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Energy and Transport Sciences Laboratory

Microstructural Variability in Graphite Electrodes

Chance Norris[1], Aashutosh Mistry[1], Scott Roberts[2] and Partha P. Mukherjee[1]

[1] School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

[2] Engineering Sciences Center, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA

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subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

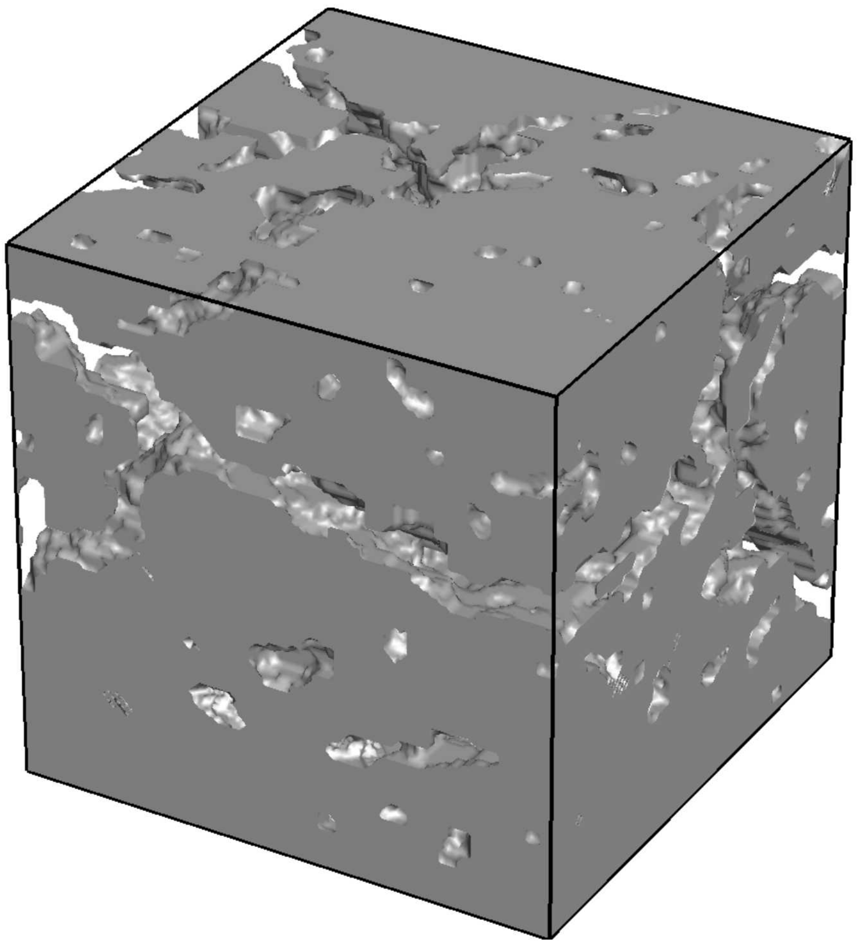
Motivation

Q. Why are we interested in microstructural variations in graphite electrodes?

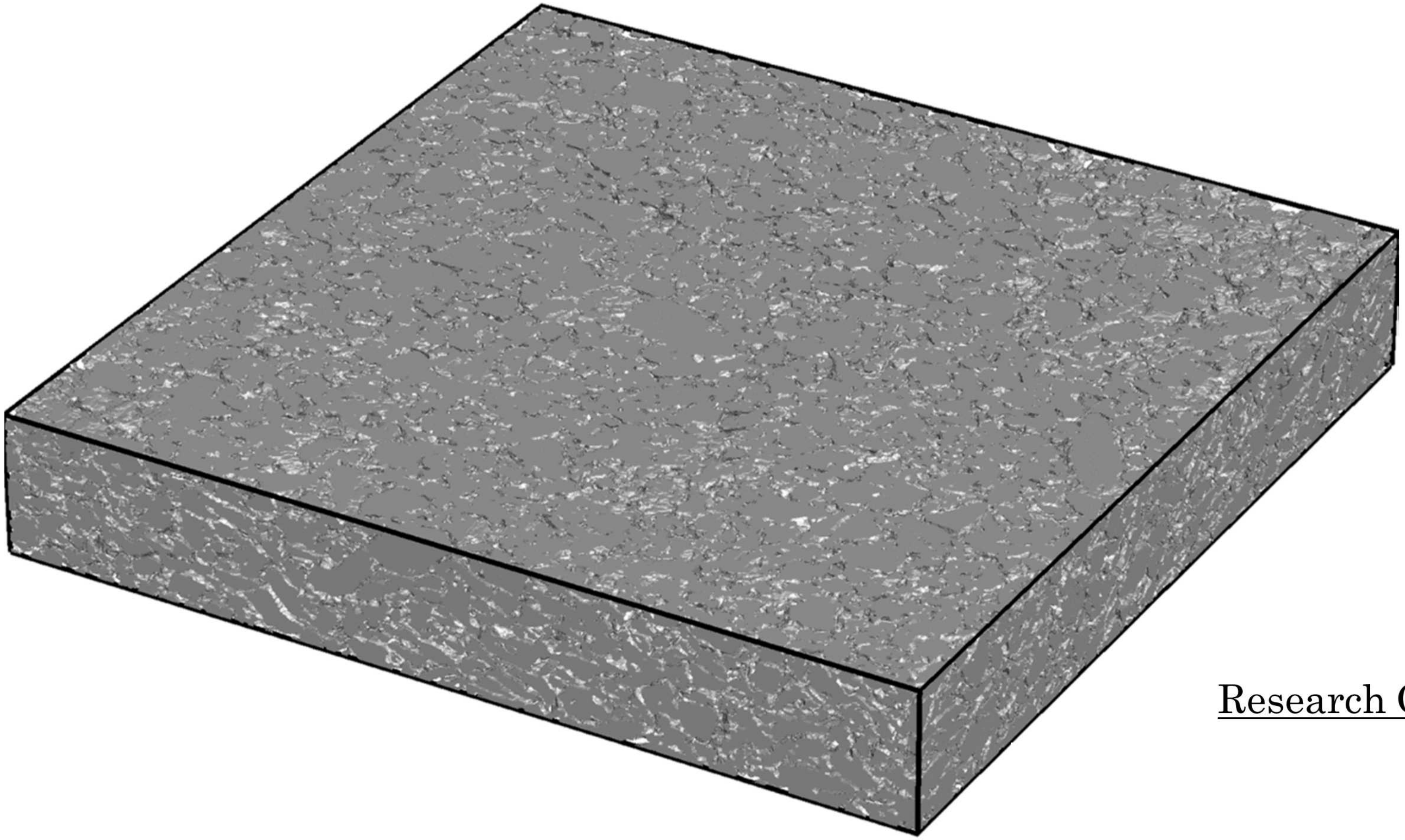
Fast charging or long-term cycling is negative electrode limited.

Graphite is one of the most used anodes in Li-ion batteries to date.

Many varying particle morphologies in graphite.



Objective



Research Questions

Muller, S. et. al. *Journal of The Electrochemical Society,* **2018**, 165(2), A339-A344.

Graphite Anodes

Numbered Electrodes			
Ia	IIa	IIIa	IVa
Ib	IIb	IIIb	IVb
Ic	IIc	IIIc	IVc

Where a, b and c denotes three samples taken from one commercial sheet

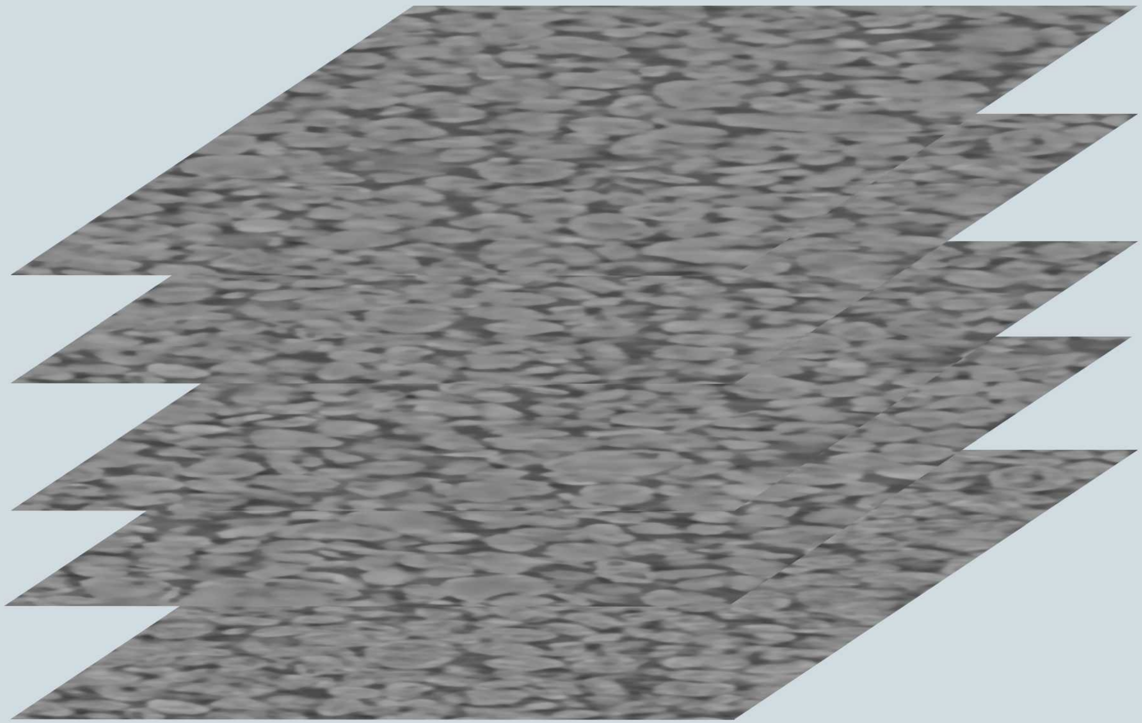
Named Electrodes					
Litarin	Tesla	SamsungE35	Samsung 25R6	GCA400	GCA2000

All electrode data is open source provided by Vanessa Woods group from ETH Zurich

Muller, S. et. al. *Journal of The Electrochemical Society,* **2018**, 165(2), A339-A344. and Pietsch, P. et al. Sustainable Energy and Fuels, **2018**, 2(3), 598-605

Methodology

Q. How are structures acquired?



Stacks of images are acquired

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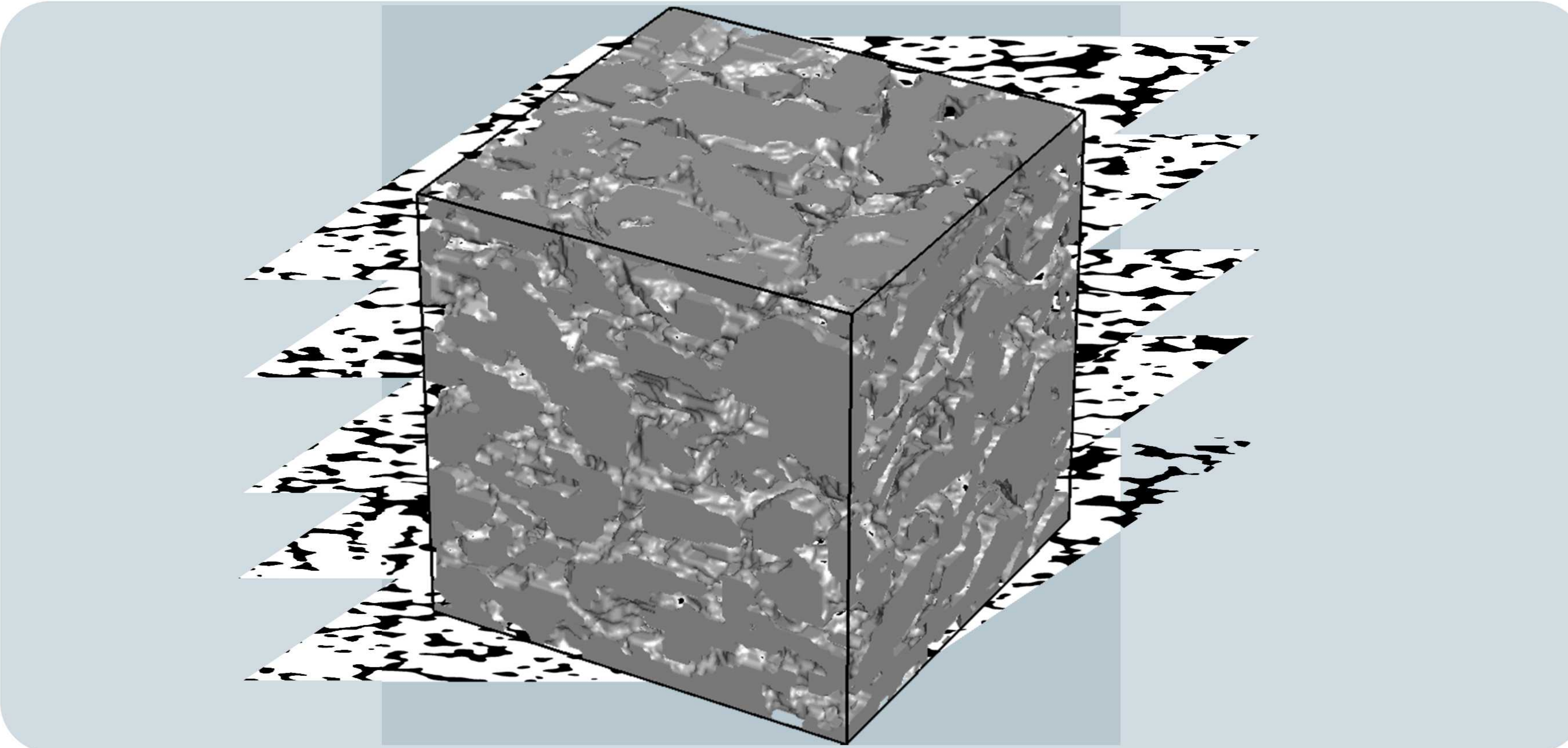


Stacks of images are acquired

Greyscale images are binarized to black and white

These can then be made into a two-phase 3D structure

Muller, S. et. al. *Journal of The Electrochemical Society,* **2018**, 165(2), A339-A344.

Methodology

Q. What can these structures tell us?

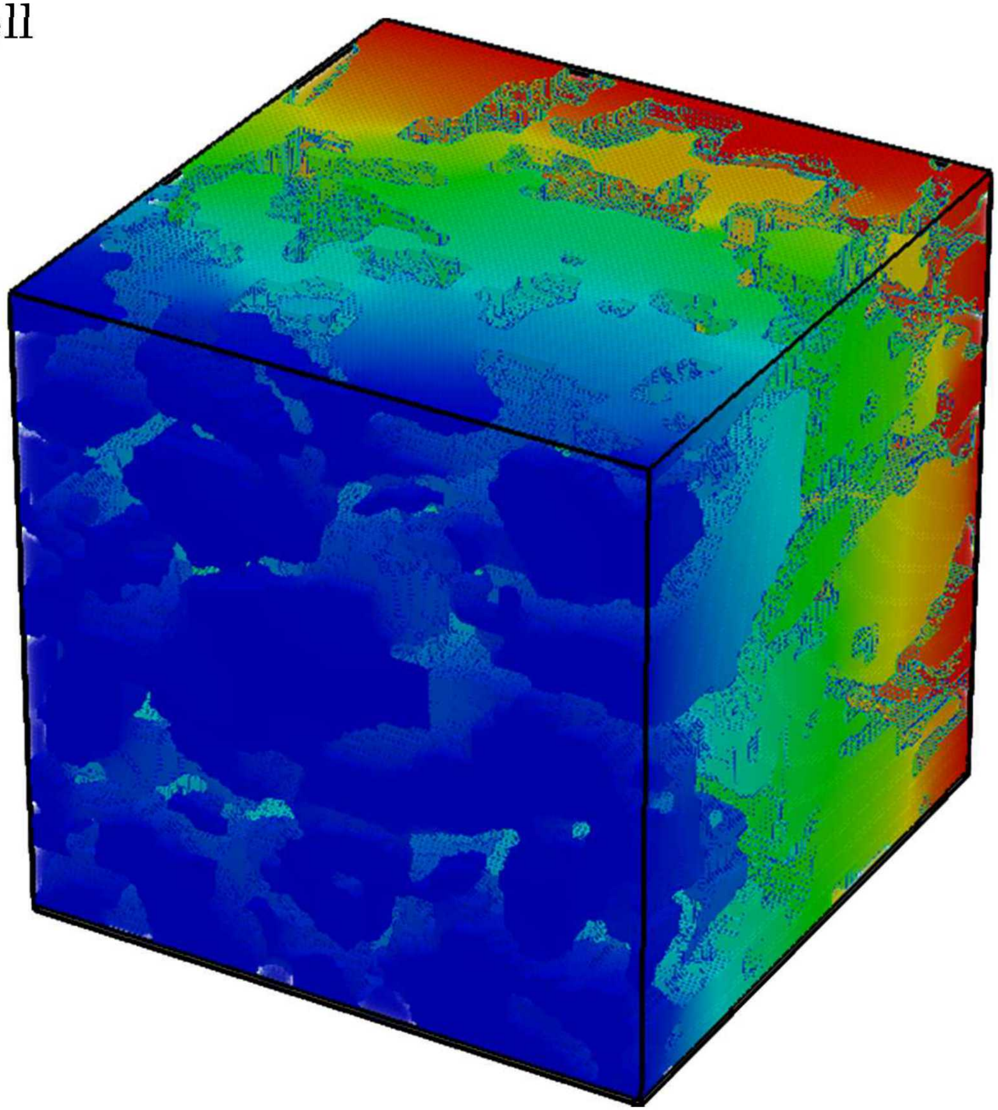
These structures can provide:

1. Porosity

2. Tortuosity

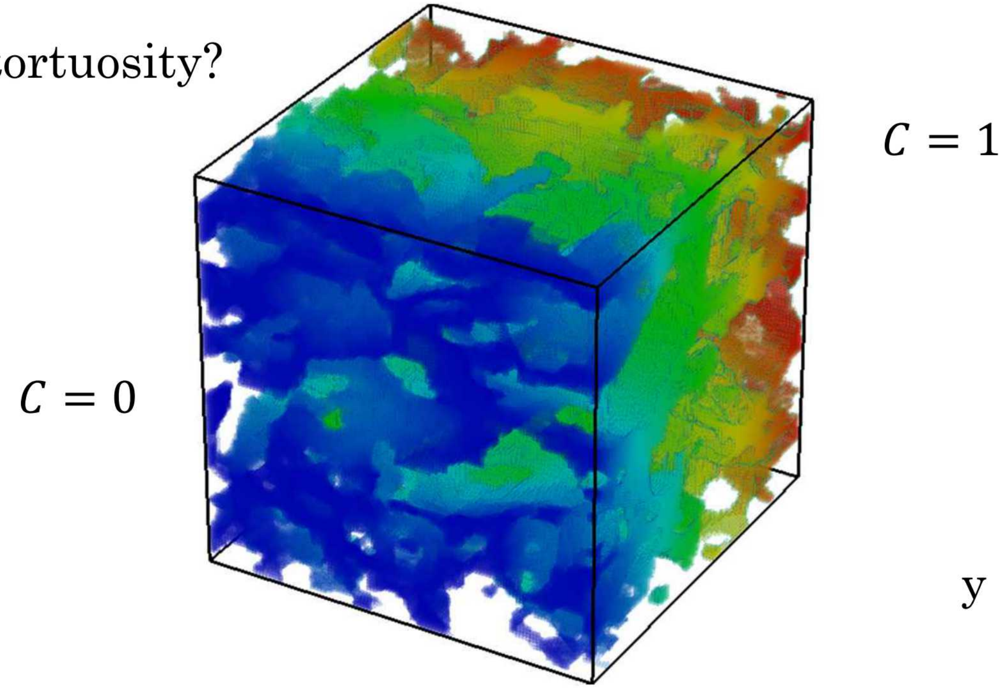
3. Conductivity

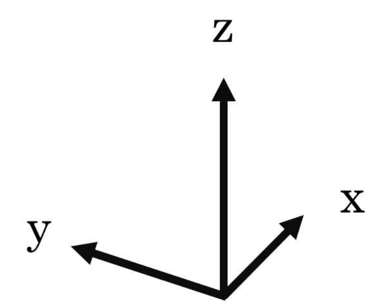
4. Surface Area



Methodology

Q. How to find tortuosity?





Tortuosity

$$\nabla^2 C = 0$$

Boundary Conditions

$$C(x = 0) = 0 \qquad C(x = L_x) = 1$$

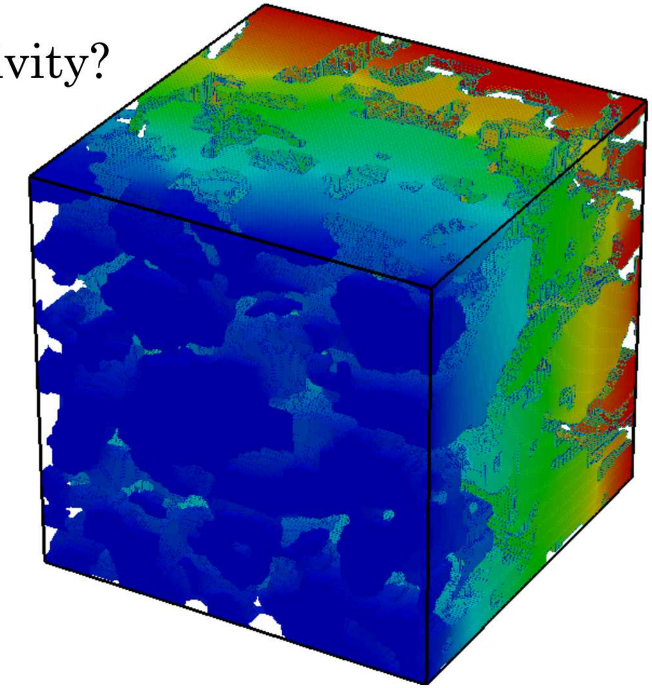
Four planes (y=0, z=0, y=L_y, z=L_z)

$$\frac{\partial C}{\partial n} = 0$$

Mistry, A. et. al. *ACS Appl. Mater. Interfaces,* **2018**, 10, 6317-6326.

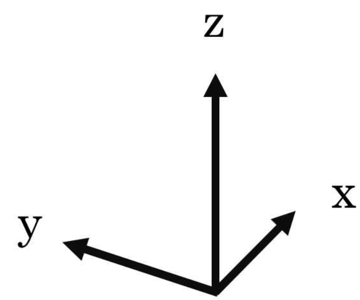
Methodology

Q. How to find conductivity?



$\varphi = 0$

$\varphi = 1$



Conductivity

$$\nabla \cdot (\sigma \nabla \varphi) = 0$$

Boundary Conditions

$$\varphi(x = 0) = 0 \qquad \varphi(x = L_x) = 1$$

Four planes (y=0, z=0, y=L_y, z=L_z)

$$\frac{\partial \varphi}{\partial n} = 0$$

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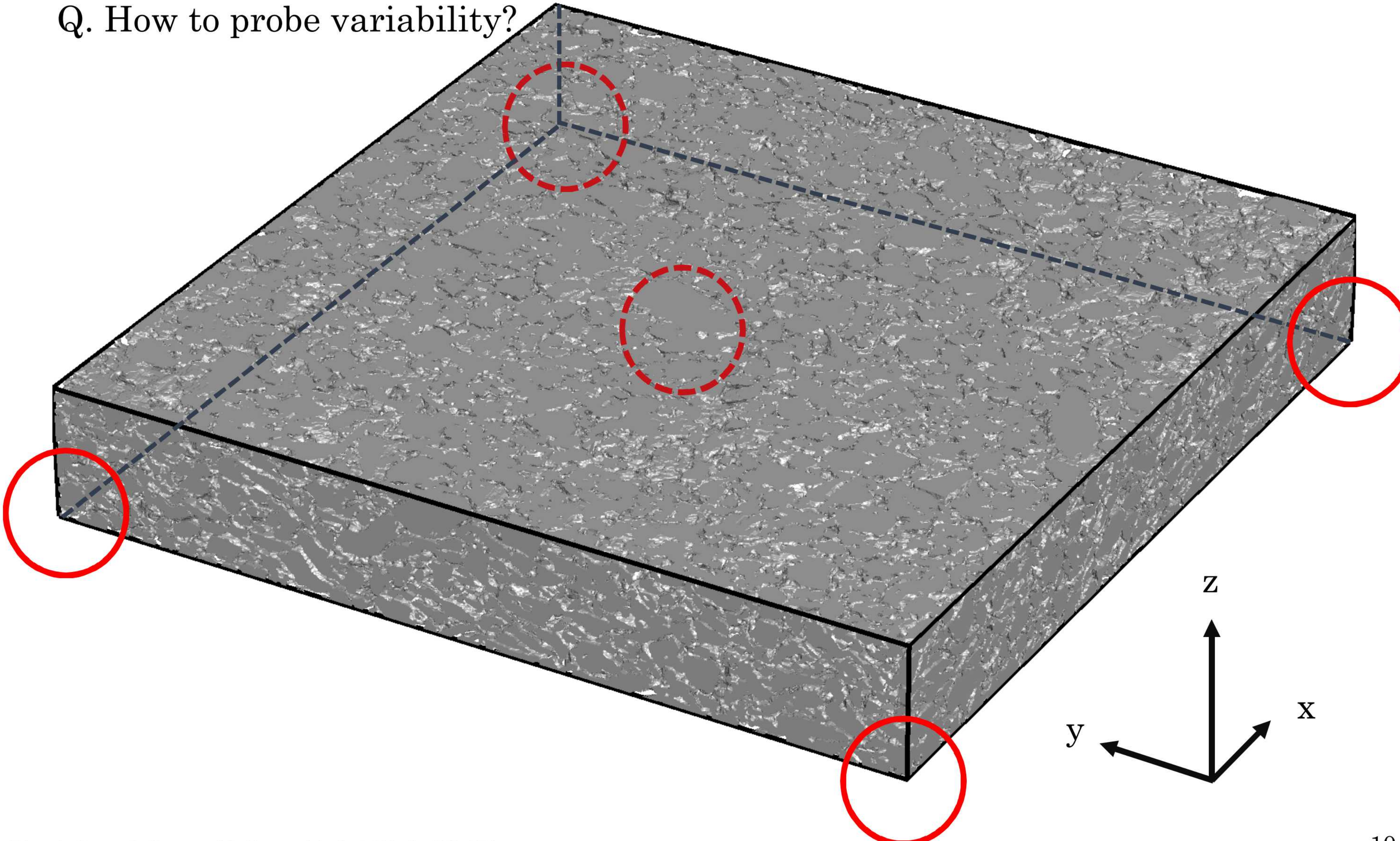
Methodology

Q. How to probe variability?



Pietsch, P. et. al. *Sustainable Energy Fuels,* **2018**, 2, 598-605.

Methodology

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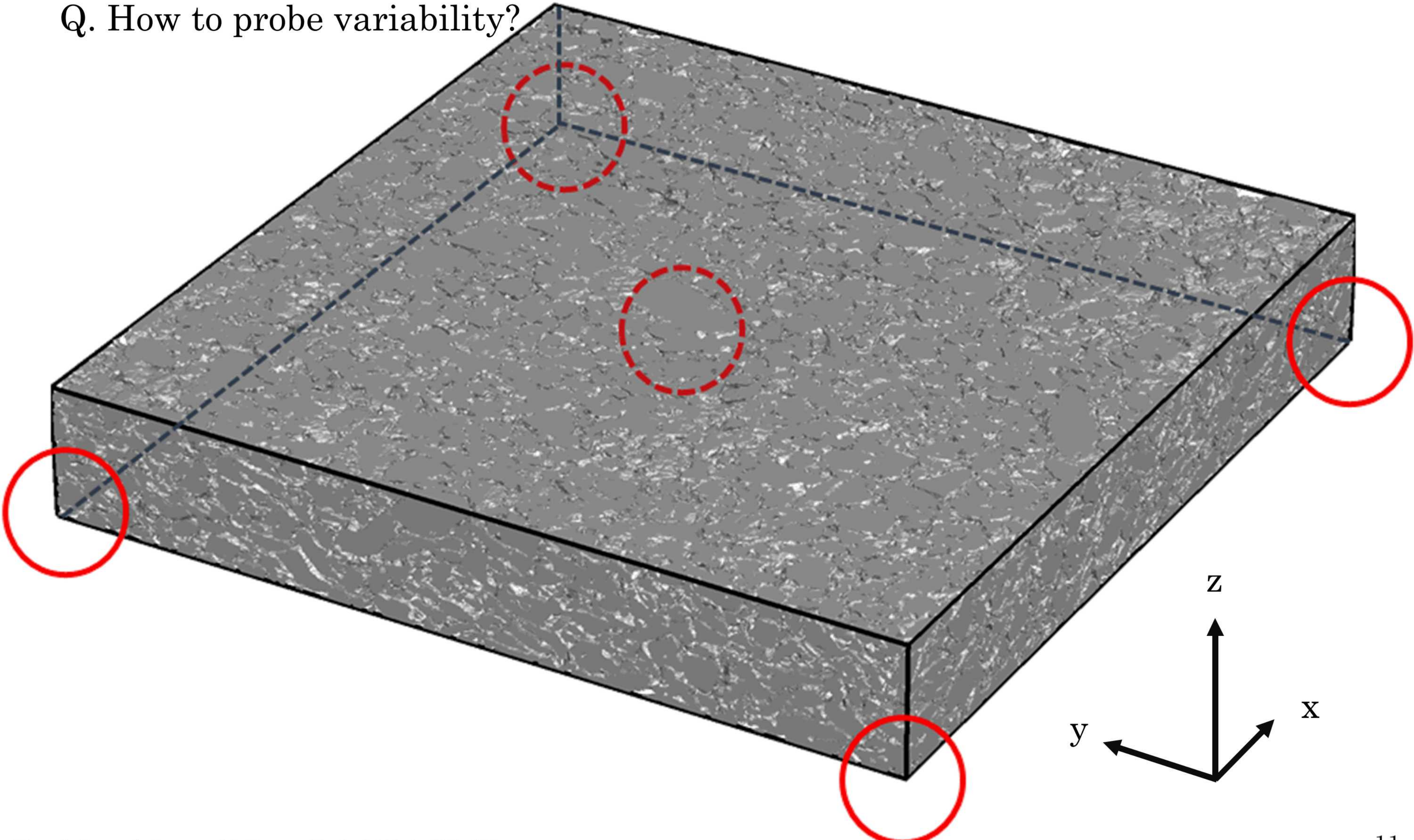

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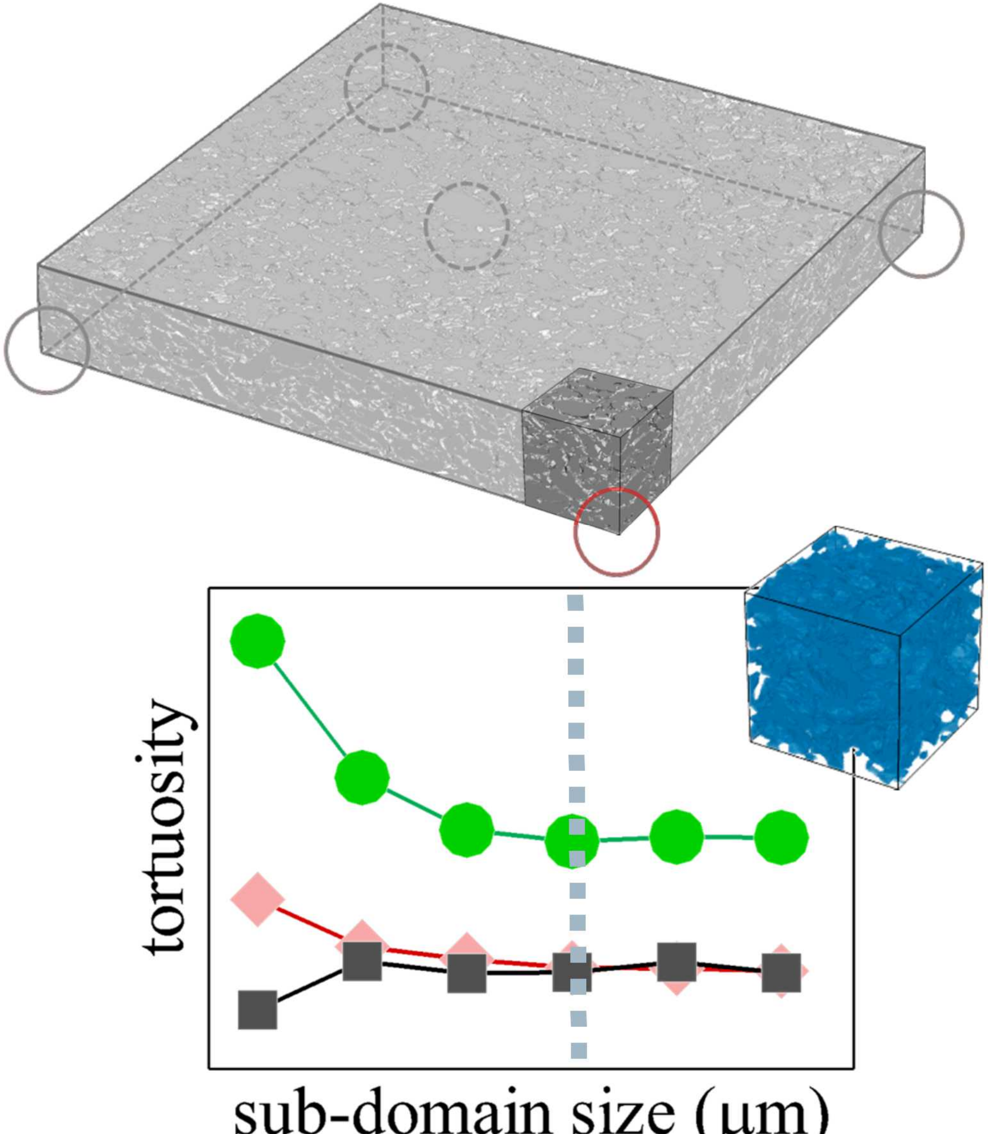

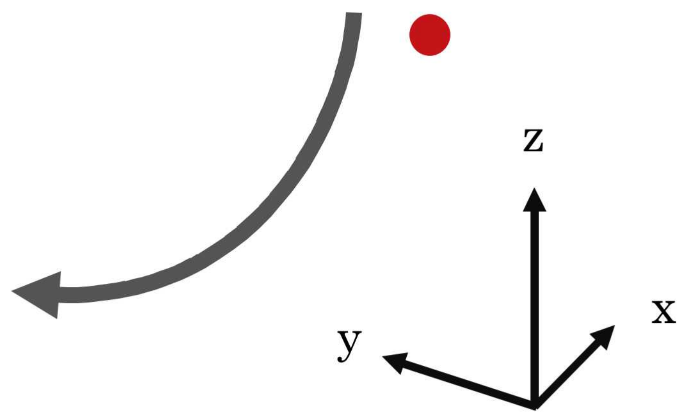

Pietsch, P. et. al. *Sustainable Energy Fuels,* **2018**, 2, 598-605.

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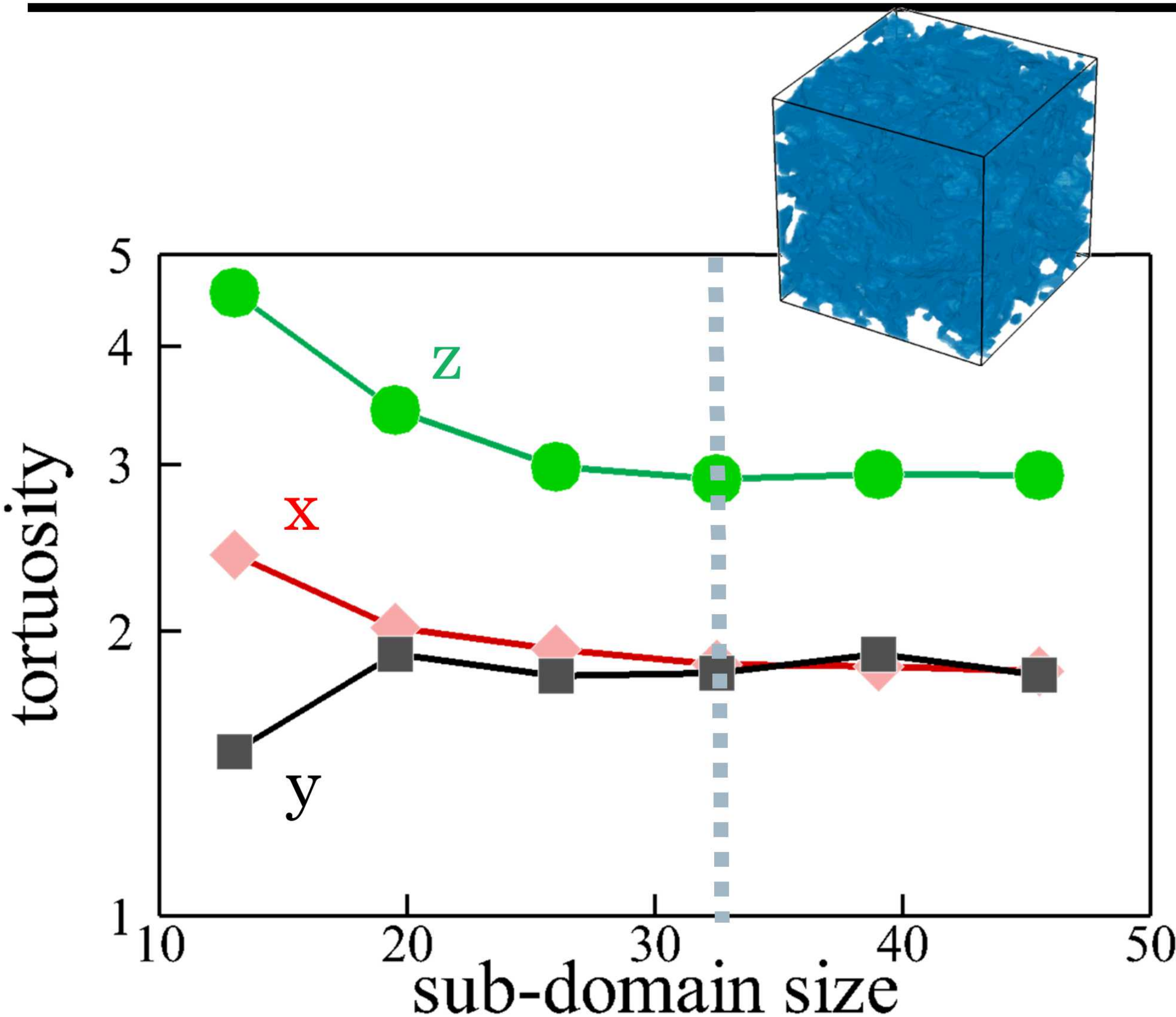


tortuosity variability in *IIIa*

Visual convergence of values as sub-domain size increases.

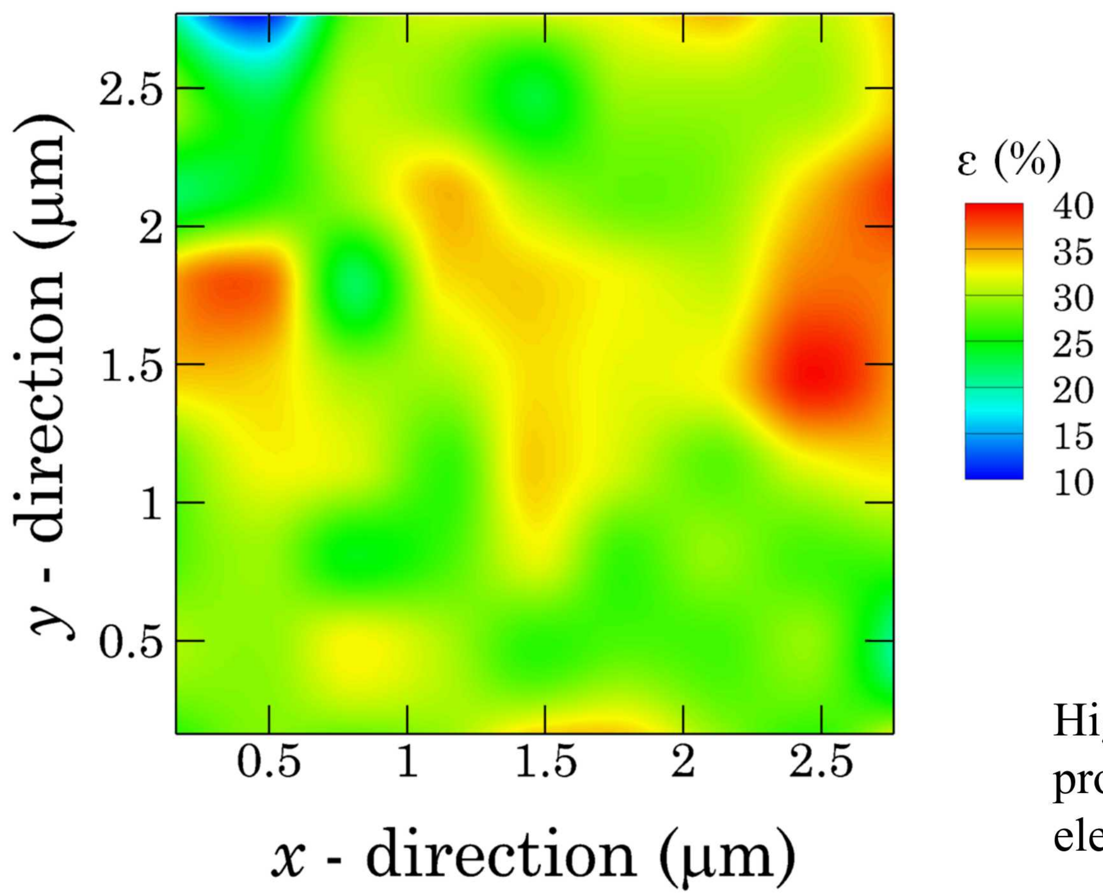
Choosing the smallest value where visual convergence occurs among all nodes.

This value can then be used to probe spatial variability.

Coker, D. A. et. al. *Journal of Applied Physics*, **1995,** *77*(12), 6087-6099.

Variability Within an Electrode

Q. How can variability be quantified?

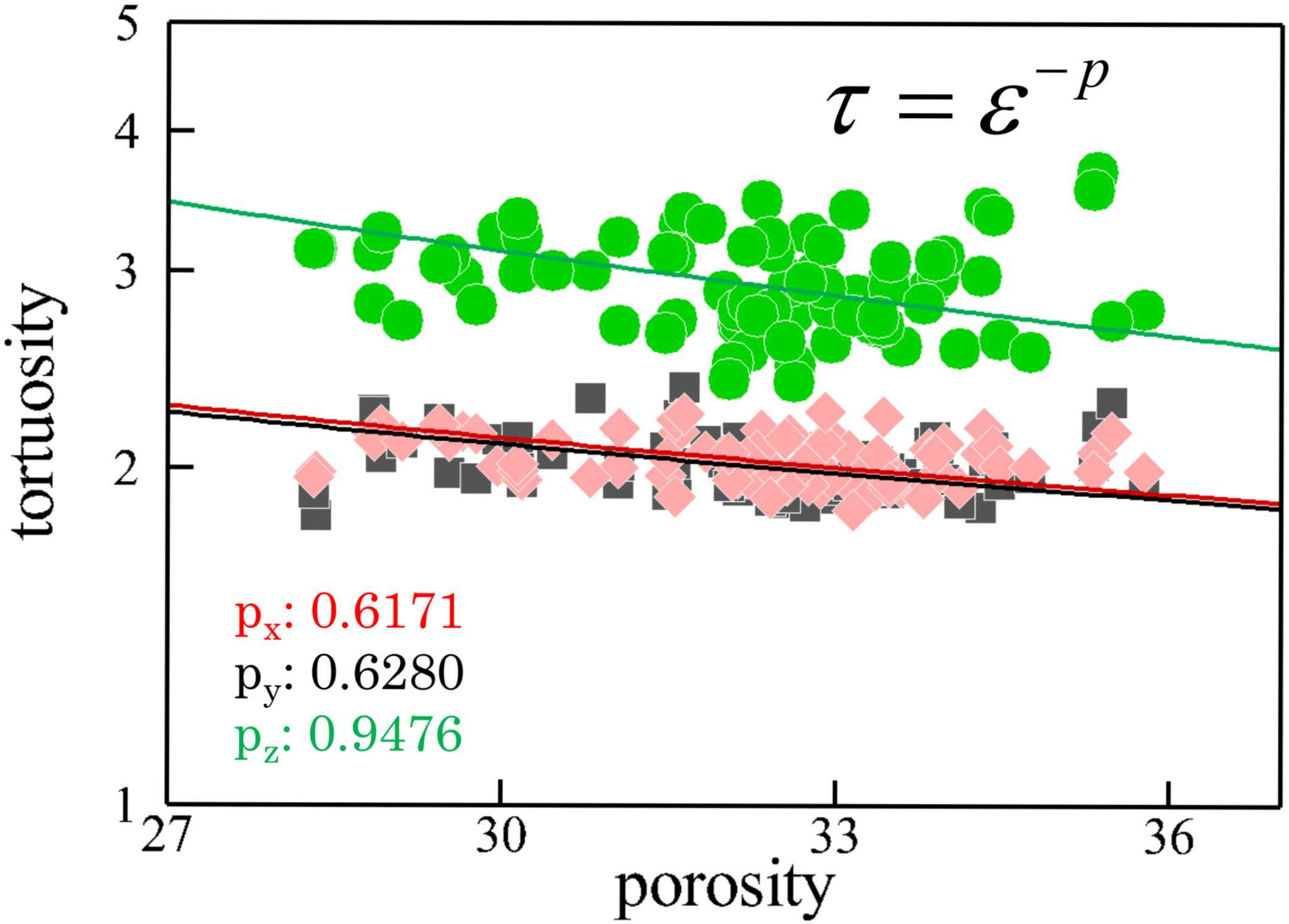


Porosity (%) variation in electrode Ib

Higher local regions of effective properties can be seen in every electrode.

Variability Within an Electrode

Q. How can variability be quantified?



tortuosity variability in IIc

In the limit,
$\varepsilon \to 100\%$
$\tau \to 1$

Variability Within an Electrode

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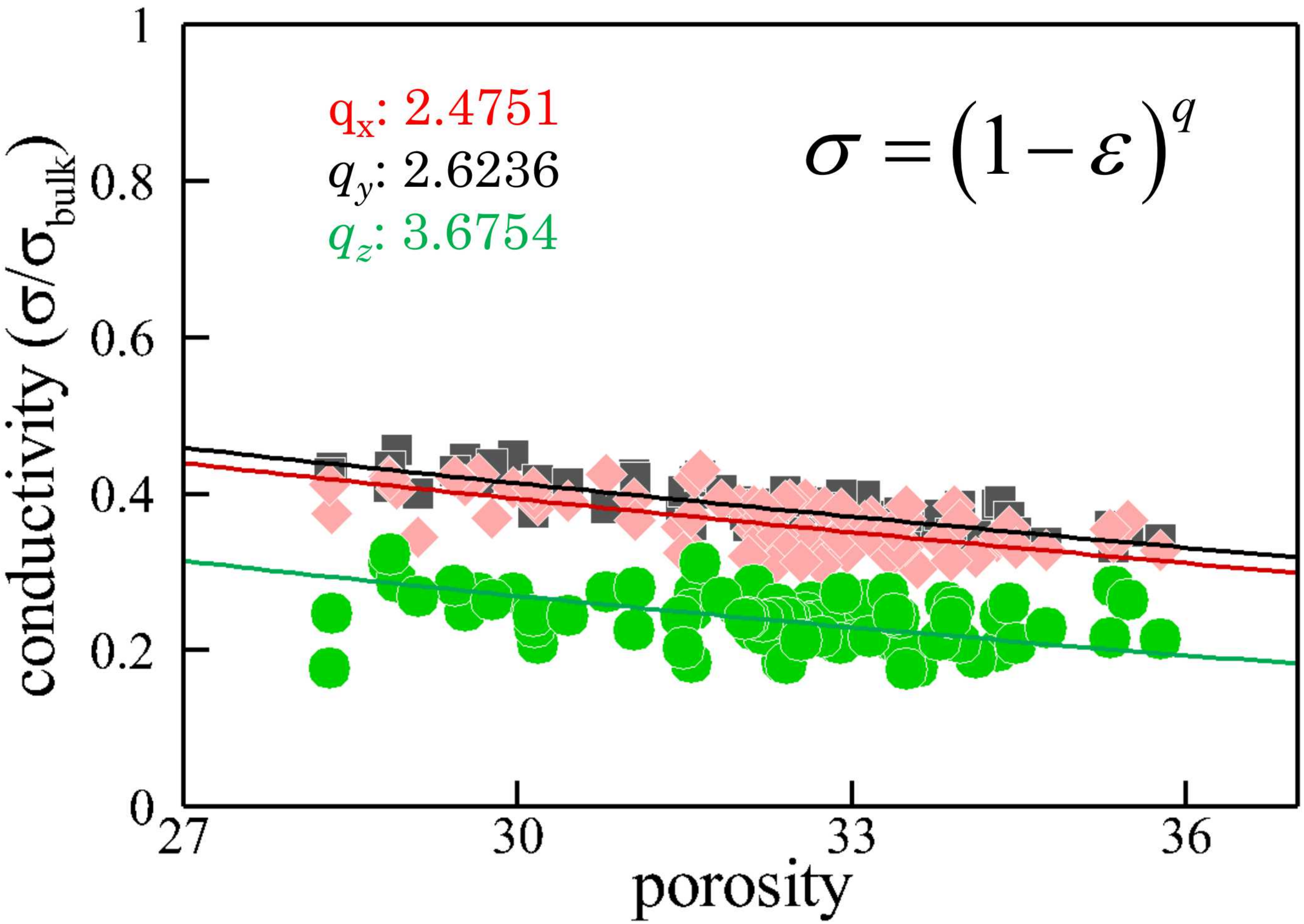


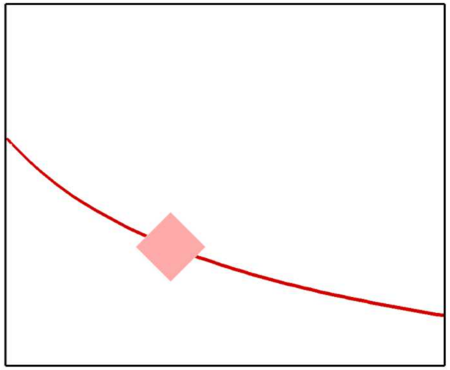
conductivity variability in IIc

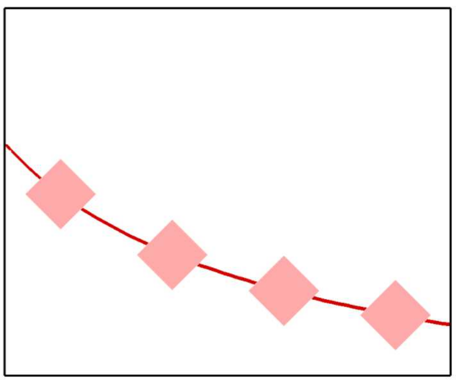
In the limit,

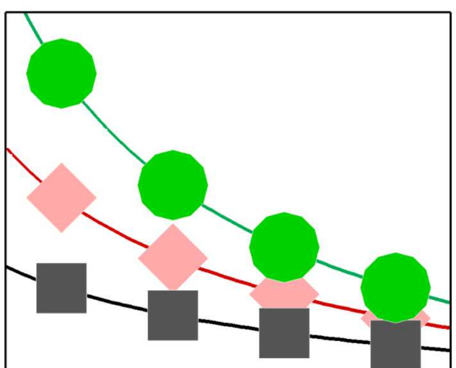
$\varepsilon \rightarrow 0\%$
$\sigma/\sigma_{bulk} \rightarrow 1$

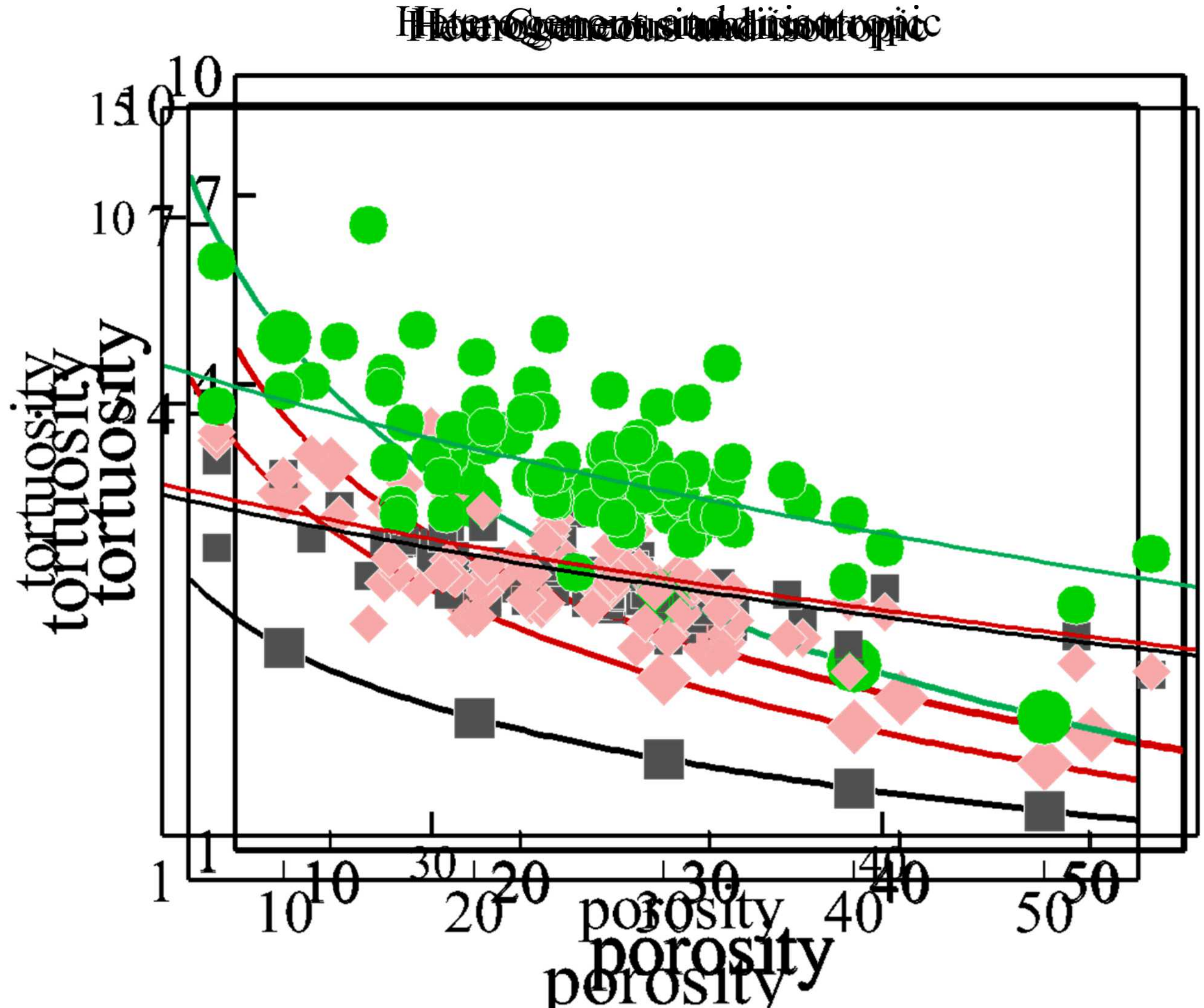
$\varepsilon \rightarrow 100\%$
$\sigma/\sigma_{bulk} \rightarrow 0$

Variability Within an Electrode



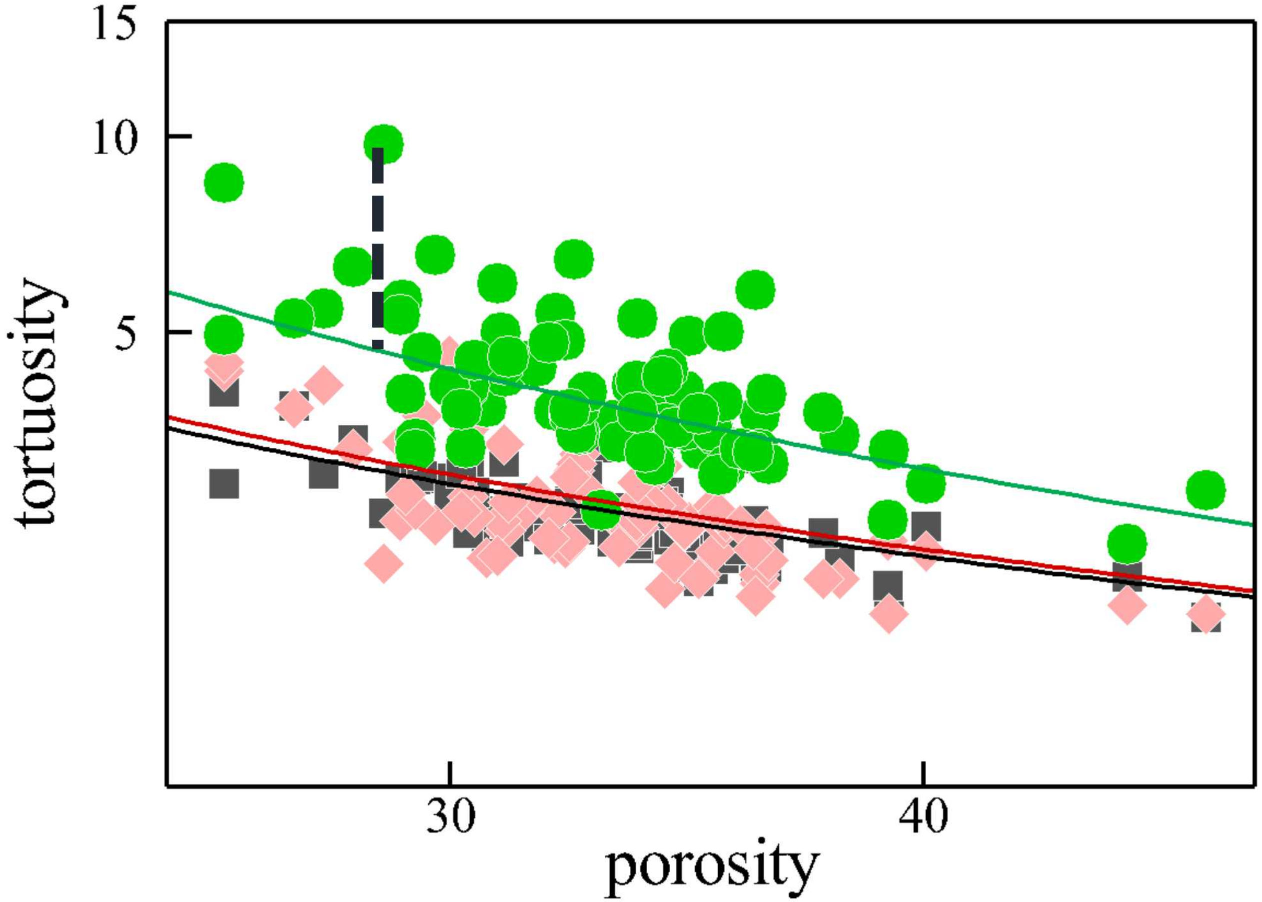






Variability Within an Electrode

Deviation, δ



tortuosity variability in Ic

Individual δ values for each point

$$\delta_\tau = \frac{\tau_{measured} - \tau_{fitted}}{\tau_{fitted}}$$

These normalized points now act as another data point

This can be seen as the internal RVE variability.

Particle Characterization

By implementing a 3D Sobel operator we can apply this to three dimensions for our particles.

1	2	1
2	4	2
1	2	1

$h_z(:,:,-1)$

0	0	0
0	0	0
0	0	0

$h_z(:,:,0)$

-1	-2	-1
-2	-4	-2
-1	-2	-1

$h_z(:,:,1)$

$$G_z = h_z * I$$

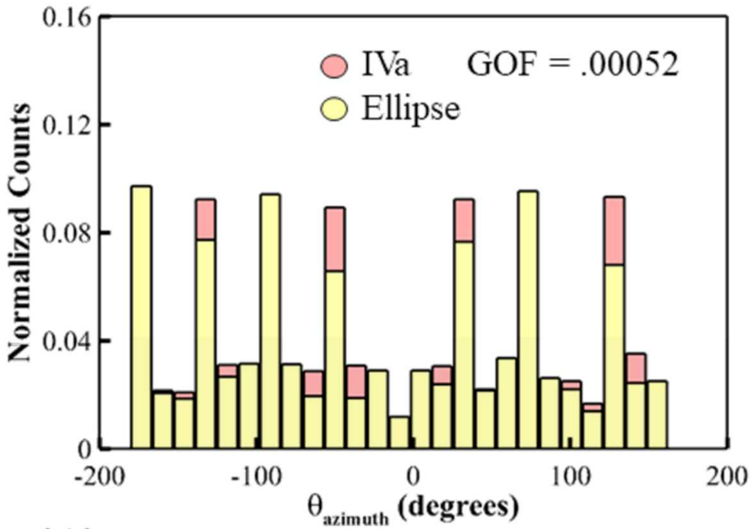
$$G_{mag} = \sqrt{G_y^2 + G_x^2 + G_z^2}$$

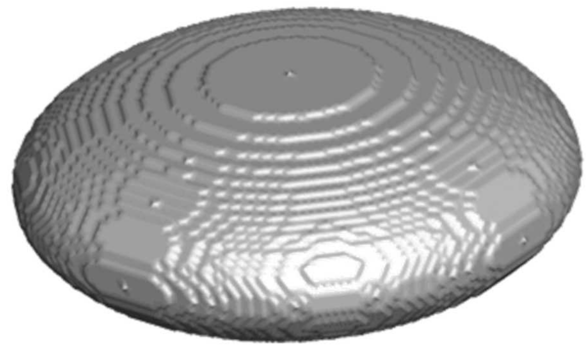
$$\phi = \arctan\left(\frac{G_z}{\sqrt{G_x^2 + G_y^2}}\right)$$

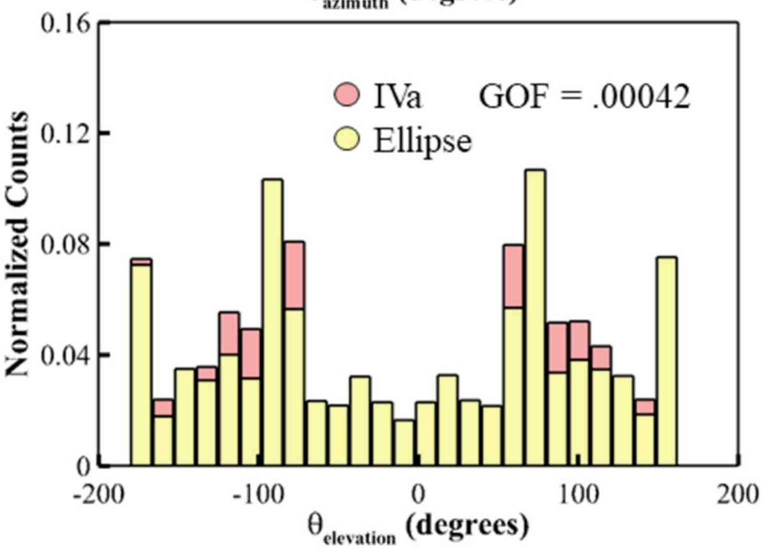
$$\theta = \arctan\left(\frac{G_y}{G_x}\right)$$

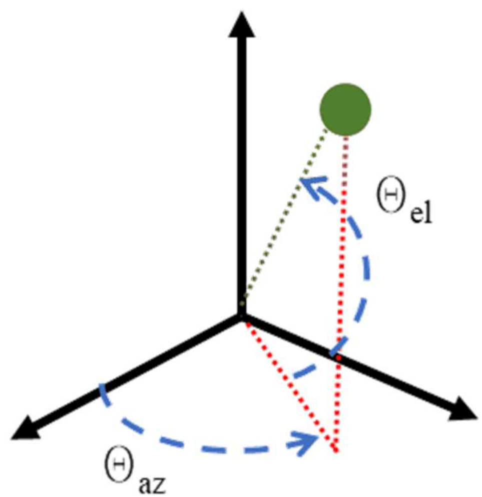
Particle Characterization

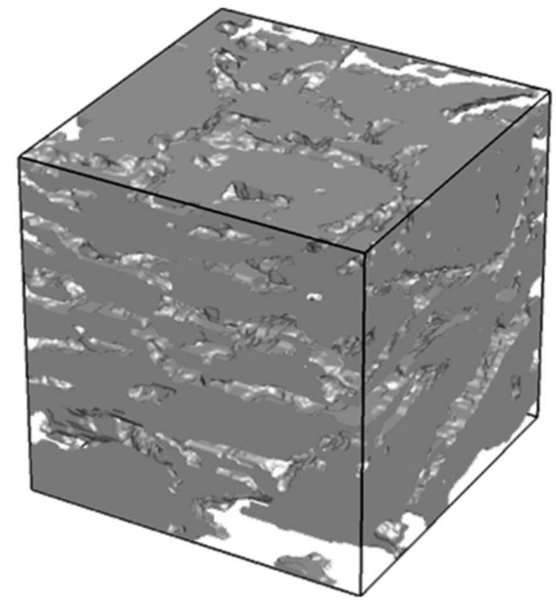
By varying ellipsoid parameters we can find reference particles to help describe the electrode.



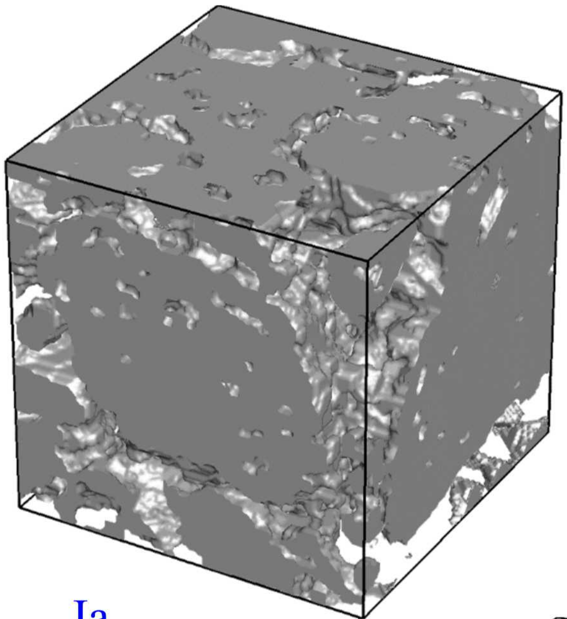




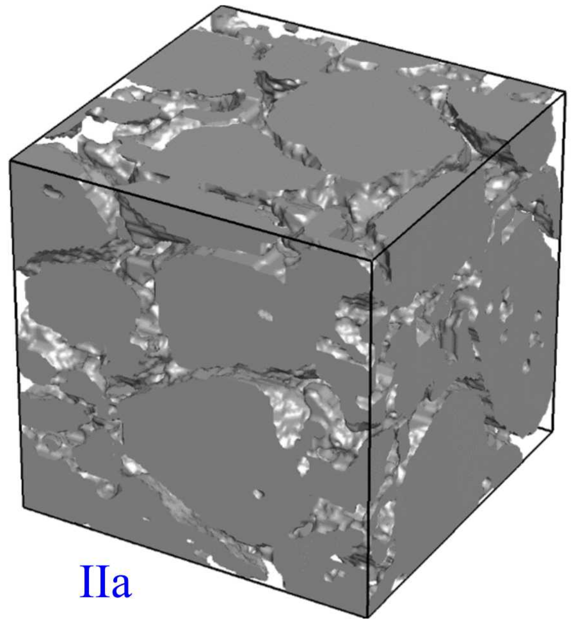




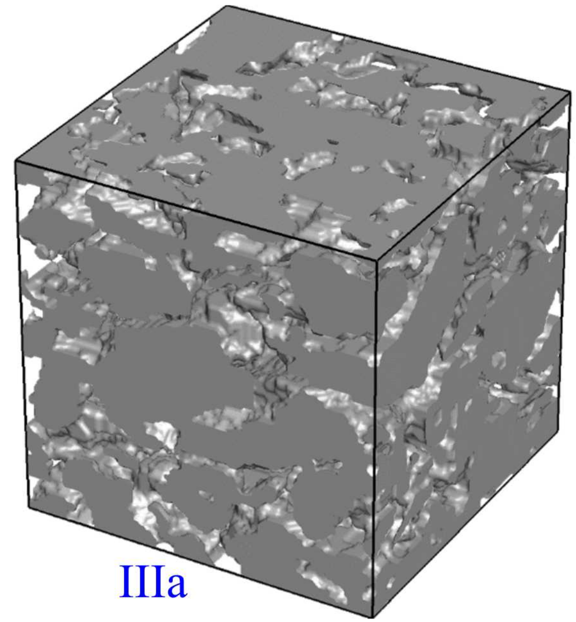
Particle Morphology Effects



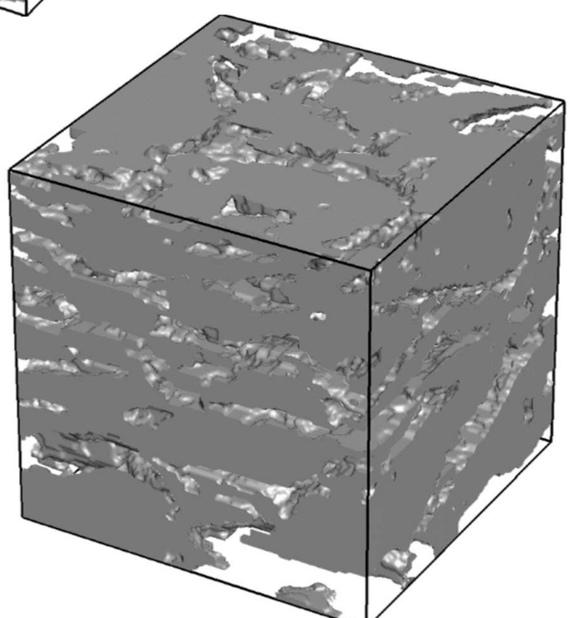
Ia



IIa



IIIa

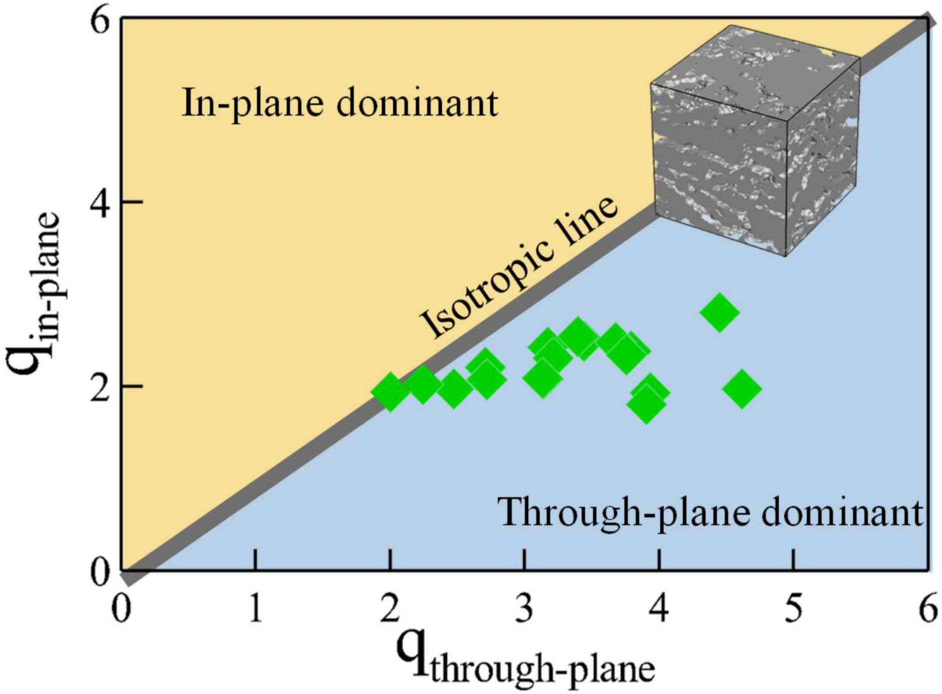


IVa

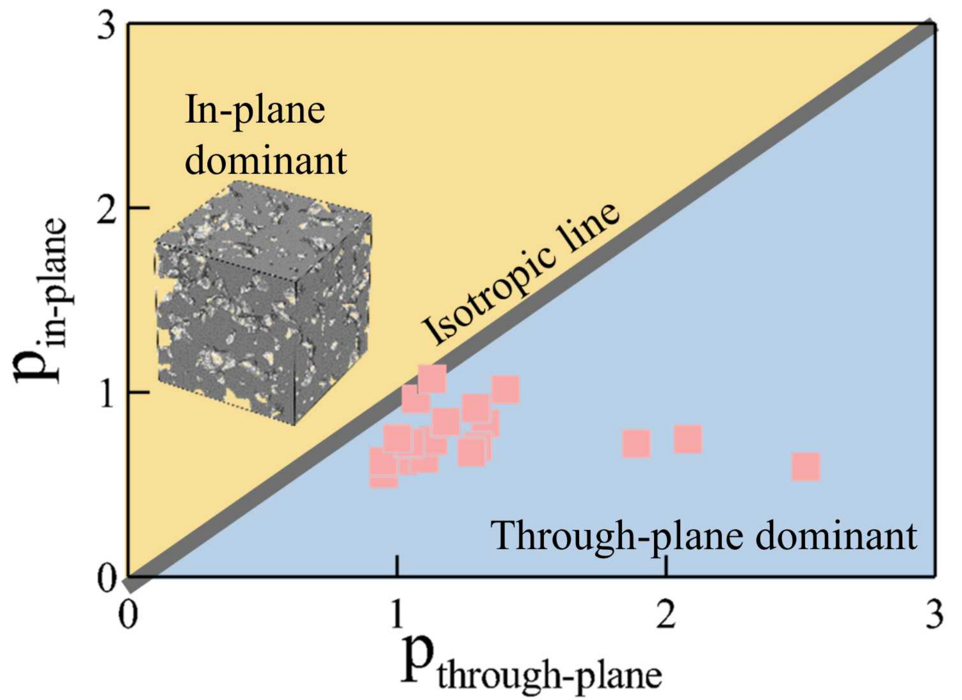
Q. How does differing morphologies influence effective properties?

Particle Morphology Effects

$\sigma = (1-\epsilon)^q$



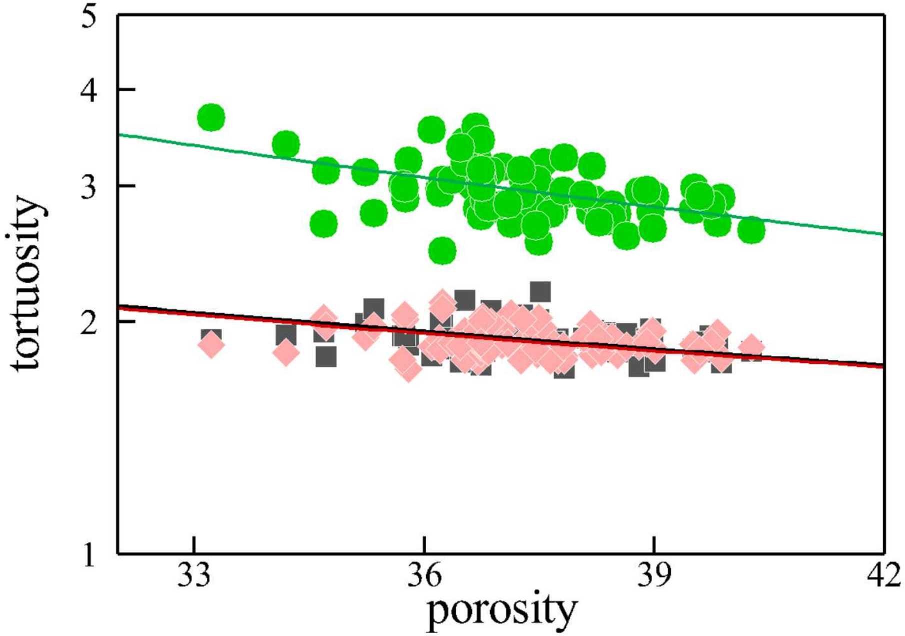
$\tau = \epsilon^{-p}$



Many electrodes show varying degrees of anisotropies

Particle Morphology Effects

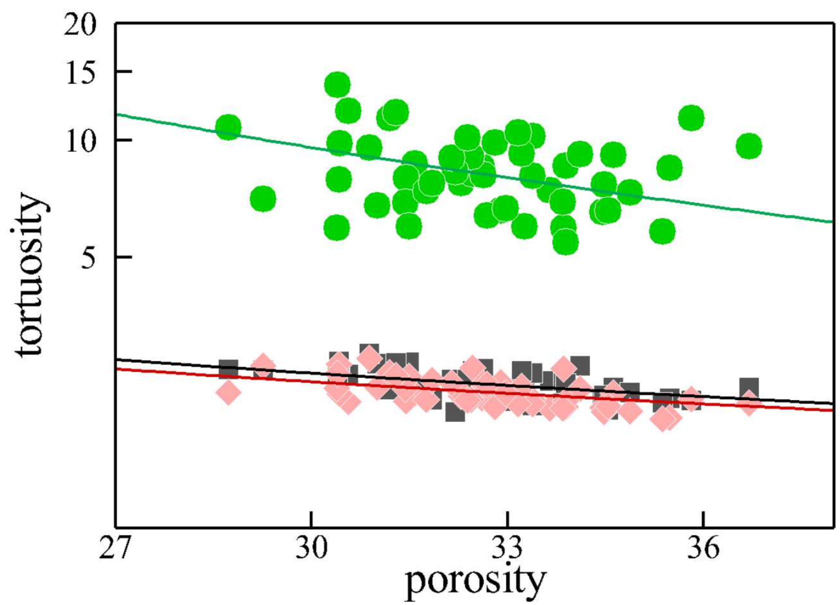
Q. What causes these variations in delta?



tortuosity variability in IIIa

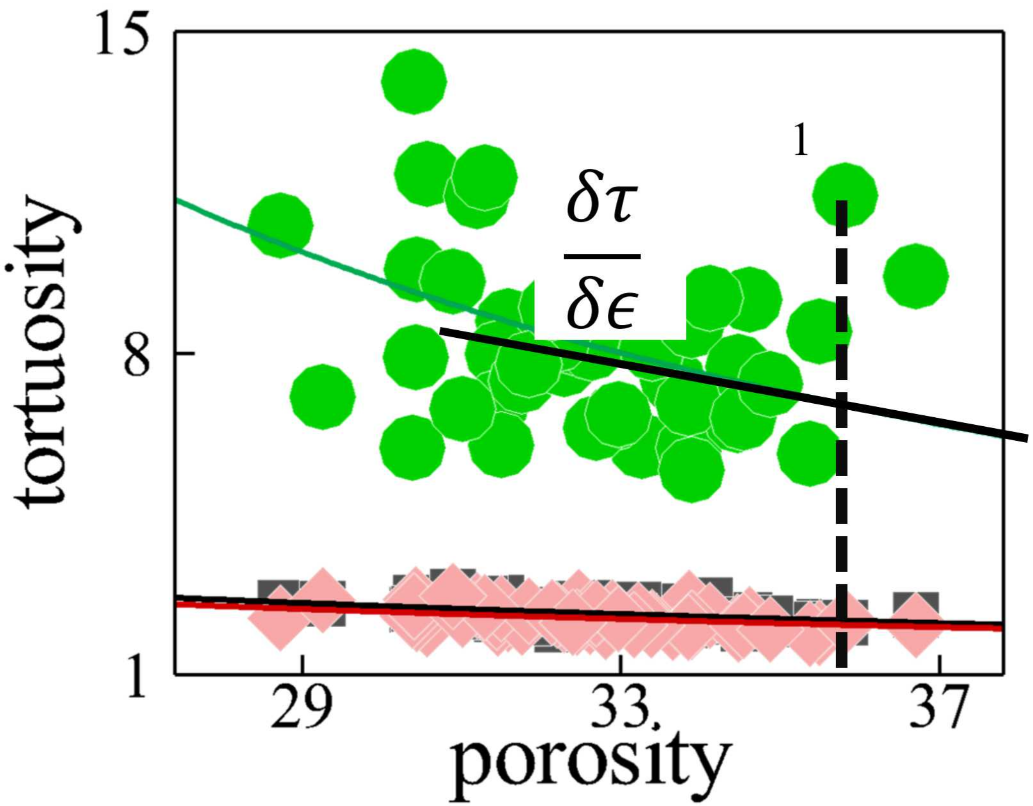
A directional correlation and proportionality to $\frac{dZ}{d\epsilon}$ is observed.

Electrode	$\overline{\delta_{\tau x}}$	$\overline{\delta_{\tau y}}$	$\overline{\delta_{\tau z}}$
IIIc	0.0331	0.0331	0.0543
IVb	0.0586	0.0602	0.1812



tortuosity variability in IVb

Particle Morphology Effects



$\frac{\delta\tau}{\delta\epsilon}$ represents the slope of the tortuosity at a given porosity value of the designated curve.

$$\tau = \epsilon^{-p}$$

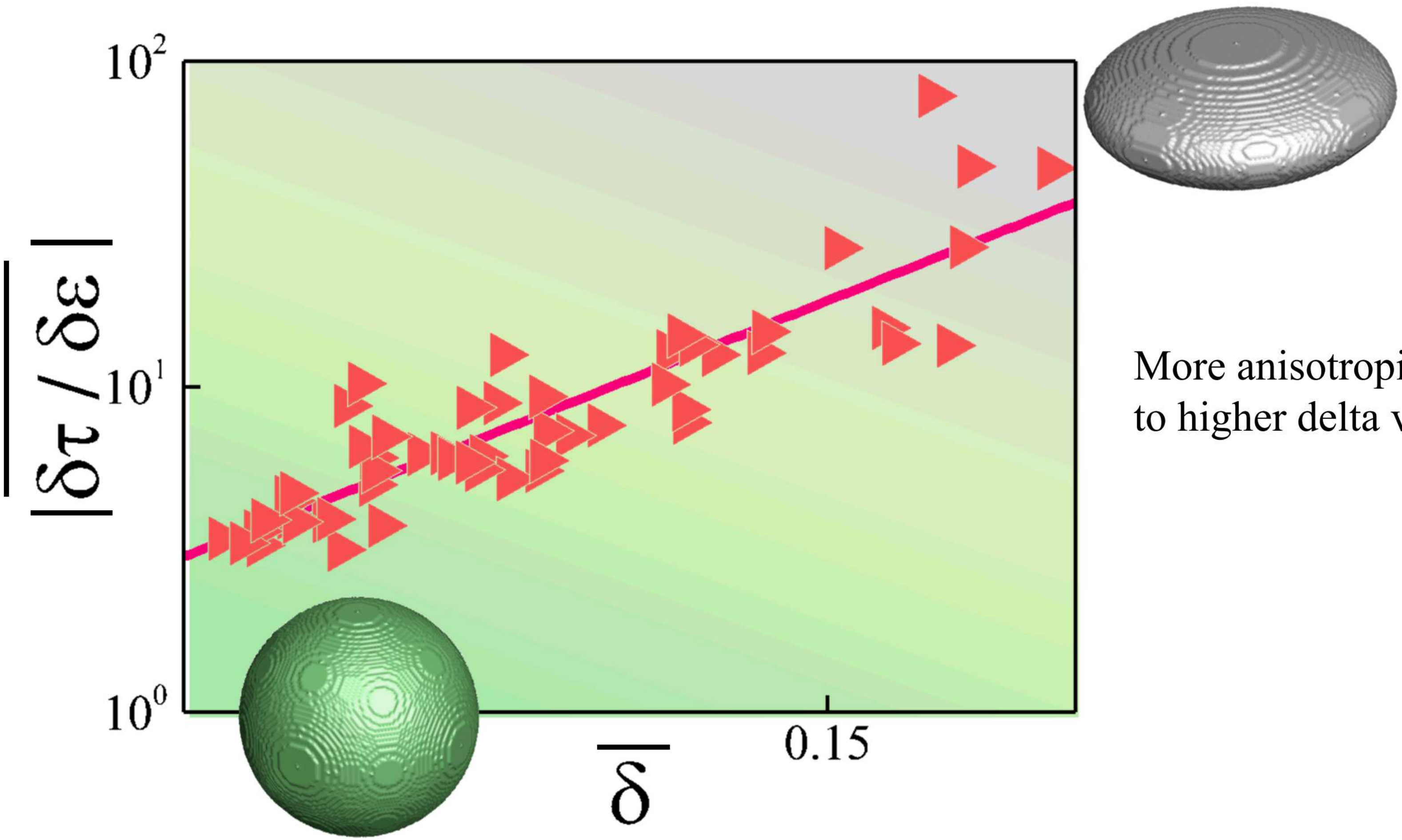
$$\frac{\delta\tau}{\delta\epsilon} = -p\epsilon^{-p-1}$$

$\tau \rightarrow tortuosity$

$\epsilon \rightarrow porosity$

$p \rightarrow exponential\ to\ curve\ fit$

Particle Morphology Effects

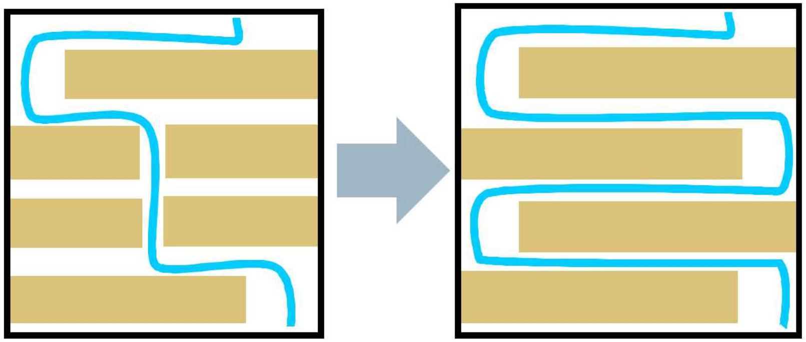


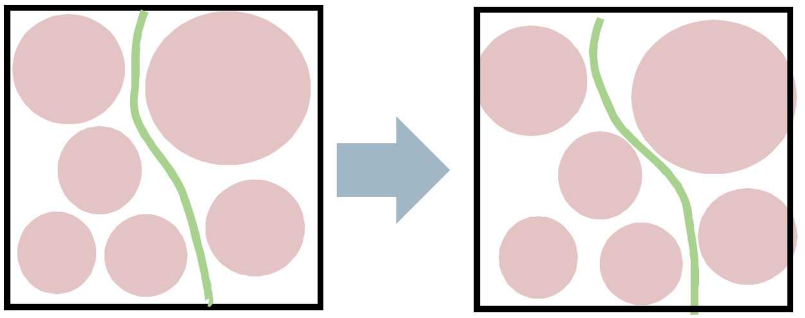
More anisotropic particles lead to higher delta values

$\bar{\delta} \rightarrow mean\ deviation\ of\ RVEs$

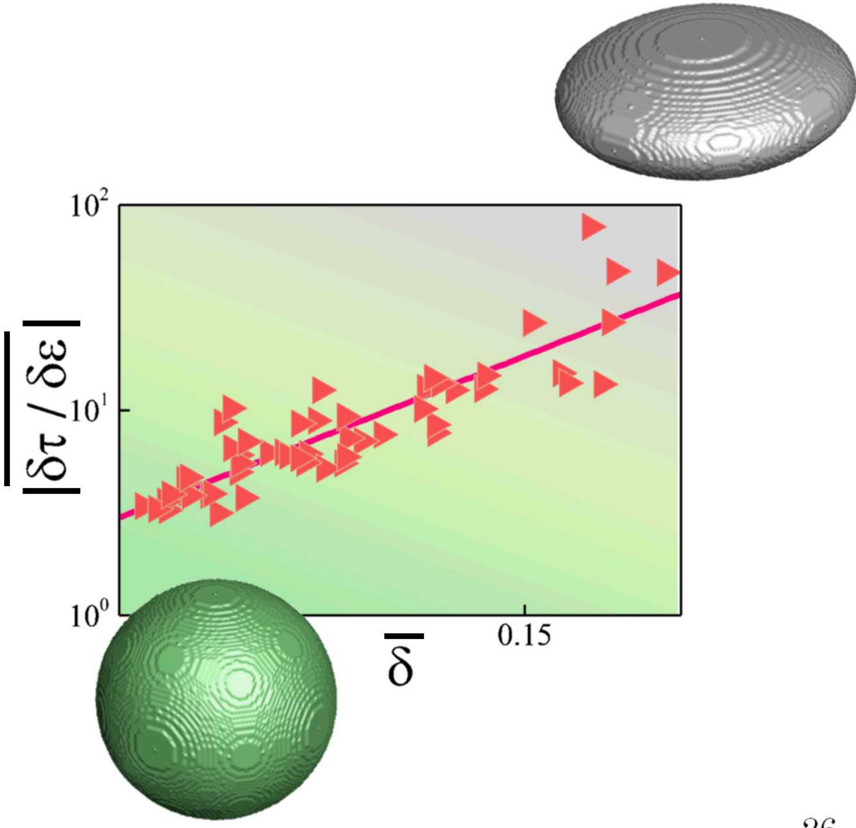
$\left|\frac{\overline{\delta\tau}}{\delta\epsilon}\right| \rightarrow mean\ magnitude\ of\ slope$

Particle Morphology Effects





The sensitive nature of the platelet like particles is mirrored in the delta reliance plot (below).



Porosity is held constant in every case.

- With small changes in particle locations large tortuosity changes are seen.

Conclusion

- Successful screening method that can compare a multitude of morphologies without segmenting particles.
- Many morphologies exhibit anisotropy given varying morphologies.
- Internal RVE tortuous dispersion can arise from particle morphology where as conductivity does not show the same.

Acknowledgements

Funding from Sandia National Lab

Scott Roberts and team

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Thank You!