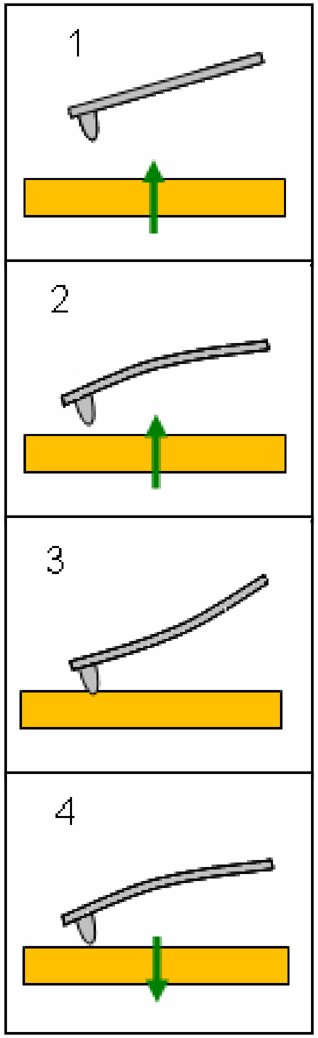
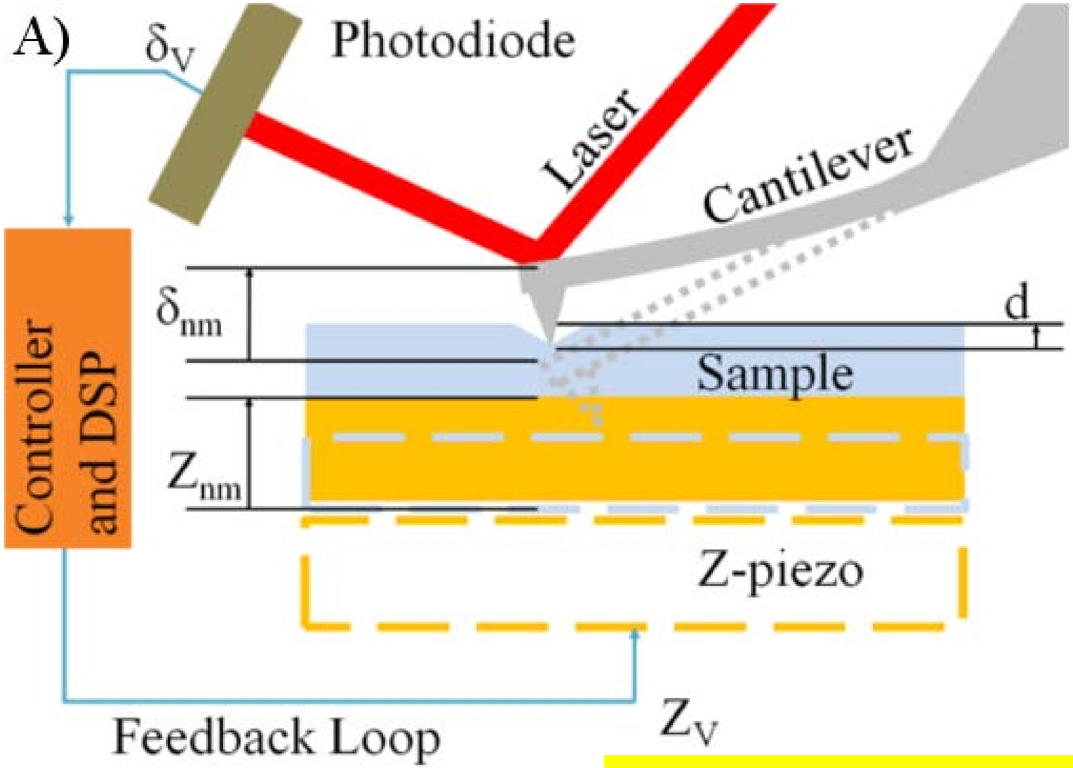
Experimental uncertainties in extracting material properties from F-Z curves

10/6/10 – Lecture 12

Ryan Wagner, Arvind Raman

AFM Force Displacement (F-Z) Curve Experiment

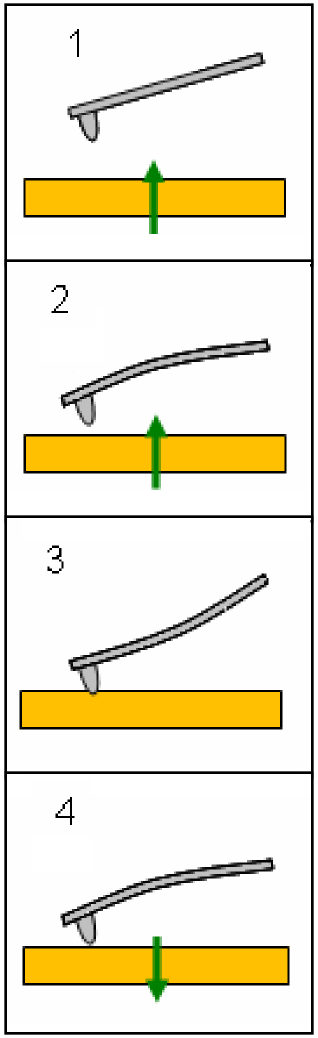


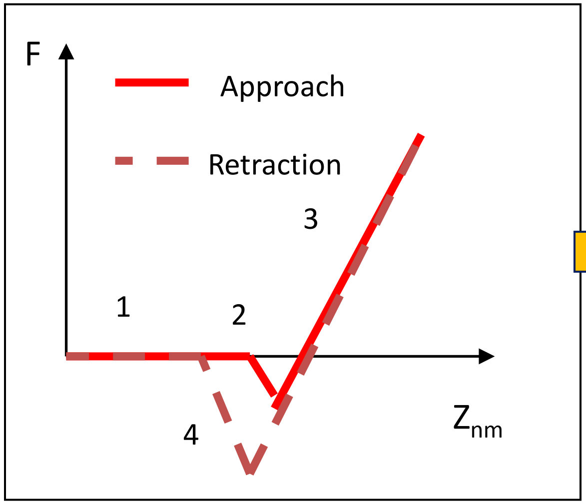


Fundamental Observables

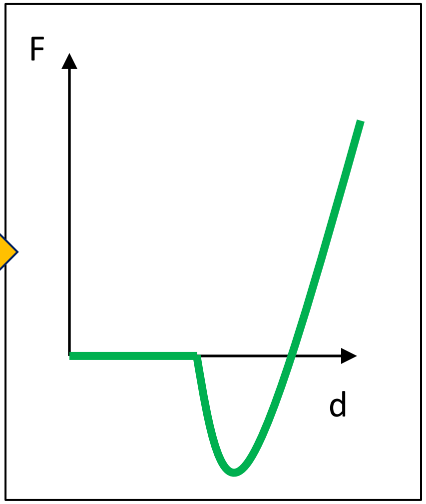
- Nomenclature:
  - **Z_V – Voltage input to the Z-piezo**
  - **δ_V – Voltage output of the Photodiode**
  - Z_{nm} – Z-piezo (Sample) Displacement in nm
  - δ_{nm} – Cantilever deflection in nm
  - d – Tip-sample distance

AFM F-Z Curve Analysis





F-Z Curve



Force Distance (F-d) Curve

$d = Z_{nm} - \delta_{nm}$

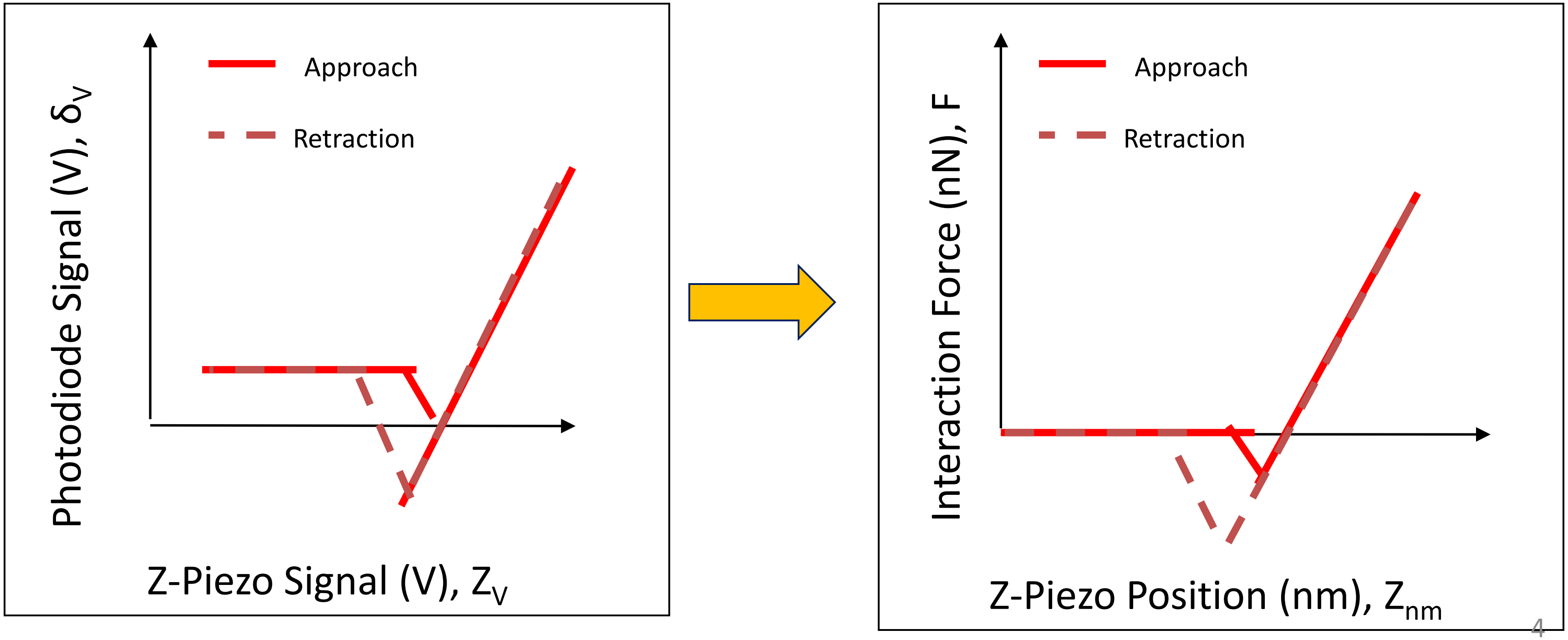
- Nomenclature:
  - F – Tip-sample force
  - Z_{nm} – Z-piezo Displacement
  - d – Tip-sample distance

Parameter of Interest

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

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**)

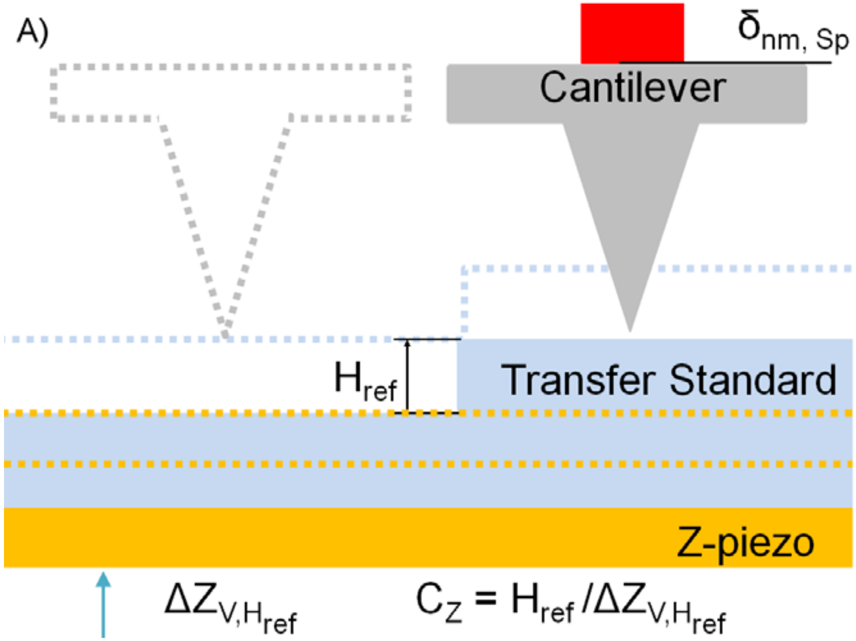


Z-Piezo calibration

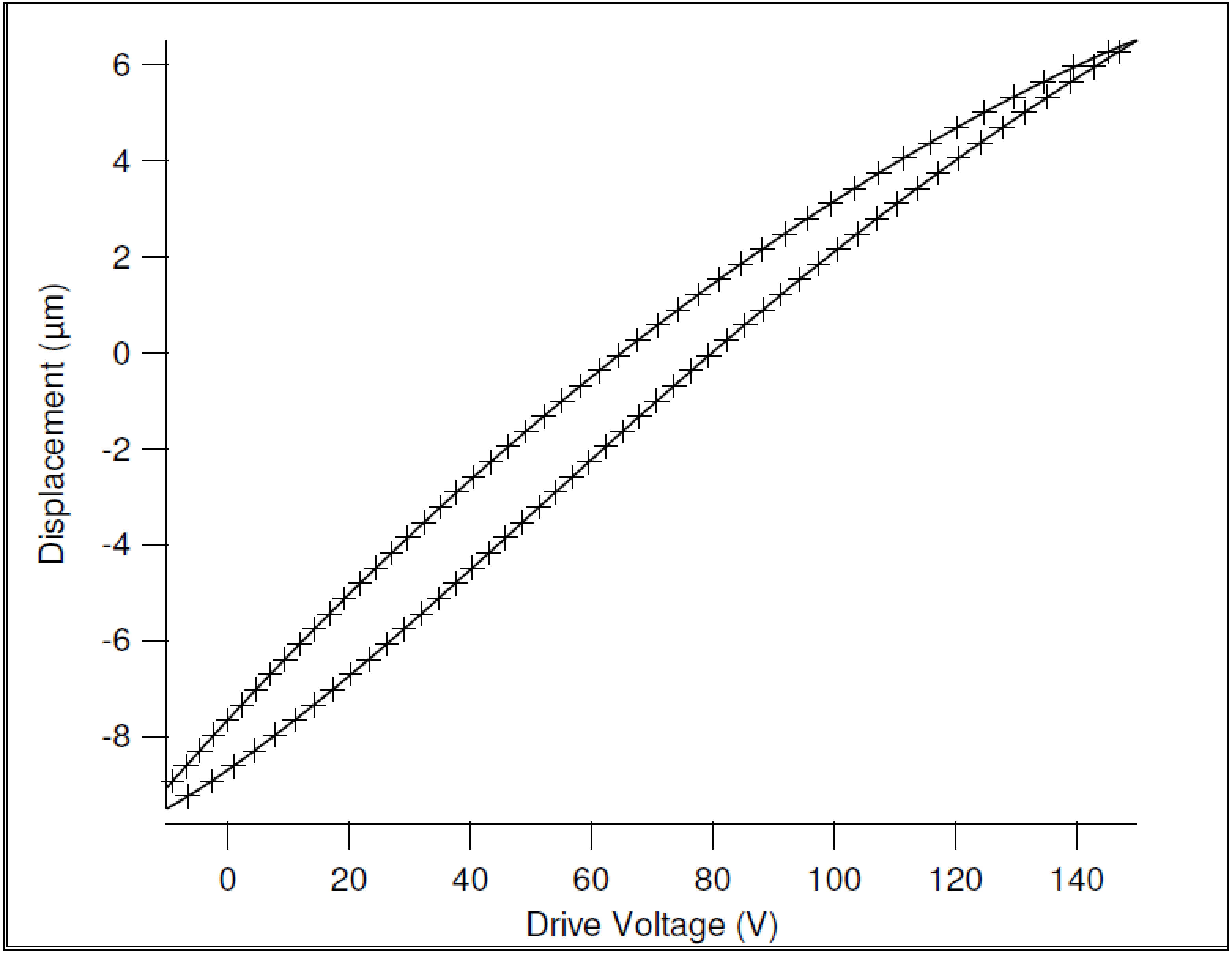
- If we assume a linear relationship between voltage input into the Z-Piezo and displacement output

$$Z_{nm} = C_Z Z_V$$

- One method:
  - Scan a sample of "known" height



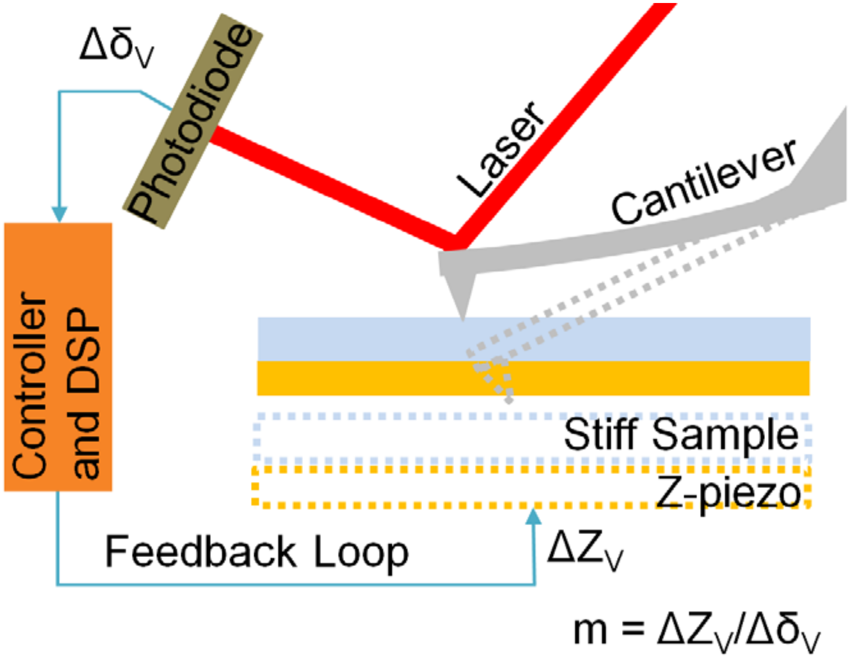
Good Assumption?

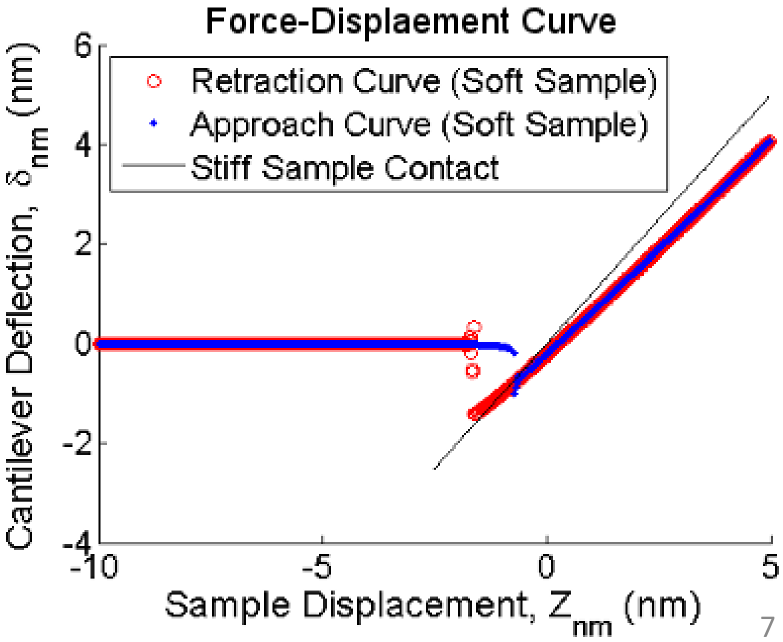


Photodiode calibration

$$\partial_{nm} = C_L \partial_V = m C_Z \partial_V$$

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





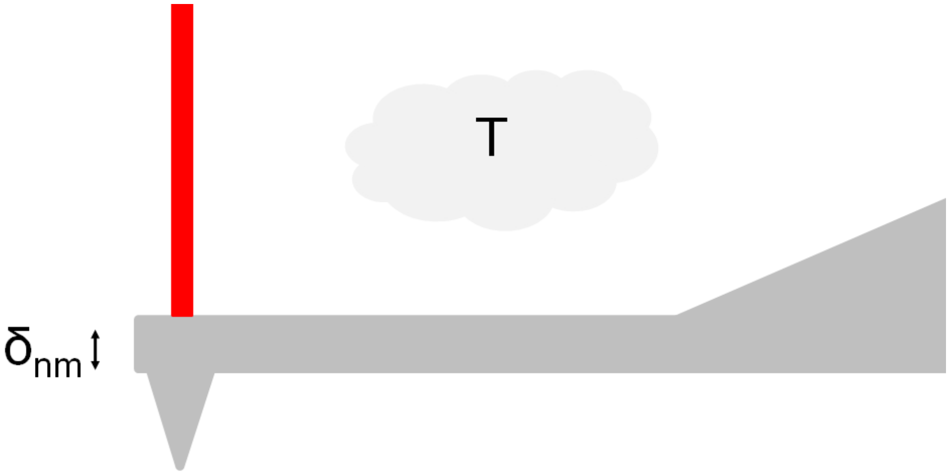
Cantilever Stiffness calibration

$$F = k_L \partial_{nm}$$

- 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:



$$k_L = 0.97 k_B T / \langle \delta_{nm}^2 \rangle$$

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.

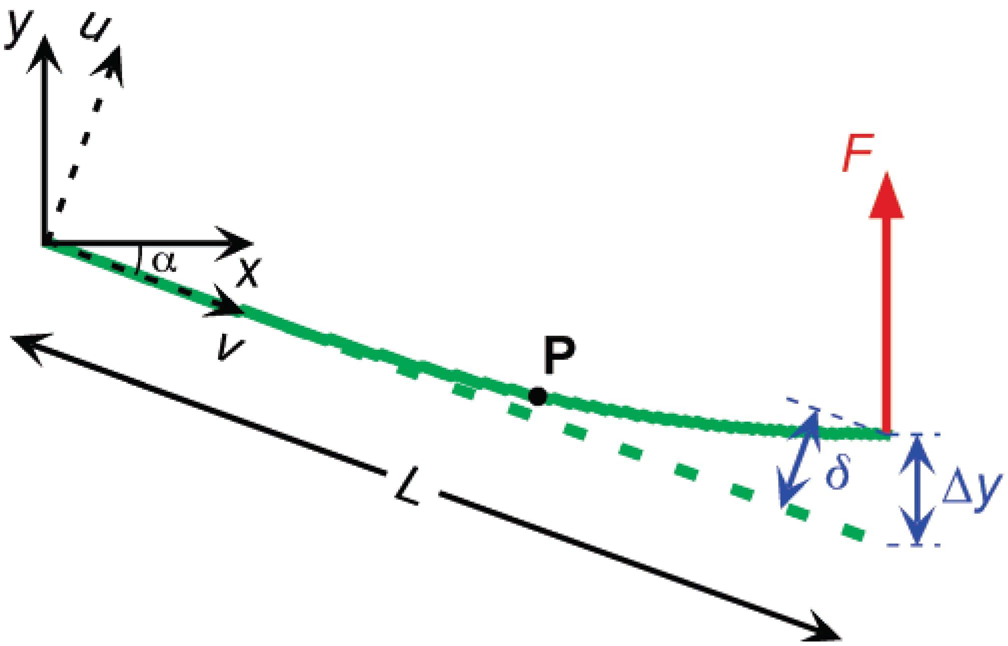
    $$C_L = f(\partial_V, Z_V, C_Z)$$

  - Measure the thermal oscillations of the cantilever:

    $$k_L = f(\partial_V, C_L, T)$$

- This is not the only method.

Cantilever tilt correction



$$F = \frac{k_L \partial_{nm}}{\cos^2(\alpha)}$$

Hutter, Comment on Tilt of Atomic Force Microscope Cantilevers: Effect on Spring Constant and Adhesion Measurements, Langmuir V 21, 2005

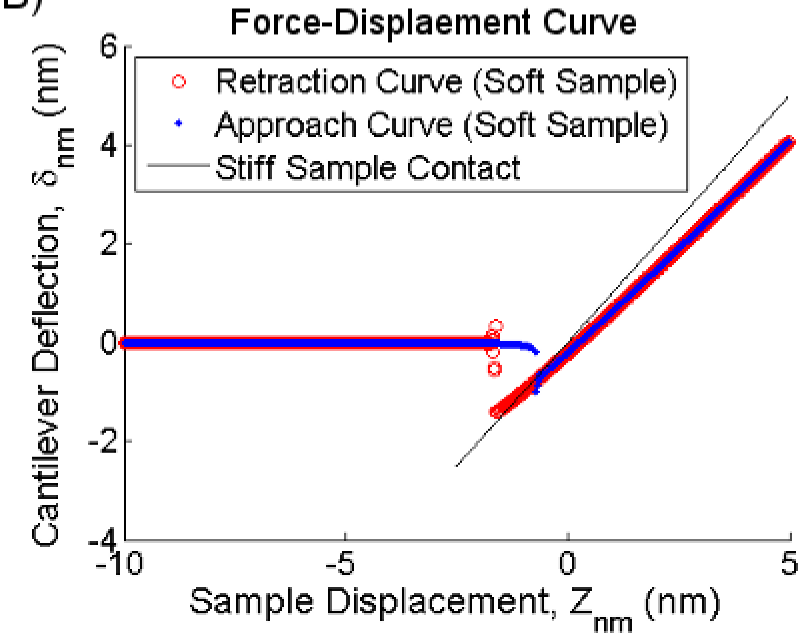
Force-Distance (F-d) Curves

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

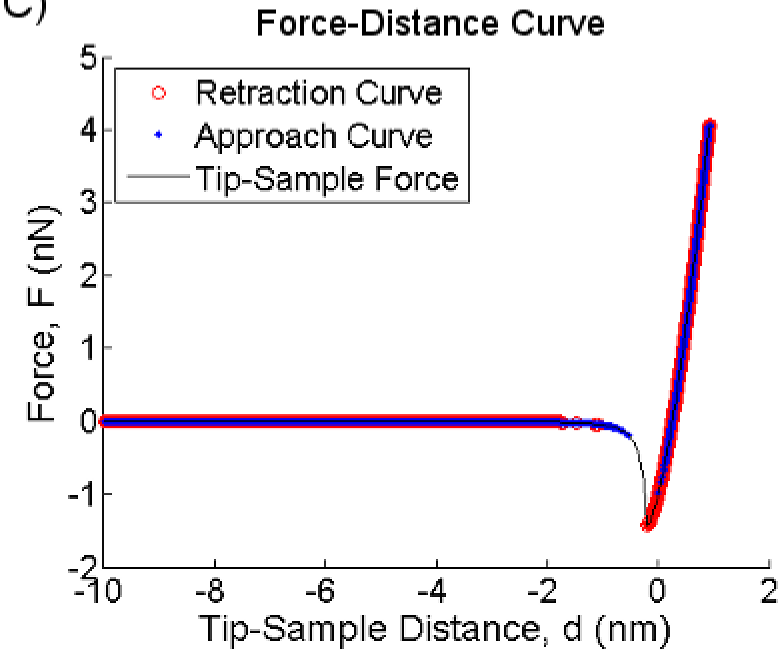
$$\begin{aligned} d &= Z_{nm} - \partial_{nm} \\ &= C_Z Z_V - C_L \partial_V \\ &= C_Z (Z_V - m\partial_V) \end{aligned}$$

$$F = \frac{k_L C_L \partial_V}{\cos^2(\alpha)}$$

B)



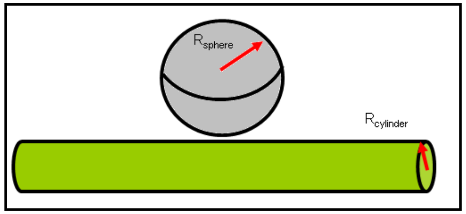
C)



Tip-Sample interaction models

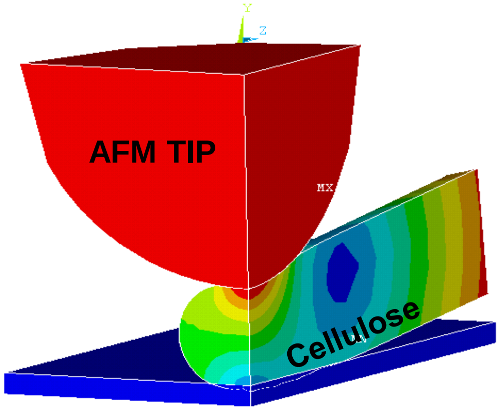
- Many ways to model the interaction of the AFM tip with the sample.

Analytic Contact Mechanics

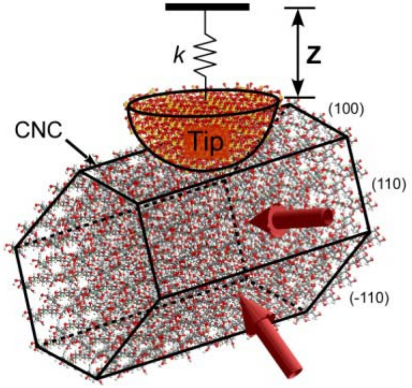


$$F = Sd^{3/2} + F_0$$

Finite Element Modeling



Molecular Dynamics Simulations



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

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

DMT contact mechanics

- Modification of Hertz model to include adhesive forces:

$$F = S(d - a_0)^{3/2} - F_0$$

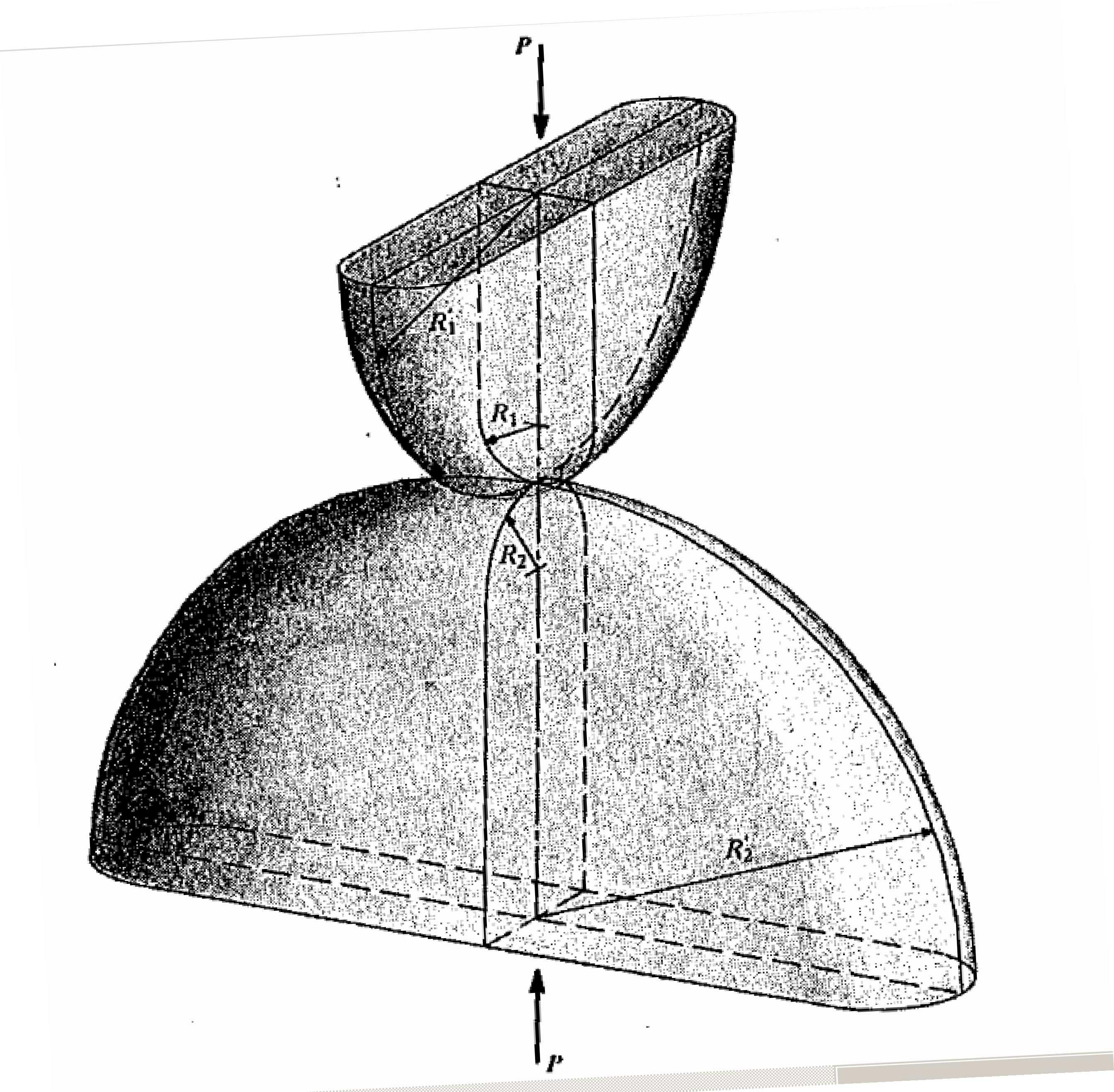
Intermolecular distance

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

$$\tilde{K}(k_p) \equiv \int_0^{\pi/2} \frac{d\theta}{\sqrt{1-k_p^2\sin^2(\theta)}} \qquad \tilde{E}(k_p) \equiv \int_0^{\pi/2} \sqrt{1-k_p^2\sin^2(\theta)}\,d\theta \qquad \hat{R} \equiv \frac{1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}+\frac{1}{R_1'}+\frac{1}{R_2'}\right)$$

$$\hat{E} \equiv \left(\frac{1-v^2}{E}+\frac{1-v_{tip}^2}{E_{tip}}\right)$$

k_p is found by solving

$$\left(\frac{\frac{1}{R_1}+\frac{1}{\mathrm{R}_2}}{\frac{1}{R_1'}+\frac{1}{R_2'}}\right) = \frac{1/(1-k_p^2)*\tilde{E}(k_p)-\tilde{K}(k_p)}{\tilde{K}(k_p)-\tilde{E}(k_p)}$$

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

*Boresi, A.P. 1978 Advanced Mechanics of Materials 3th Edition. New York: Wiley.

Effect of surface geometry on DMT model

- Common geometry in AFM
  - Sphere-Sphere:

$$S = \frac{4}{3}\frac{1}{\hat{E}}\left(\frac{1}{R_{tip}} + \frac{1}{R_{surf}}\right)^{-1/2}$$

  - Sphere-Plane:

$$S = \frac{4}{3}\frac{\sqrt{R_{tip}}}{\hat{E}}$$

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:

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

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

$$R_{gof}^2 = \frac{\sum_{\mathrm{i}=1}^{\mathrm{n}} (F_i - F_i^*)^2}{\sum_{\mathrm{i}=1}^{\mathrm{n}} (F_i - \bar{F})^2}$$

- 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.

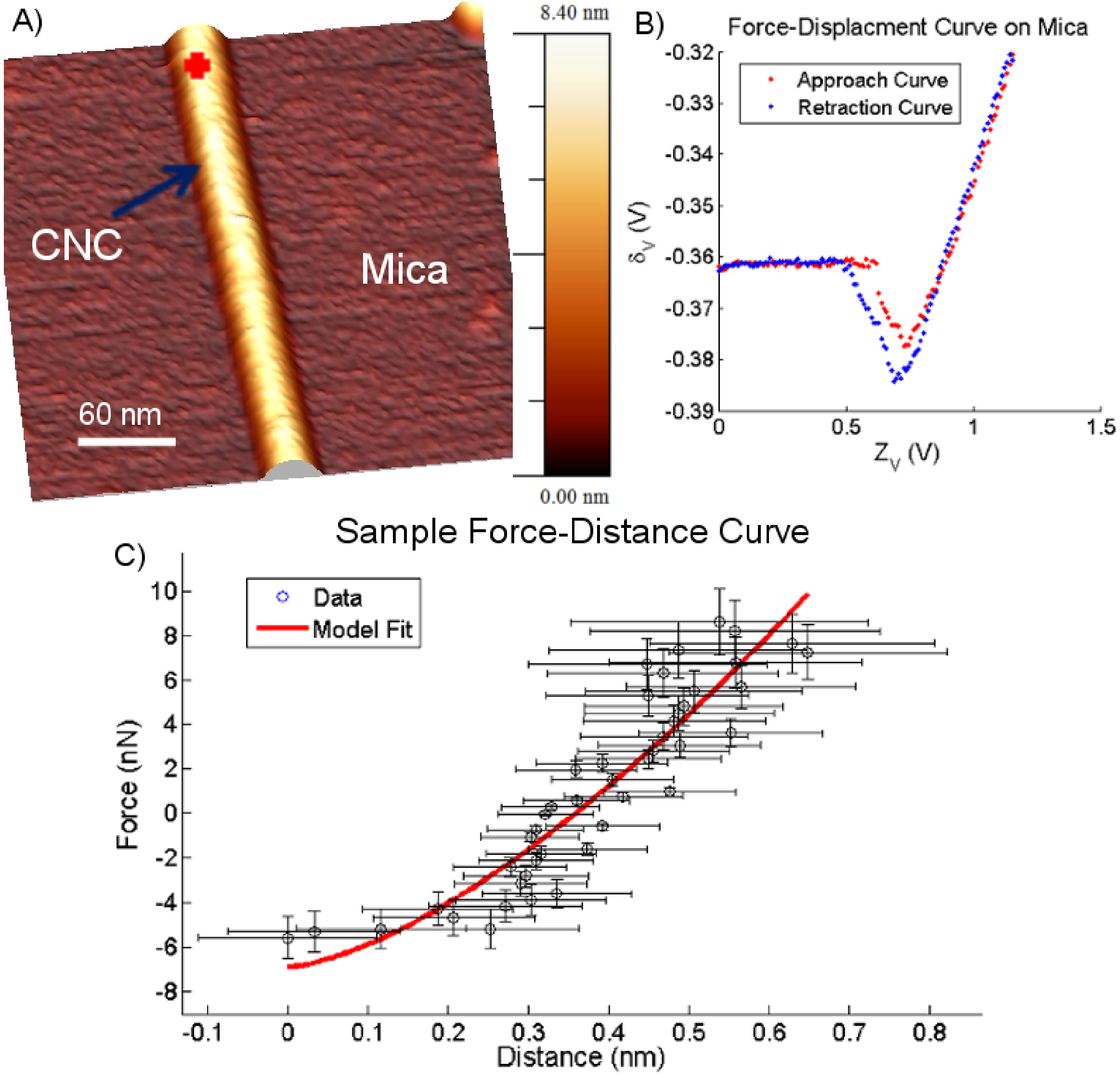
Summary

- 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

$$E = f_1(Z^*_{V_1}, \ldots, Z^*_{V_n}, \delta^*_{V_1}, \ldots, \delta^*_{V_n}, Z_{V,shift}, \delta_{V,shift}, C_Z, m, k_L, \alpha, R_V, R_{tip}, E_{tip}, \nu_{tip}, \nu)$$

$$W = f_2(Z^*_{V_1}, \ldots, Z^*_{V_n}, \delta^*_{V_1}, \ldots, \delta^*_{V_n}, Z_{V,shift}, \delta_{V,shift}, C_Z, m, k_L, \alpha, R_V, R_{tip})$$

Case study: Cellulose Nanocrystals

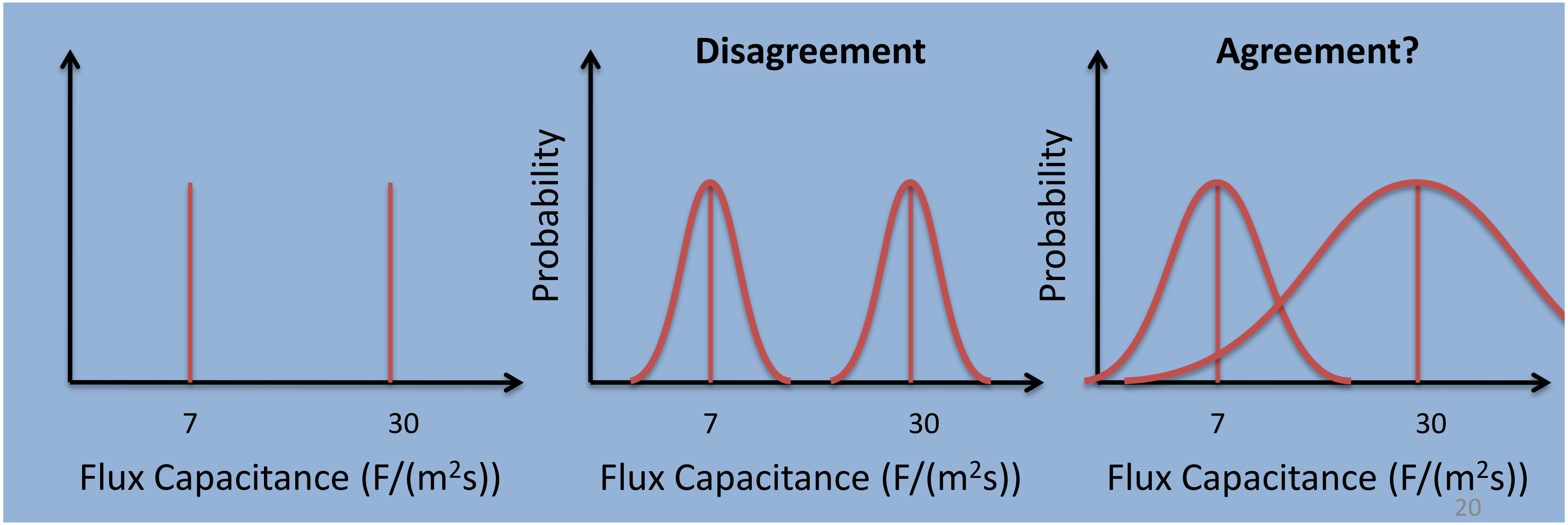


$E = 10.3$ GPa

$W = 120$ mJ/m^2

Uncertainty in measurement

- Lab A and B are given a sample, say X.
  - Lab A → flux capacitance = 7
  - Lab B → 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:

$$U_{x,r} = k_x u_r$$

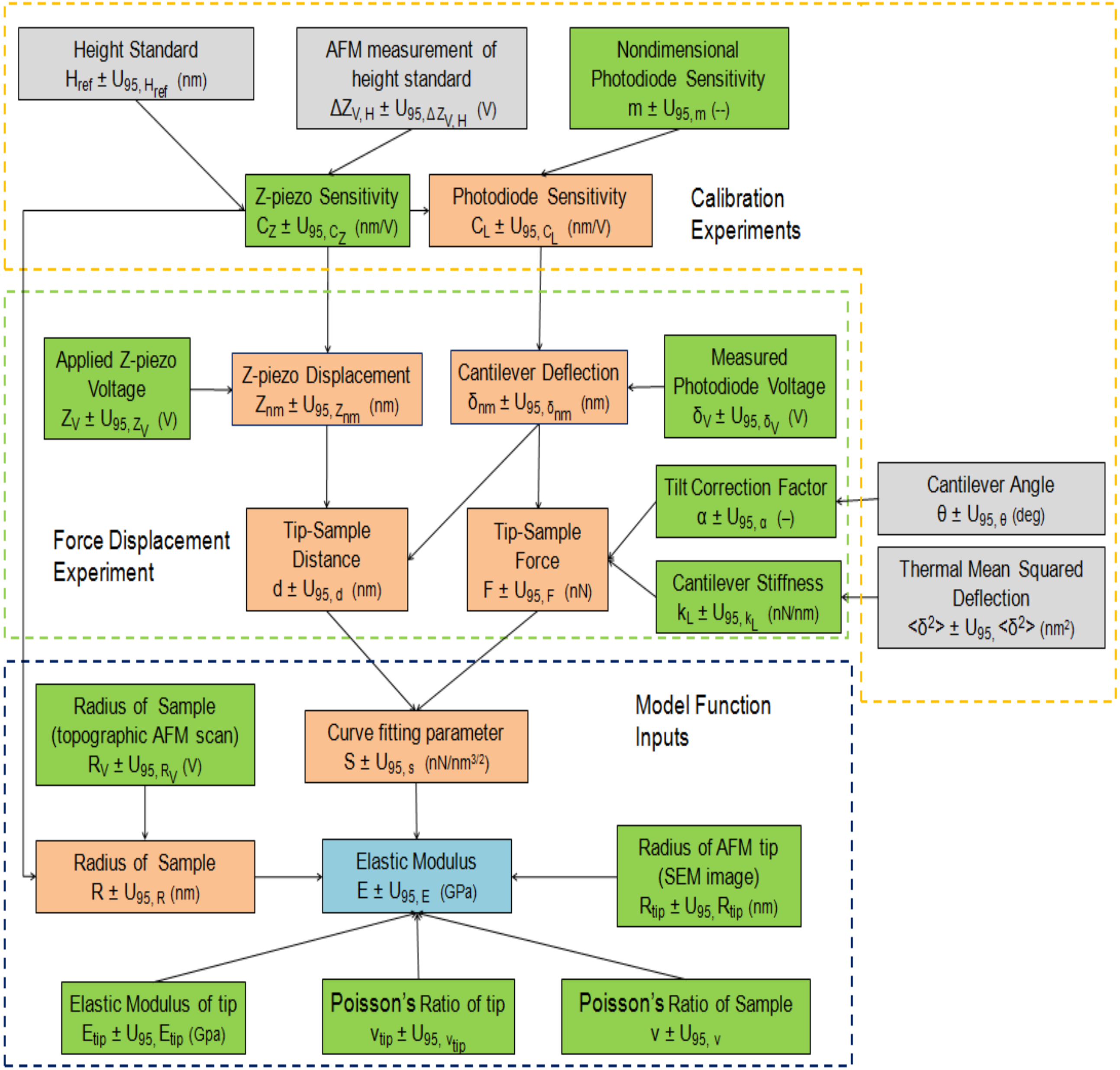
$U_{x,r}$ corresponds to the range that we are x percent confident that the true value of r falls within $r_{best} \pm U_{x,r}$

If we have $f(r_1, \ldots, r_n)$ the then 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



Height Standard
$H_{ref} \pm U_{95,H_{ref}}$ (nm)

AFM measurement of height standard
$\Delta Z_{V,H} \pm U_{95,\Delta Z_{V,H}}$ (V)

Nondimensional Photodiode Sensitivity
$m \pm U_{95,m}$ (--)

Z-piezo Sensitivity
$C_Z \pm U_{95,C_Z}$ (nm/V)

Photodiode Sensitivity
$C_L \pm U_{95,C_L}$ (nm/V)

Calibration Experiments

Applied Z-piezo Voltage
$Z_V \pm U_{95,Z_V}$ (V)

Z-piezo Displacement
$Z_{nm} \pm U_{95,Z_{nm}}$ (nm)

Cantilever Deflection
$\delta_{nm} \pm U_{95,\delta_{nm}}$ (nm)

Measured Photodiode Voltage
$\delta_V \pm U_{95,\delta_V}$ (V)

Tilt Correction Factor
$\alpha \pm U_{95,\alpha}$ (–)

Cantilever Angle
$\theta \pm U_{95,\theta}$ (deg)

Force Displacement Experiment

Tip-Sample Distance
$d \pm U_{95,d}$ (nm)

Tip-Sample Force
$F \pm U_{95,F}$ (nN)

Cantilever Stiffness
$k_L \pm U_{95,k_L}$ (nN/nm)

Thermal Mean Squared Deflection
$\langle\delta^2\rangle \pm U_{95,\langle\delta^2\rangle}$ (nm²)

Radius of Sample (topographic AFM scan)
$R_V \pm U_{95,R_V}$ (V)

Curve fitting parameter
$S \pm U_{95,s}$ (nN/nm$^{3/2}$)

Model Function Inputs

Radius of Sample
$R \pm U_{95,R}$ (nm)

Elastic Modulus
$E \pm U_{95,E}$ (GPa)

Radius of AFM tip (SEM image)
$R_{tip} \pm U_{95,R_{tip}}$ (nm)

Elastic Modulus of tip
$E_{tip} \pm U_{95,E_{tip}}$ (Gpa)

Poisson's Ratio of tip
$\nu_{tip} \pm U_{95,\nu_{tip}}$

Poisson's Ratio of Sample
$\nu \pm U_{95,\nu}$

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

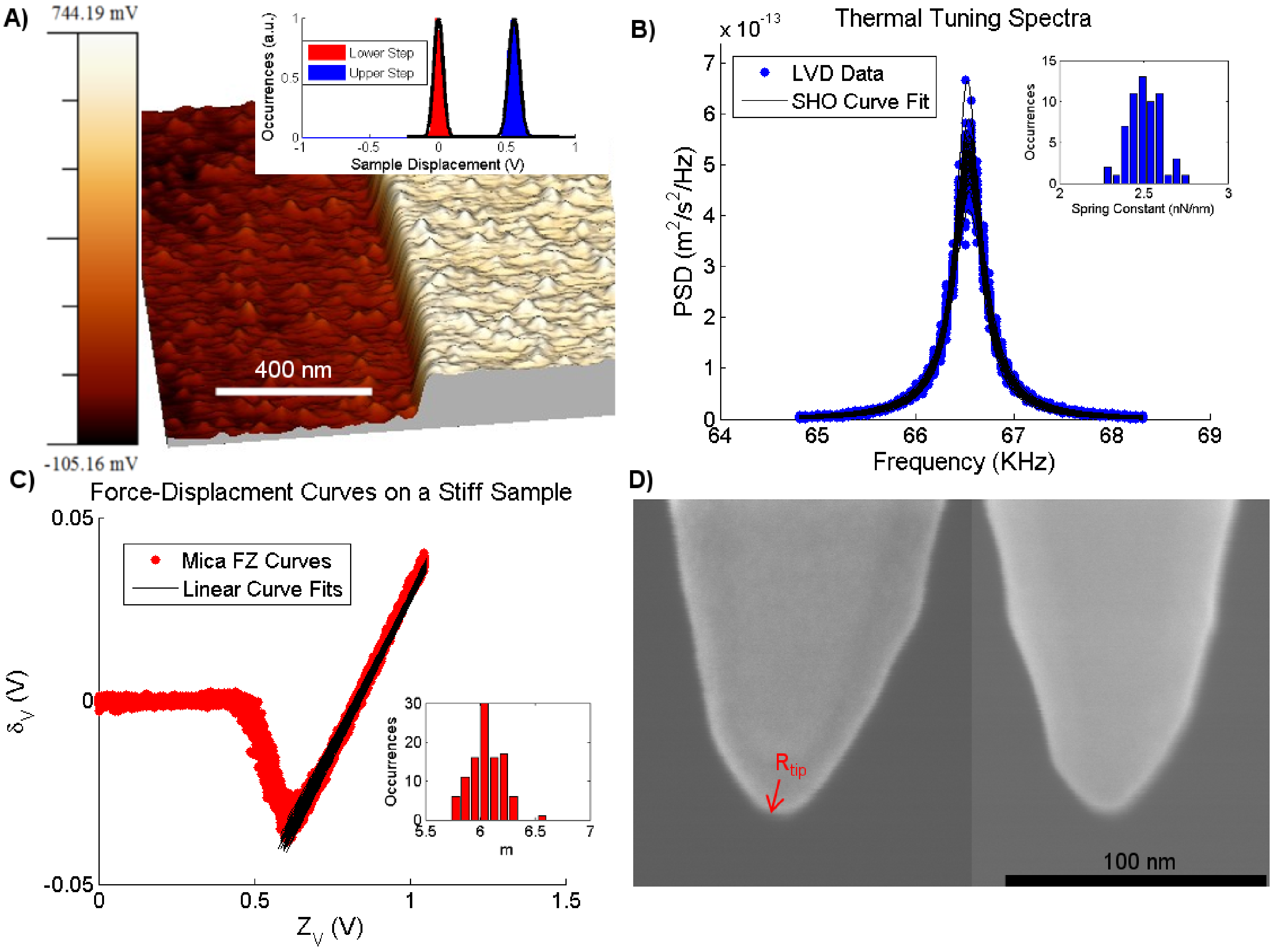
Summary

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

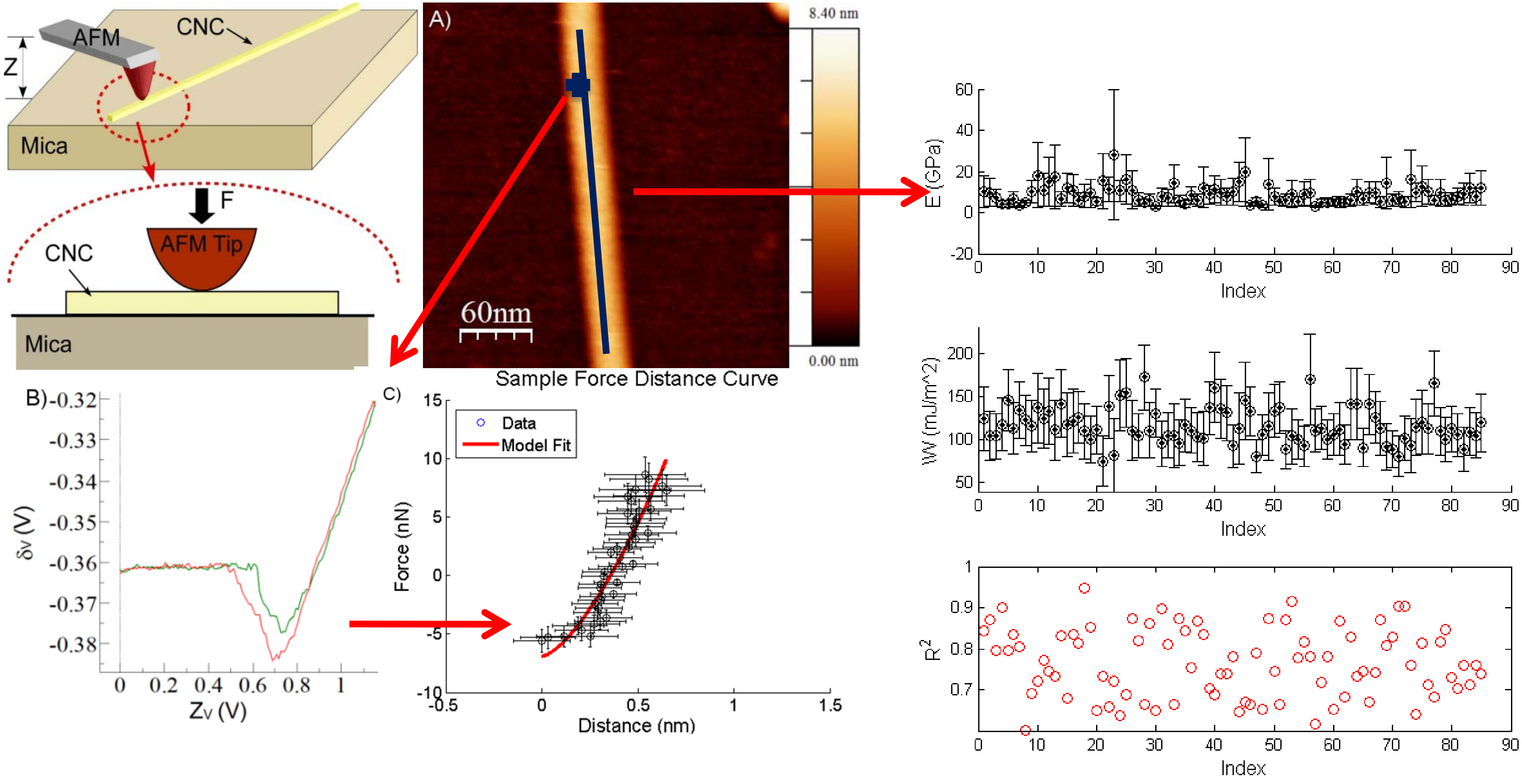
$$
\begin{aligned}
u_E = ((\frac{df_1}{dZ_{V_1}} u_{V_1})^2 + \dots + (\frac{df_1}{dZ_{V_n}} u_{Z_{V_n}})^2 + (\frac{df_1}{d\delta_{V_1}} u_{\delta_{V_1}})^2 + \dots + (\frac{df_1}{d\delta_{V_n}} u_{\delta_{V_n}})^2 + \\
(\frac{df_1}{dZ_{V,shift}} u_{Z_{V,shift}})^2 + (\frac{df_1}{d\delta_{V,shift}} u_{\delta_{V,shift}})^2 + (\frac{df_1}{dC_Z} u_{C_Z})^2 + (\frac{df_1}{dm} u_m)^2 + \\
(\frac{df_1}{dk_L} u_{k_L})^2 + (\frac{df_1}{d\alpha} u_\alpha)^2 + (\frac{df_1}{dR_V} u_{R_V})^2 + (\frac{df_1}{dR_{tip}} u_{R_{tip}})^2 \\
+ (\frac{df_1}{dE_{tip}} u_{E_{tip}})^2 + (\frac{df_1}{d\nu_{tip}} u_{\nu_{tip}})^2 + (\frac{df_1}{d\nu} u_\nu)^2)^{1/2}
\end{aligned}
$$

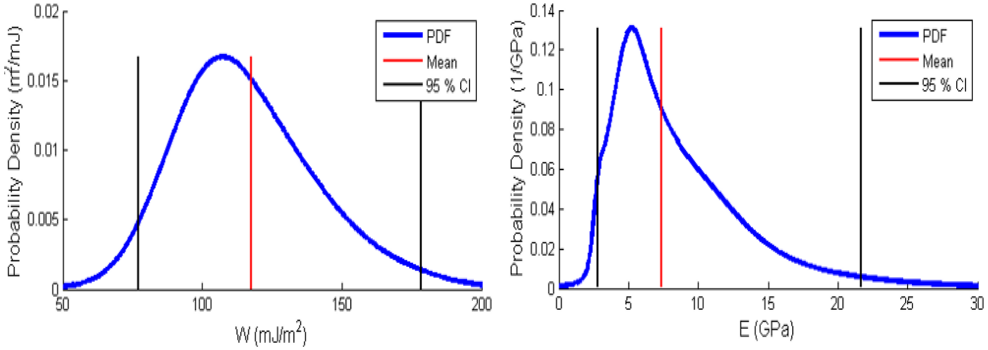
(Result for W is similar)

Case Study Cellulose Nanocrystals



Case Study: Cellulose Nanocrystals[1]





Value	Mean	95 % CI	Units
E_t	7.9	[2.9, 22.0]	GPa
W	116	[77, 180]	mJ/m^2

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[1] Wagner R., Raman A., Moon. R. "Uncertainty quantification in nanomechanical measurements using the Atomic Force Microscope" *In Preparation* 2010.

Sensitivity Analysis

Sample Uncertainty Table for Elastic Modulus Analysis

Variable (x)	Description	Value	Standard Uncertainty (u_x)	Sensitivity (dE/dx)	Contribution to Elastic Modulus Variance $(dE/dx\ u_x)^2$	
Calibration Parameters:						
C_Z	Z-piezo Sensitivity	14 (nm/V)	1 (nm/V)	0.5 (GPa V/nm)	0.03 (GPa^2)	
m	Nondimentional Photodiode Sensitivity	6.1 (--)	0.15 (--)	25 (GPa)	14 (GPa^2)	
α	Tilt Correction Factor	1.037 (--)	0.007 (--)	10 (GPa)	0.01 (GPa^2)	
k_L	Cantilever Stiffness	2.5 (nN/nm)	0.1 (nN/nm)	5 (GPa nm/nN)	0.02 (GPa^2)	
$\delta_{V,\ Shift}$	Photodiode voltage Shift Factor	-0.36 (V)	0.01 (V)	0.0002 (GPa/ V)	4 E -12 (GPa^2)	
Model Parameters:						
R_{tip}	Radius of AFM tip	10 (nm)	1 (nm)	0.4 (Gpa/nm)	0.16 (GPa^2)	
E_{tip}	Elastic Modulus of AFM tip	100 (GPa)	3 (GPa)	0.01 (--)	0.001 (GPa^2)	
ν_{tip}	Poisson's Ratio of AFM tip	0.28 (--)	0.02 (--)	0.6 (GPa)	0.001 (GPa^2)	
R_V	Radius of Sample measured with AFM	0.31 (V)	.04 (V)	6 (GPa/V)	0.05 (GPa^2)	
ν	Poisson's Ratio of Sample	0.28 (--)	0.05 (--)	6 (GPa)	0.01 (GPa^2)	
Data pairs sampled during experiment :				Mean Sensitivity	Mean Variance Contribution	Total Variance Contribution
Z_{V_i}	Z-piezo voltage	-- (V)	0.0002 (V)	30 (GPa/V)	0.00004 (GPa^2)	0.004 (GPa^2)
δ_{V_i}	Photodiode voltage	-- (V)	0.0002 (V)	170 (GPa/V)	0.001 (GPa^2)	0.2 (GPa^2)
Total:				Expanded Uncertainty ($k_p = 2$)	Variance	
E	Elastic Modulus	10 .3 (Gpa)	3.8 (GPa)	7.6 (GPa)	15 (GPa^2)	