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Microscopic Electrical Study of Carbon Nanofiber Composites Using Conducting-tip Atomic Force Microscopy

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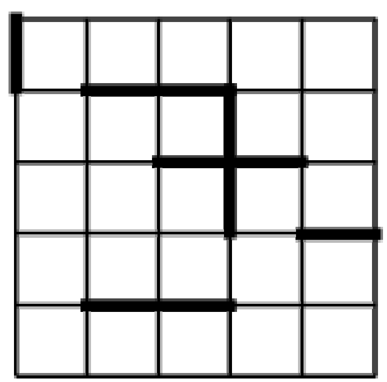
Outline

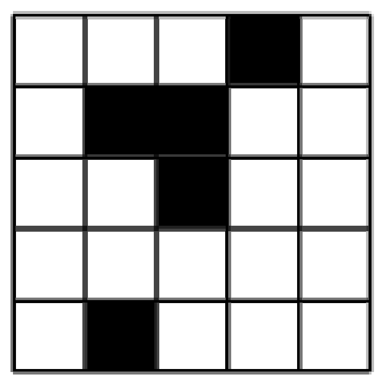
- Percolation Theory
  - Lattice Model
  - Carbon nanofiber (CNF) composite exhibiting properties of percolation
  - Bulk measurement results
- Atomic Force Microscopy (AFM) Measurements of CNF composite
  - Conducting-tip AFM (C-AFM)
  - Analysis using Principle of Delesse
- Conclusions

Intro to Percolation Theory

- **Question:** If I submerge a porous rock into water, what is the probability water will wet the center of the rock?
- Percolation theory deals with fluid flow (or any other similar process) in random media.
- The most basic percolation model is known as lattice percolation and actually has two forms: **bond percolation** and **site percolation**.



bond percolation



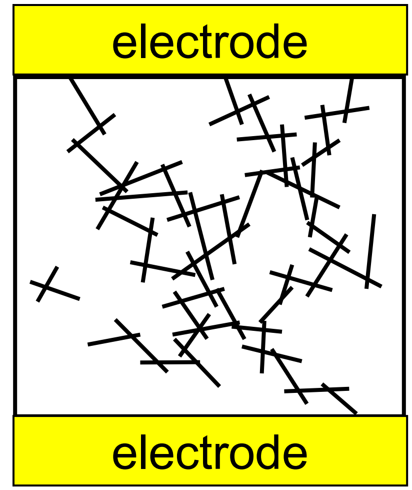
site percolation

Real Systems

- Oil Exploration – how is oil dispersed in porous bedrock and how do you get it out of the rock?
- Forest Fires – can one simulate how forest fires spread?
- Electrical transport in metal/insulator composites – how do charge carriers traverse a system of randomly placed metal particles embedded in an insulating matrix.

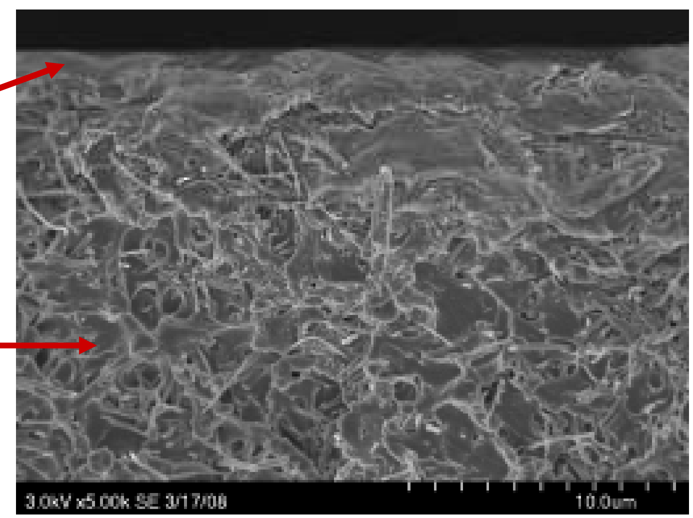
Our System

- CNF dispersed in a insulating polymer matrix
- Why CNF?
  - Aspect ratio results in lower percolation thresholds.
- The material is a **flexible conductor** with a conductivity dependent on the nanotube loading.



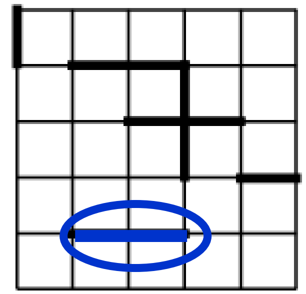
Polymer-rich skin layer

Isotropic, uniform dispersion

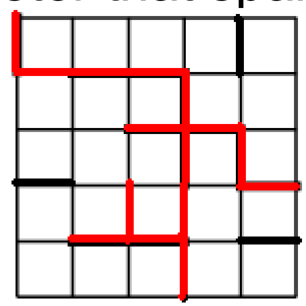


Intro to Percolation Theory

- **Cluster** – a group of connected lattice points.



- **Infinite Cluster** – a cluster that spans the entire lattice.



- **Occupation probability** (p) – the ratio of occupied bonds to that of all lattice edges
- **Percolation threshold** (p_c) – the minimum occupation probability required to create an infinite cluster in the lattice.

Intro to Percolation Theory

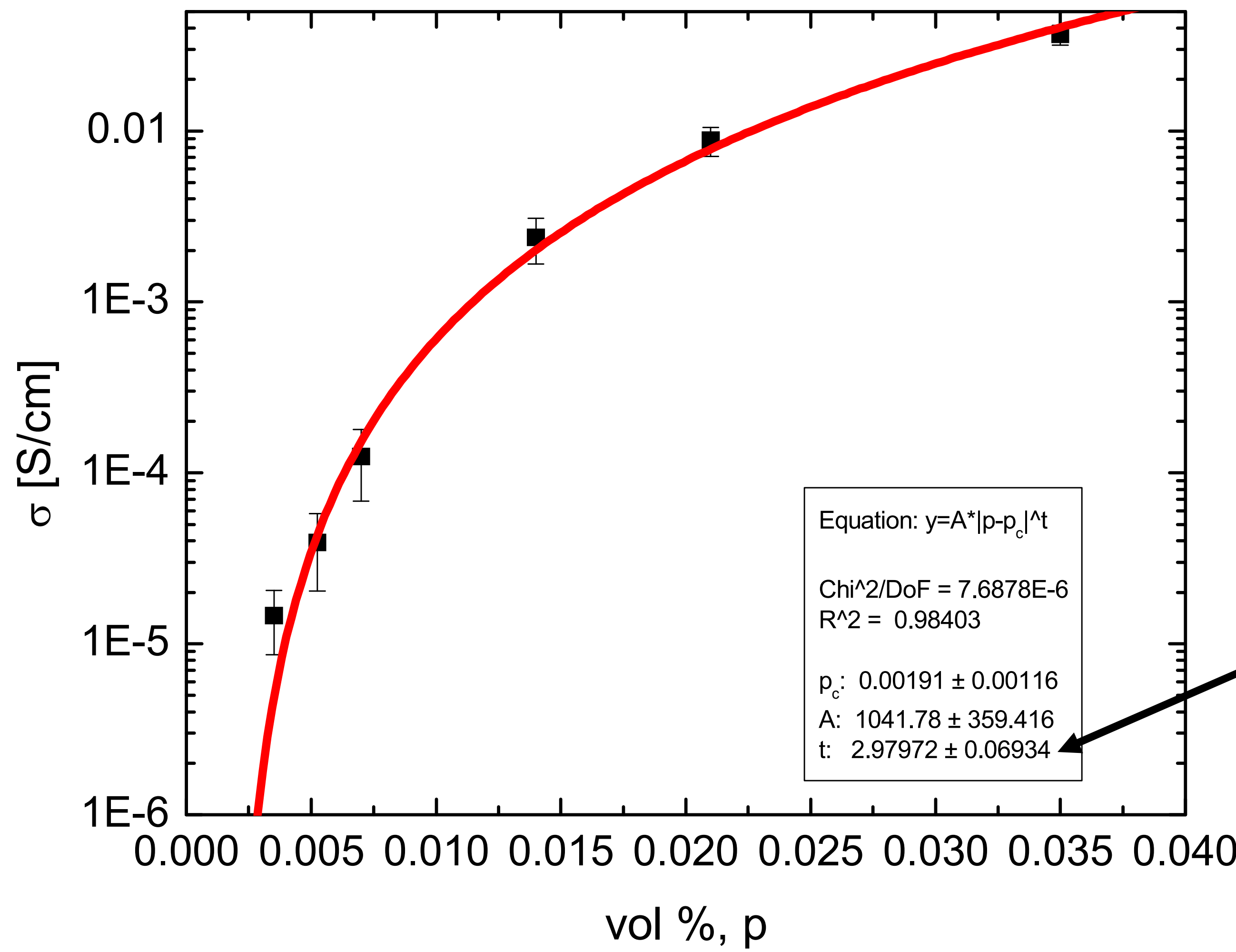
- The change at p_c from the absence of an infinite cluster to the presence of one without a latent heat implies a **second order phase transition**
- Second order phase transitions have 2 characteristics:
  - Universality
  - Scaling laws (i.e. critical exponents)
- Universality implies that critical exponents of properties in percolation system (such as σ) should be dependent on dimensionality only.
- Scaling law implies:

$$\sigma(p) \propto (p - p_c)^t$$

Typically measured

C.-W. Nan, Progress in Materials Science **37**, 1 (1993).

Composite Bulk Conductivity



t ~ 3

Bulk Conductivity

- Critical exponent, t, of the DC conductivity for the material is ~ **3**.
- Lattice percolation model predicts a t value of ~ **2** for the electrical conductivity in a 3D percolation network.

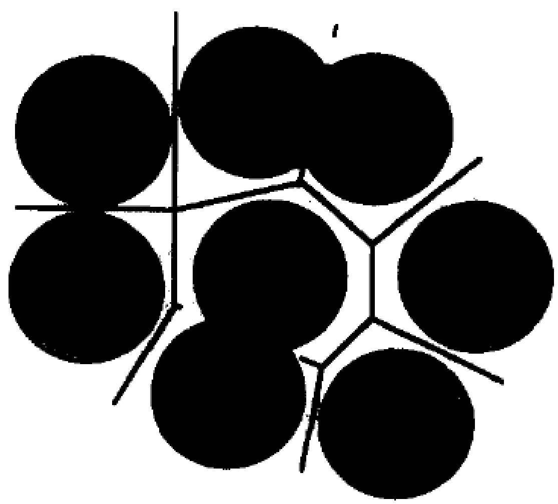
Composite	t
Glass/Indium	3.1
Epoxy/Graphite	3.4
Polymer/Carbon Black	2.8
Glass/RuO_2	3-5

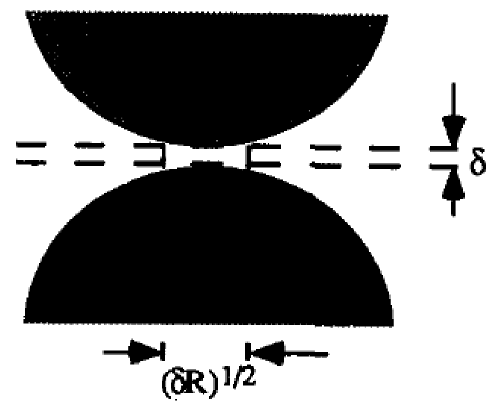
C.-W. Nan, Progress in Materials Science **37**, 1 (1993).

Possible Explanation

- Inverted Random Void (IRV) Tunneling Model
  - Conducting particles have a small gap between them leading to a tunneling resistance.
  - Gap size has a distribution

Conducting particle





Percolation Probability $\theta_\infty(p)$

- Percolation probability, $\theta_\infty(p)$, is the probability that any one occupied site (or nanotube in our system) is part of the infinite cluster

$$\theta_\infty(p) \propto (p - p_c)^\beta$$ $\beta \approx 0.4$ in 3D

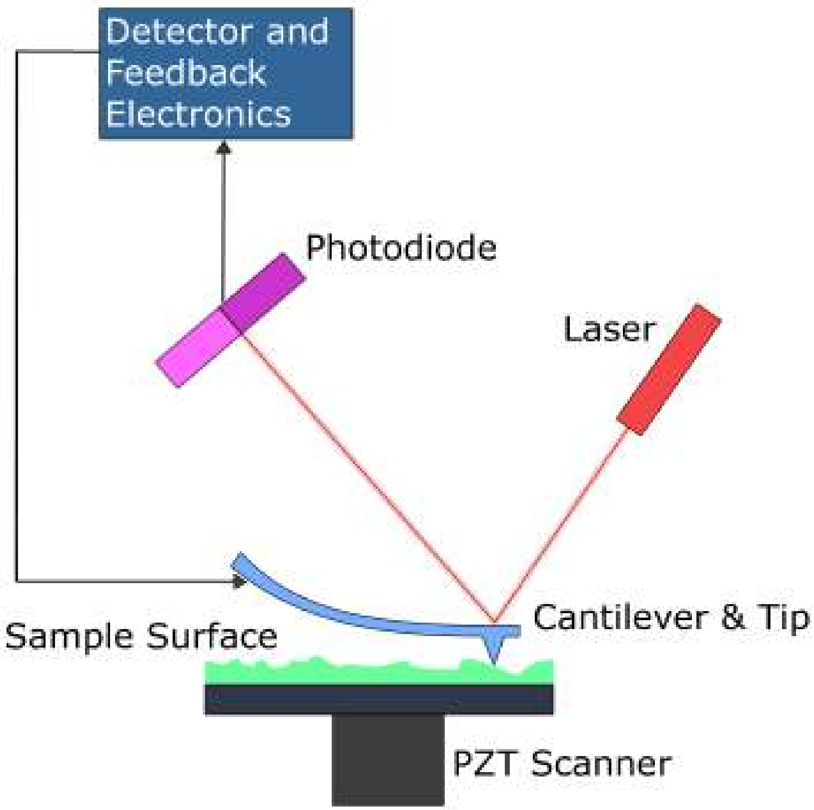
- While the IRV tunneling model predicts a non-universal critical exponent for t, it has been shown that **geometrical critical exponents (such as β) should be the same in all percolation systems*.**

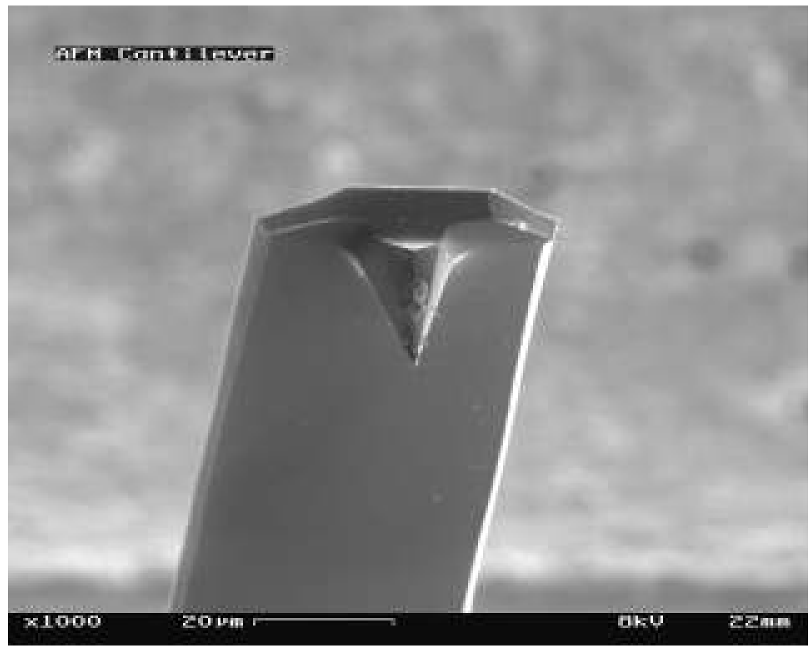
*I. Balberg, Phys. Rev. B **37**, 2391 (1988).

What we propose

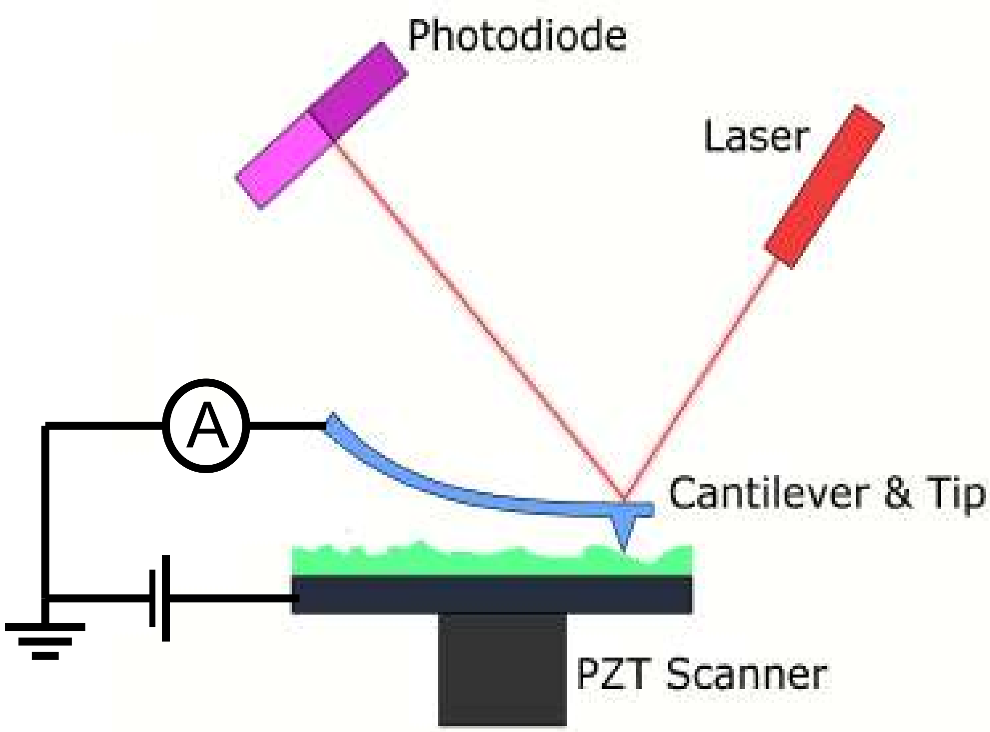
- Determine β and compare with lattice model prediction of $\beta \approx 0.4$.
- **How can we measure the percolation probability????**
  - We will need to do the measurement at the microscopic scale!
- Atomic Force Microscopy allows us to probe electrical properties at the microscopic level.
- This measurement has never been performed in an electrical percolation system.

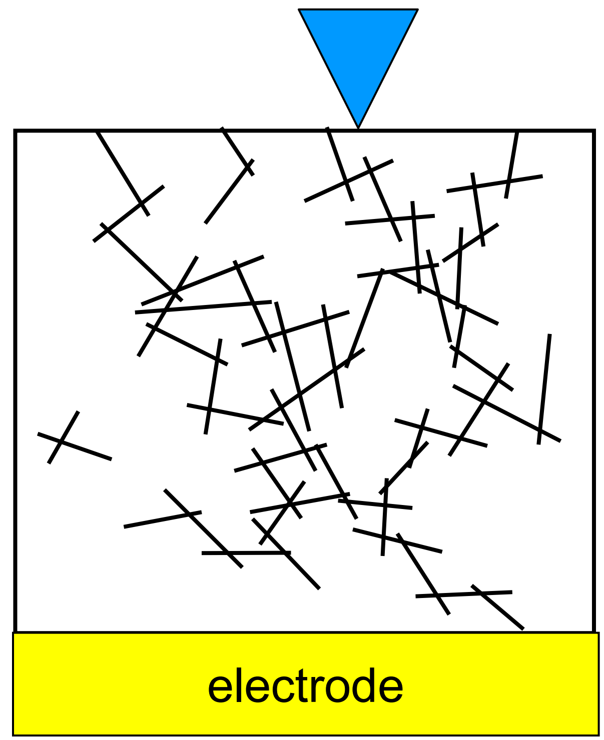
Atomic Force Microscopy



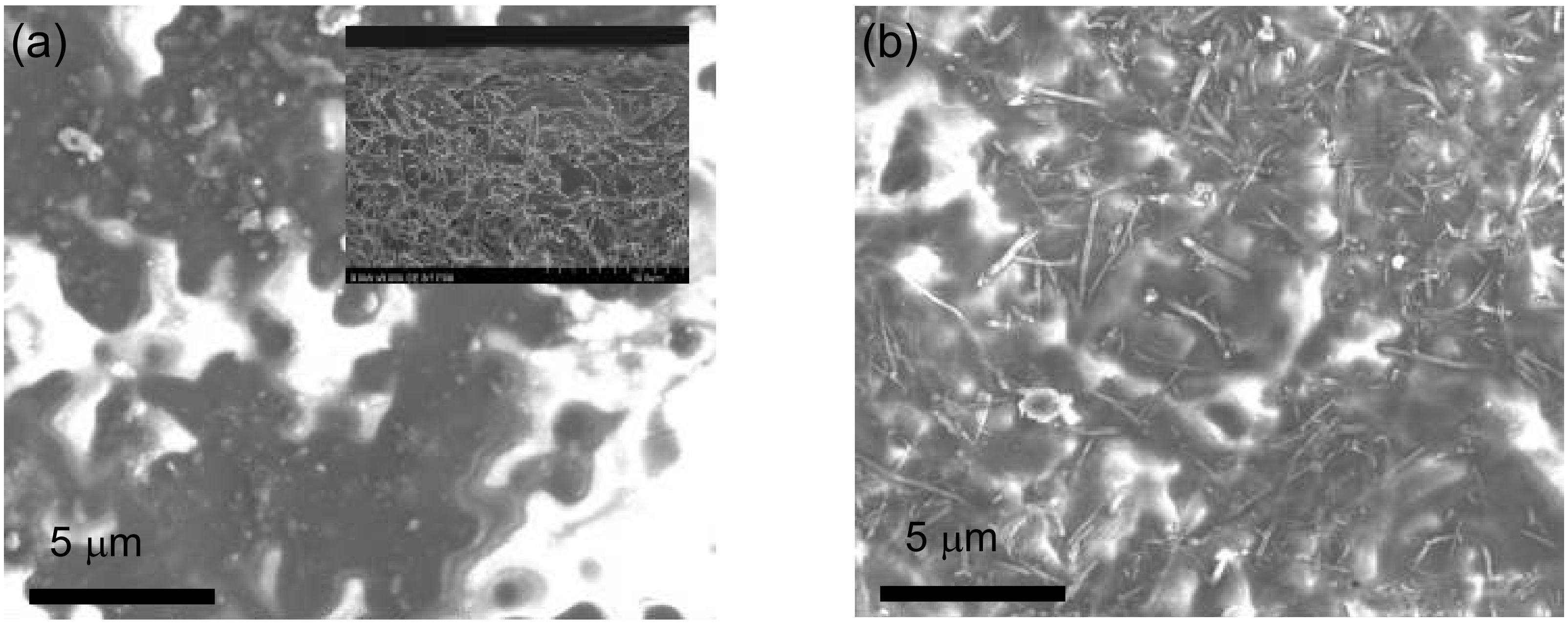


Conducting-tip AFM



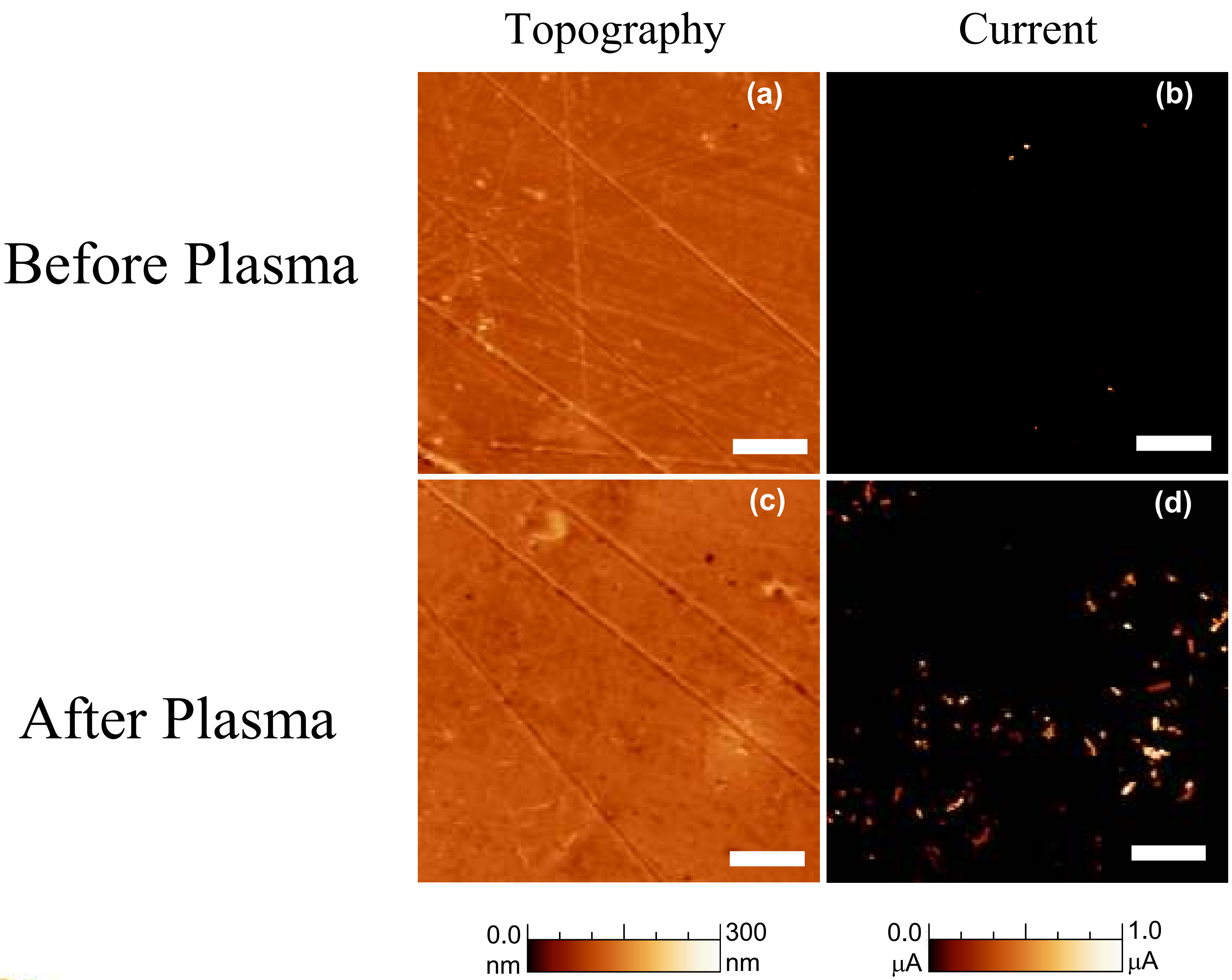


Problem with the Native Surface?!



Before (a) and after (b) exposure to an oxygen plasma. Clearly, there is a significant absence of tubes at native surfaces of material.

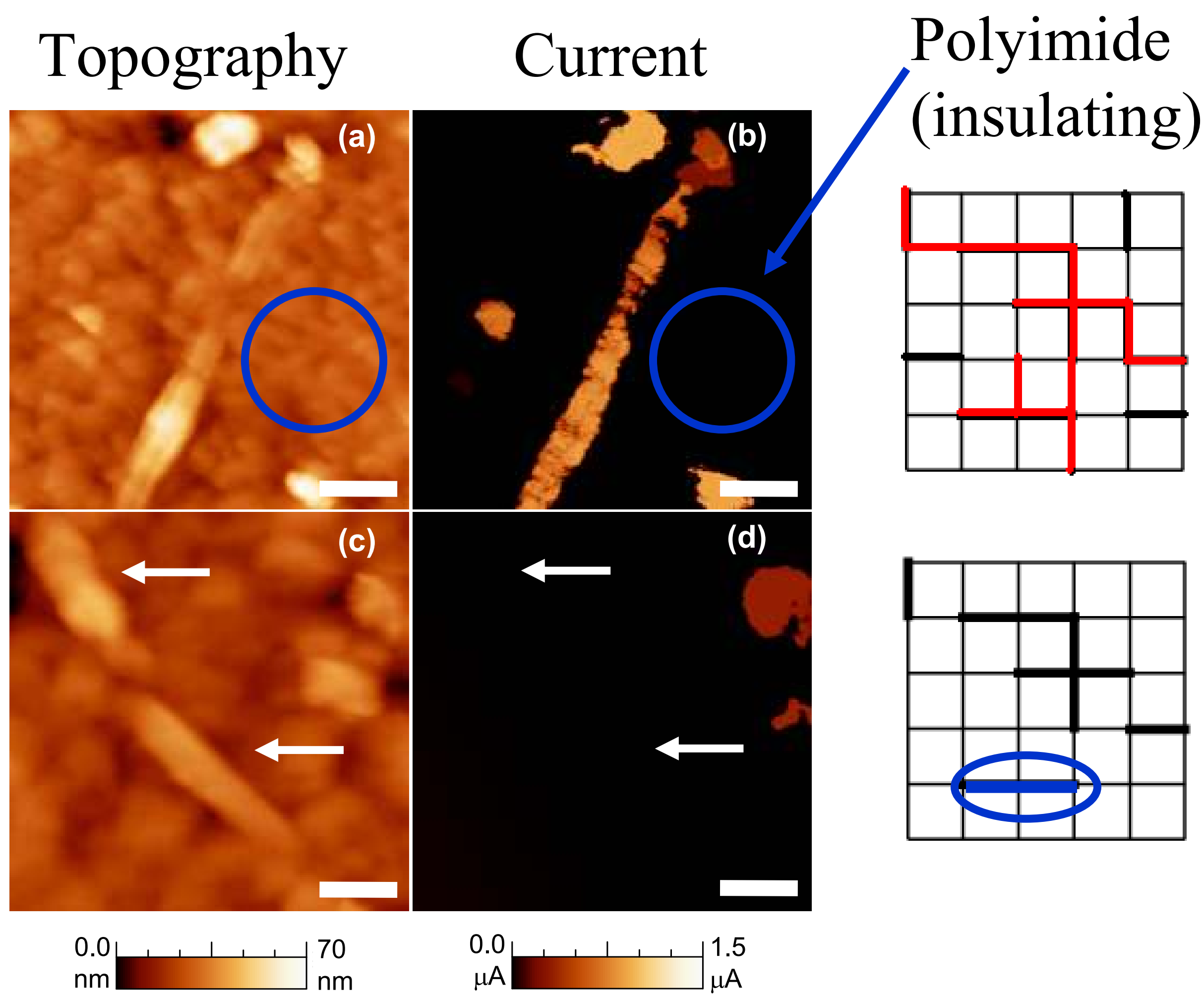
3.5 vol % composite before and after plasma treatment



High Resolution CAFM Results of 3.5 vol % composite

MWNT (part of infinite cluster).

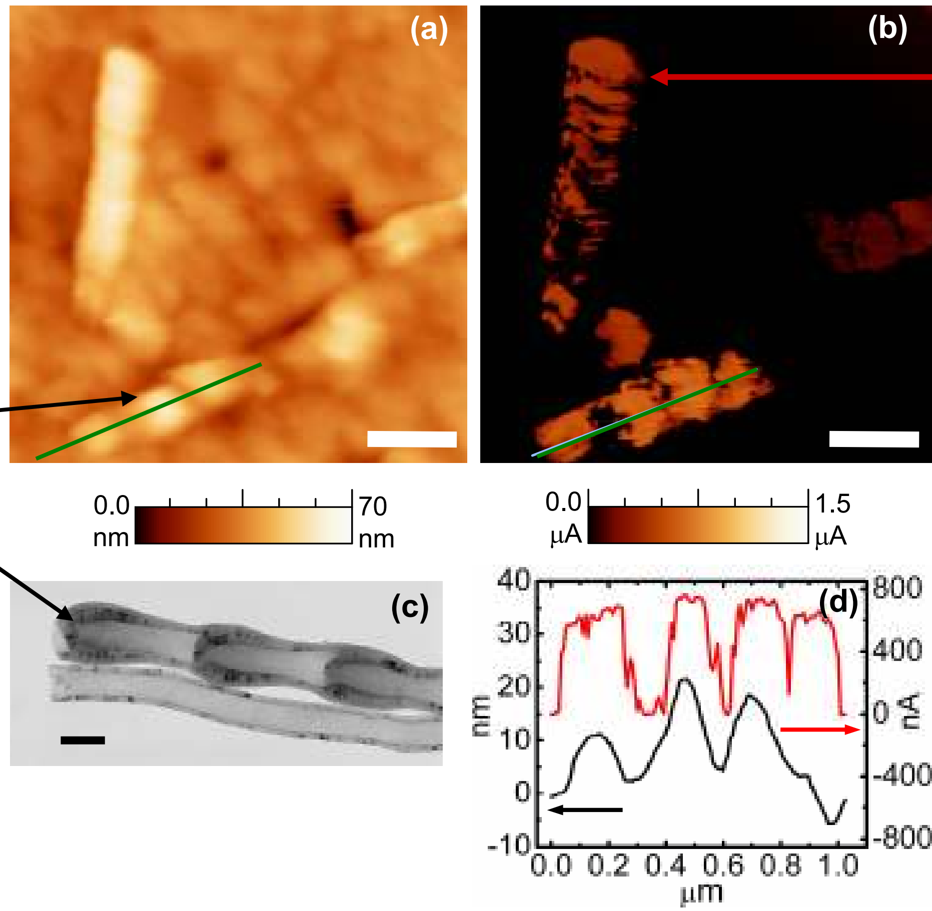
MWNT? (not part of infinite cluster).



C-AFM details

Current banding?

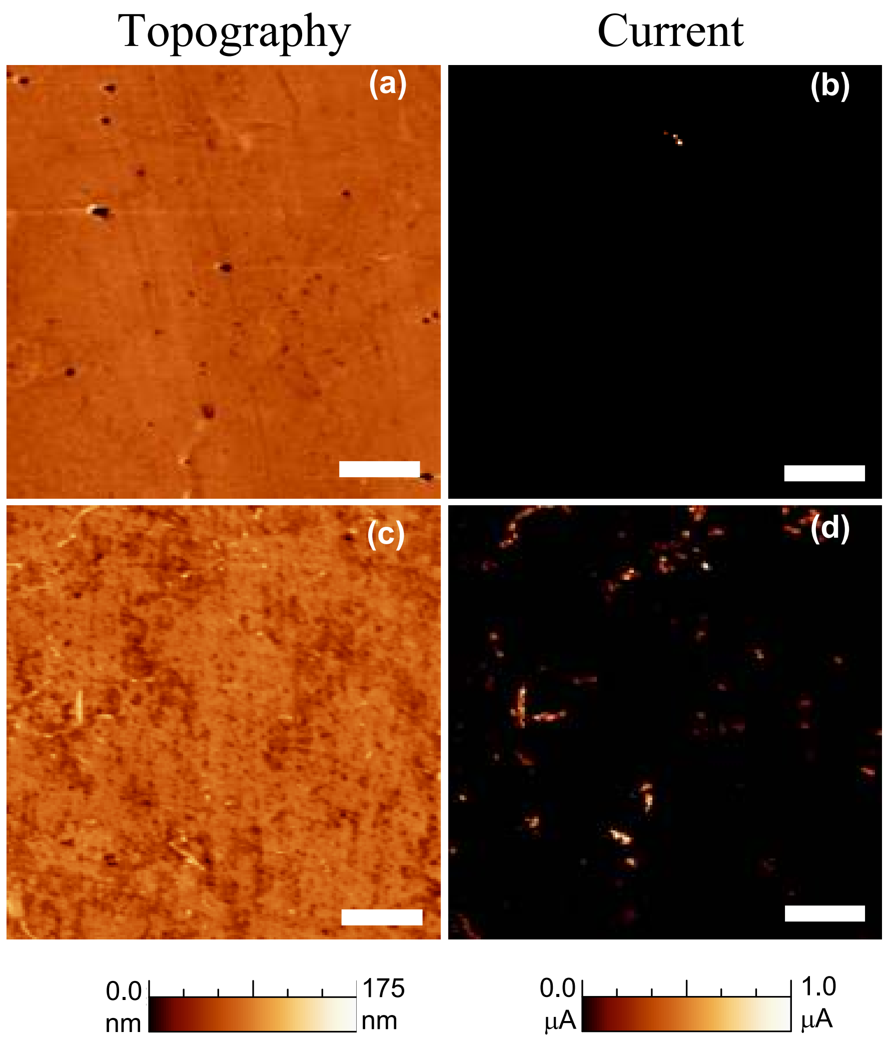
Dixie-cup nanofiber



Different MWNT Loading

p =0.35 vol %

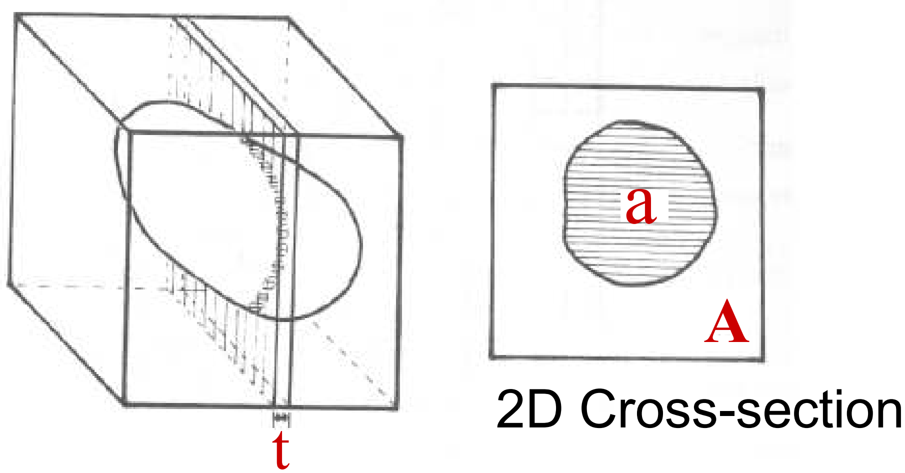
p =3.5 vol %



$$\theta_\infty(p) \propto (p - p_c)^\beta$$

Principle of Delesse

- **In a random isotropic composite, the areal density of a phase in a representative 2D cross-section is statistically equal to expected 3D volume fraction of that phase.**



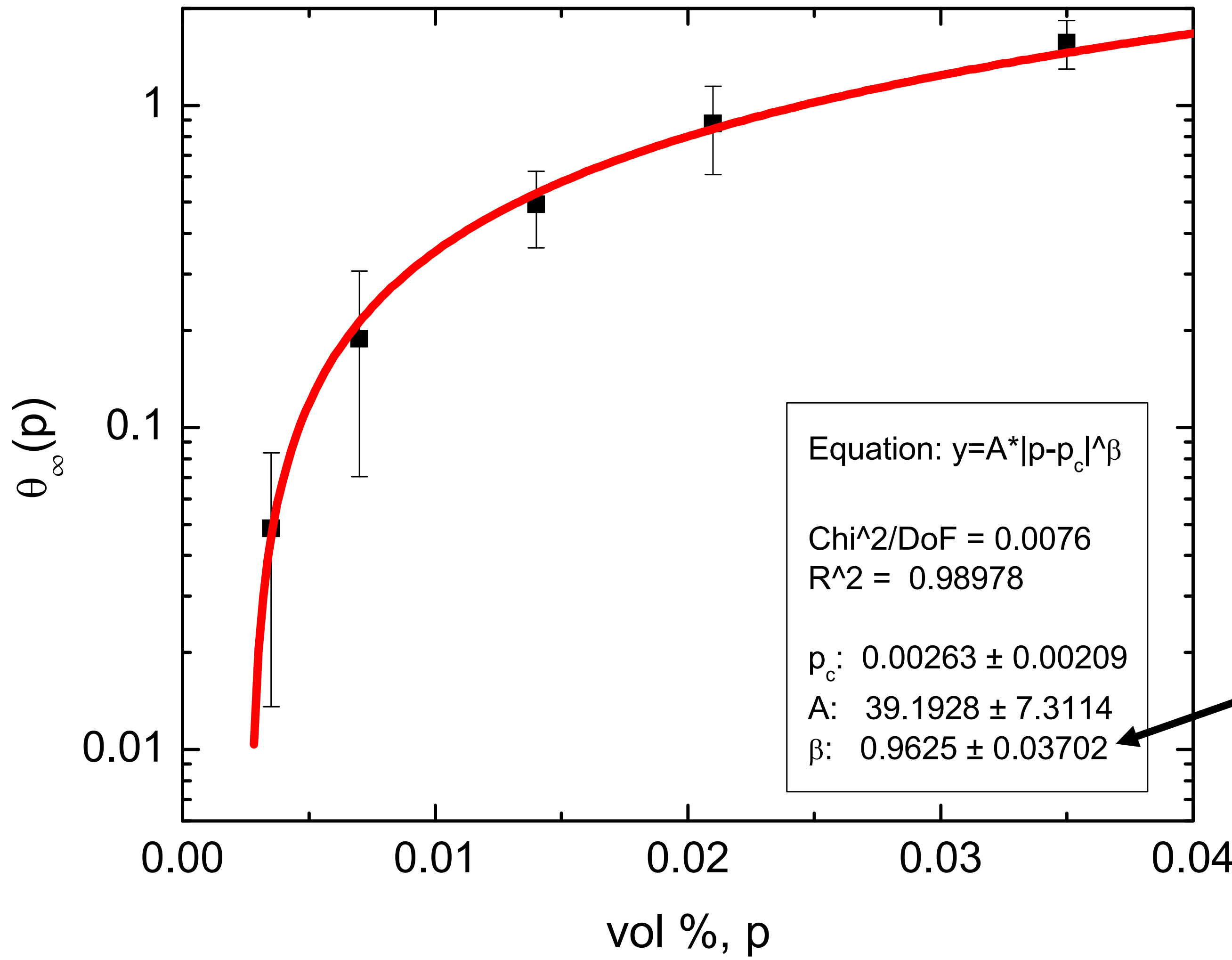
$$V_V = \frac{v_1}{V} = \frac{\sum_i a_i t}{\sum_i A_i t} = \frac{\sum_i a_i}{\sum_i A_i} \approx \frac{Na_1}{NA} = A_A$$

How to measure the percolation probability

- Given an average areal density of conducting tubes (A_A^{CT}).
- Using the principle of Delesse, average areal density will be equal to volume fraction of conducting tubes (V_V^{CT}).
  - This will give us the volume fraction of the infinite cluster!
- Total volume fraction of tubes (p) is known from synthesis.

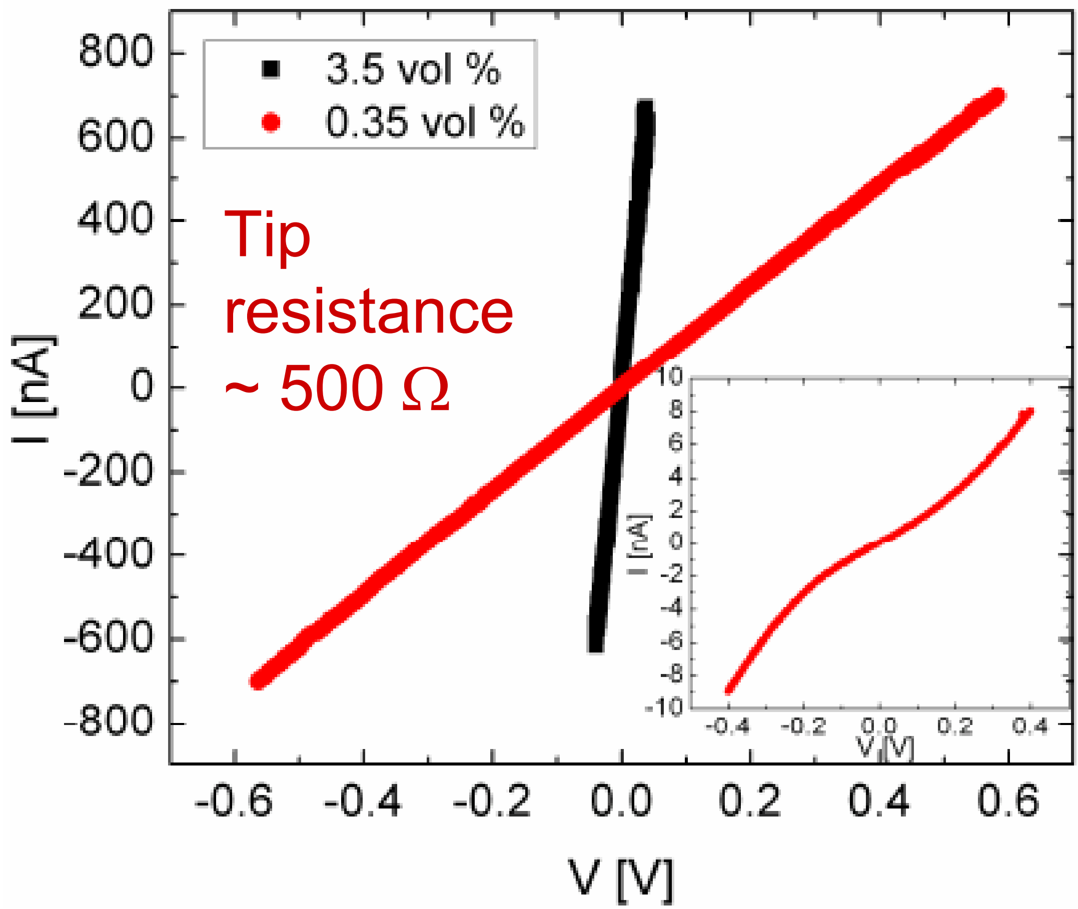
$$\theta_\infty(p) = \left(A_A{}^{CT}(p)/p\right) \propto (p - p_c)^\beta$$

Percolation Probability Results



$\beta \approx .96$

CAFM Local I-V Data



- Ohmic I-Vs likely indicate no tunneling behavior
- Non-ohmic I-Vs are present indicating some tunneling transport is possible.

Conclusion

- Bulk transport measurements of CNF composites give a critical exponent t = 3, possibly suggesting IRV tunneling model as theoretical model of the material
- Native surfaces of material are not bulk representative of carbon nanofiber network
  - Oxygen plasma treatment removes polymer-rich skin layer without damaging CNF
- Percolation Probability can be measured by Principle of Delesse analysis of conducting-tip AFM scans
- Microscopic analysis of CNF composite does not support tunneling percolation model
  - Percolation Probability critical exponent β not in agreement with lattice theory prediction of 0.4.
  - Ohmic I-V indictate that tunneling is not the dominant transport mechanism in the material

Acknowledgements

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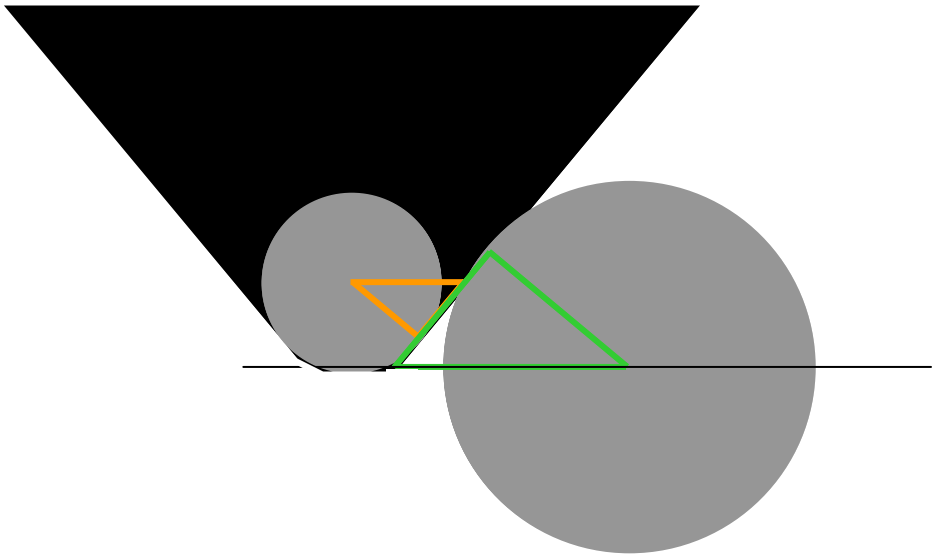
AFM Tip Convolution



AFM-measured CNF radius can be over twice as large as actual value!