piezo Sensitivity</td>
<td>14 (nm/V)</td>
<td>1 (nm/V)</td>
<td>0.5 (GPa V/nm)</td>
<td>0.03 (GPa²)</td>
</tr>
<tr>
<td>$m$</td>
<td>Nondimensional Photodiode Sensitivity</td>
<td>6.1 (--)</td>
<td>0.15 (--)</td>
<td>25 (GPa)</td>
<td>14 (GPa²)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Tilt Correction Factor</td>
<td>1.037 (--)</td>
<td>0.007 (--)</td>
<td>10 (GPa)</td>
<td>0.01 (GPa²)</td>
</tr>
<tr>
<td>$k_L$</td>
<td>Cantilever Stiffness</td>
<td>2.5 (nN/nm)</td>
<td>0.1 (nN/nm)</td>
<td>5 (GPa nm/nN)</td>
<td>0.02 (GPa²)</td>
</tr>
<tr>
<td>$\delta_{V,\text{Shift}}$</td>
<td>Photodiode voltage Shift Factor</td>
<td>-0.36 (V)</td>
<td>0.01 (V)</td>
<td>0.0002 (GPa/V)</td>
<td>4 E -12 (GPa²)</td>
</tr>
<tr>
<td><strong>Model Parameters:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$R_{\text{tip}}$</td>
<td>Radius of AFM tip</td>
<td>10 (nm)</td>
<td>1 (nm)</td>
<td>0.4 (Gpa/nm)</td>
<td>0.16 (GPa²)</td>
</tr>
<tr>
<td>$E_{\text{tip}}$</td>
<td>Elastic Modulus of AFM tip</td>
<td>100 (GPa)</td>
<td>3 (GPa)</td>
<td>0.01 (--)</td>
<td>0.001 (GPa²)</td>
</tr>
<tr>
<td>$v_{\text{tip}}$</td>
<td>Poisson’s Ratio of AFM tip</td>
<td>0.28 (--)</td>
<td>0.02 (--)</td>
<td>0.6 (GPa)</td>
<td>0.001 (GPa²)</td>
</tr>
<tr>
<td>$R_{\text{V}}$</td>
<td>Radius of Sample measured with AFM</td>
<td>0.31 (V)</td>
<td>.04 (V)</td>
<td>6 (GPa/V)</td>
<td>0.05 (GPa²)</td>
</tr>
<tr>
<td>$v$</td>
<td>Poisson’s Ratio of Sample</td>
<td>0.28 (--)</td>
<td>0.05 (--)</td>
<td>6 (GPa)</td>
<td>0.01 (GPa²)</td>
</tr>
<tr>
<td><strong>Data pairs sampled during experiment:</strong></td>
<td>Mean Sensitivity</td>
<td>Mean Variance Contribution</td>
<td>Total Variance Contribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Z_{\text{vi}}$</td>
<td>Z-piezo voltage</td>
<td>-- (V)</td>
<td>0.0002 (V)</td>
<td>30 (GPa/V)</td>
<td>0.00004 (GPa²)</td>
</tr>
<tr>
<td>$\delta_{V_i}$</td>
<td>Photodiode voltage</td>
<td>-- (V)</td>
<td>0.0002 (V)</td>
<td>170 (GPa/V)</td>
<td>0.001 (GPa²)</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td>Elastic Modulus</td>
<td>10.3 (Gpa)</td>
<td>3.8 (GPa)</td>
<td>7.6 (Gpa)</td>
<td>15 (GPa²)</td>
</tr>
</tbody>
</table>

The highlighted contributions are calculated from the table above.