SAND2021-4955C

Measuring the Dielectric Constant of Ferroelectric Nanoparticles

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Professional Liaison: Dr. Todd Monson

Sandia National Laboratories

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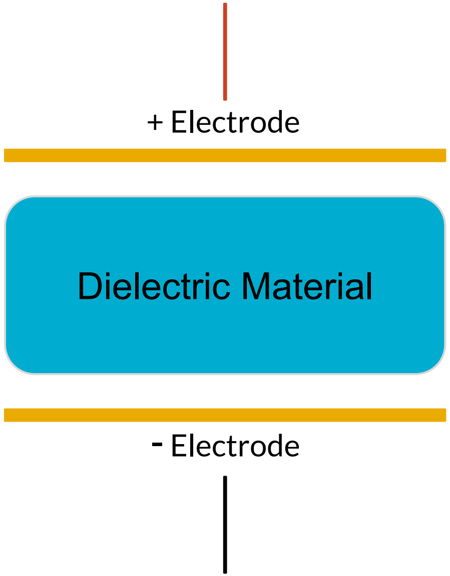
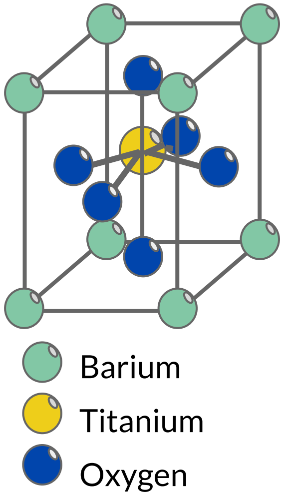
HARVEY MUDD COLLEGE

Background and Motivation



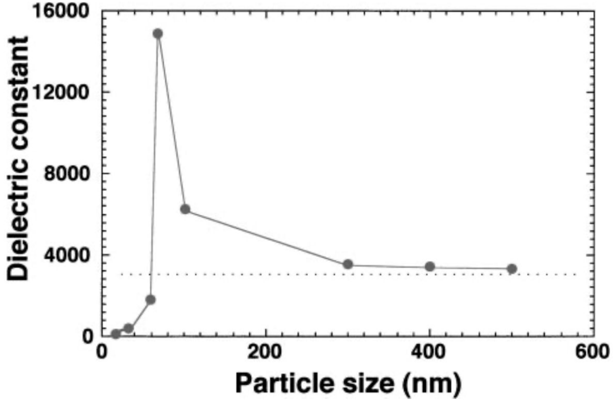
Dielectric Constant
A measure of the amount of electric potential energy that can be stored in a given material (per unit volume)

Dielectric Constant of Barium Titanate (BTO)



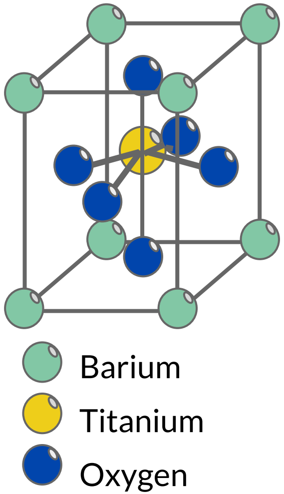
BTO Powder

(contested results)



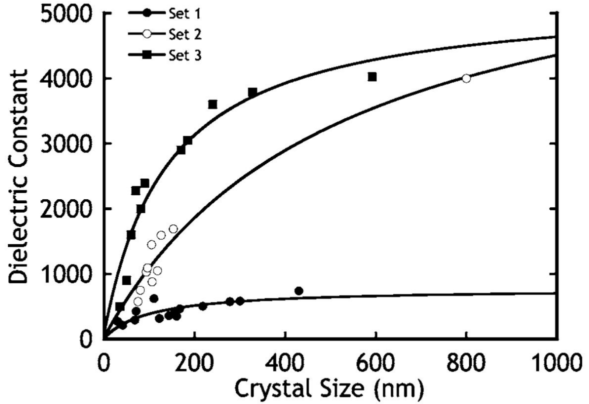
Wada, Satoshi, et al. "Preparation of nm-sized barium titanate fine particles and their powder dielectric properties." *Japanese journal of applied physics* 42.9S (2003): 6188.

Dielectric Constant of Barium Titanate (BTO)



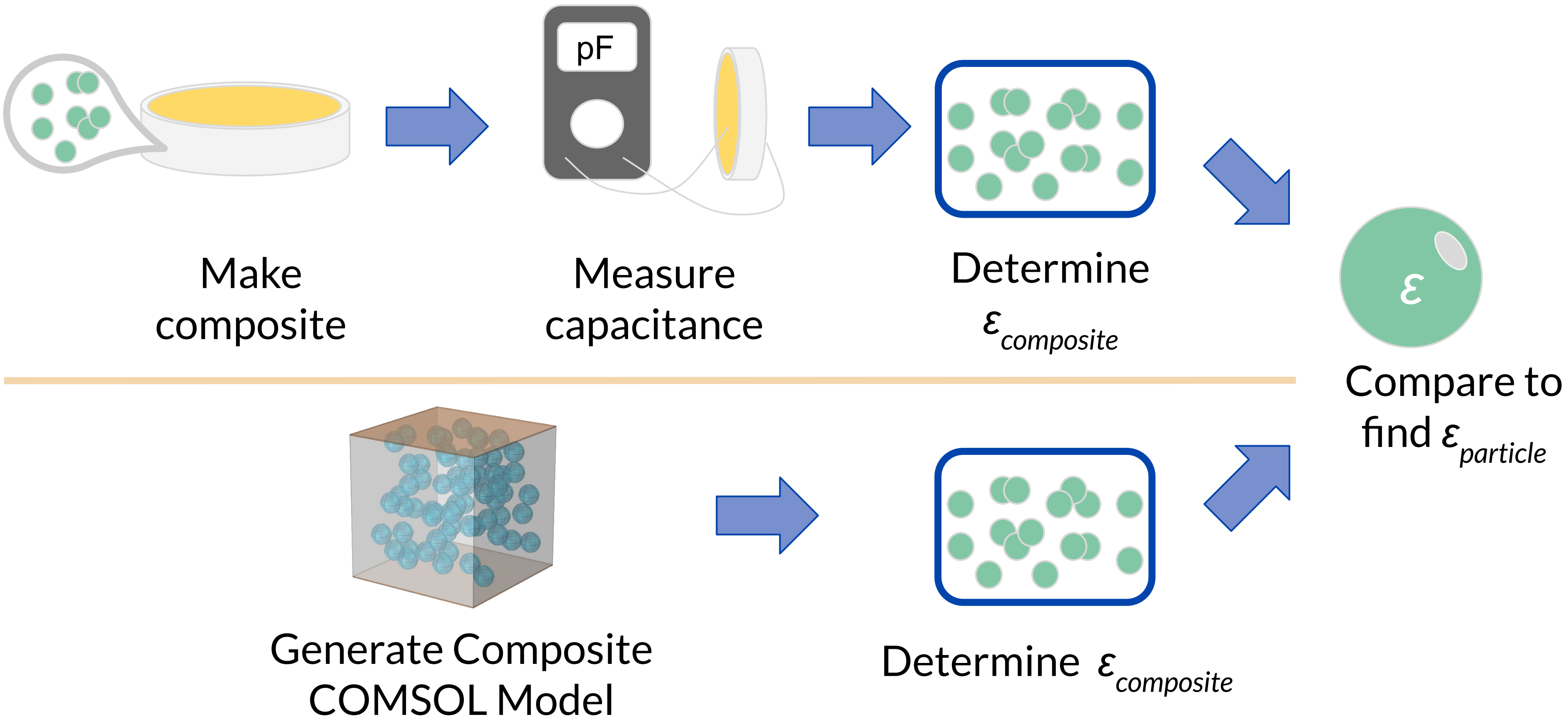
Sintered BTO

(widely reported behavior)



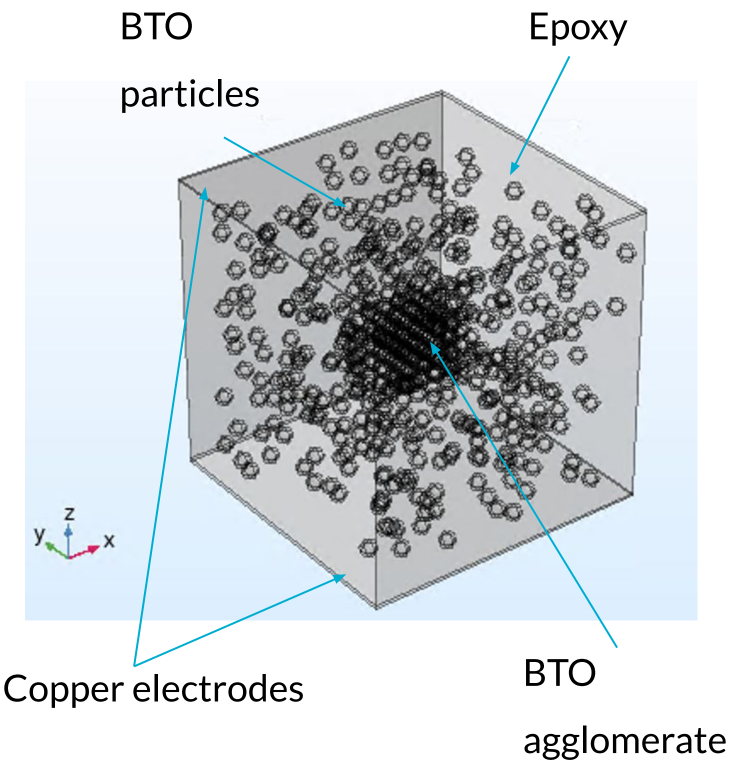
Aygün, Seymen, et al. "Permittivity scaling in Barium Titanate thin films and ceramics" *Journal of applied physics* 109S (2011): 034108.

Fabrication Process & Techniques



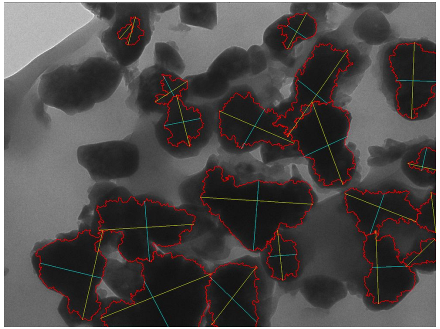
Prior Work on COMSOL Modelling

- In 2018 Kauffman et al modelled BTO-Epoxy nanocomposites
- Factors that significantly impact composite dielectric constant
  - Volume fraction
  - Level of agglomeration in BTO particles
  - BTO particle diameter

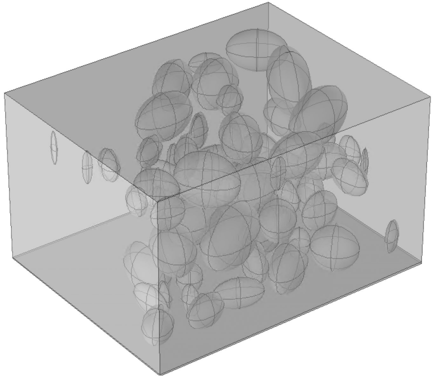


Overview

Python image processing pipeline calculates particle positions, size, rotation



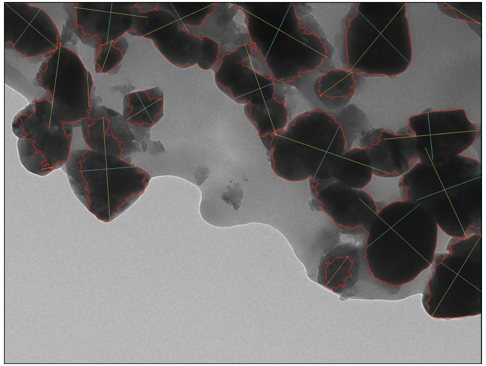
COMSOL model calculates composite dielectric constant



Use model to investigate impact of volume loading, BTO diameter, position

Image Processing Overview

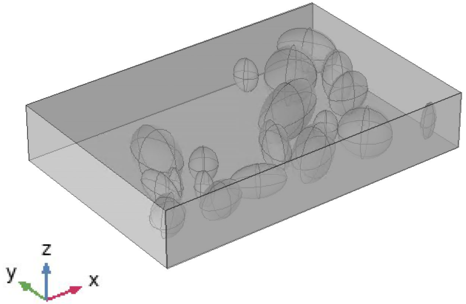
TEM Image processed by pipeline



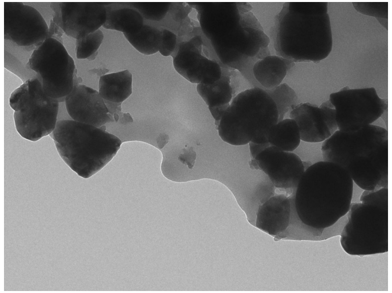
Particle data file

```
a1 224.4727378102044[nm]
b1 128.3381973462805[nm]
c1 183.64168260311894[nm]
x1 590.8097600900303[nm]
y1 143.6509966409194[nm]
z1 184.64168260311894[nm]
theta1 -158.0978596407897[degrees]
a2 167.95575111230593[nm]
b2 116.71643778910794[nm]
c2 151.18331973463887[nm]
x2 274.6185102278307[nm]
y2 225.19127647811584[nm]
z2 213.18331973463887[nm]
•
•
•
*****************
total_particles 60
total_volume_ellipsoids 353695839.634434
x_length_prism 1801.7971601415672[nm]
y_length_prism 1411.5889999306992[nm]
z_length_prism 1053.6548232241637[nm]
x_position_prism -36.46783608004786[nm]
y_position_prism -80.82174116928499[nm]
volume_fraction 0.13198282759810015
```

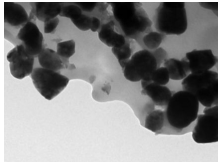
COMSOL Model



Python Pipeline Overview

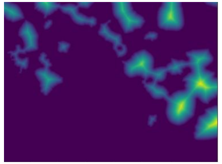


Input



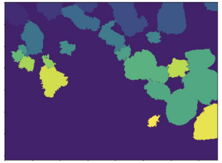
Gaussian Blur

Binary Threshold

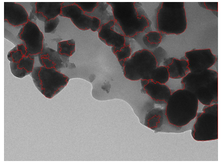


Distance Transform

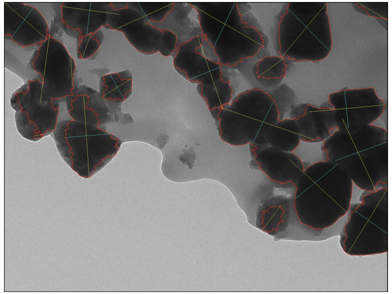
Connected Components



Watershed

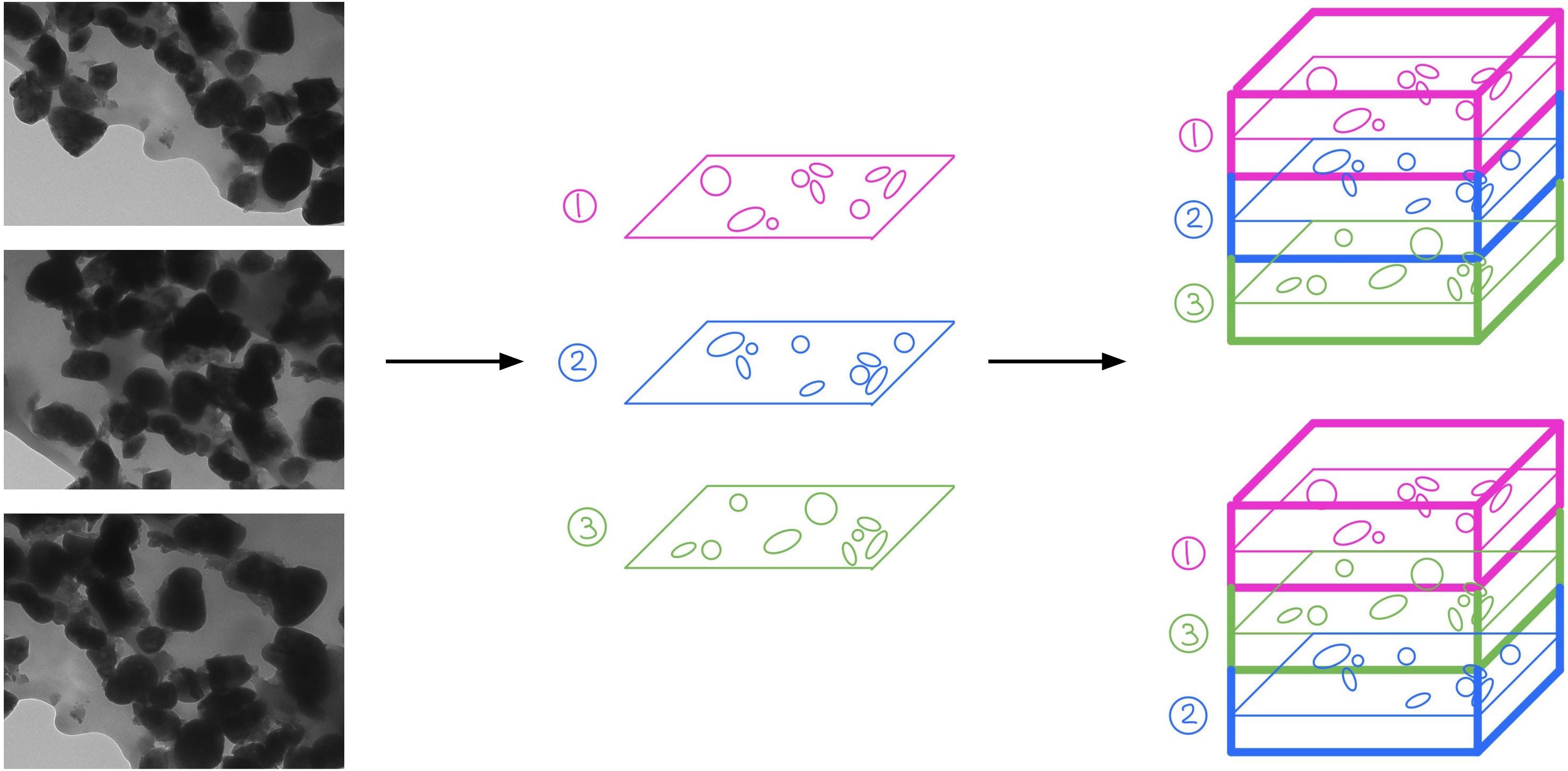


Contours

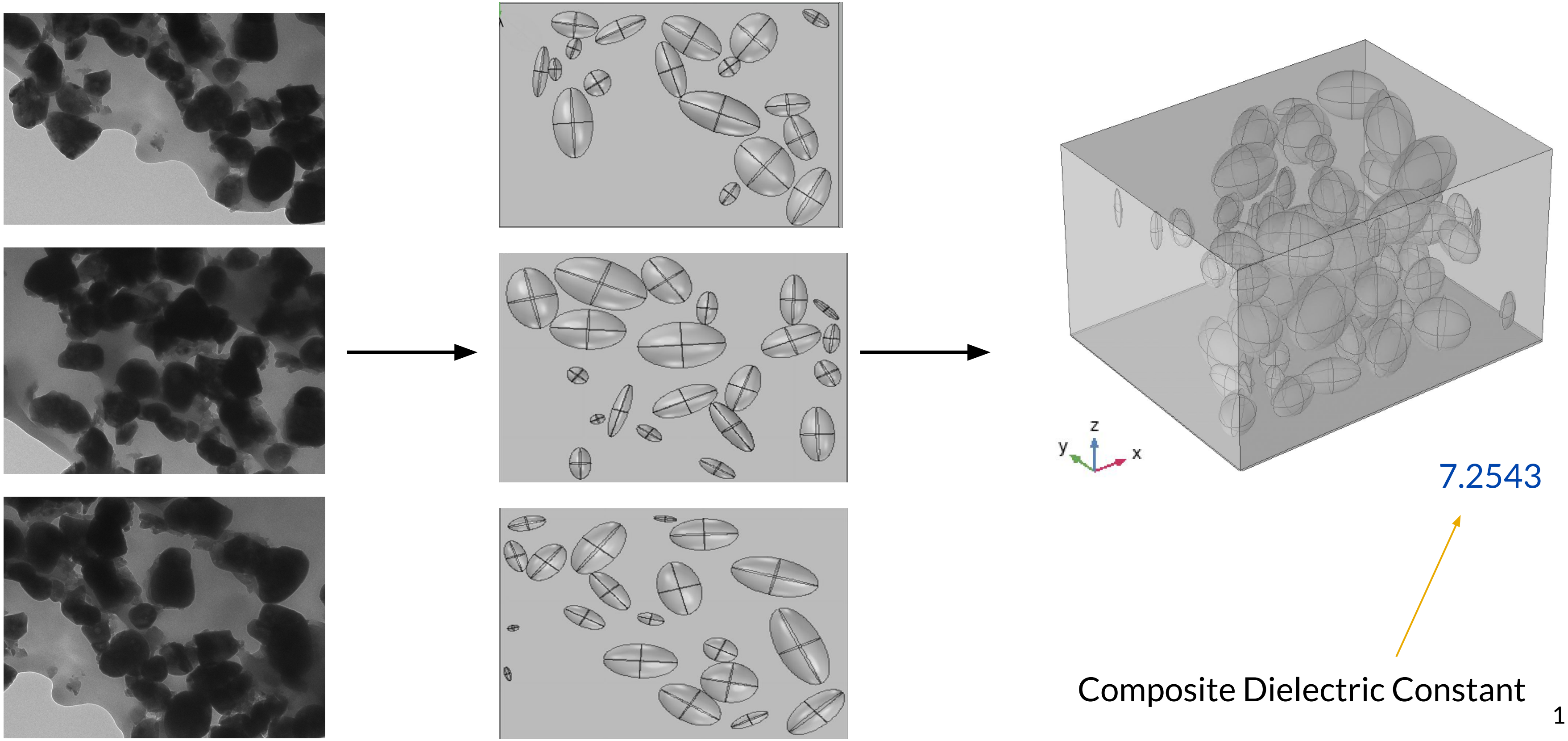


Output

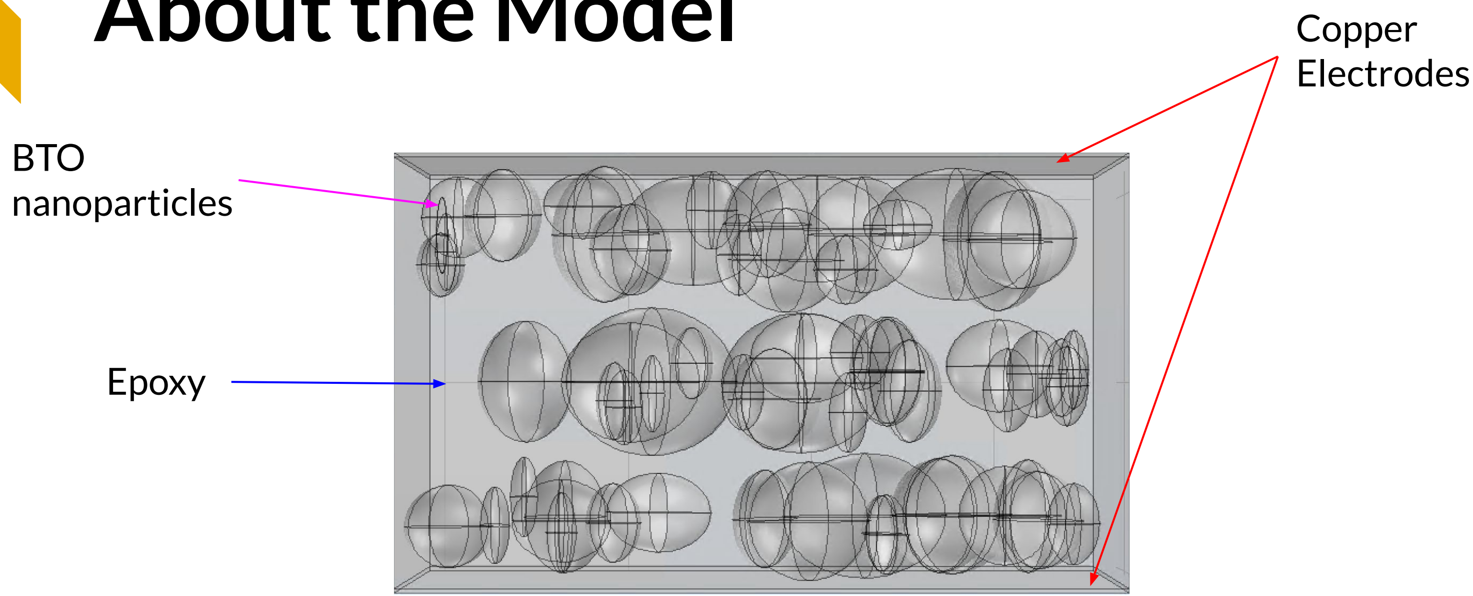
Layered Approach



3 Layers Model COMSOL



About the Model



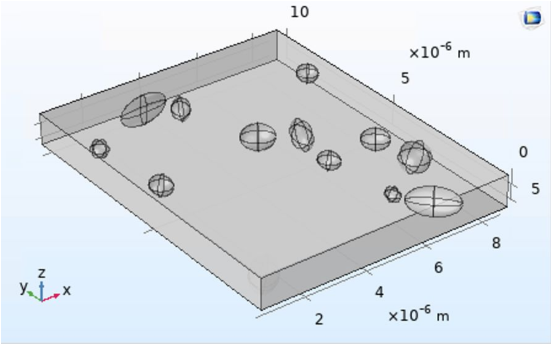
~ 15% Volume Loading

*The data given to us with the TEM images are BTO in epoxy with a 20% volume loading, they have dielectric constant of ~10.4

$$\text{volume loading} = \frac{\text{volume of BTO particles}}{\text{volume of composite}} \cdot 100\%$$

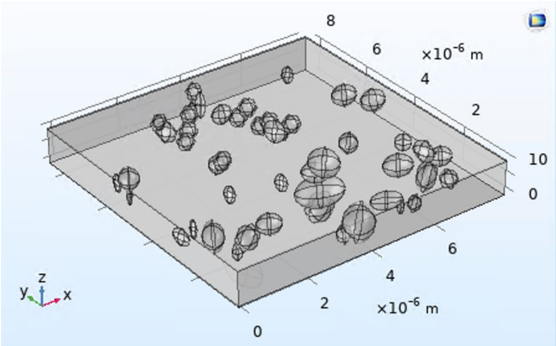
Single Layer Models (500 nm)

Layer 15



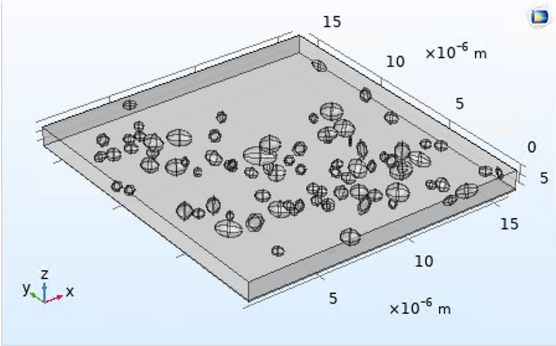
7.9213 (3.54% vol fraction)

Layer 22



8.7042 (6.7% vol fraction)

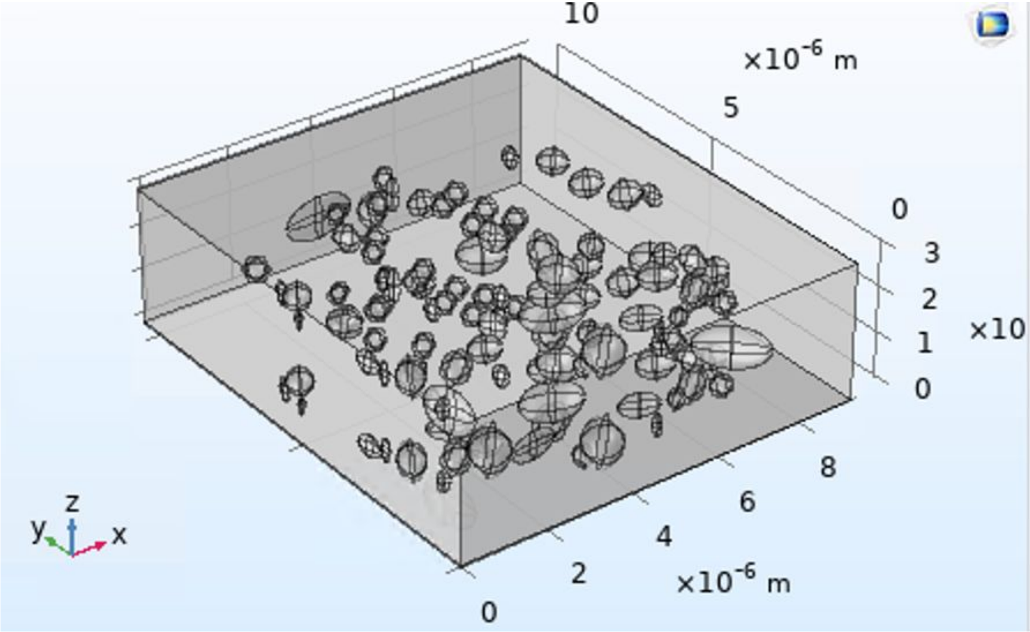
Layer 2



7.8997 (4.97% vol fraction)

Experimental value 5% vol loading 500 nm BTO in LDPE : 7.032832294 +/- 0.136

3 Layer Model (500 nm)



7.3730
Layers 22, 15 and 22
4.19% vol loading

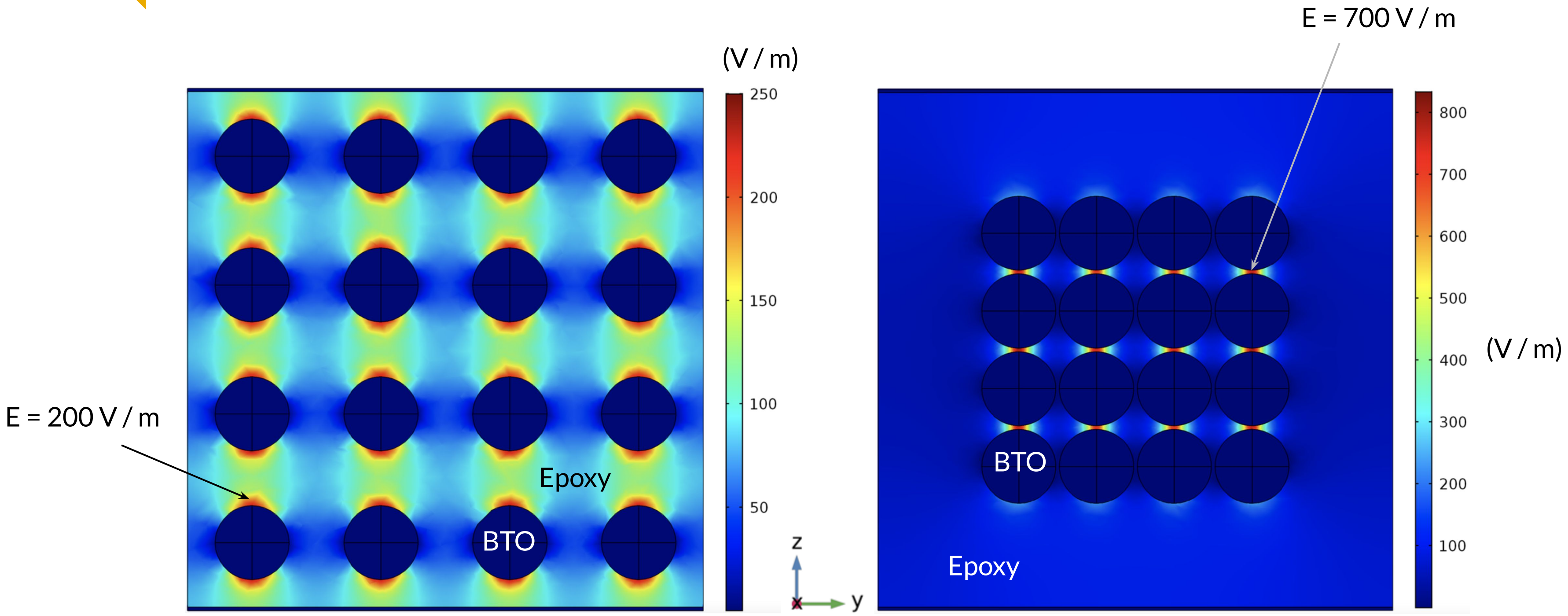
Calculating the Composite Dielectric Constant ε_c

$$\varepsilon_c = \frac{2Ud}{V^2 \varepsilon_o A}$$

$$U = \iiint \frac{1}{2} \varepsilon \varepsilon_0 E^2$$

$$\varepsilon = \begin{cases} 2000, & \text{for BTO nanoparticles} \\ 4.5, & \text{for epoxy} \end{cases}$$

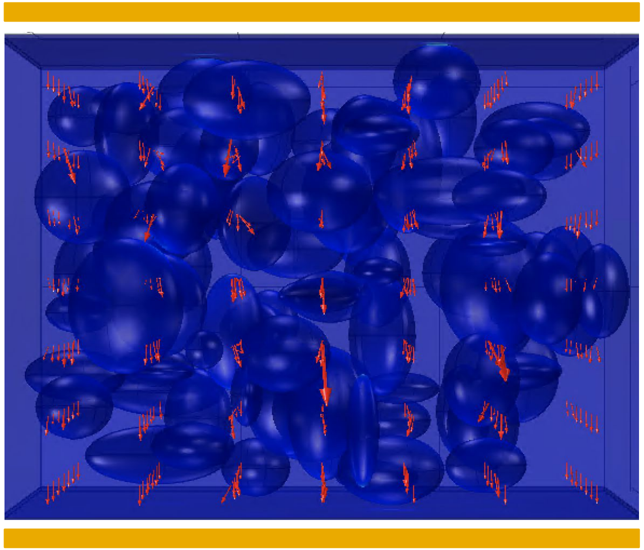
Enhanced Field Regions



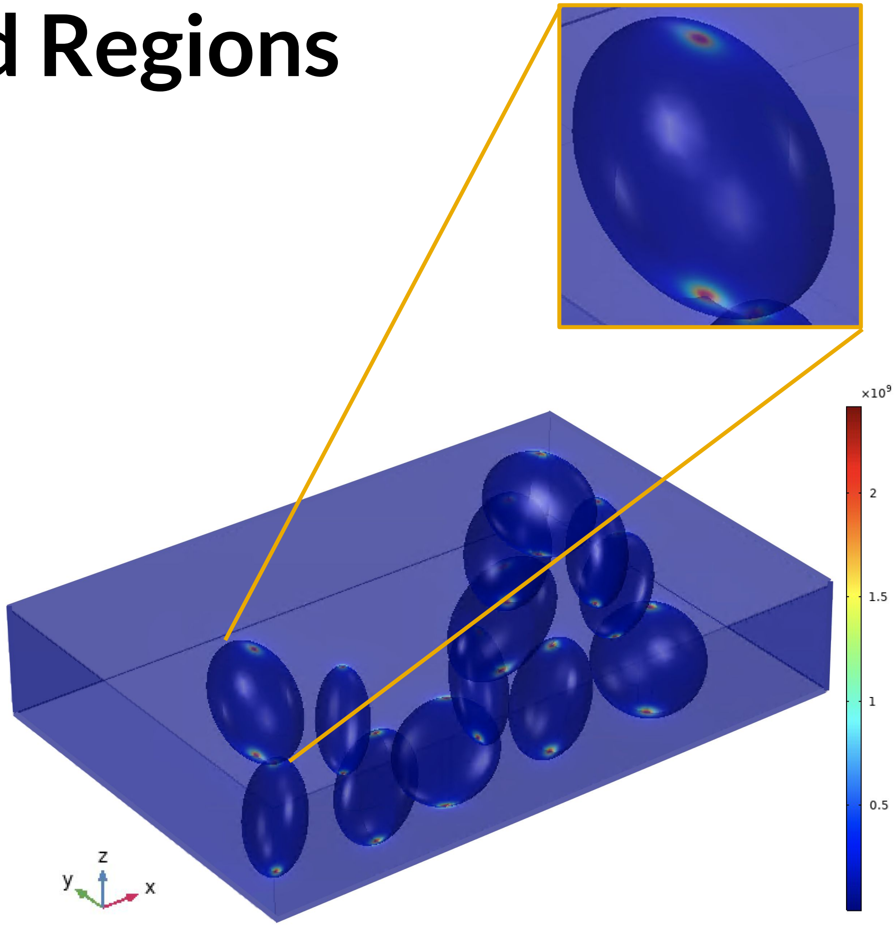
Kaufman, J. L.; Tan, S. H.; Lau, K.; Shah, A.; Gambee, R. G.; Gage, C.; MacIntosh, L.; Dato, A.; Saeta, P. N.; Haskell, R. C.; Monson, T. C. Permittivity Effects of Particle Agglomeration in Ferroelectric Ceramic-Epoxy Composites Using Finite Element Modeling. AIP Advances 2018, 8 (12), 125020. https://doi.org/10.1063/1.5053442.

Enhanced Field Regions

Voltage = 5 V

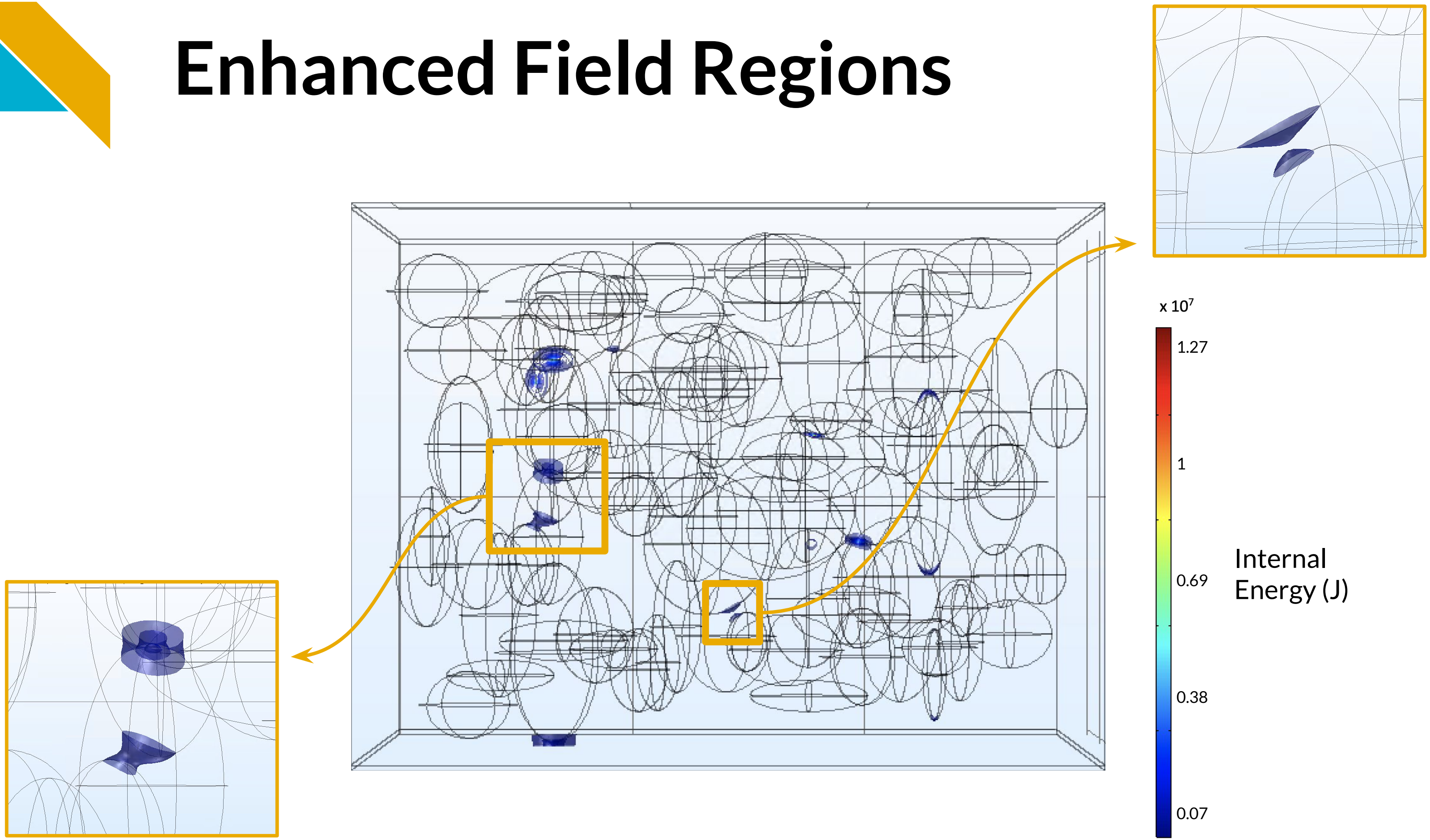


Voltage = – 5 V



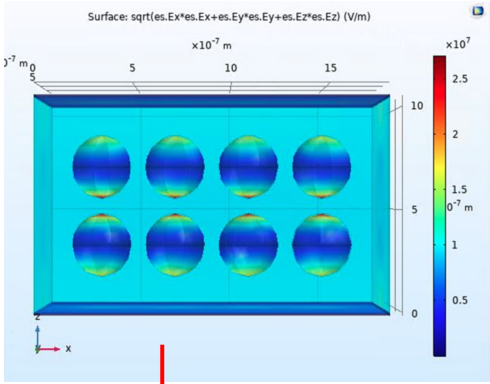
Electric Field (V / m)

Enhanced Field Regions



Particle Interactions

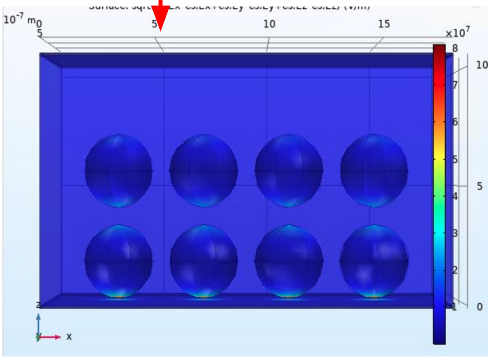
- Particle-particle and particle-electrode
  - Impact on dielectric constant depends on direction
- Magnitude of electric field varies significantly with position in z
  - Want to better understand these effects



Dielectric constant

= 5.3226

Moving particle layers closer to electrode

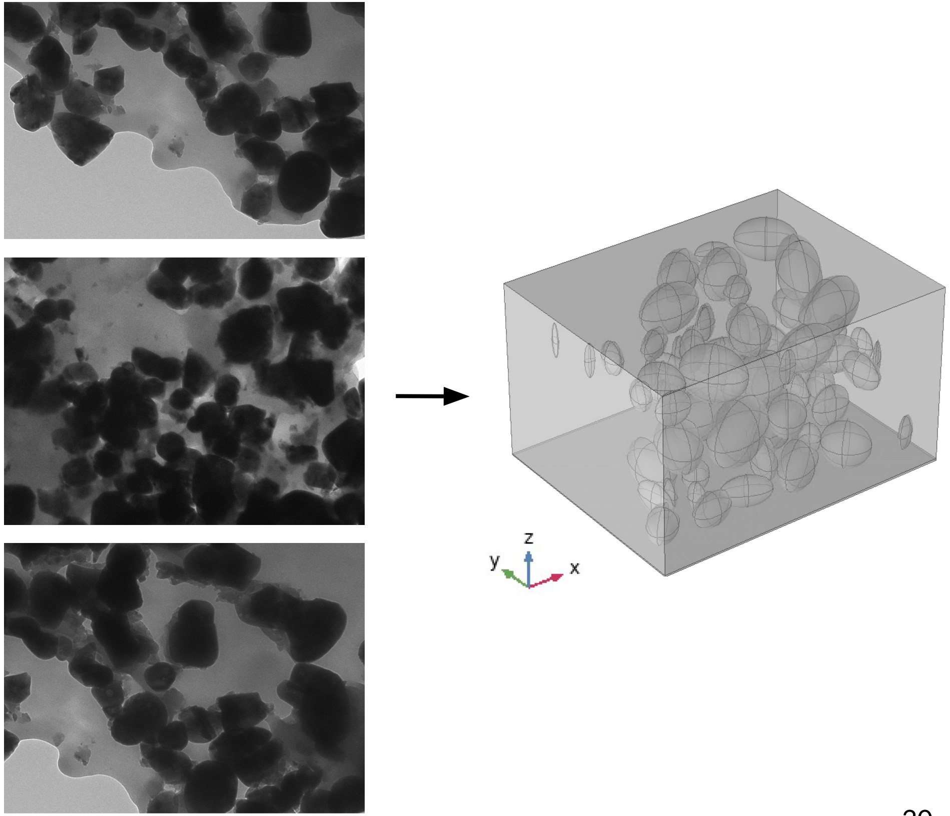


Dielectric constant

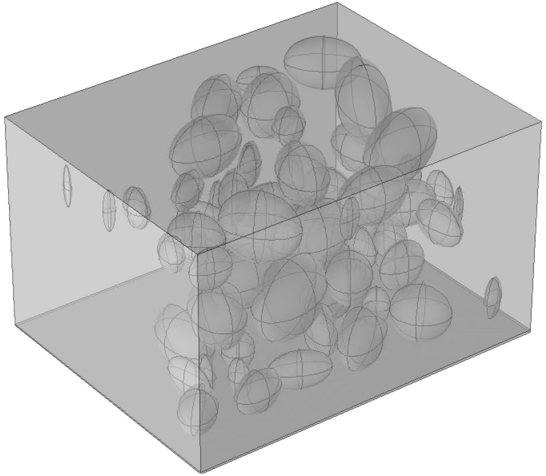
= 5.4660

To Summarize

- Developed a more accurate COMSOL model using information from the TEM images
- Designed an image processing pipeline to find centerpoints and chord lengths from TEM images of agglomerated BTO composites



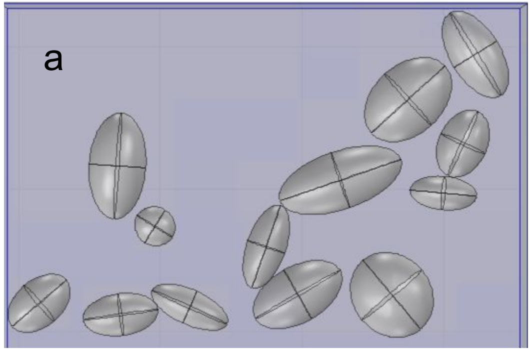
Thank you!

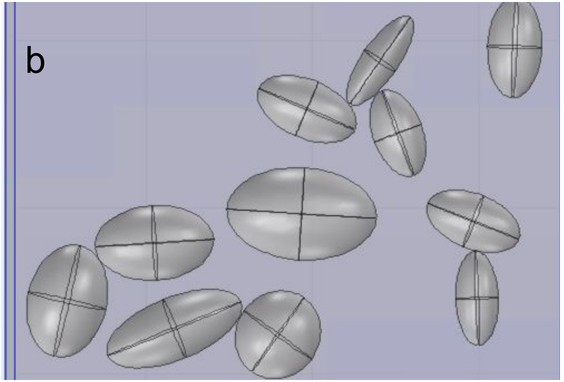


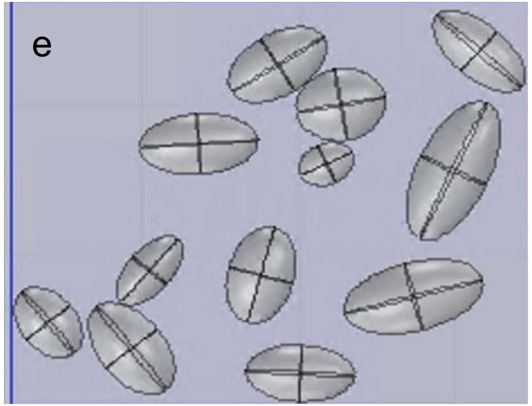
Questions?

Revised Dielectrics - Scaled Single Layer

Layer	Volume Fraction	Dielectric Constant
a	16.15%	8.4259
b	17.44%	8.8044
e	16.06%	8.5942

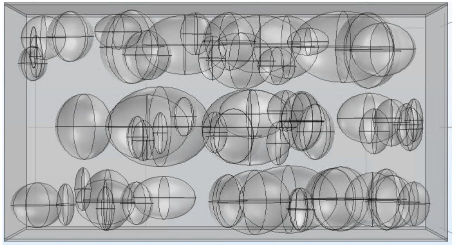


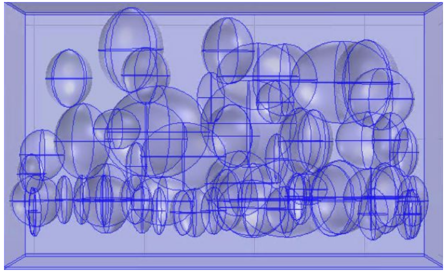


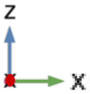


Understanding Particle Interactions: Investigations

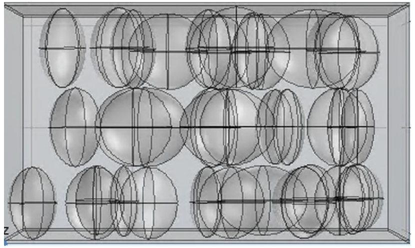
Pushing particles together

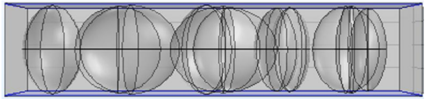




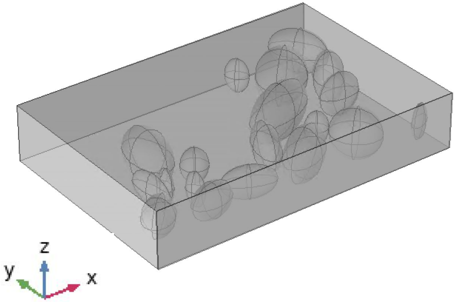


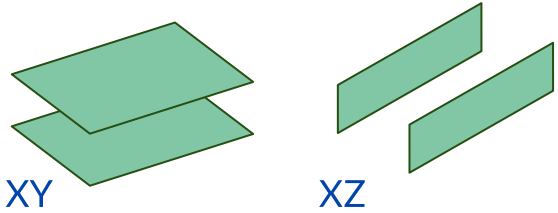
Maximizing C radii (particle ‘height’)





Changing electrode position





Glossary of Important Terms

TEM

Transmission
Electron
Microscopy

High magnification images of nanocomposites.

Real data that informs our model

Dielectric Constant

A measure of the amount of electric potential energy that can be stored in a given material (per unit volume)

Agglomerate

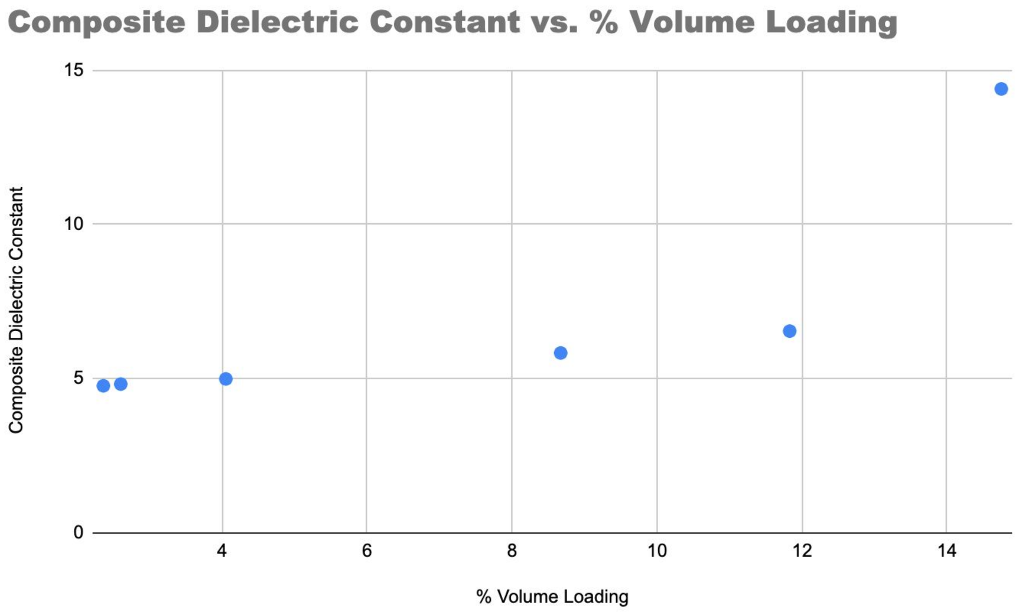
(fluid definition)

An ensemble of two or more particles that in our model requires special treatment

BTO Volume Loading (%)

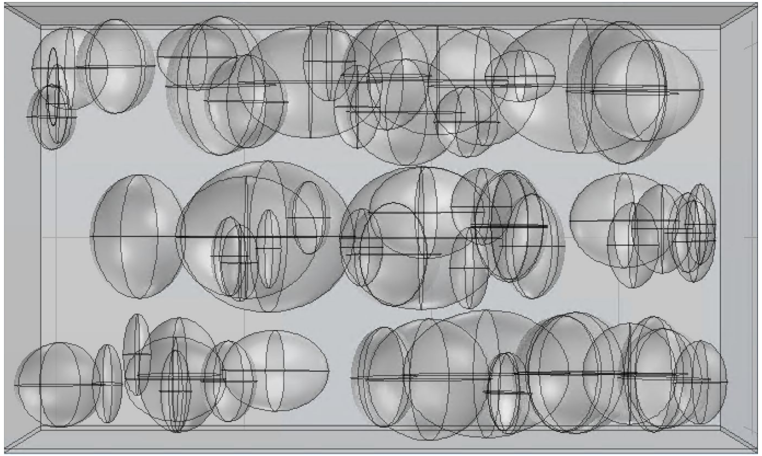
$$\text{volume loading} = \frac{\text{volume of BTO particles}}{\text{volume of composite}} \cdot 100\%$$

Relationship between Composite Dielectric Constant and % Volume Loading (Computational)

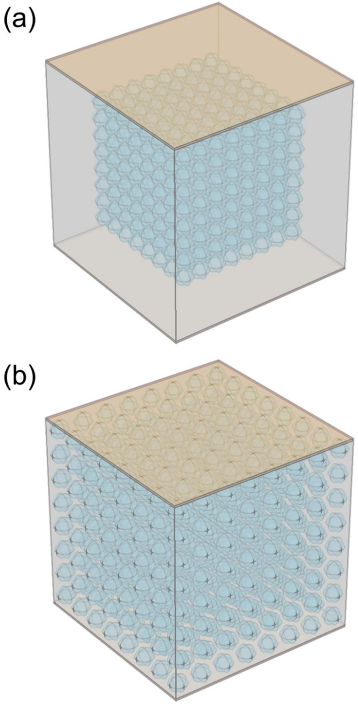


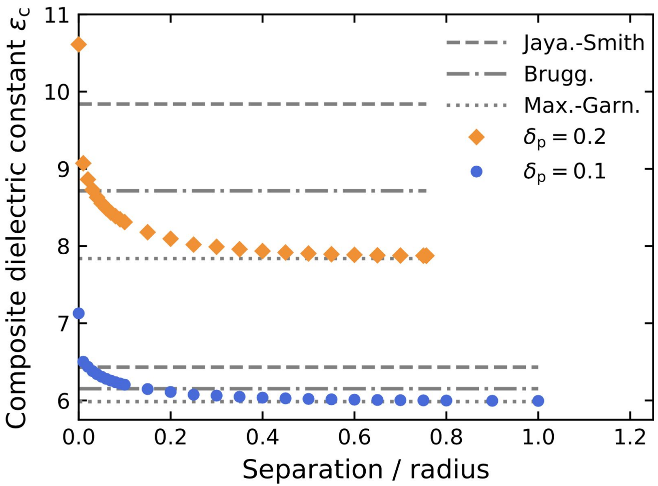
Adjustments to Model

- Randomized the z position to better simulate particle interactions in the z-direction
- Added particles to create a composite with 20% volume loading
    - Composite dielectric of 9.8583

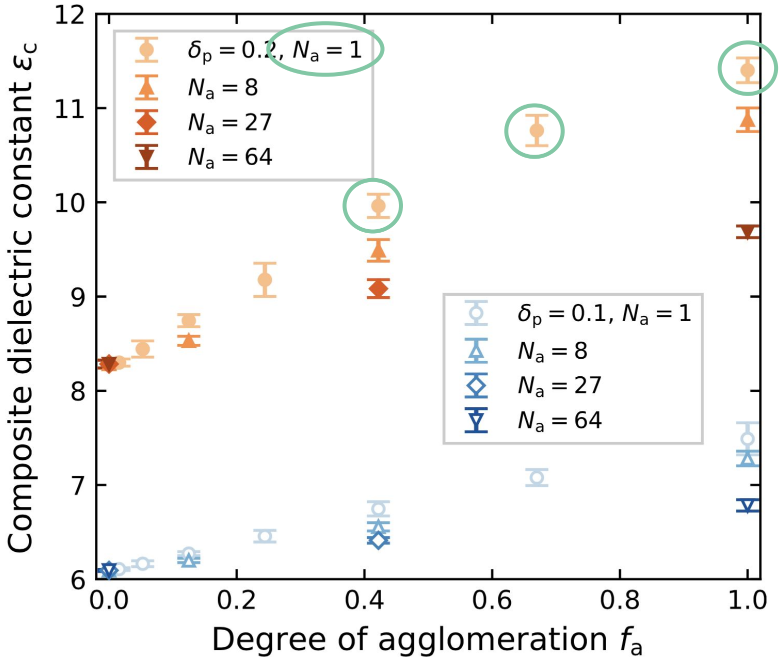


Pushing Particles Together: Minimizing z-distance





Pushing Particles Together: Minimizing z-distance



$$f_a = \frac{N_a n^3}{N_p}$$

$$N_p = 512$$

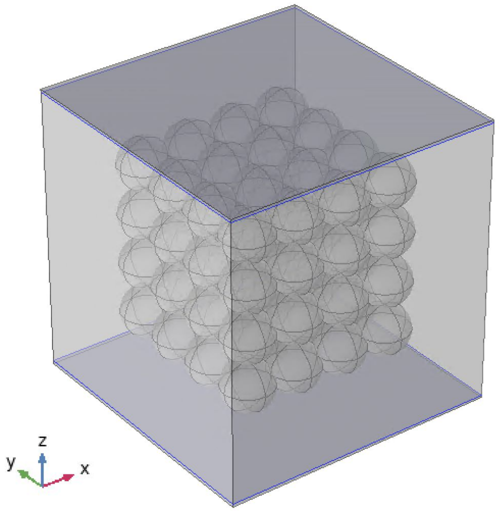
Pushing Particles Together: Minimizing z-distance

maybe we are just 0.5 nm away?

- How much does particle distance ACTUALLY matter?

distance = 1 nm

9.0911

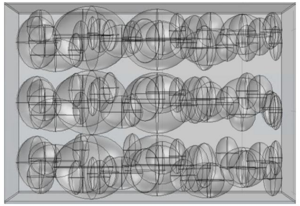


distance = 0 nm

10.0240

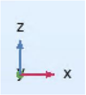
Pushing Particles Together: Minimizing z-distance

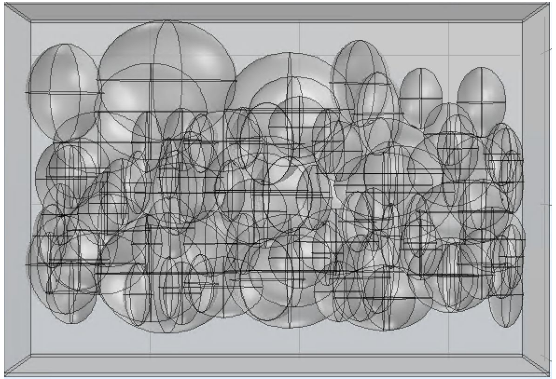
- Minimizing z-distance **EVEN** more
- Three layer model “bbb”
- 20% volume fraction



BTO dielectric constant = **2000**

9.8583

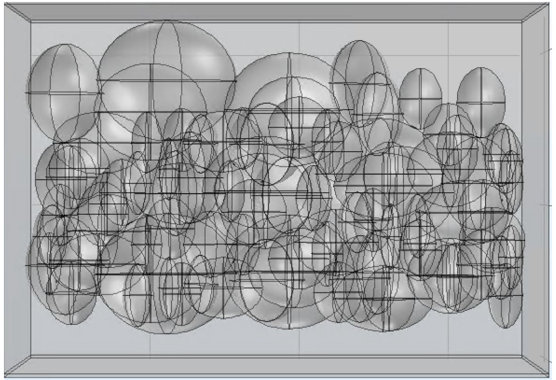




9.2555

Making particles a bit bigger in z-direction

Increasing c-radius



9.6238

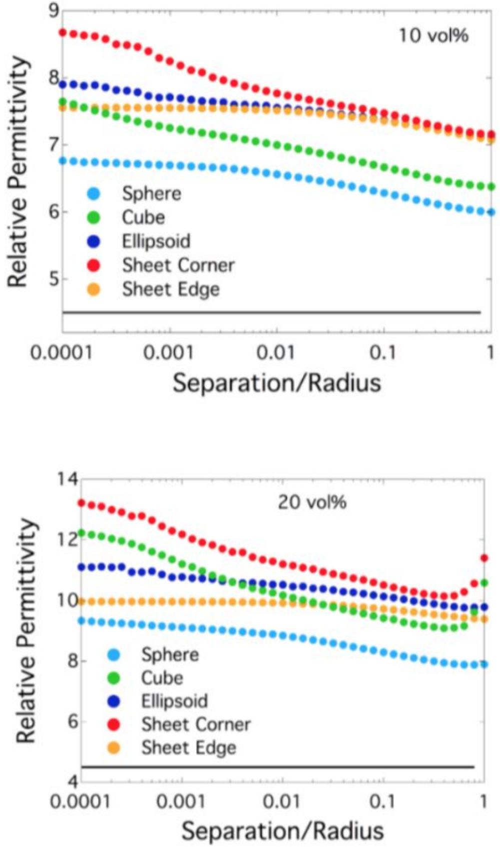
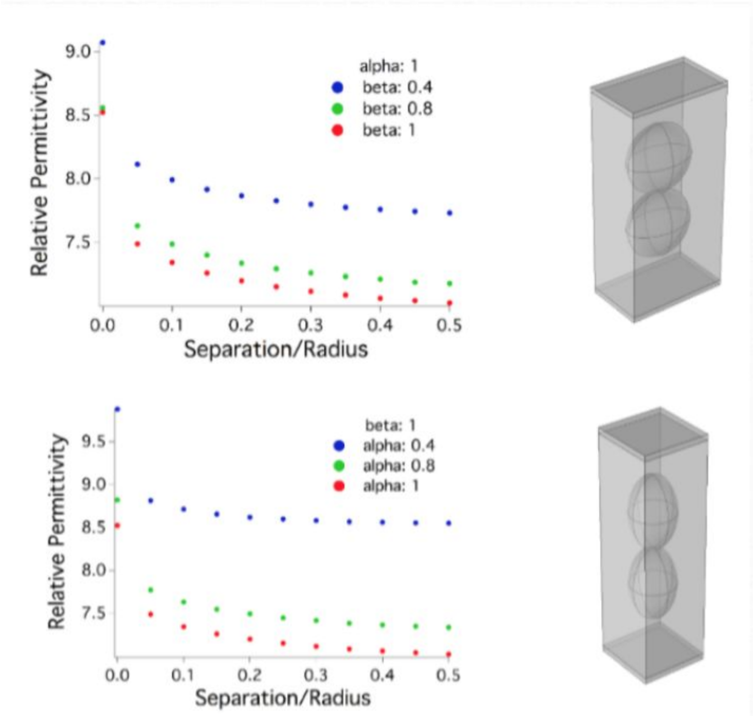


Figure 11: Comparison of the relative permittivity for cubes, spheres, sheets, and ellipsoids at 10 vol% (top) and 20 vol% (bottom). The sudden increase in the sheet and cube models at large separations come from particles intersecting with the copper plates. The black line shows the epoxy baseline.[Team, 2017]



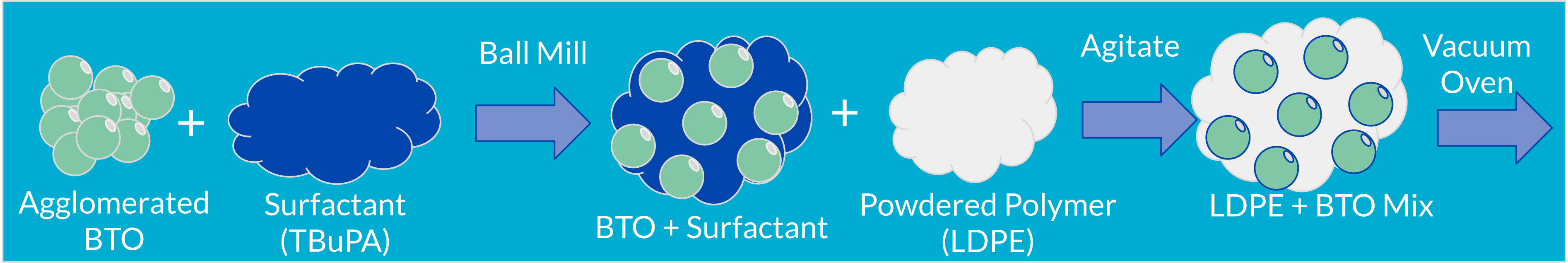
Alpha length of y-axis:z-axis (relative length of the long axis)

Beta length of x-axis :y-axis (geometry of the cross section)

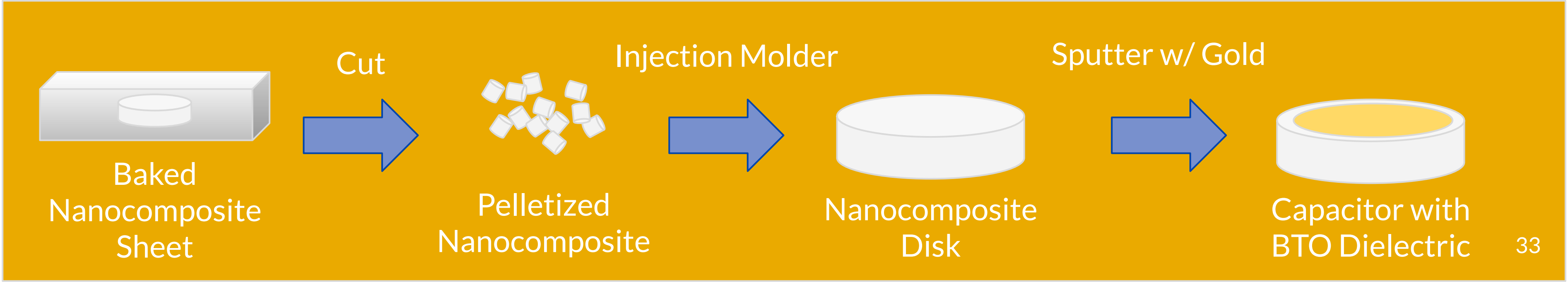
Figure 12: Plots showing the results of changing beta (top) and alpha (bottom). Models shown are for 15.5 vol%, though higher volume fractions were tested as well. [Team, 2017]

Fabrication Process & Techniques

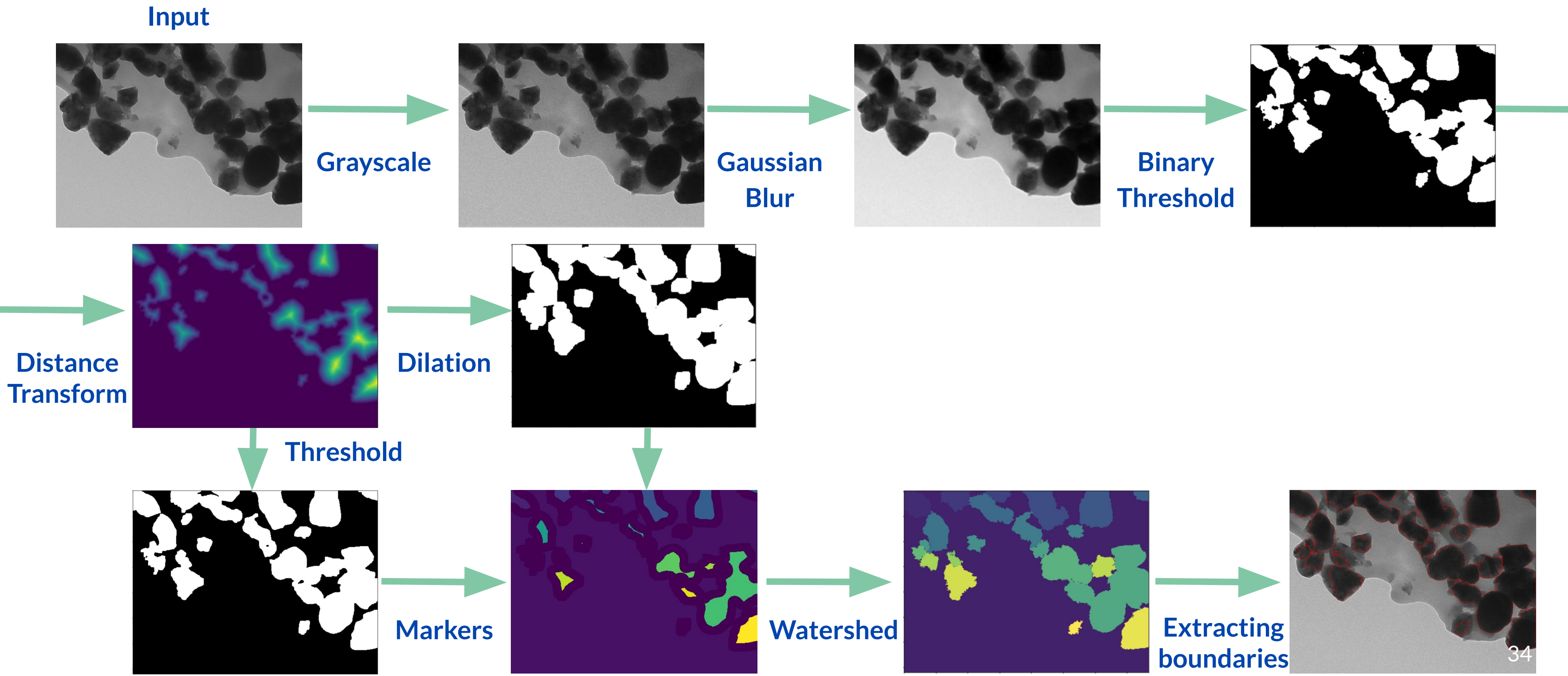
1. *Mixing Stage*



2. *Fabrication Stage*



Python Pipeline Overview



A Composite of Just Organic Matrix

THE MATH

(1)

$$\varepsilon_m = 6.29 \text{ or } 4.5 \qquad \text{(LDPE or epoxy)}$$

$$\varepsilon_o = 8.8541878128 \text{ x } 10^{-12}$$

$$E = \frac{V}{d}$$

$$V_c = \text{x-length-prism} \cdot \text{y-length-prism} \cdot \text{z-length-prism}$$

(2)

constant

$$U = \iiint_V \frac{1}{2}\varepsilon_{\text{x}}\varepsilon_o E^2 dV = \frac{1}{2}\varepsilon_m\varepsilon_o E^2 \iiint_V dV = \frac{1}{2}\varepsilon_m\varepsilon_o E^2 V_c$$

volume of composite

(3)

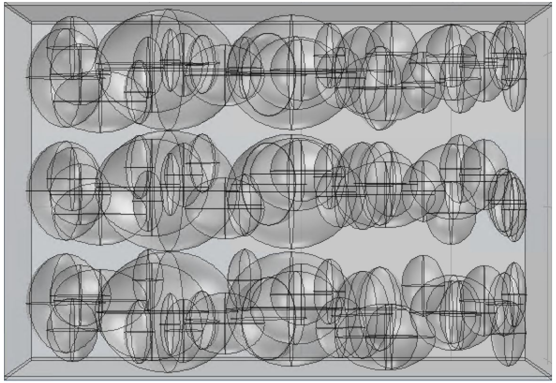
composite dielectric constant

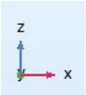
$$\varepsilon_c = \frac{2Ud}{\varepsilon_o A V^2} = \frac{2\left(\frac{1}{2}\varepsilon_m\varepsilon_o E^2 V_c\right)d}{\varepsilon_o A V^2} = \frac{\varepsilon_m E^2 V_c d}{AV^2} = \frac{\varepsilon_m E^2 (Ad) d}{AV^2} = \frac{\varepsilon_m E^2 d^2}{V^2} = \frac{\varepsilon_m \left(\frac{V}{d}\right)^2 d^2}{V^2} = \frac{\varepsilon_m \left(\frac{V^2}{d^2}\right) d^2}{V^2} = \varepsilon_m$$

matrix dielectric constant

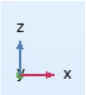
A Truly 20% Vol. Fraction Model

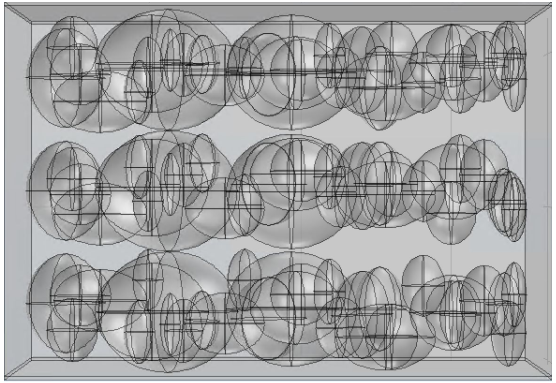
- Large dielectric constant but still below experimental: **10.4 ± 0.1**
- Increasing the BTO dielectric constant still does not take us to 10.4 ± 0.1





Increasing BTO dielectric constant →



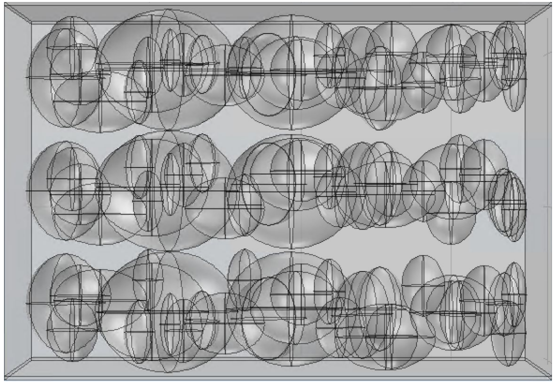


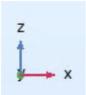
BTO dielectric constant = **2000** — 9.8583

BTO dielectric constant = **4800** — 9.9359

A Truly 20% Vol. Fraction Model

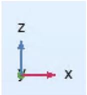
- For this 20% vol. fraction model (three times layer b) pushing particles together resulted in a **decrease** in the composite dielectric constant

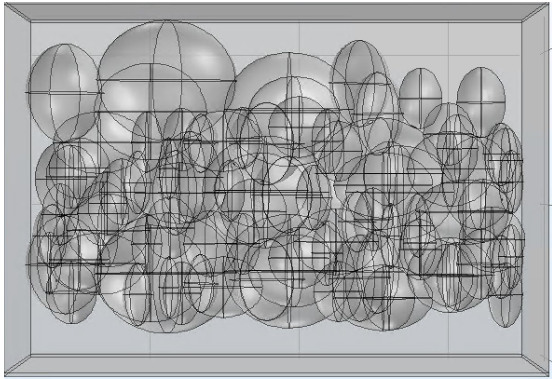




Minimizing
z-distance

(pushing particles together)





BTO dielectric constant = **2000**

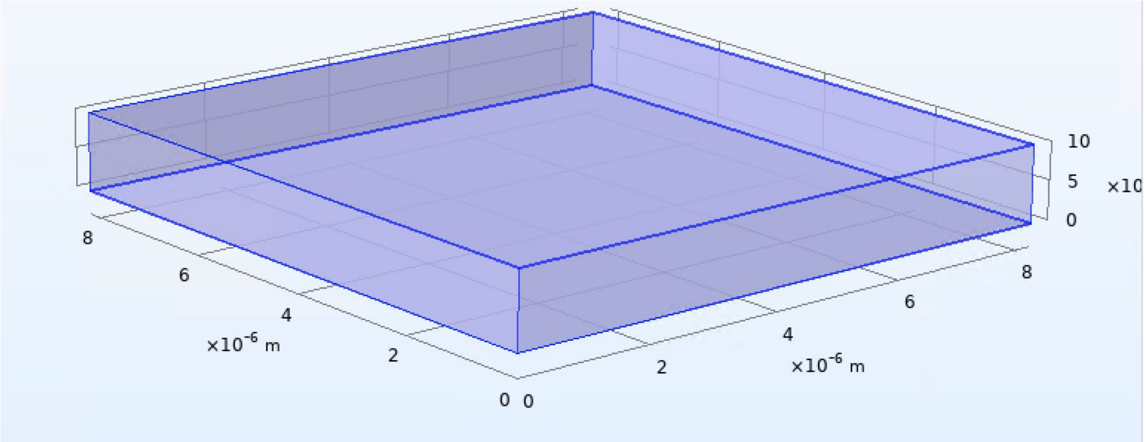
9.8583

BTO dielectric constant = **2000**

9.2555

A Composite of Just Organic Matrix

THE MODEL



In epoxy:
4.5000

In LDPE:
6.2900

The Jayasundere-Smith EMA

$$\varepsilon_c = \frac{\varepsilon_m(1-\delta_p) + \varepsilon_p\delta_p\left(\frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m}\left(1 + \frac{3\delta_p(\varepsilon_p - \varepsilon_m)}{\varepsilon_p - 2\varepsilon_m}\right)\right)}{(1-\delta_p) + \delta_p\left(\frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m}\left(1 + \frac{3\delta_p(\varepsilon_p - \varepsilon_m)}{\varepsilon_p - 2\varepsilon_m}\right)\right)}$$

- ε_c composite dielectric constant
- ε_p particle dielectric constant
- ε_m medium dielectric constant