# AFM Metrology of Cellulose Nanocrystals

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2/17/11

PURDUE UNIVERSITY

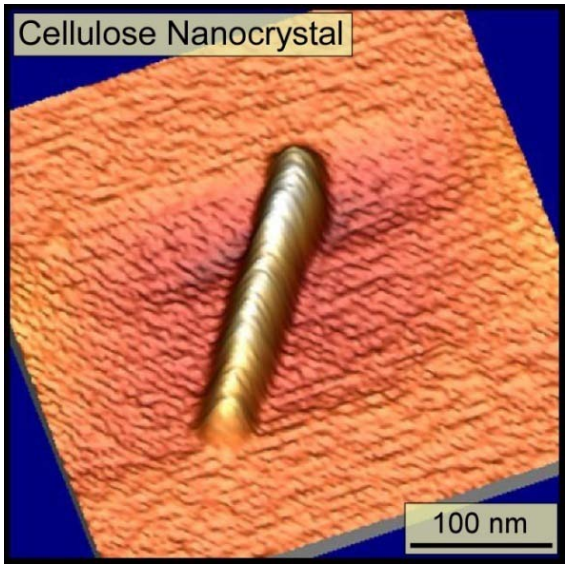
FOREST SERVICE US DEPARTMENT OF AGRICULTURE

NIST

# Outline

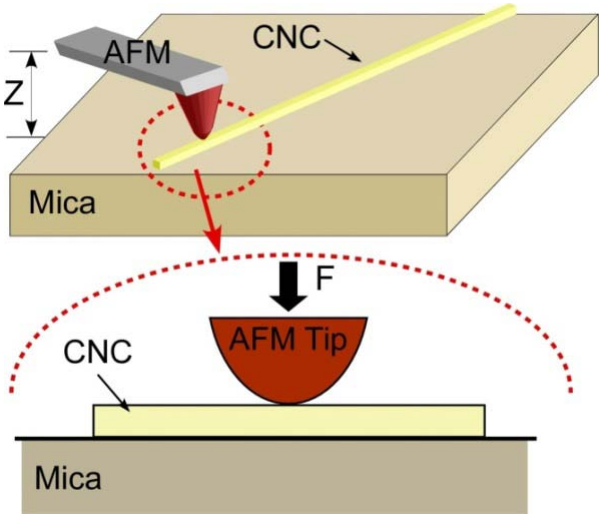
## Cellulose Nanoparticles (CN)

- CN Particle & Composites
- Motivation for AFM



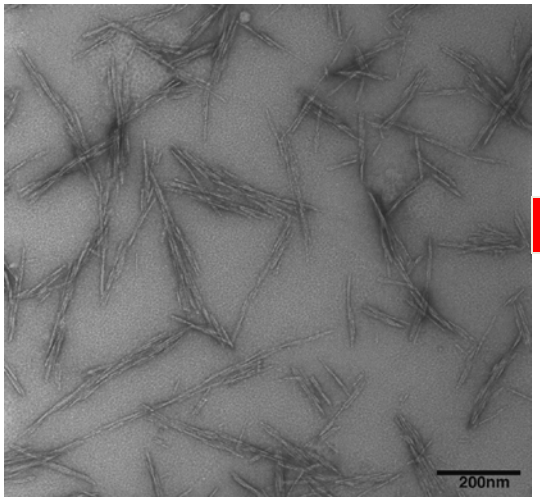

## AFM Characterization of CNs

- Force-Displacement Data
- Uncertainty Quantification



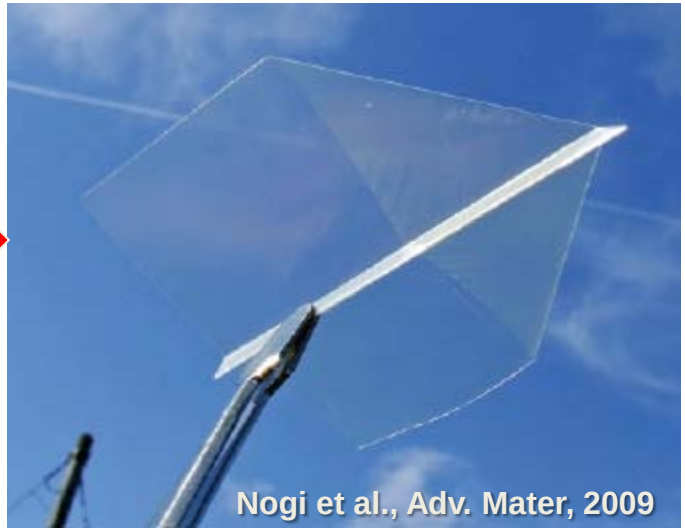
# Unique Nanoparticle – Unique Composites

## Isolated CNs




- Uniform “Building Block”
- High Aspect Ratio
- Good Mechanical Properties
- Low Density (1.6g/cm$^3$)
- “Reactive” Surfaces
- “Green”

## Designed CN Composites



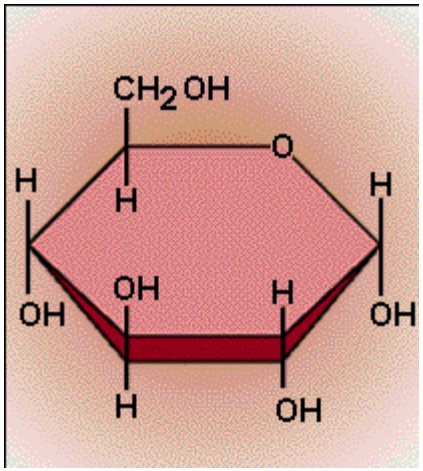

- Several Composite Types
- Unique Optical Properties
- Mechanical Properties
- Low Density
- Multifunctional
- “Green”

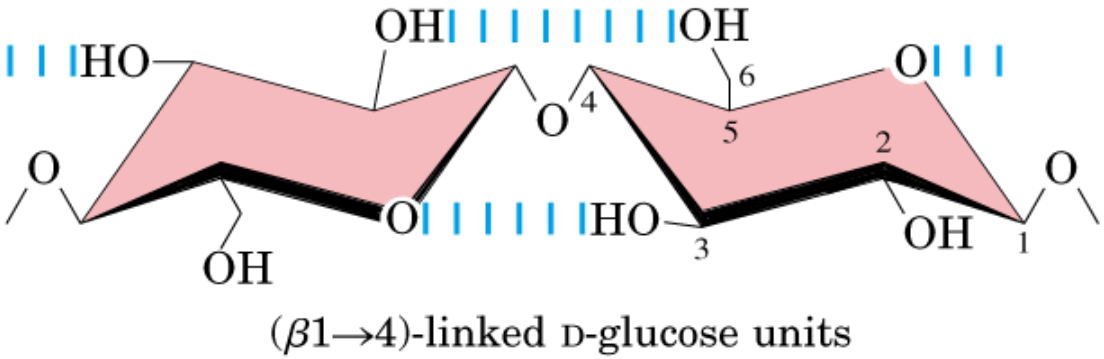
# Cellulose Structure

**Carbohydrates** **(Simple sugars: monomers)**

- **Monosaccharides (1 sugar units)**
- **Disaccharides (2 → 10 sugar units)**
- **Polysaccharides (many sugar units)** ← **Cellulose**

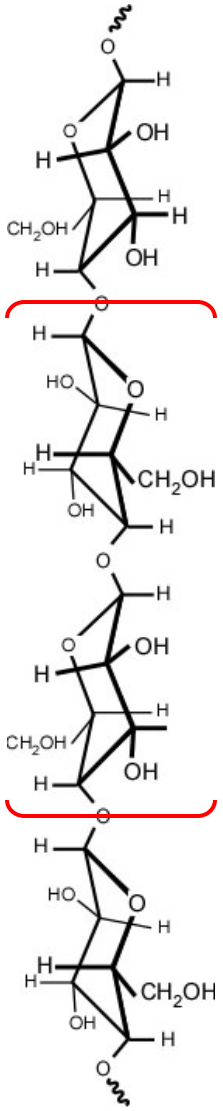
**$C_6H_{12}O_6$**




(β1→4)-linked D-glucose units

# Cellulose Structure

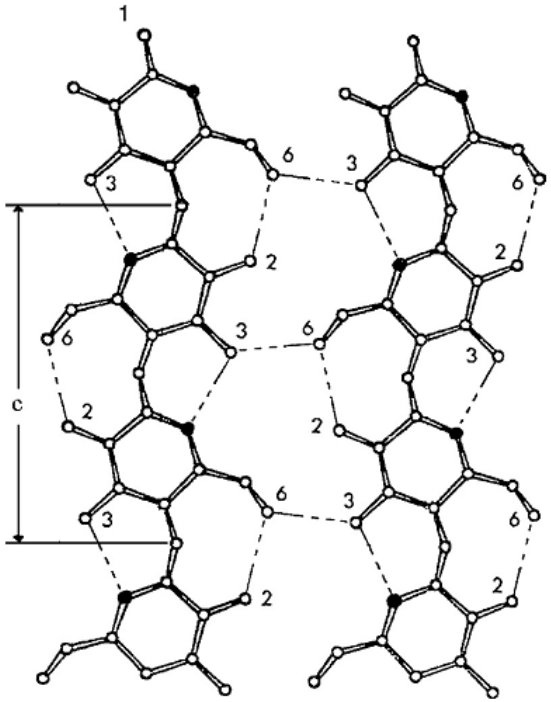


## Cellulose

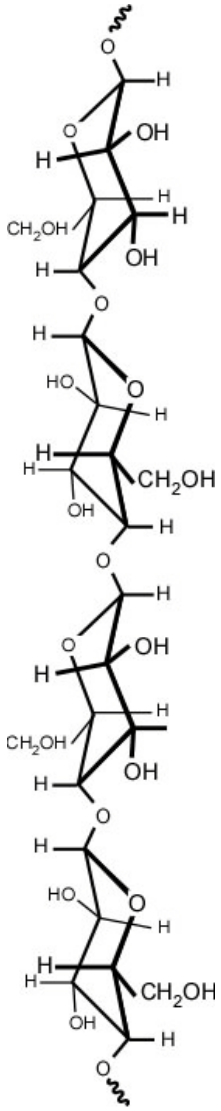
- 1,4-β-D- linked polyanhydro glucopranose
- Repeat unit = 2 glucose units
- N= 1,000 – 15,000
- Chain length up to 5 µm
- MW= 10,000 – 150,000

## Hydrogen Bonding

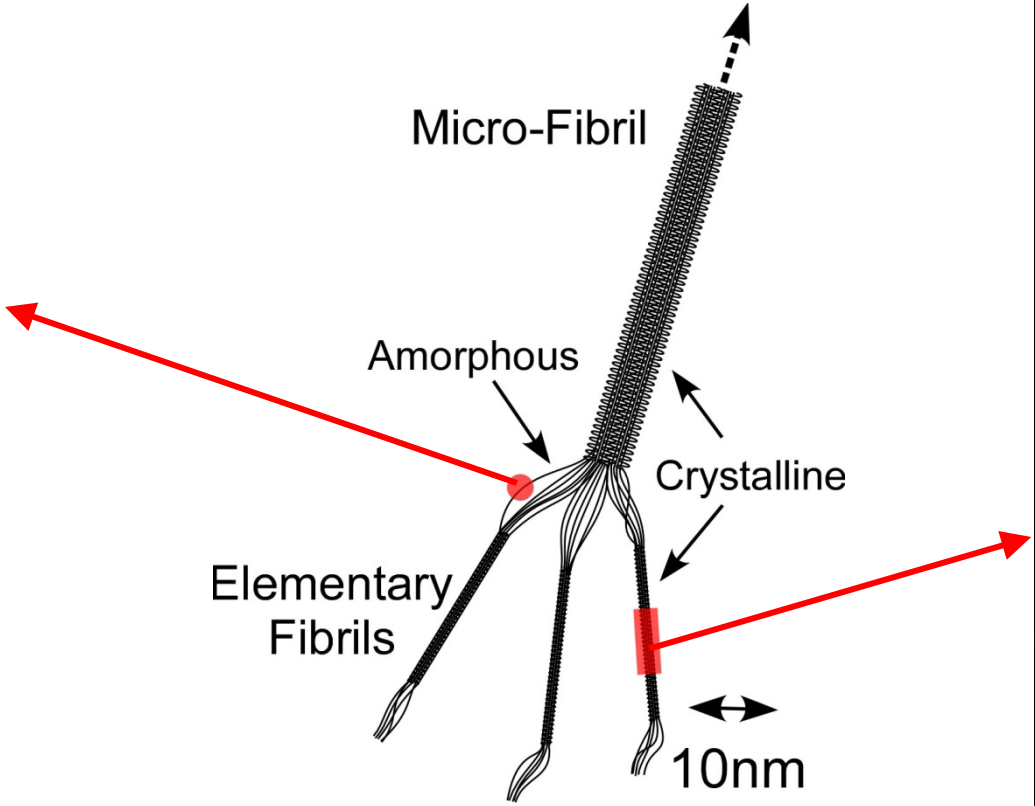
- -OH Groups & O
- Intra & Inter Bonding
- Makes Cellulose Stiff & Rigid

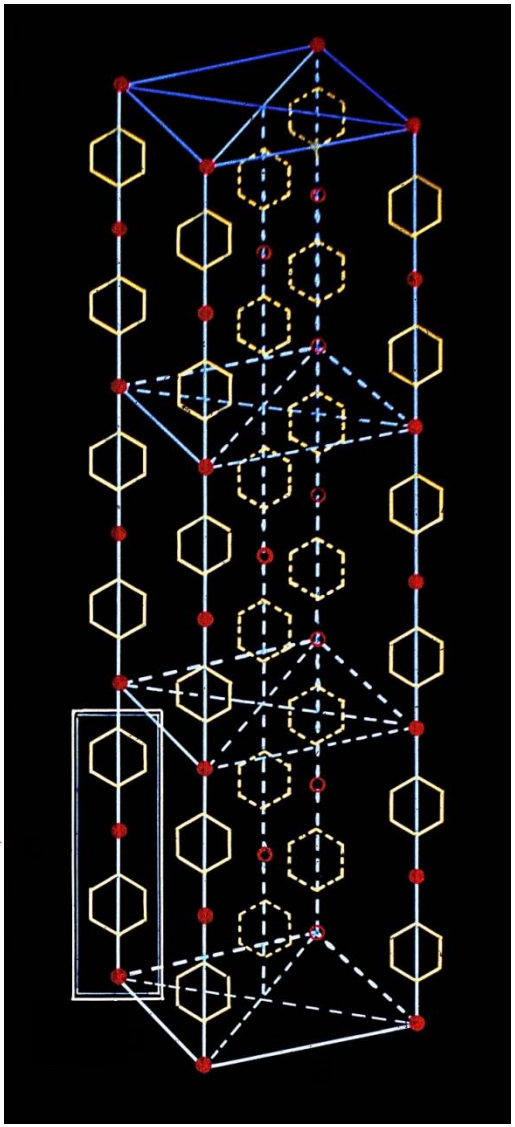


# Cellulose I Fibril

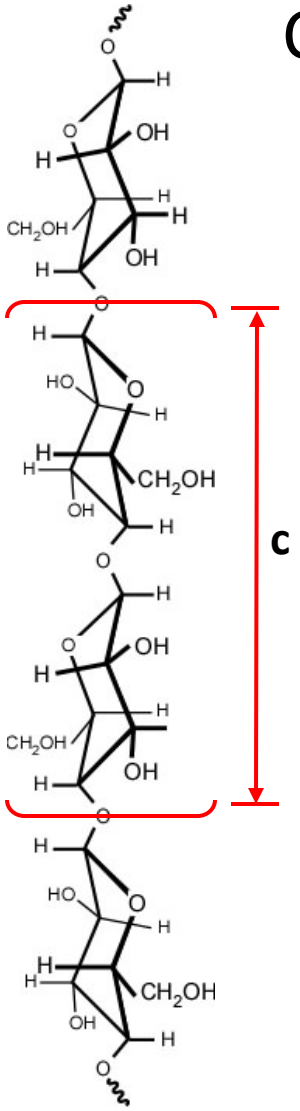


- Cellulose Chains Combine
- Elementary Fibrils
- Micro-Fibrils



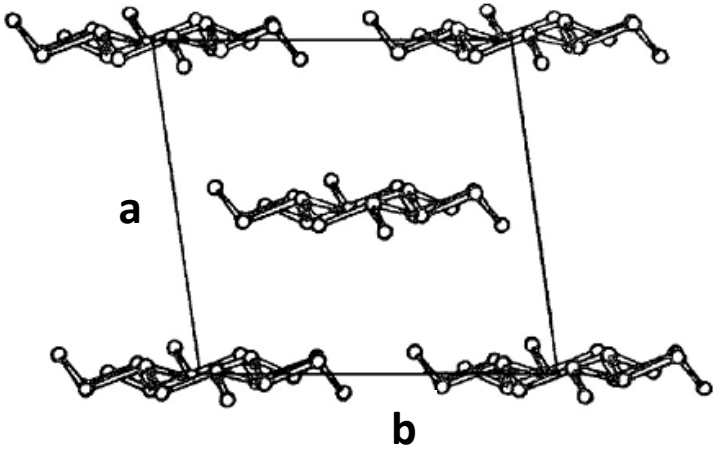



# Cellulose Structure

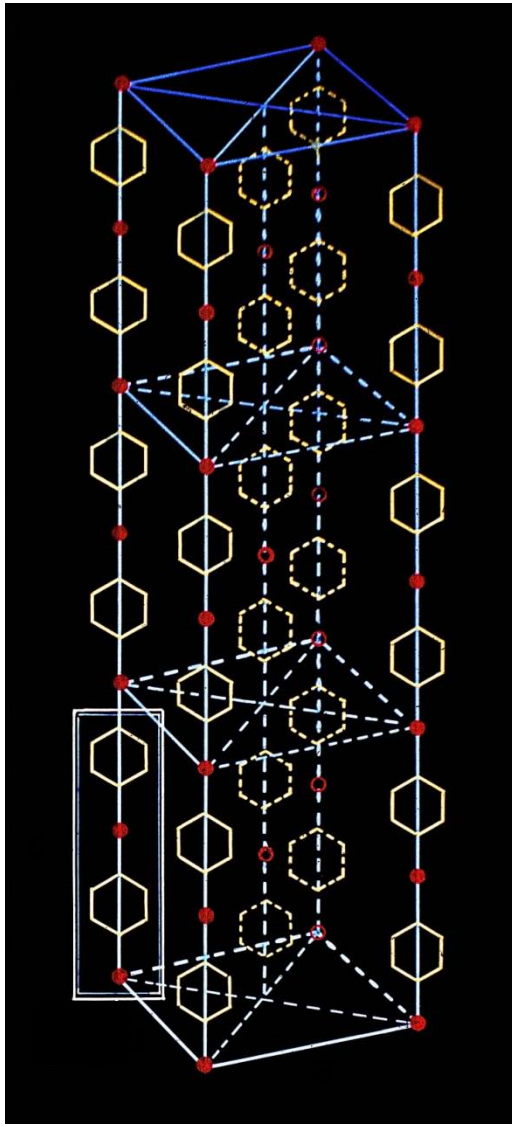



## Cellulose I: "Natural"

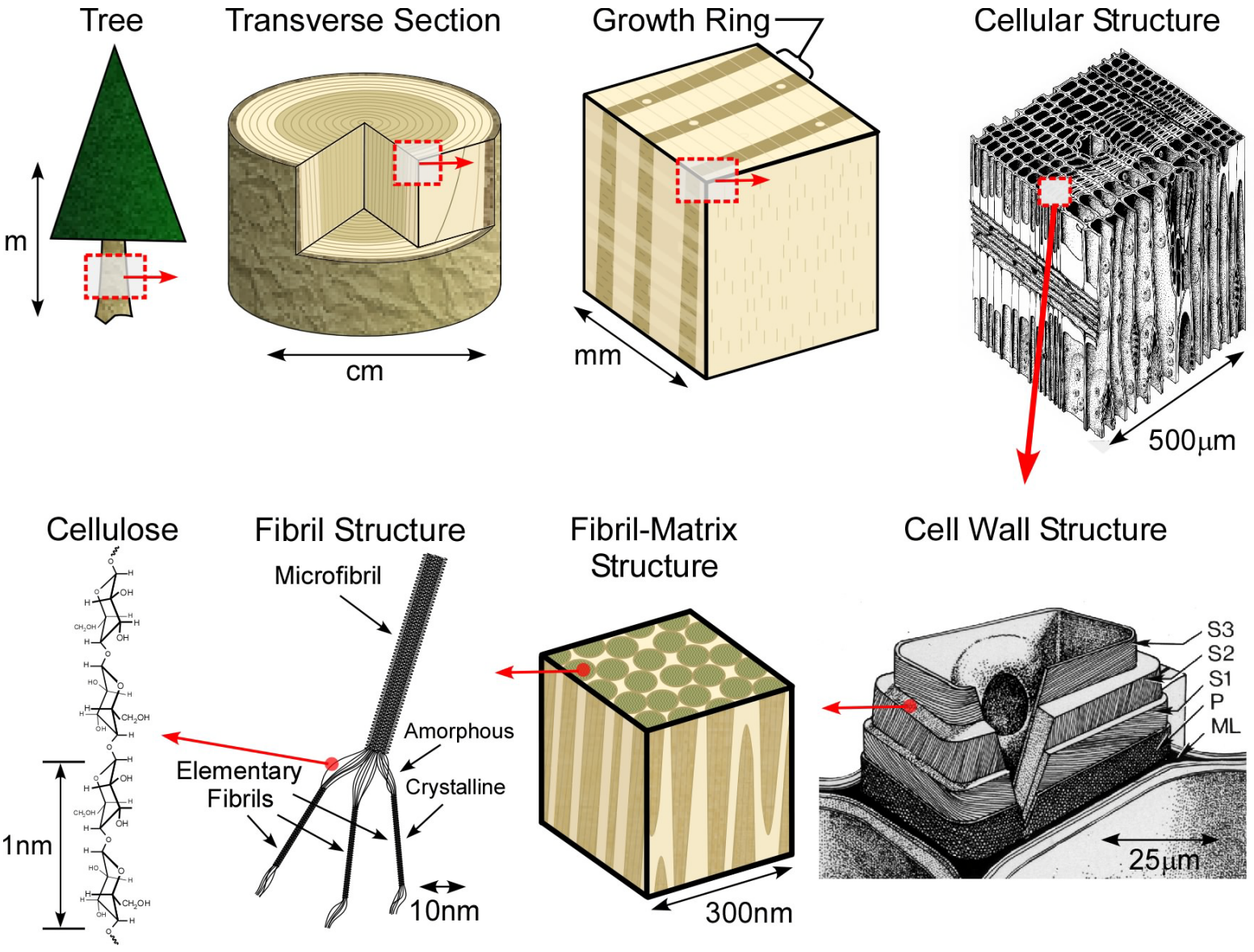
- Hydrogen Bonding
- Crystalline Unit Cell
  - a=7.78 Å
  - b=8.20 Å
  - c=10.38 Å




- Source Independent
- Cellulose II, III, IV



# Wood-CNs

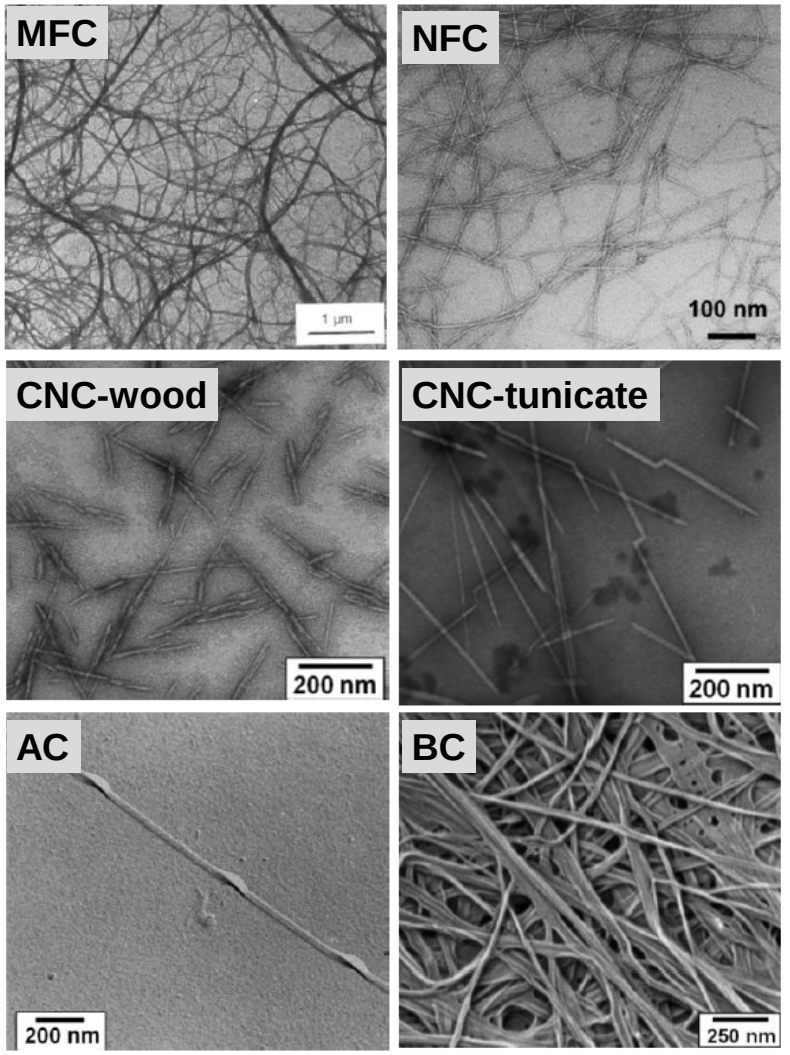



Moon et al., submitted to Chem Soc Rev 2010..

# Cellulose Particle Types

- Microfibrillated Cellulose (MFC)
- Nanofibrillated Cellulose (NFC)
- Cellulose Nanocrystals (CNC)
- Algae Cellulose (AC)
- Bacterial Cellulose (BC)

| CNC Source | Length | Cross-Section |
|---|---|---|
| **Algal** | >1000nm | 10-20nm |
| **Bacterial** | 100 to >1000nm | 5-10nm by 30-50nm |
| **Cotton** | 200-350nm | 5nm |
| **Tunicate** | 100 to >1000nm | 10-20nm |
| **Wood** | 100-300nm | 3-5nm |




MFC: Dufresne et al., J. App. Poly. Sci., 1997
NFC: Saito et al., Biomacromolecules, 2007
AC: Hanley et al., Cellulose, 1997.
BC: Ifuku et al., Biomacromolecules, 2007

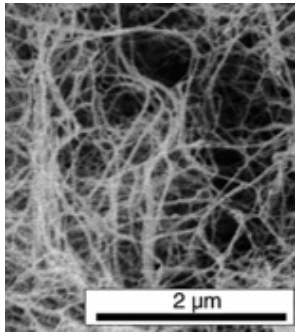
# CN Comparison

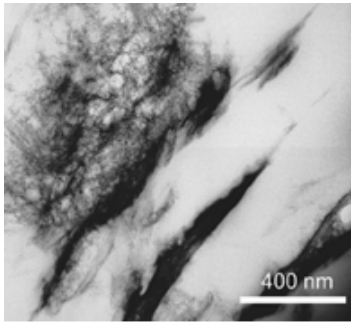
| Material | Density ($g/cm^3$) | CTE ($10^{-6}/K$) Axial | Tensile Strength (GPa) Axial | Elastic Modulus (GPa) Axial | Elastic Modulus (GPa) Transverse |
|---|---|---|---|---|---|
| **Crystalline Cellulose** | **1.6** | **0.1** | **7.5** | **120-220** | **11-57** |
| Kevlar-49 fiber | 1.4 | 2 | 3.5 | 124-130 | 2.5 |
| Glass fiber | -- | 4 | 4.8 | 86 | -- |
| Carbon fiber | 1.8 | 1.6-2.1 | 1.5 - 5.5 | 150-500 | -- |
| Steel Wire | 7.8 | 9-17 | 4.1 | 210 | -- |
| Clay Nanoplatelets | -- | -- | -- | 170 | -- |
| Carbon Nanotubes | -- | -- | 11-63 | 270-950 | 0.8-30 |
| Boron Nanowhiskers | -- | 6 | 2-8 | 250-360 | -- |

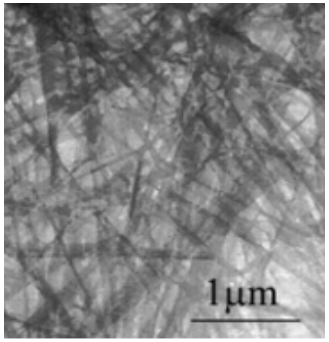
- Comparable to other Reinforcement materials

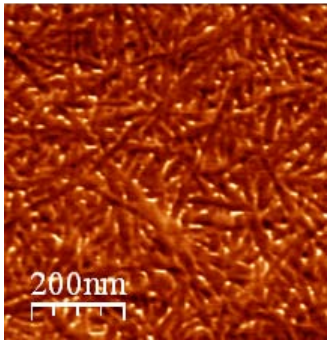
# CN Composite Types

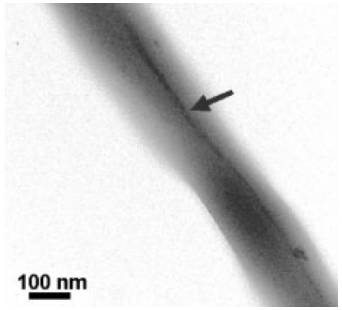
**Aerogel** | **Modified Matrix** | **"Filler"** | **Modified Network** | **Neat Network**



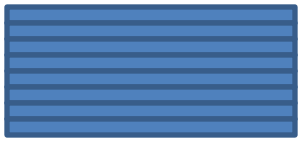



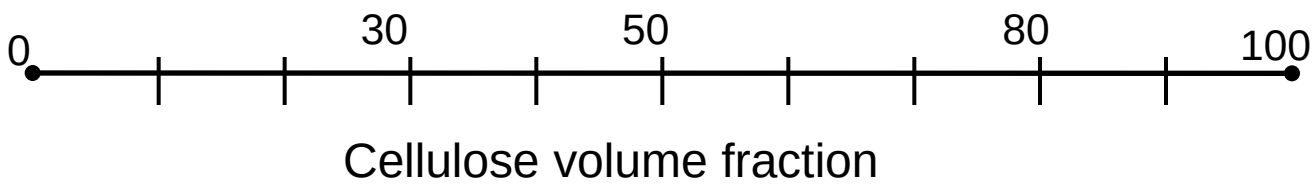




**Fibers**

**Laminates**






Paakko et al., Soft Matter, 2008, 4, 2492-2499

Bondeson and Oksman, Composite Interfaces, 2007, 14, 617-630

Park et al., Macromol Symp., 2007, 249-250, 289-294

Noichiki et al., J. Appl. Poly. Sci., 2002, 86, 3425-3429

# CN Composites

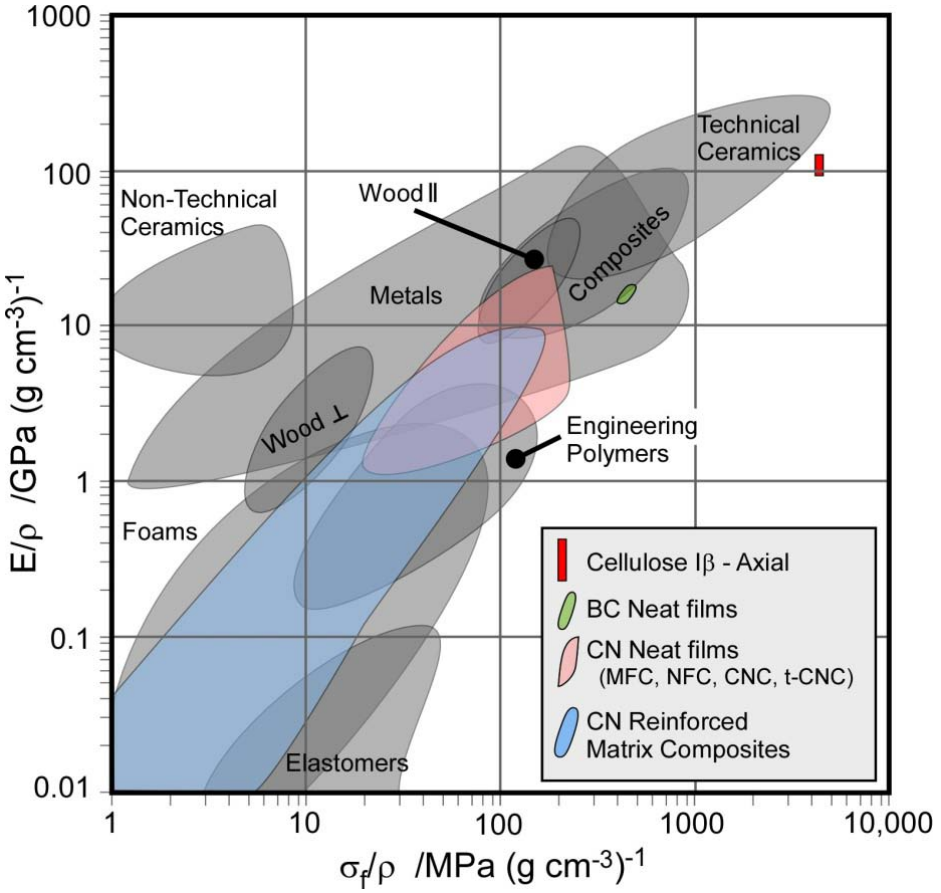
## Transparent:

Nogi et al. , Adv. Mater , 2009, 20:1-4.

## Low Thermal Expansion:

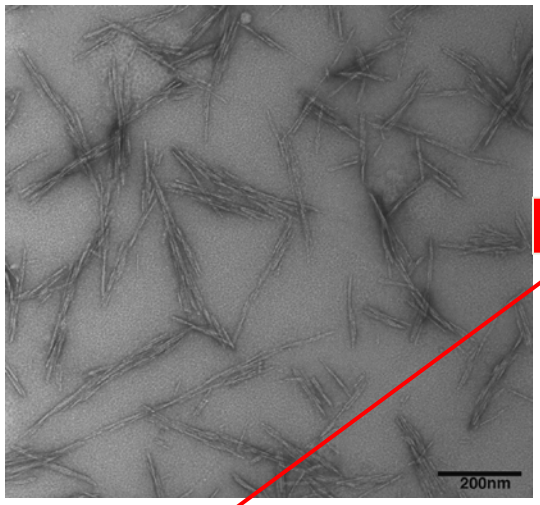
Okahisa et al., Composites Science and Technology, 2009, 69:1958-1961.

## High Elasticity & Strength:



# CN Research @Purdue

**Isolated CNs**




**CN Composites**

**Processing**

- CNC
- NFC

**Metrology**

- Particles
- Composites

**Modeling**

- Atomistic
- Continuum
- Laminate

**Coatings**

- Chemical
- Metallic

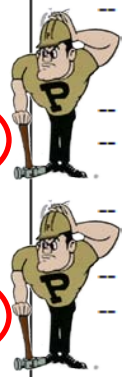
**Composite Processing**

- Neat Films
- Modified Neat films
- Matrix Reinforced
- Laminate

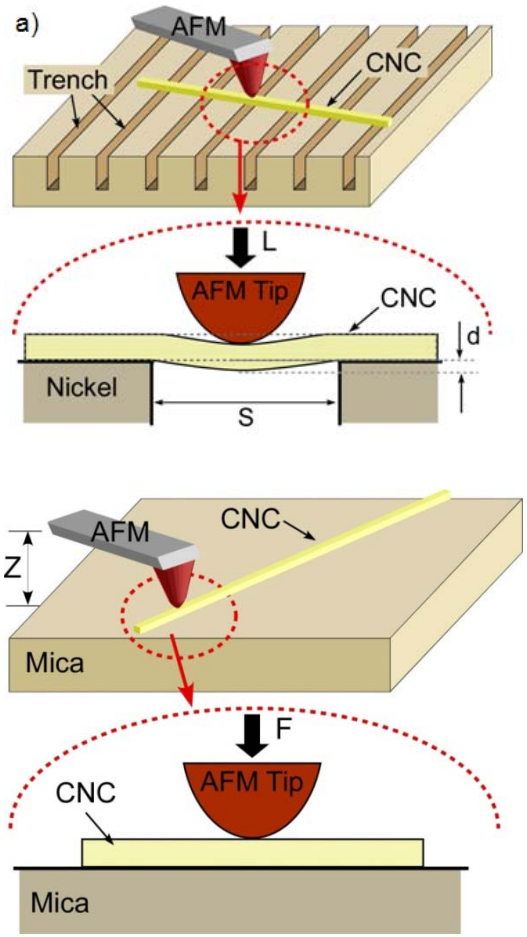
- **Engineered CN Composites**

# Properties of Cellulose

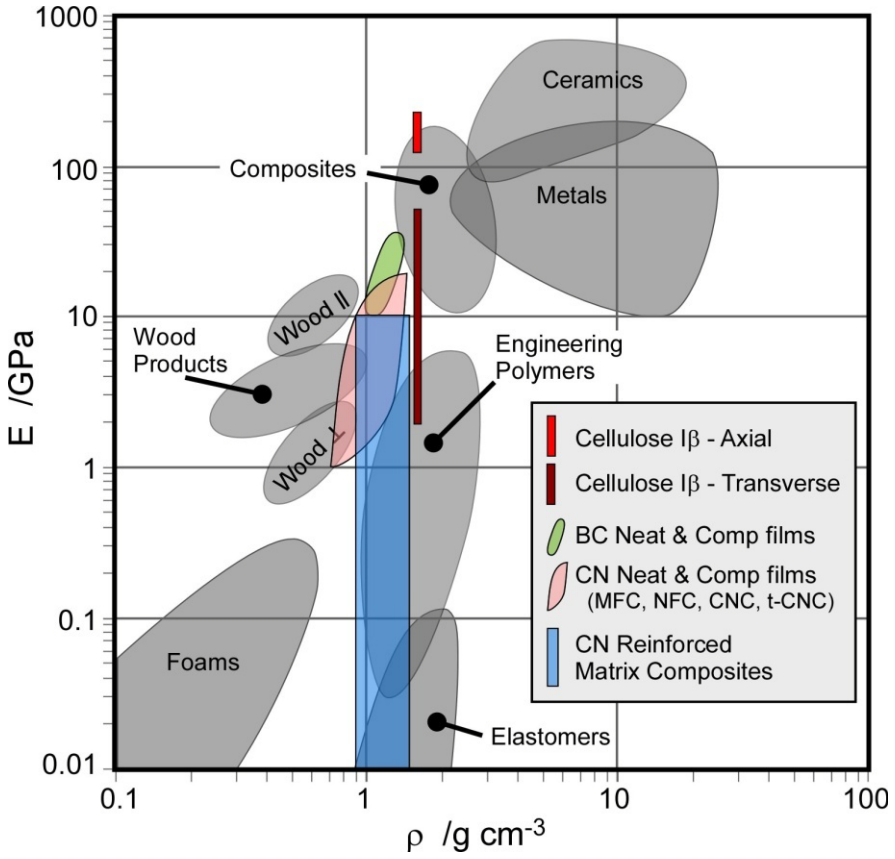
| Material | $E_A$ (GPa) | $E_T$ (GPa) | $\sigma_f$ (GPa) | $\varepsilon_f$ (%) | Technique |
|---|---|---|---|---|---|
| **Wood fiber** | 14-27 | -- | 0.3-1.4 | 4-23 | Tensile |
| **Plant fiber** | 5-45 | -- | 0.3-0.8 | 1.3-8 | Tensile, Raman |
| **MCC** | 25±4 | -- | -- | -- | Raman |
| **MFC & NFC** | N/A | -- | -- | -- | |
| **CNC** | | | | | |
| plant | 57, 105 | -- | -- | -- | Raman |
| wood | -- | 18-50 | -- | -- | AFM indentation |
| **t-CNC** | 143 | -- | -- | -- | Raman |
| Acid* | 151±29 | -- | -- | -- | AFM-3pt bend |
| TEMPO* | 145±31 | | -- | -- | |
| | -- | 9±3 | -- | -- | AFM indentation |
| **BC** | 78±17 | -- | -- | -- | AFM-3pt bend |
| | 114 | -- | -- | -- | Raman |
| **Cellulose Iβ** | | | | | |
| Experimental | 120-138 | | -- | -- | XRD |
| | 220±50 | 15±1 | -- | -- | IXS |
| Modeling | 110-179 | -- | -- | -- | |
| | 124-155 | 10-57 | -- | -- | |
| | 137 | 27 | 7.5 | -- | |







# Motivation for AFM of CNs

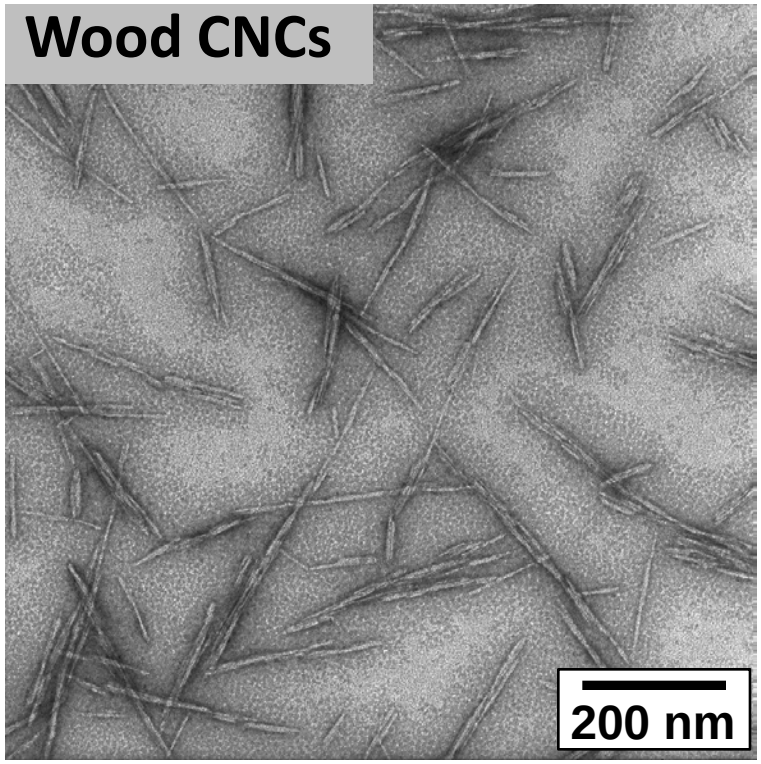


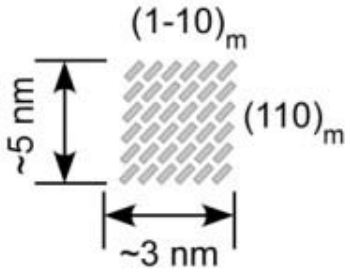

- Characterize CNs
  - Mechanical Properties
  - Anisotropy
  - CN-CN differences
- Elasticity: Insight for…
  - Predictive Modeling
  - Composite Design
- Why AFM:
  - Size Scale
  - Sensitivity

Moon et al., submitted to Chem Soc Rev 2010..

# Elastic Properties CNs

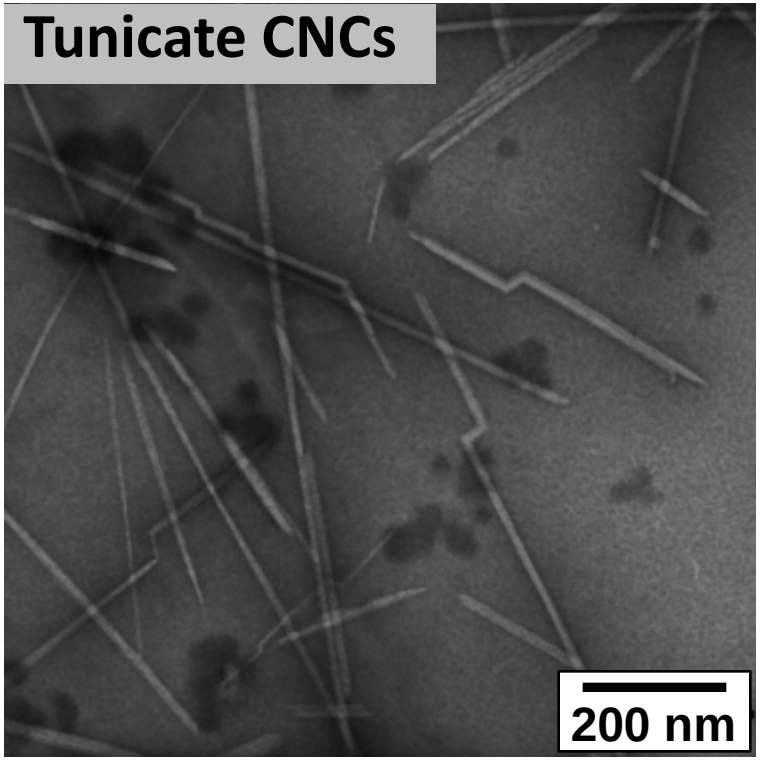
**Wood CNCs**

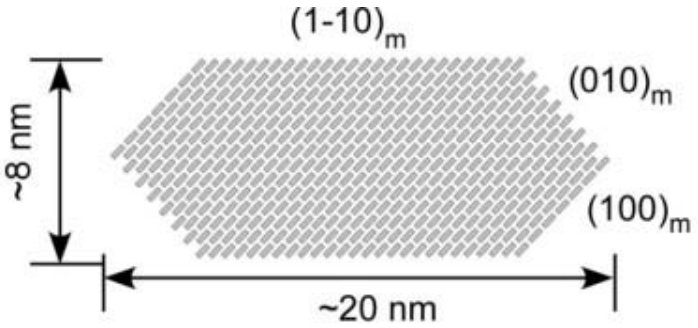



a)

**Tunicate CNCs**

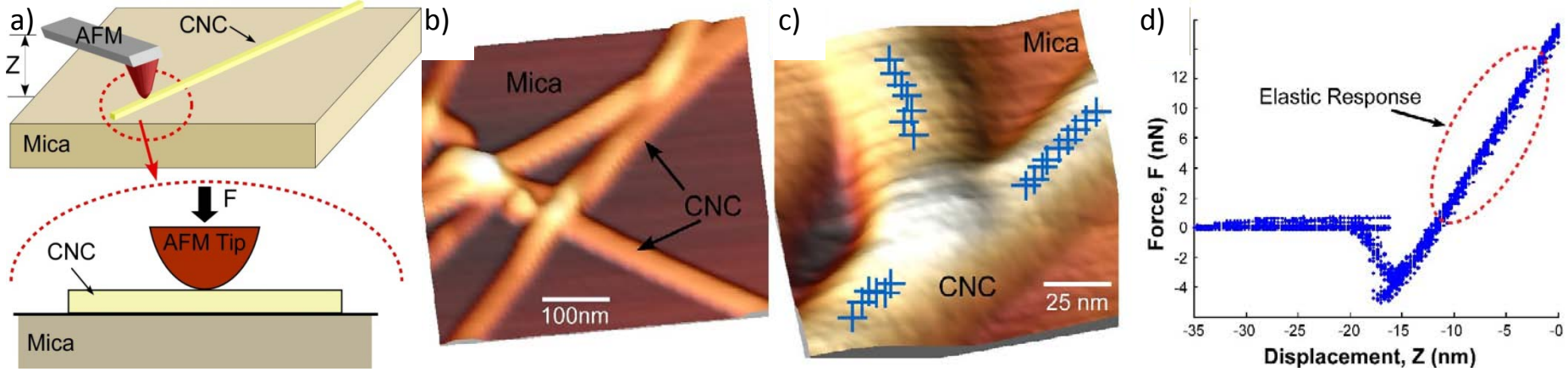


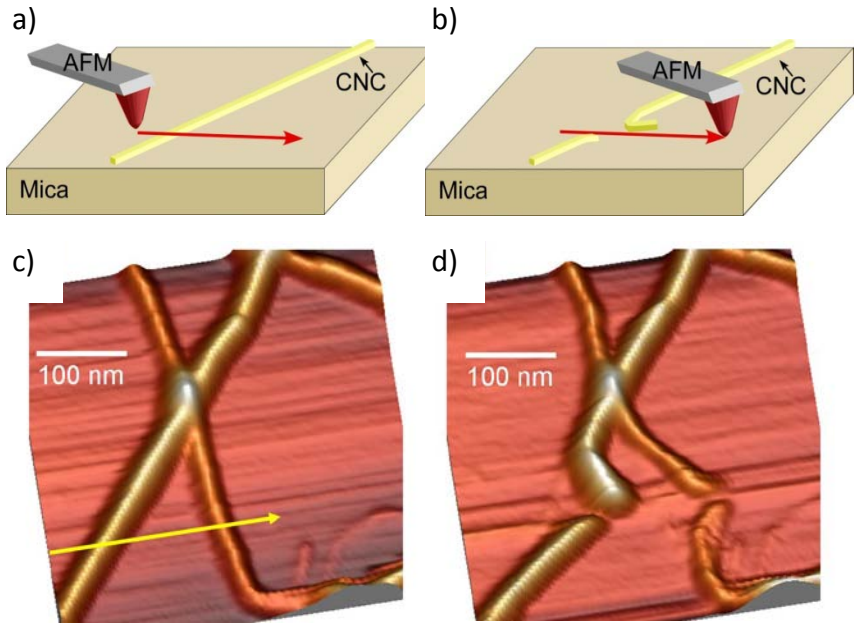

b)

Moon et al. submitted to Chem Soc Rev 2010..

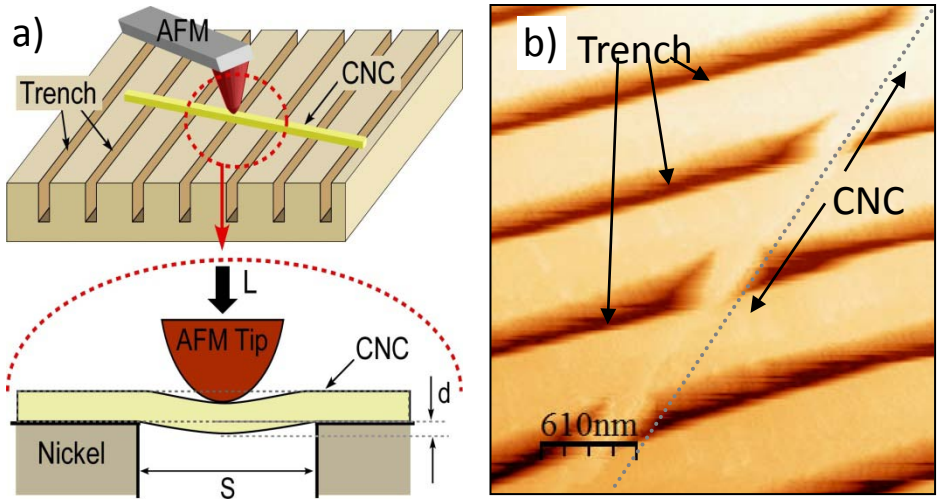
# Characterization of CNCs via AFM: Material Properties




Measure Transverse Elastic Modulus and Surface energy

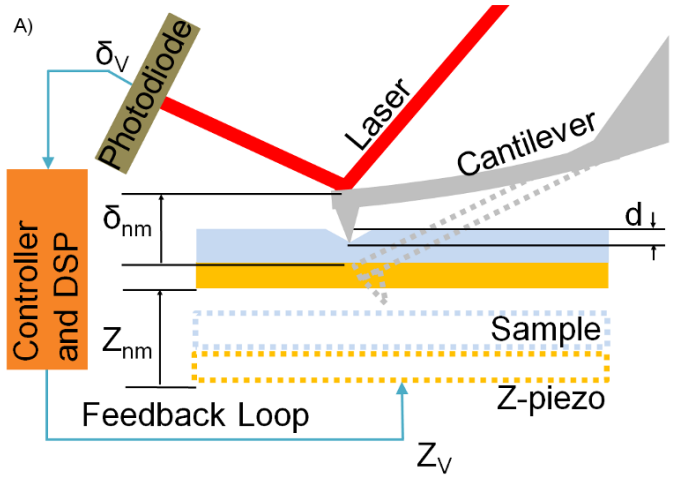


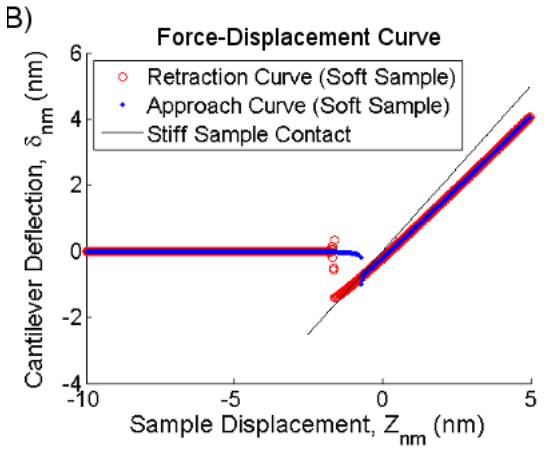

Measure Transverse Strength

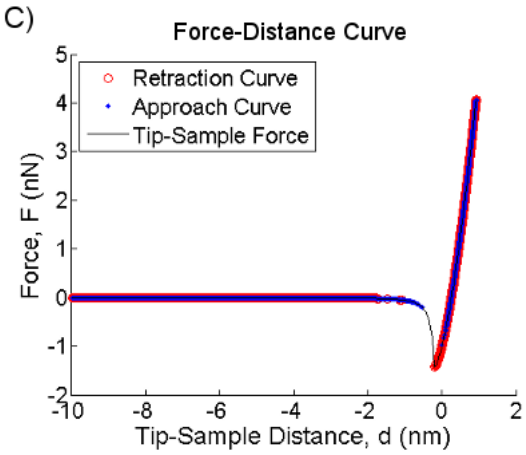



Measure Axial Modules

# Force-Displacement (F-Z) Curves



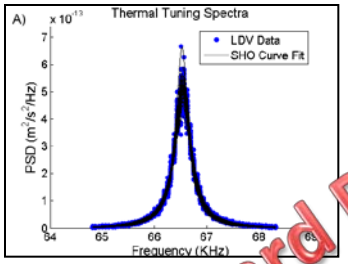



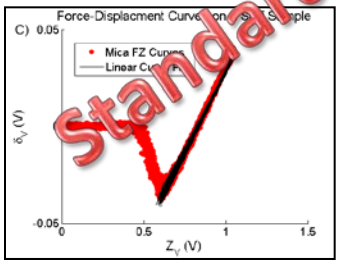



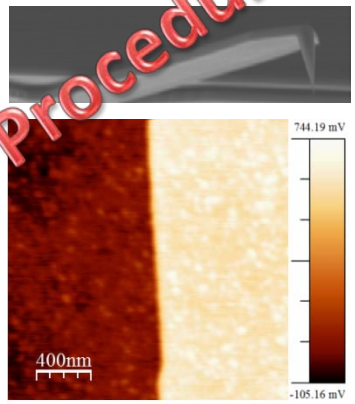

- Measure ΔF due to ΔZ
- Standard AFM technique
- Over a thousand published articles

# Elastic Modulus and Surface Energy Measurements: Procedure

## 1. Calibration Experiments

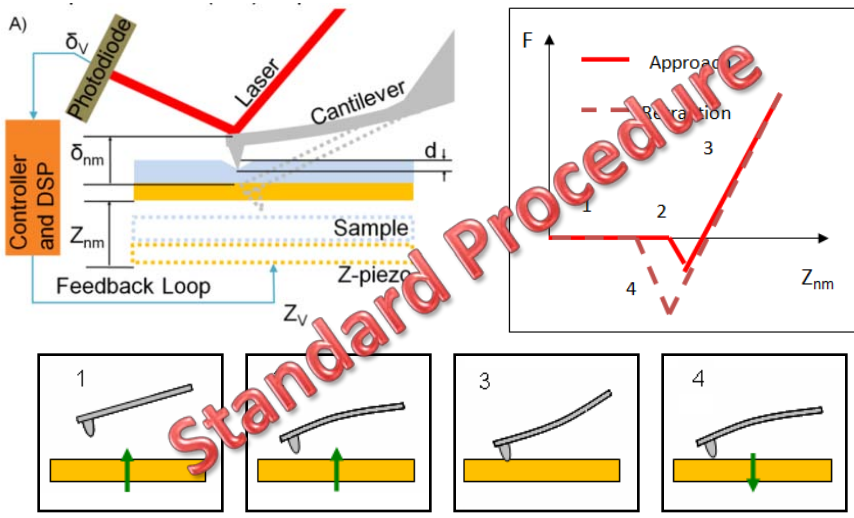


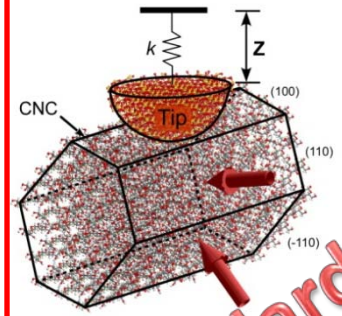

Standard Procedure

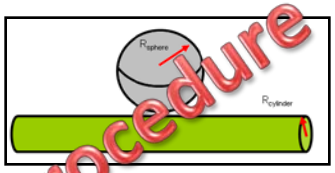
## 2. Force-Displacement (F-Z) Experiments

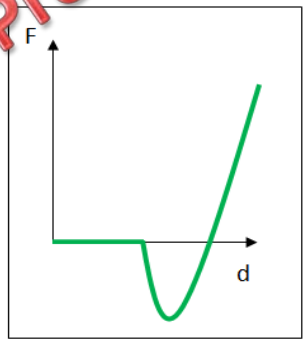


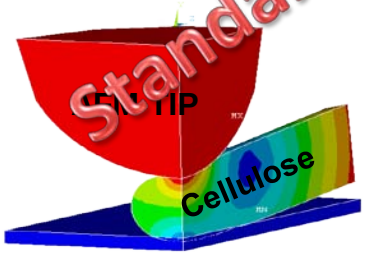

Standard Procedure

## 3. Model Fitting



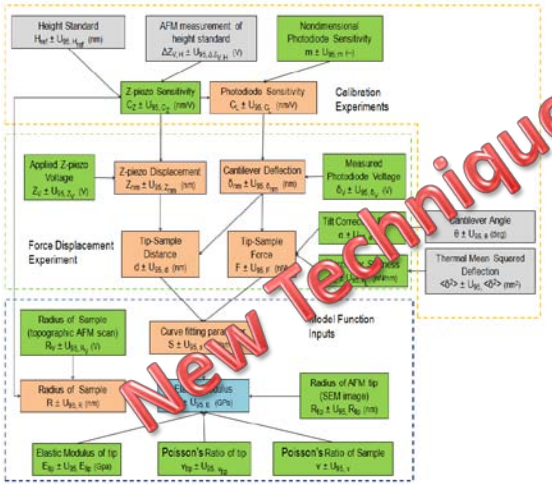



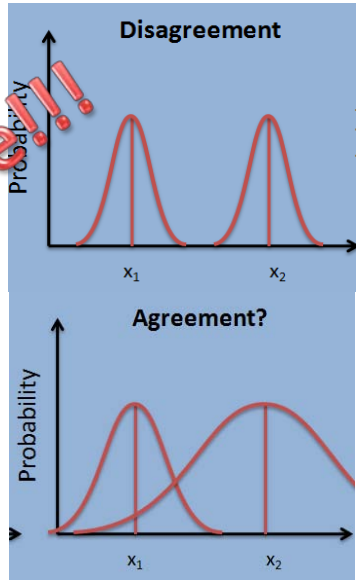




Standard Procedure

## 4. Uncertainty Quantification

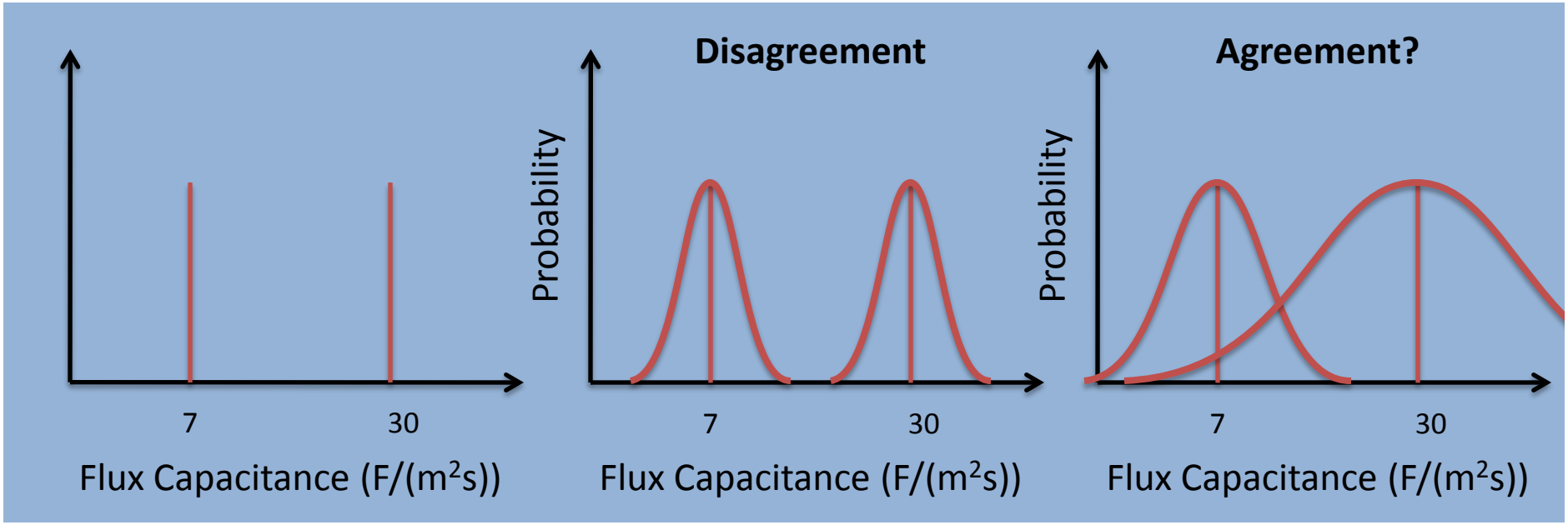



New Technique!!!

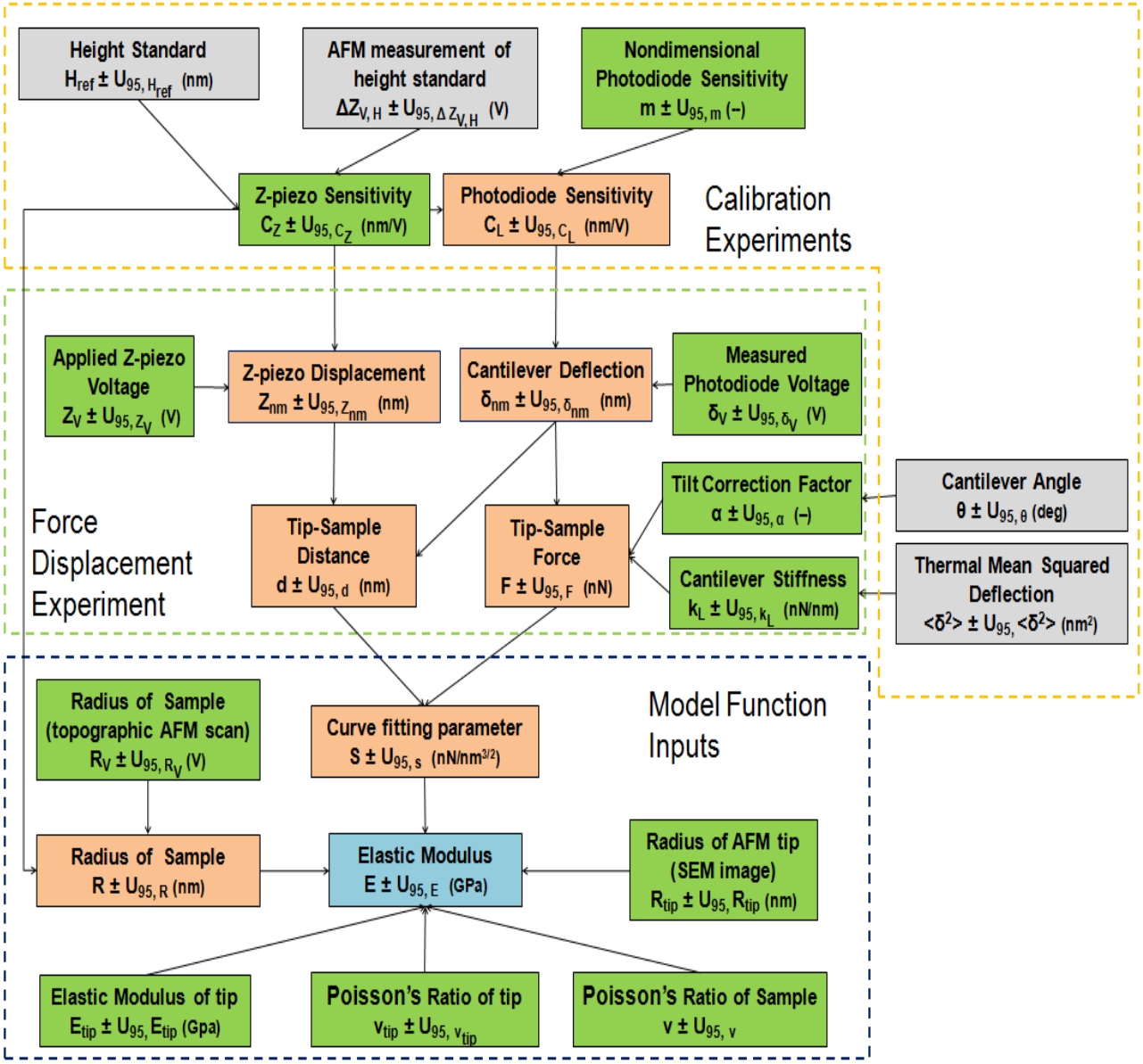


# Uncertainty Quantification (UQ)

- 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?

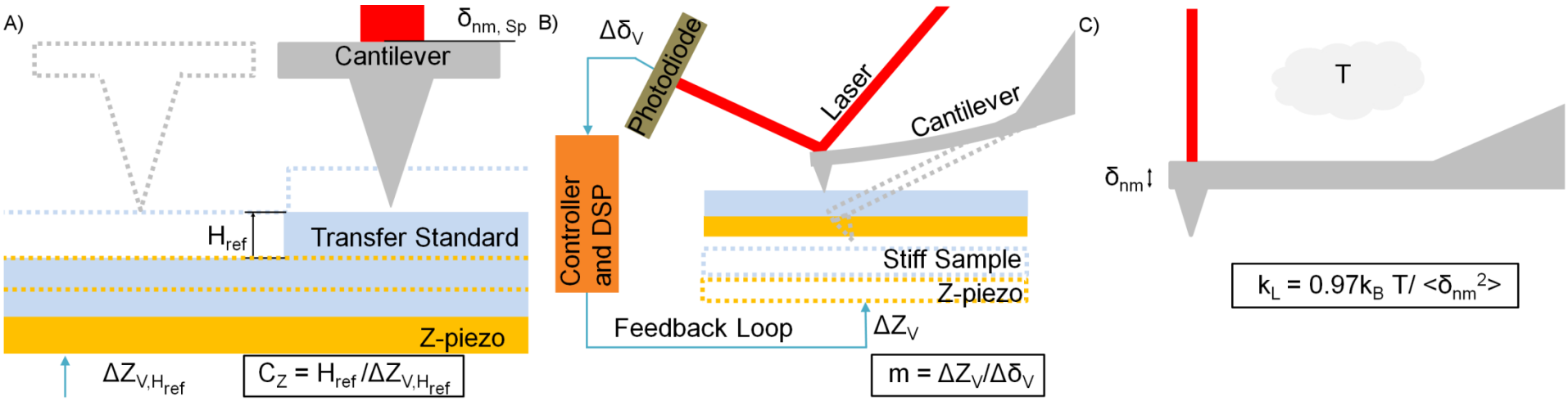


# DRE for elastic modulus



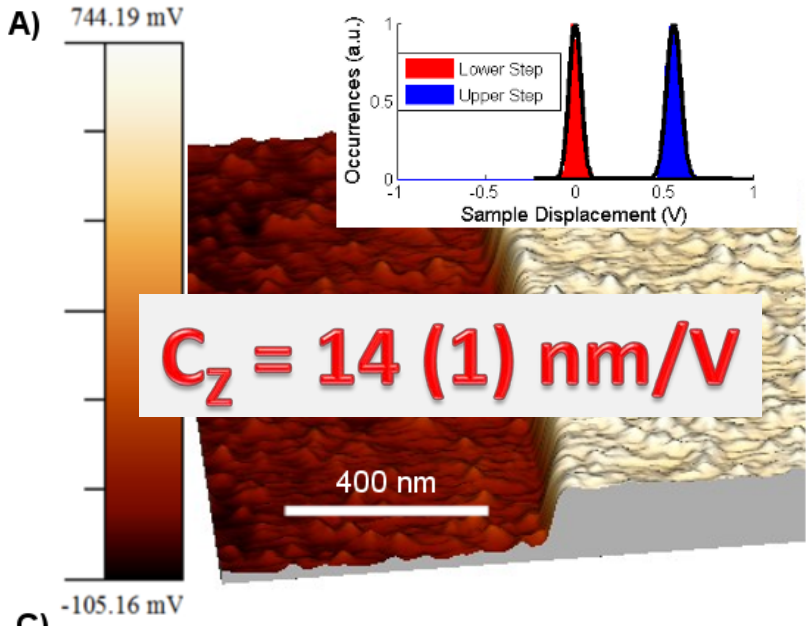

1. Identify Input Parameters and uncertainties
2. Propagate input uncertainties to output uncertainty
3. Identify Dominate Contribution to Output Uncertainty
4. Try to improve experiment based on uncertainty analysis

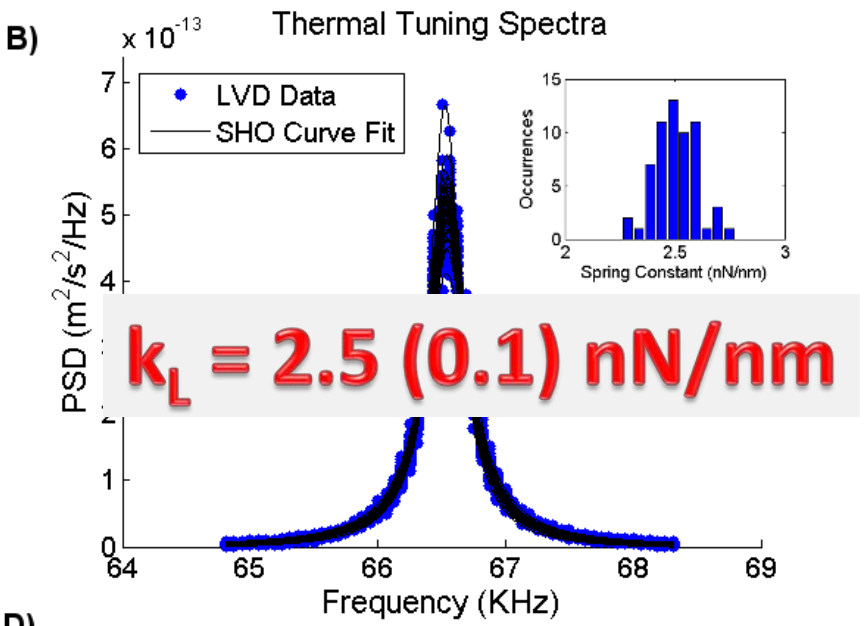
# Calibration

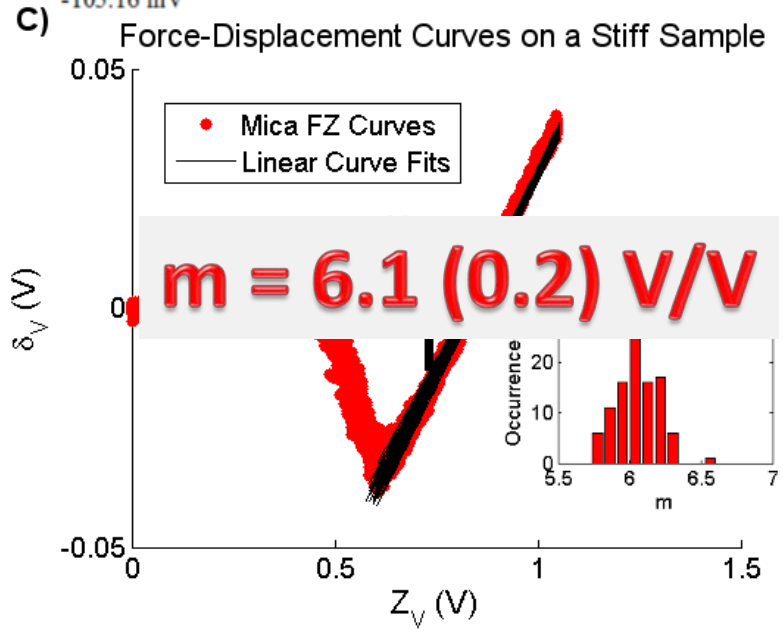


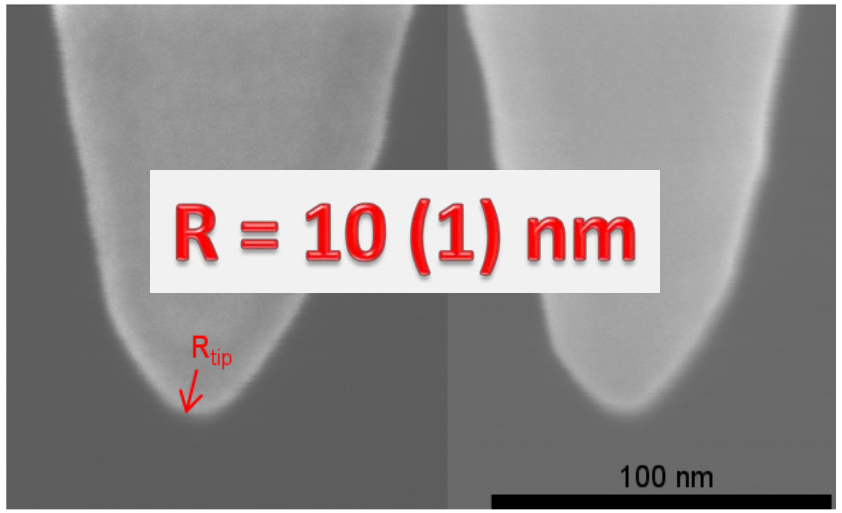

- Convert voltage outputs into force and displacement
- 3 Calibrations
  - A) Z-piezo voltage into Z-piezo displacement ($C_Z$)
  - B) Cantilever voltage into cantilever displacement ($C_L$)
  - C) Cantilever displacement into force ($k_L$)

# Sample Calibration Experiments



# Property Extraction (Data reduction equation)

- Data reduction equation (DRE) for elastic modulus can be constructed in three steps.
  1. Force displacement curve is converted into force-distance curve
  2. Force-distance curve is fit to a material model
  3. Elastic modulus is found by comparing to material model to the fit parameters.

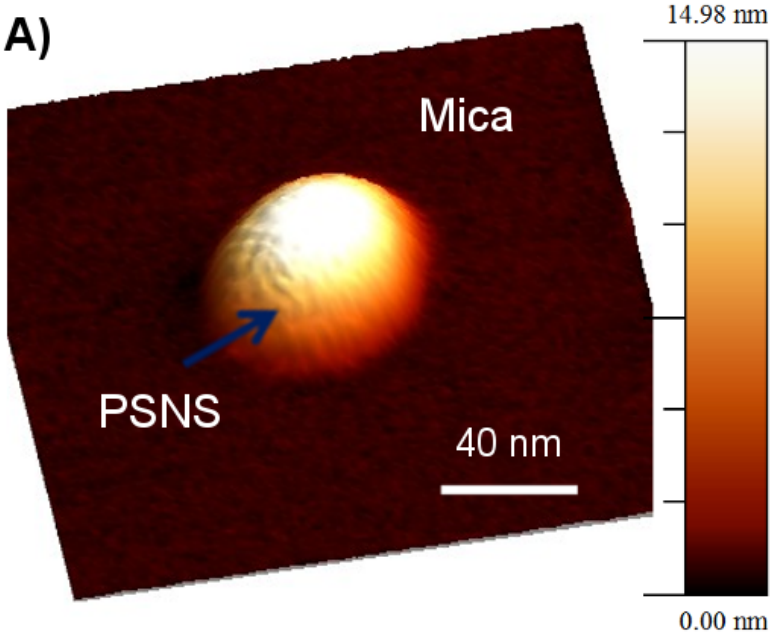
- DRE:

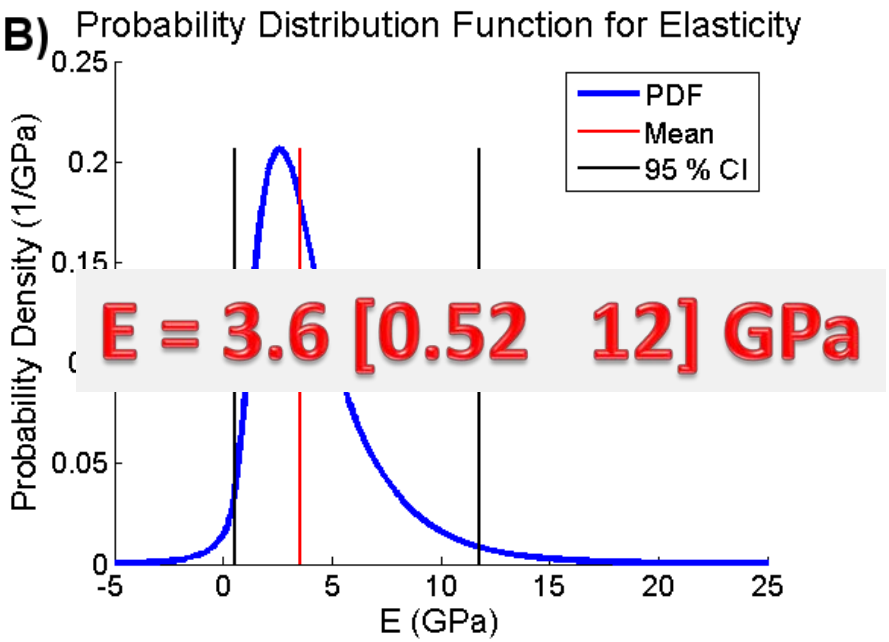
$$E = f_1(Z^*_{V_1}, ..., Z^*_{V_n}, \delta^*_{V_1}, ..., |\delta^*_{V_n}, Z_{V,shift}, \delta_{V,shift}, C_Z, m, k_L, \alpha, R_V, R_{tip}, E_{tip}, \nu_{tip}, \nu)$$

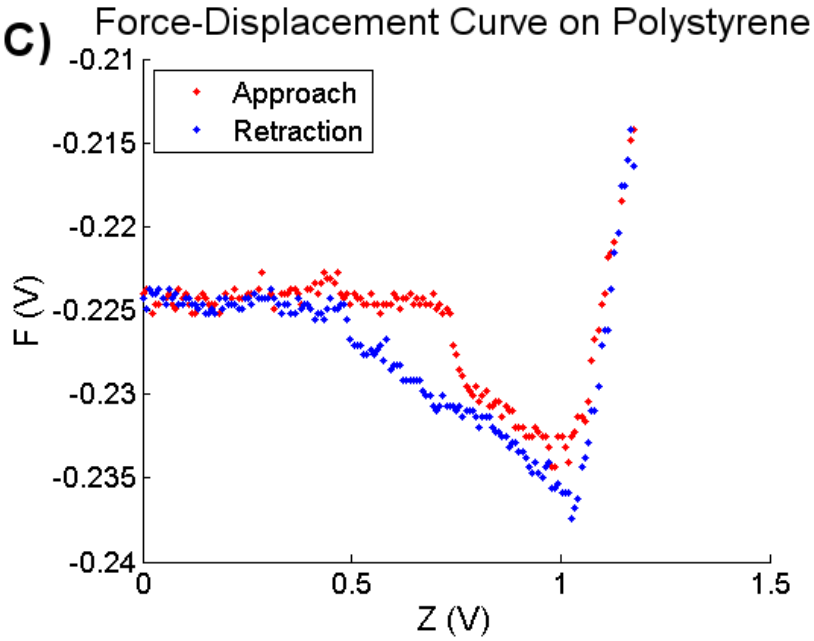
- Uncertainty (Taylor series method):

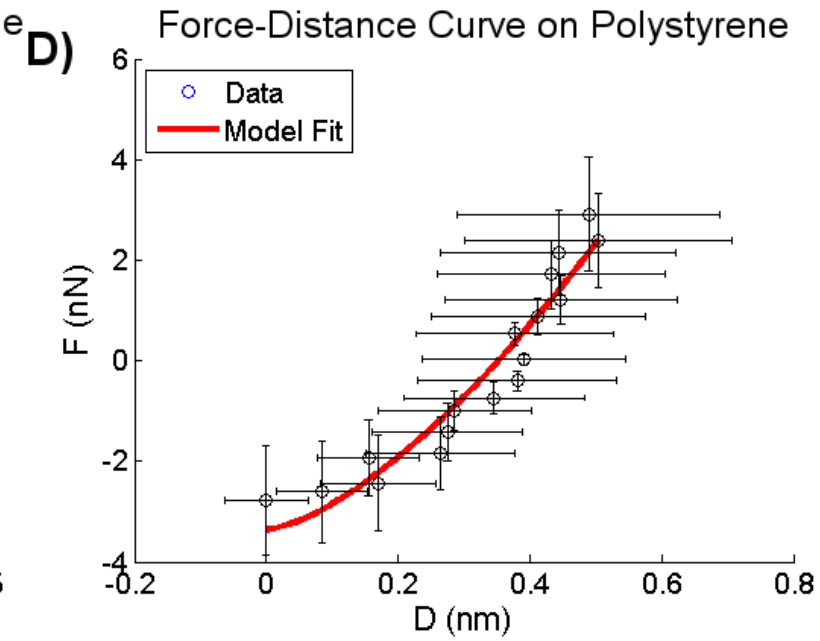
$$u_E = ((\frac{df_1}{dZ_{V_1}}u_{V_1})^2 + ... + (\frac{df_1}{dZ_{V_n}}u_{Z_{V_n}})^2 + (\frac{df_1}{d\delta_{V_1}}u_{\delta_{V_1}})^2 + ... + (\frac{df_1}{d\delta_{V_n}}u_{\delta_{V_n}})^2 +$$
$$(\frac{df_1}{dZ_{V,shift}}u_{Z_{V,shift}})^2 + (\frac{df_1}{d\delta_{V,shift}}u_{\delta_{V,shift}})^2 +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

# Polystyrene Nanosphere Data

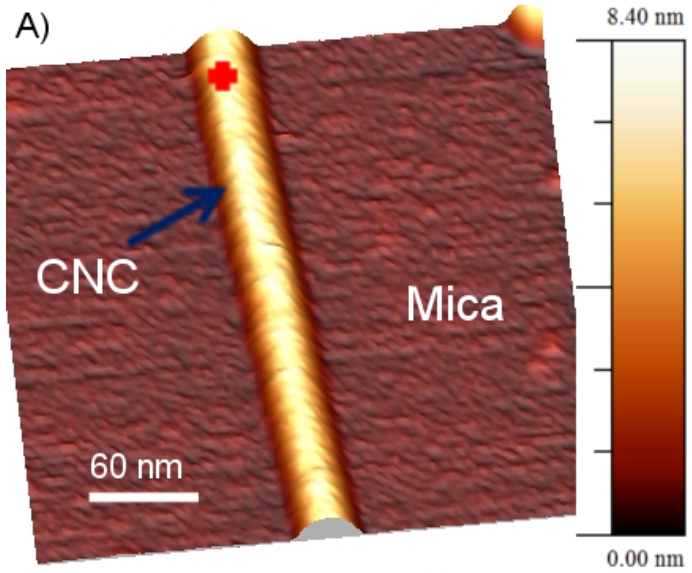


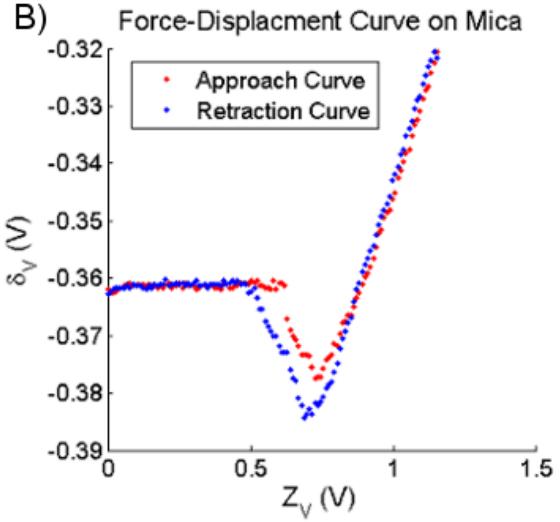



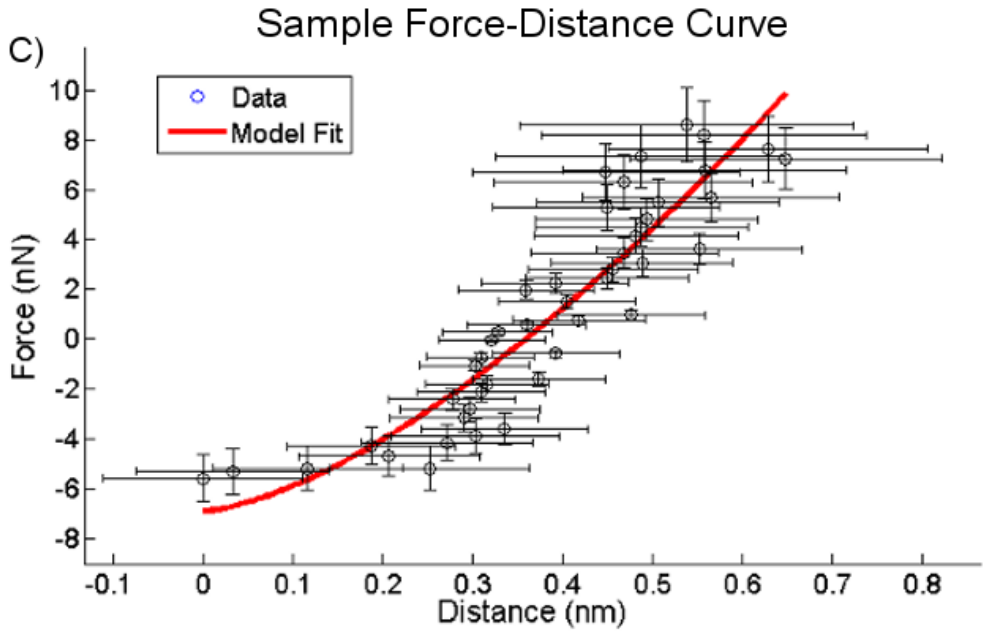



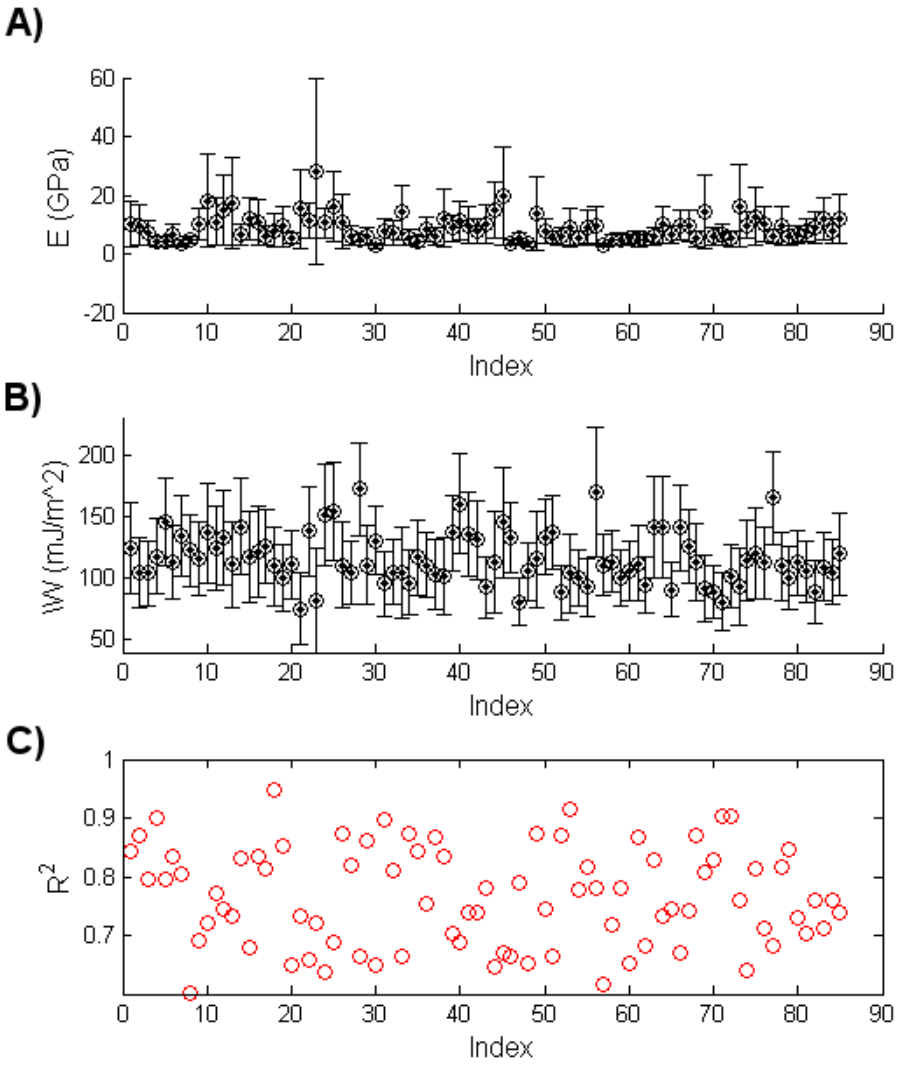
# Cellulose Nanocrystal Data

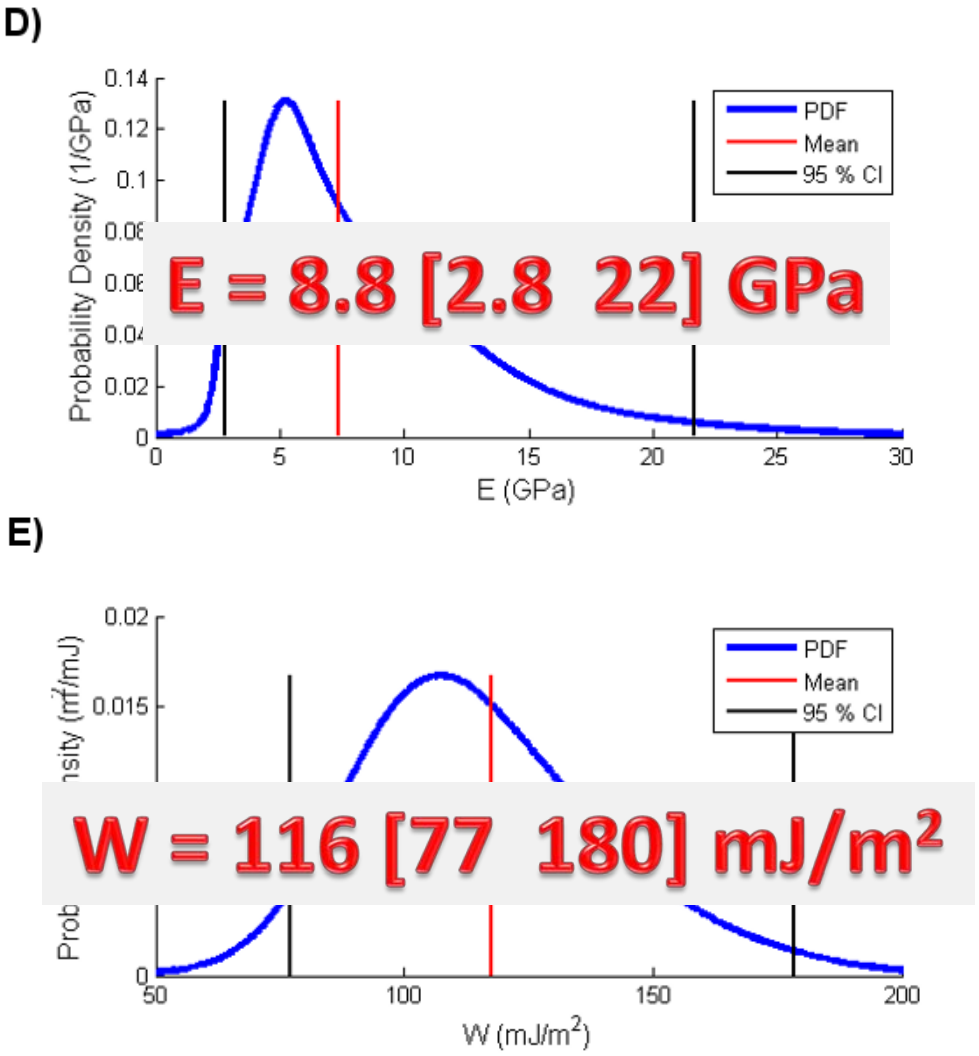


# Cellulose Nanocrystal Data



# Uncertainty Breakdown

**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) | 0.25 (GPa²) | |
| m | Nondimentional Photodiode Sensitivity | 6.1 (--) | 0.15 (--) | 25 (GPa) | 14 (GPa²) | |
| α | Tilt Correction Factor | 1.037 (--) | 0.007 (--) | 10 (GPa) | 0.005 (GPa²) | |
| $k_L$ | Cantilever Stiffness | 2.5 (nN/nm) | 0.1 (nN/nm) | 5 (GPa nm/nN) | 0.25 (GPa²) | |
| $\delta_{V,s}$ | | | | | | |
| **Mode** | | | | | | |
| $R_t$ | | | | | | |
| $E_{tip}$ | tip | | | | | |
| $\nu_{tip}$ | Poisson's Ratio of AFM tip | 0.28 (--) | 0.02 (--) | 0.6 (GPa) | 0.001 (GPa²) | |
| $R_V$ | Radius of Sample measured with AFM | 0.31 (V) | .04 (V) | 6 (Gpa / V) | 0.06 (GPa²) | |
| ν | Poisson's Ratio of Sample | 0.28 (--) | 0.05 (--) | 6 (GPa) | 0.1 (GPa²) | |
| **Data pairs sampled during experiment :** | | | | Mean Sensitivity | Mean Variance Contribution | Total Variance Contribution |
| $Z_{v_i}$ | Z-piezo voltage | -- (V) | 0.001 (V) | 30 (Gpa / V) | 0.001 (GPa²) | 0.11 (GPa²) |
| $\delta_{V_i}$ | Photodiode voltage | -- (V) | 0.0003(V) | 170 (Gpa / V) | 0.003 (GPa²) | 0.38 (GPa²) |
| **Total:** | | | | Expanded Uncertainty ($k_p$ = 2) | Variance | |
| E | Elastic Modulus | 10 .3 (Gpa) | 3.9 (GPa) | 7.8 (GPa) | 15 (GPa²) | |

**m is the dominant contributor to uncertainty in E**

# Comparison to Literature

Data from Literature:

| Reference | Material | Elastic Modulus (GPa) $E_A$ | $E_{T1}$ | $E_{T2}$ | Method |
|---|---|---|---|---|---|
| **Cellulose I Modeling** | | | | | |
| Jaswon 1968 | -- | 76 | 51 | 57 | w/ H bonding |
| Tashiro 1985 | -- | 173 | -- | -- | w/ H bonding |
| Kroon-Batenburg 1986 | -- | 136±6 | -- | -- | w/ H bonding |
| | Flax | 78-108 | -- | -- | Wave propagation |
| Sakurada 1962 | Ramine | 137 | -- | -- | X-ray Diffraction |
| Sakurada 1964 | Ramine | 130 | -- | -- | X-ray Diffraction |
| Matsuo 1990 | Ramine | 120-135 | -- | -- | X-ray Diffraction |
| Nishino 1995 | Ramine | 138 | -- | -- | X-ray Diffraction |
| **Cellulose NanoCrystals** | | | | | |
| Šturcová 2005 | Tunicate | 143 | -- | -- | Raman* |

**First Group to Report Transverse Properties from Experiments!**

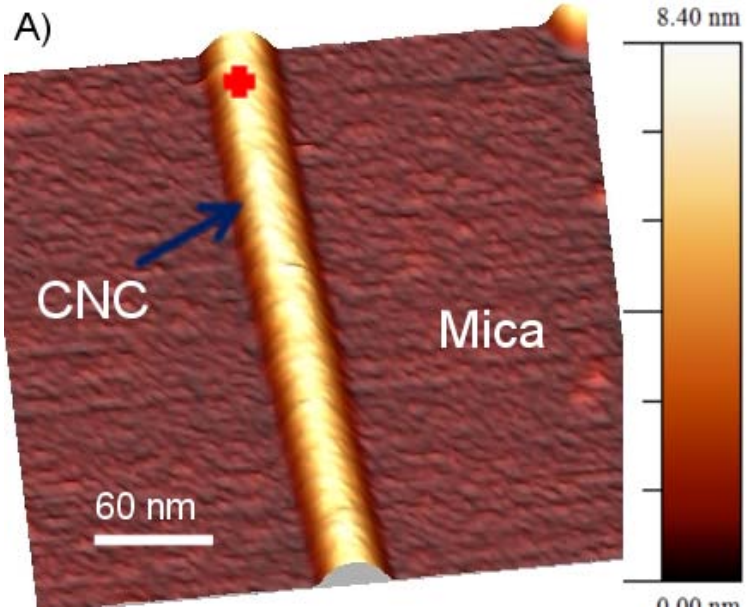
Our Data:

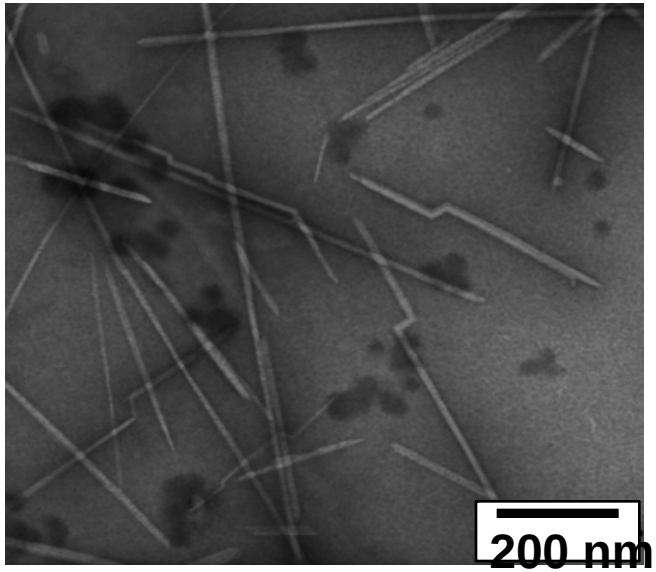
| Material | Parameter | Value | 95 % CI | Units |
|---|---|---|---|---|
| Tunicate CNC[1] | $E_t$ | 8.8 | [2.8, 22.0] | GPa |

1. Wagner, J.; Shaw, G.; Pratt, J.; Moon, R.J.; Raman, A. Uncertainty quantification in nanomechanical measurements using the Atomic Force Microscope *In Preparation.*

# Questions?

- Thank you for your attention.



# Supplement

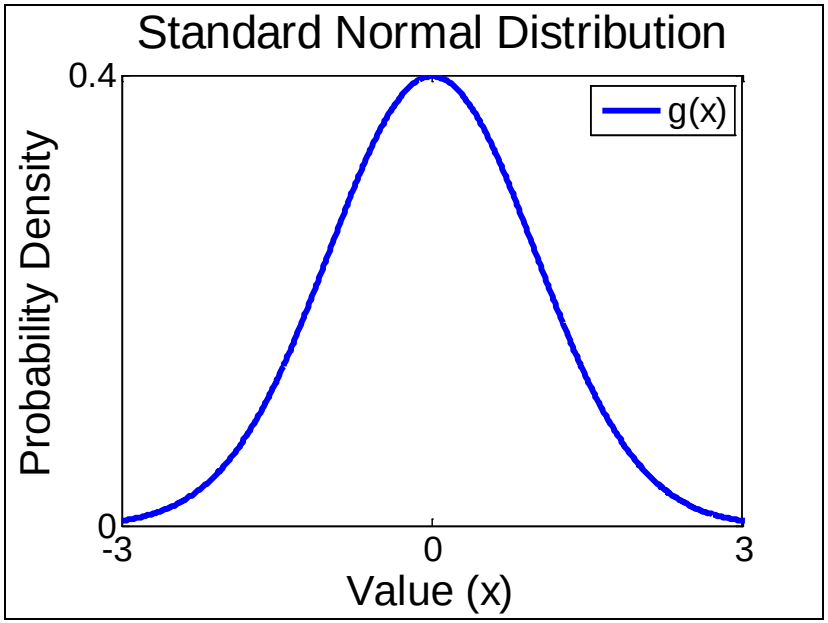
# Uncertainty Propagation

- Uncertainty in input parameters needs to be propagated to the DRE output

- Goal is to create a probability density function (PDF) describing the DRE output

- Three common methods
  - Experimental replicates
  - Monte Carlo method
  - Taylor series method

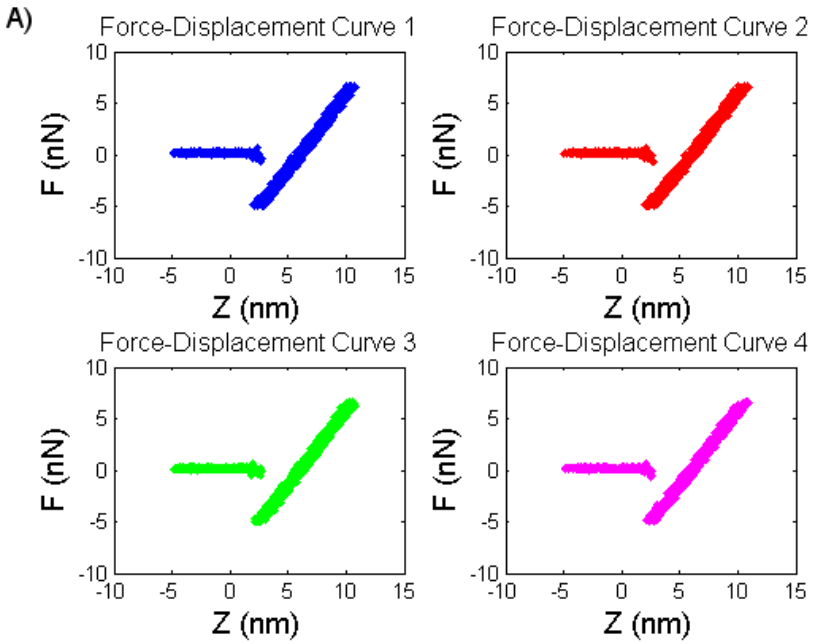
$$P(a<x<b)=\int_a^b g(x)dx$$

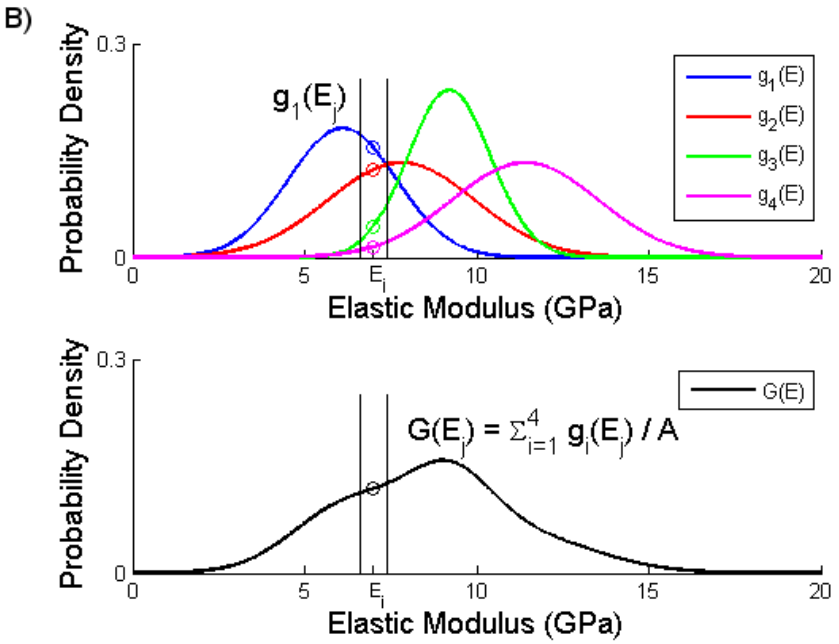


# Combining Uncertainties

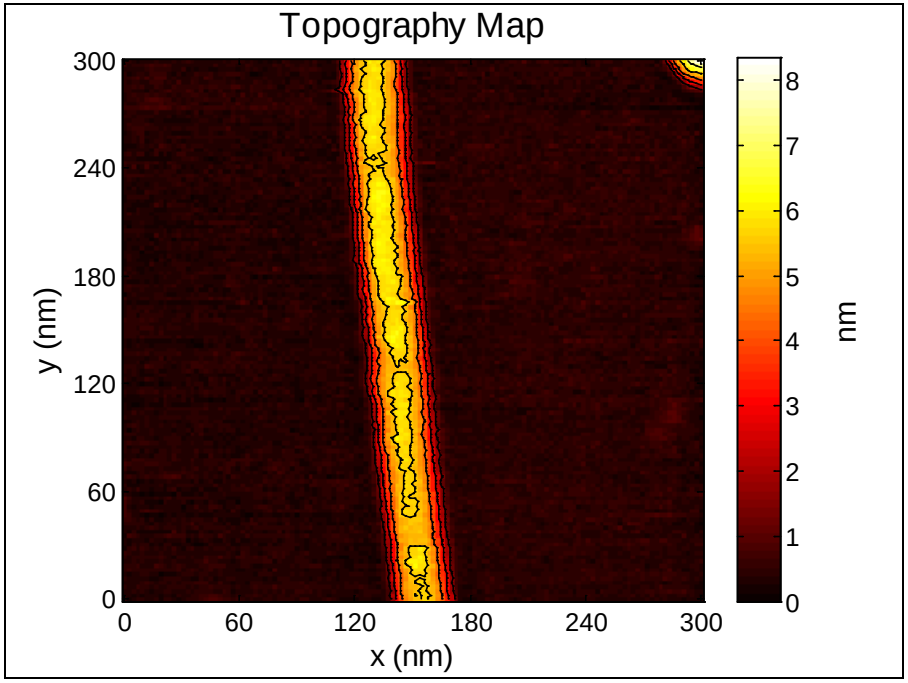
- Each F-Z curve gives a PDF for elastic modulus.

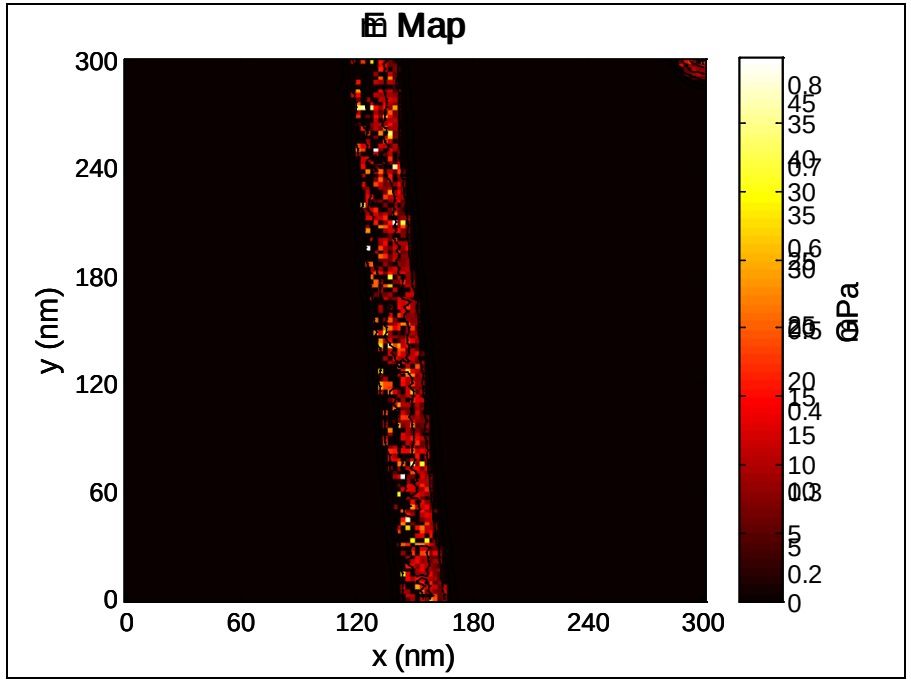
- Multiple F-Z curve PDFs can be combined

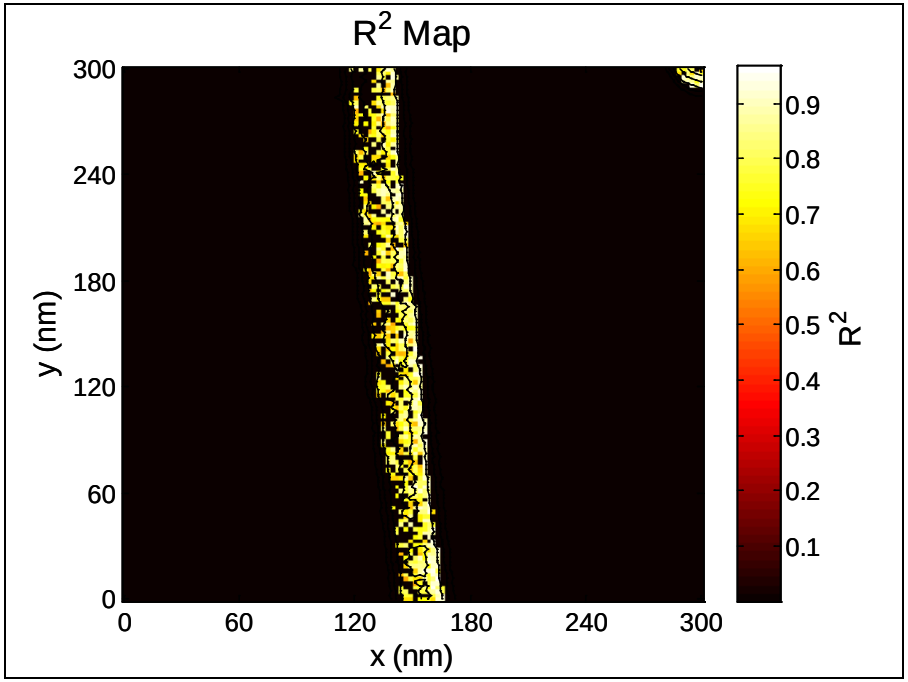


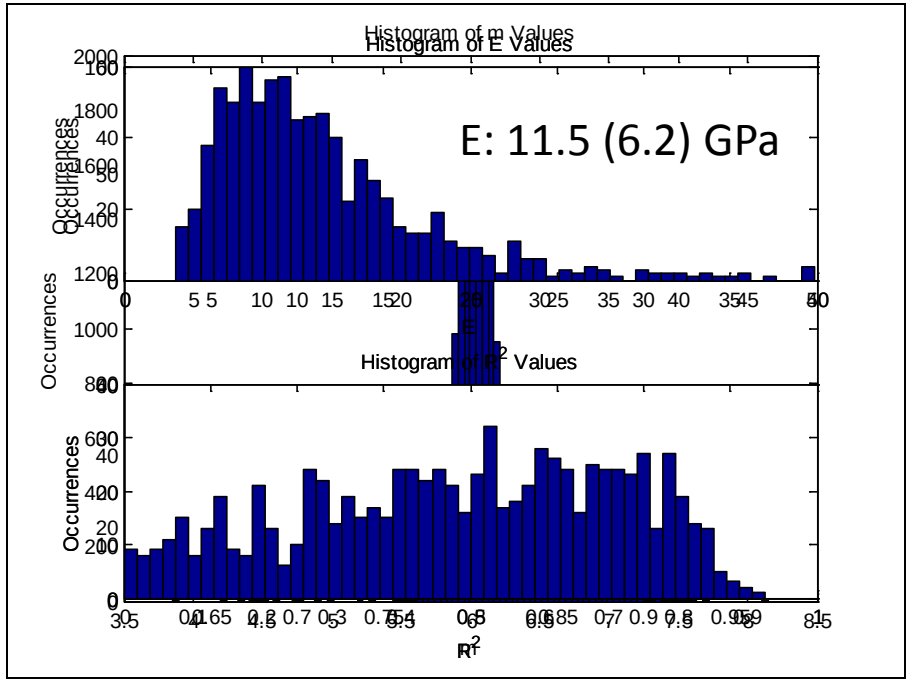



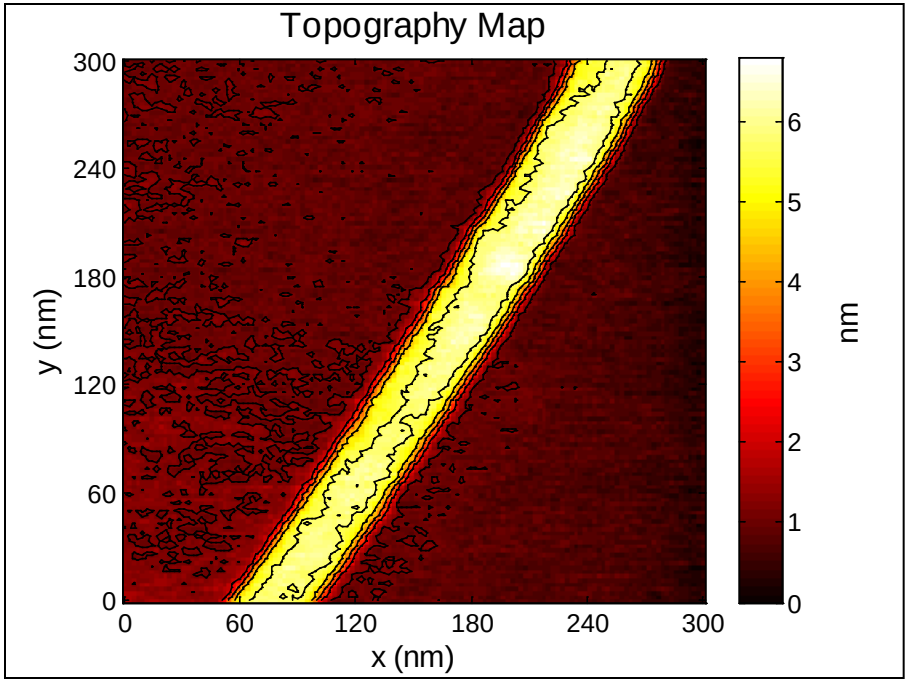
# Mapping Data

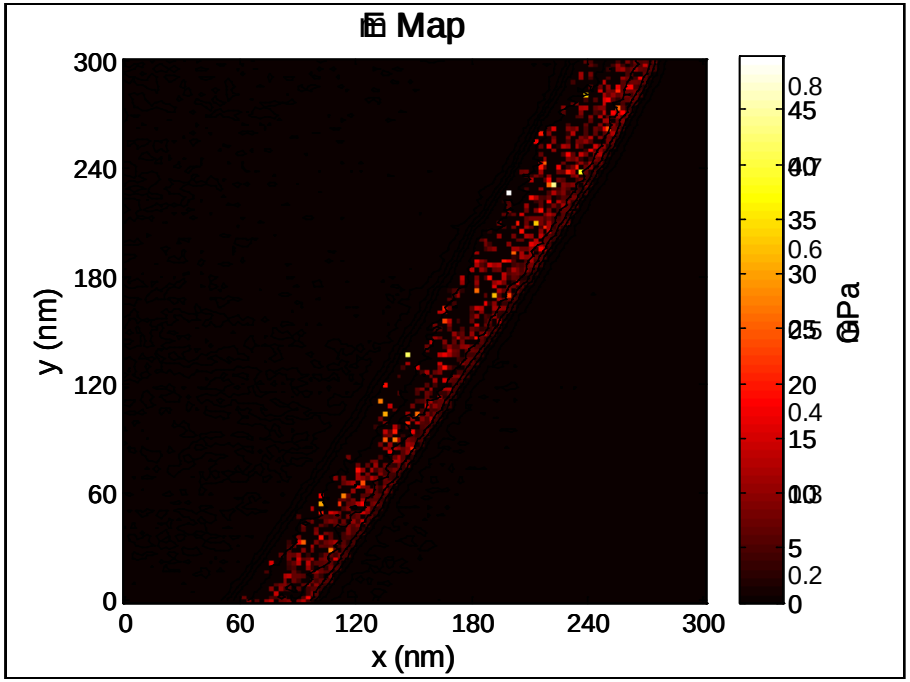


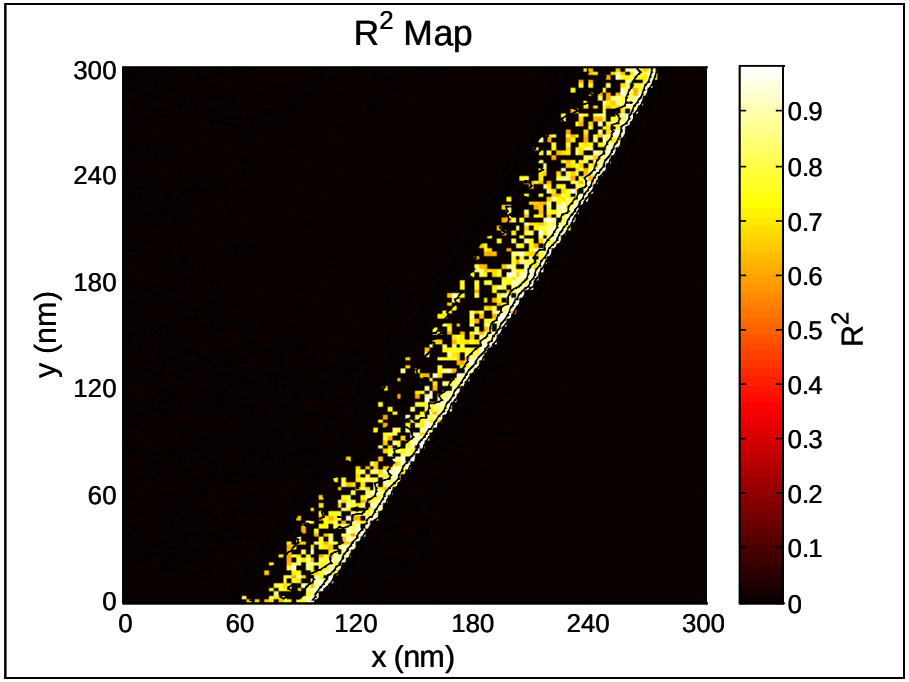



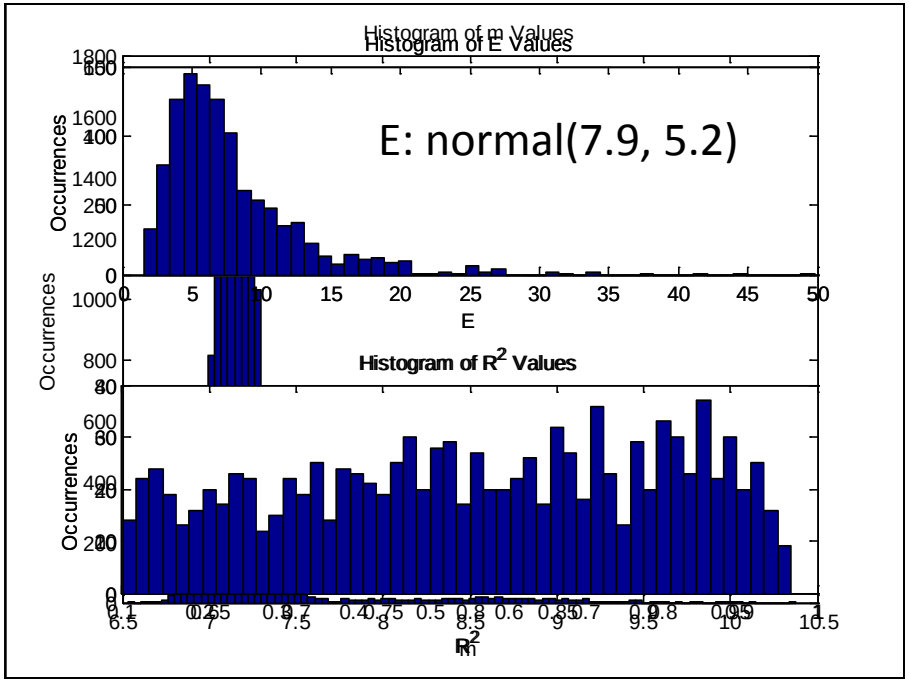




Topography Map
y (nm)
x (nm)
nm
0
60
120
180
240
300
0
1
2
3
4
5
6

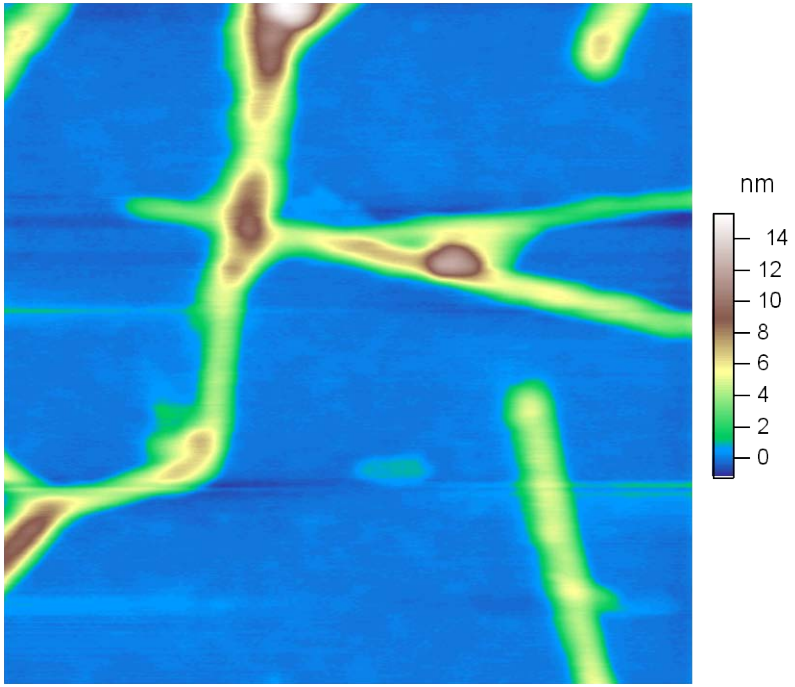

E Map
y (nm)
x (nm)
GPa
0
60
120
180
240
300
0
0.2
0.4
0.6
0.8


R2 Map
y (nm)
x (nm)
R2
0
60
120
180
240
300
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9

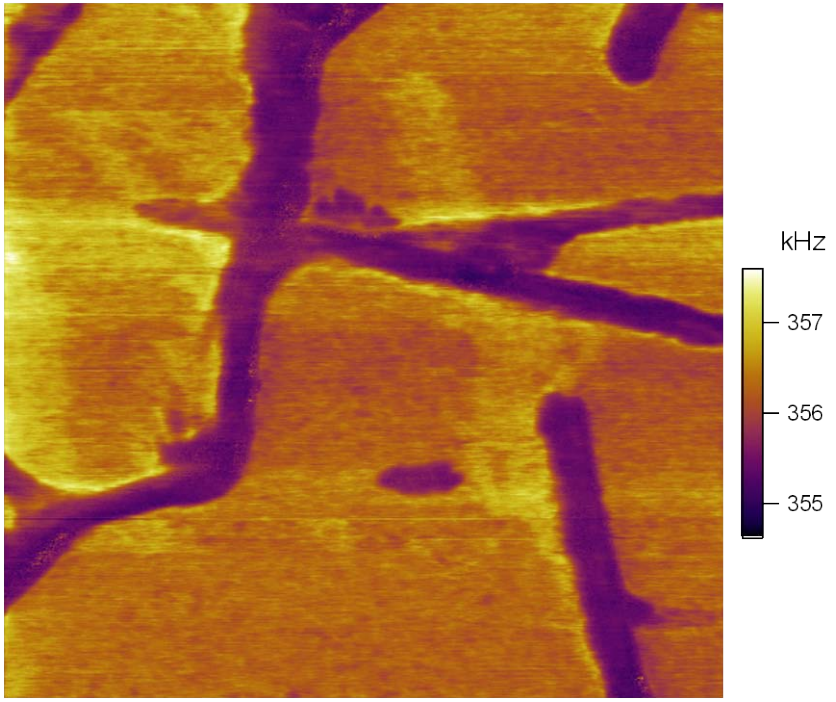

Histogram of E Values
E: normal(7.9, 5.2)
Occurrences
E
Histogram of R2 Values
Occurrences
R2

# Contact resonance scans in Air

Topography




First contact resonance frequency




F1_mica = 356.3 kHz, F1_CNC = 355.4 kHz -> k*_mica=91.2 N/m, k*_CNC=88.1 N/m.
You convert these contact stiffnesses into elastic moduli by using the appropriate contact model.
For example, if we use Hertz contact model with the assumption that both mica and CNC are flat and the elastic modulus of mica is E=60 GPa, then the CNC will have an elastic modulus of 56 GPa.
The substrate contribution and the non-flat contact geometry on CNC, probably will change these numbers; both these two contribution will increase the difference between CNC and mica.