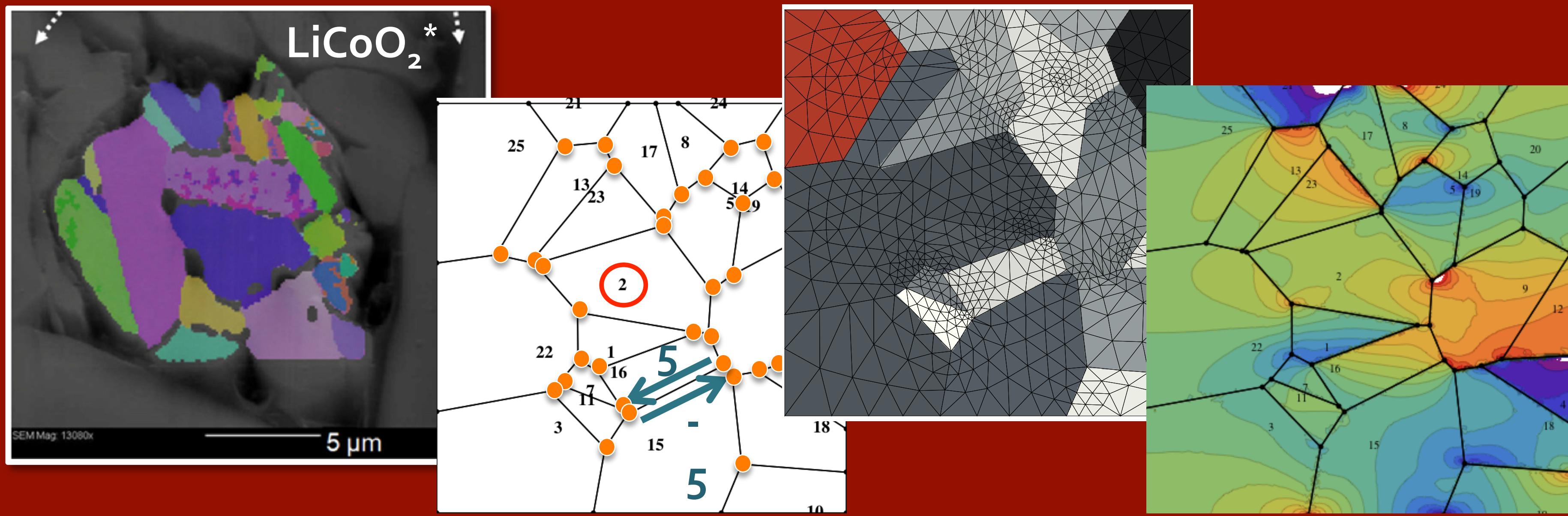


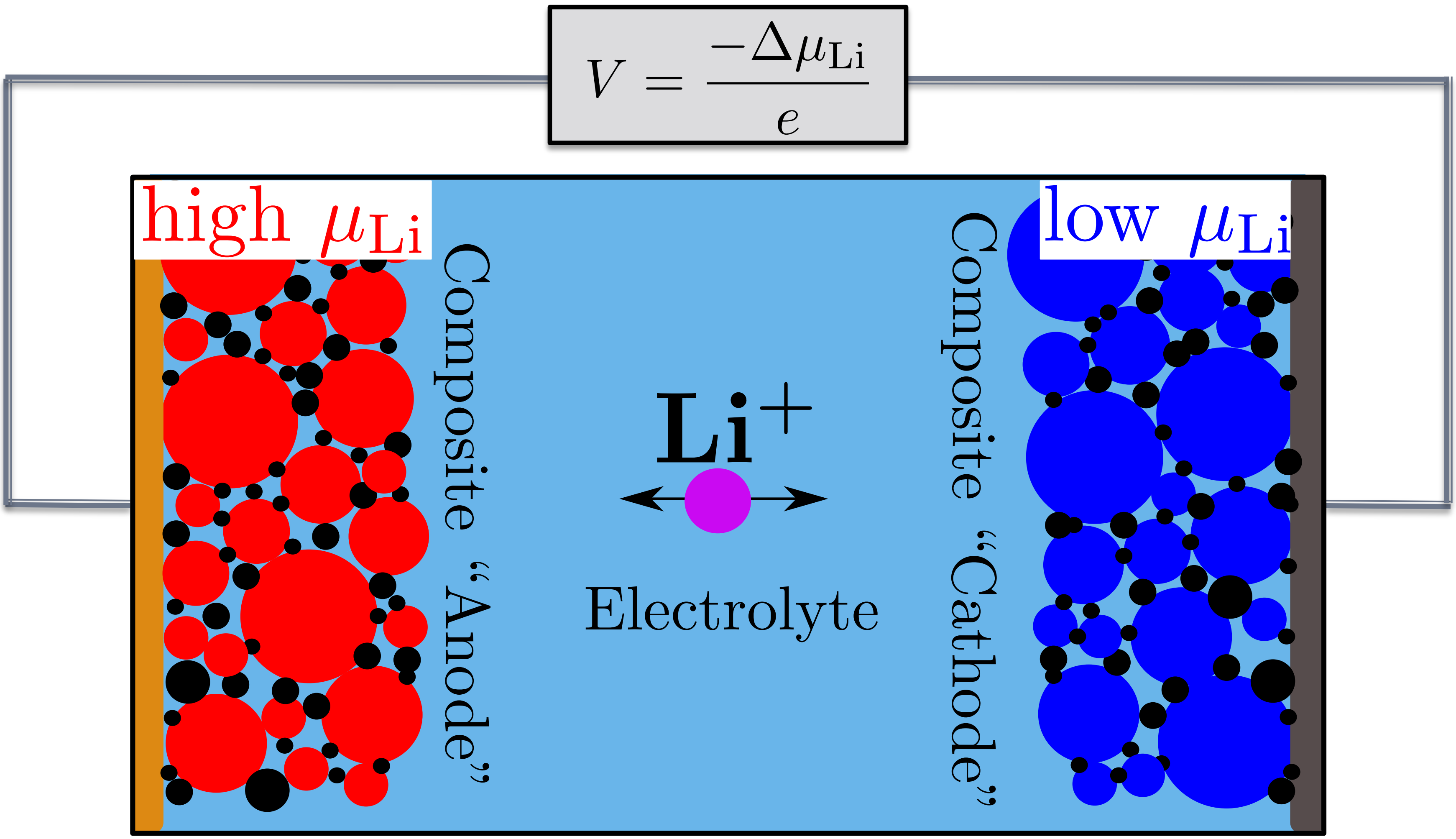
Electrochemical Shock in Polycrystalline Lithium Storage Materials

William H. Woodford, Yet-Ming Chiang, and W. Craig Carter
Department of Materials Science and Engineering, MIT

"Whiskers, Wires, and Walls" Workshop – NIST
30 September 2010

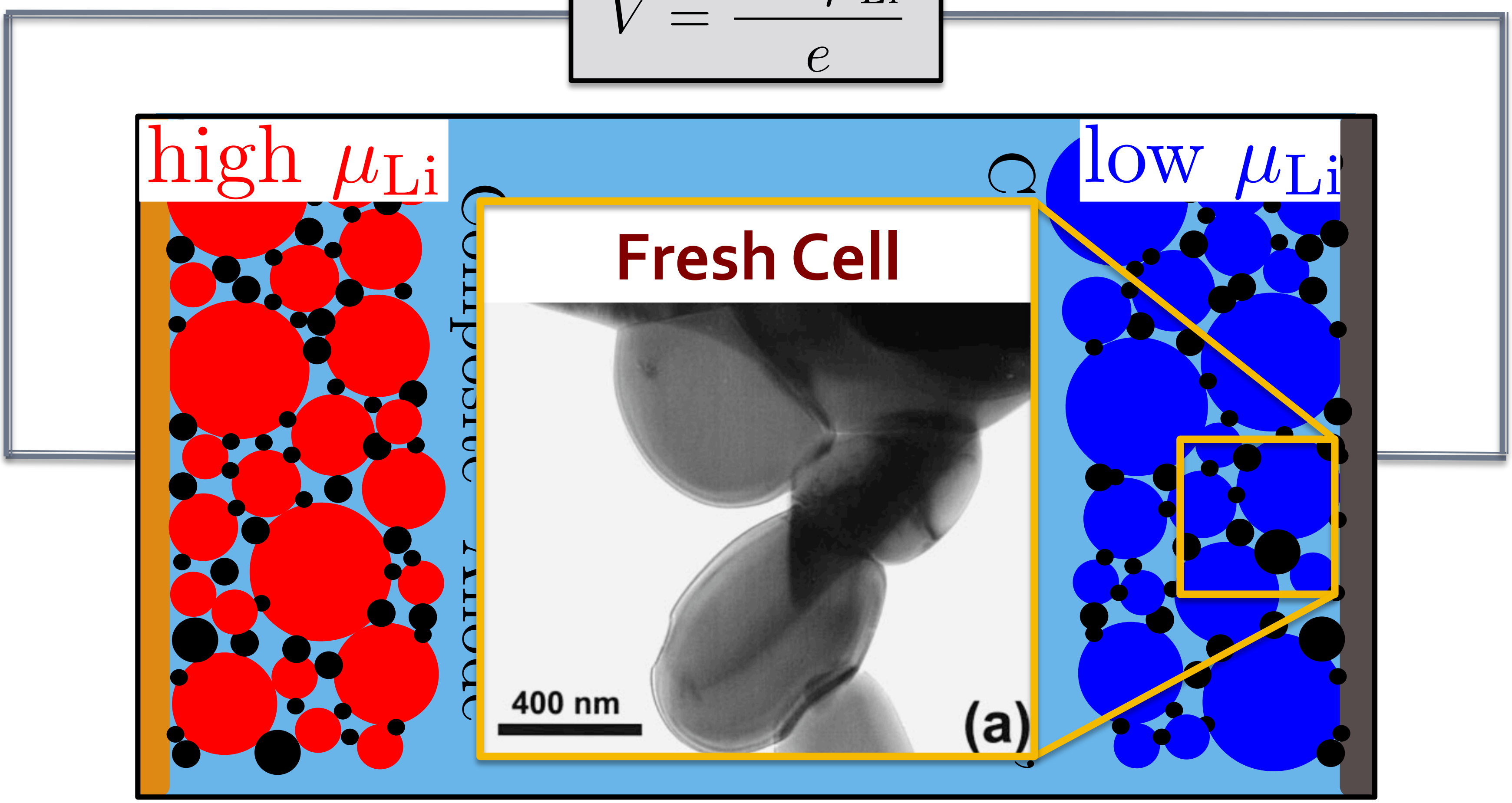
*J.R. Wilson, et al., *J. Power Sources* (2010), doi:10.1016/j.jpowsour.2010.04.066

Lithium-ion Batteries – Operating Principles



Lithium-ion Batteries – Operating Principles

$$V = \frac{-\Delta \mu_{\mathrm{Li}}}{e}$$



H. Wang, Y.-I. Jang, B. Huang, D. Sadoway, and Y.-M. Chiang, *J. Electrochem. Soc.*, **146** (2) 473-480 (1999).

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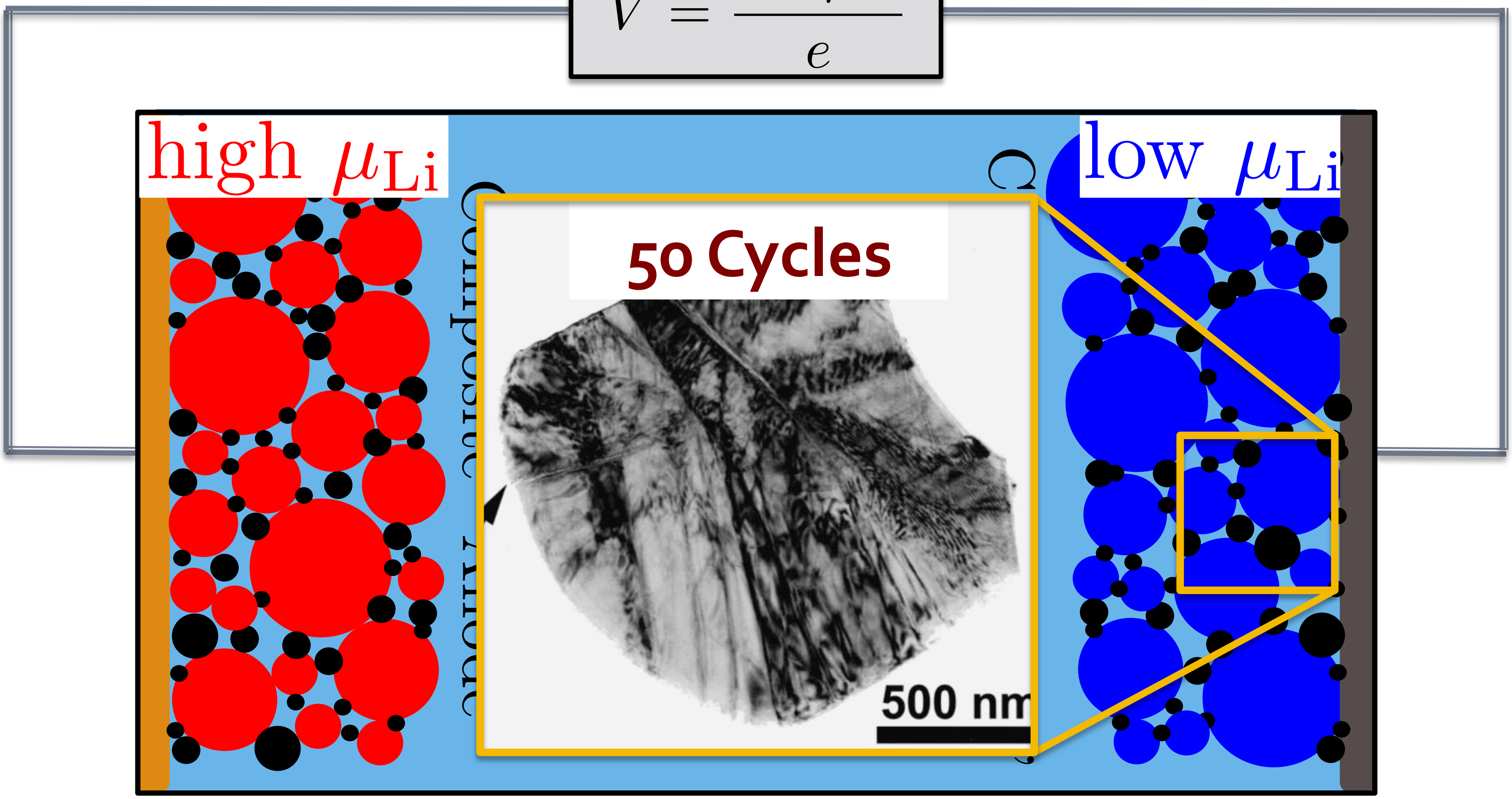


H. Wang, Y.-I. Jang, B. Huang, D. Sadoway, and Y.-M. Chiang, *J. Electrochem. Soc.*, **146** (2) 473-480 (1999).

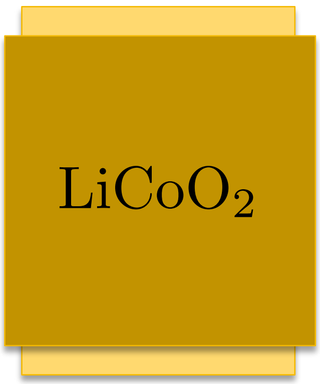
Most Materials Change Shape with Varying Lithium Content

$LiCoO_2$

$LiMn_2O_4$

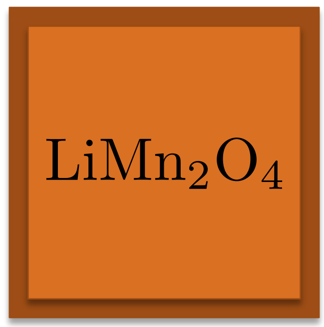
Si

Most Materials Change Shape with Varying Lithium Content



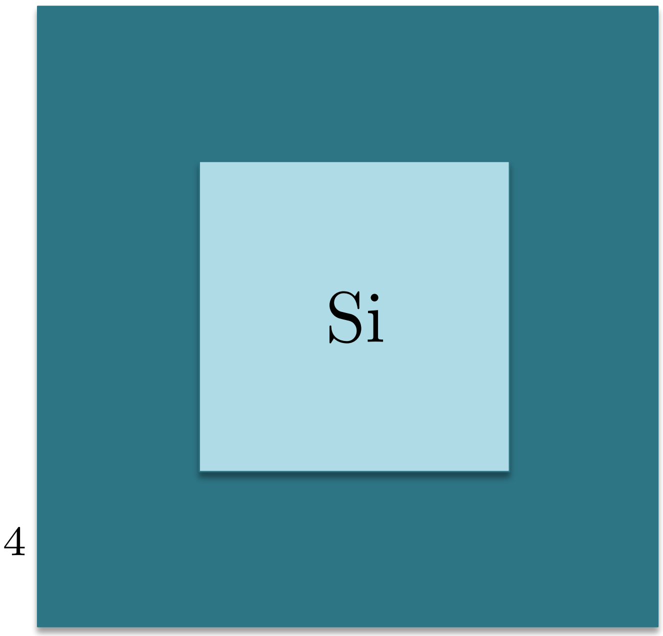
$LiCoO_2 \rightarrow Li_{0.5}CoO_2$

$\Delta V = +1.9\%$



$LiMn_2O_4 \rightarrow Mn_2O_4$

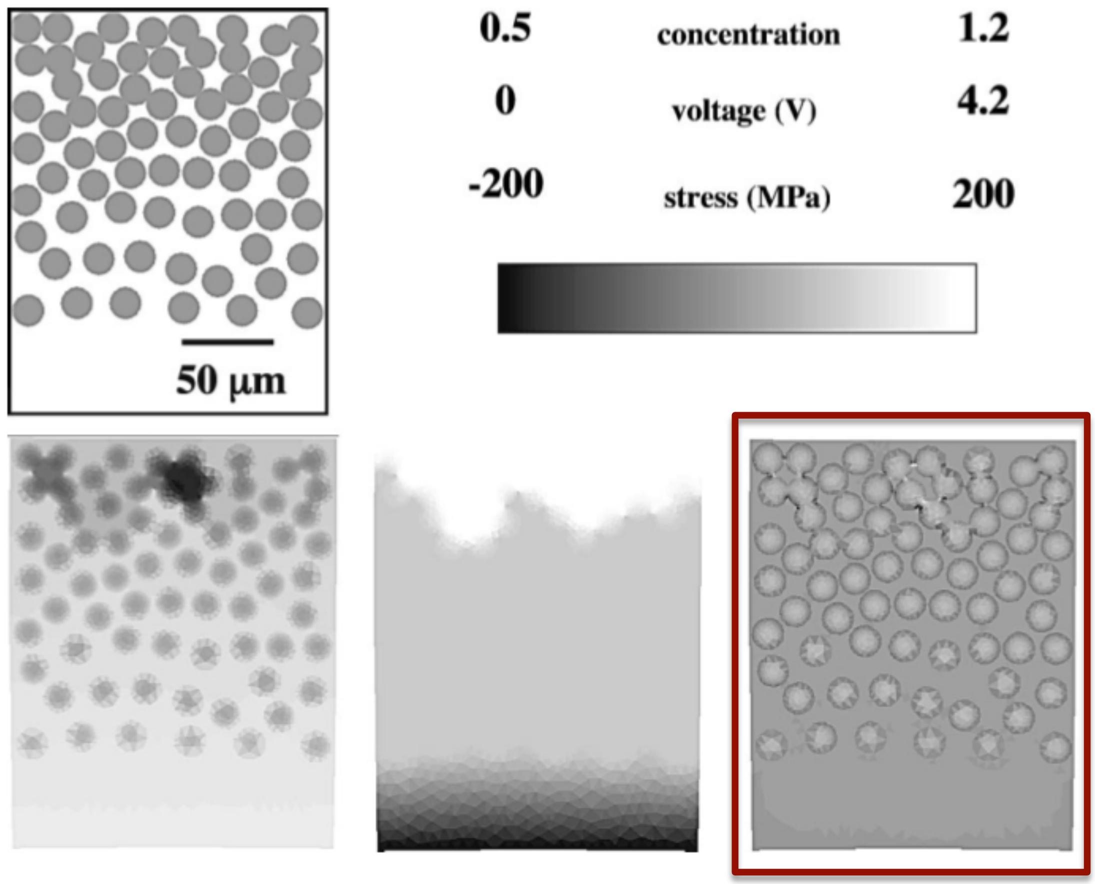
$\Delta V = -7.3\%$



$Si \rightarrow Li_{4.4}Si$

$\Delta V = +311\%$

Previous Models Have Calculated Diffusion-Induced Stresses



Concentration Voltage Stress

R.E. García, *et al.*, *J. Electrochem. Soc.* **152**[1] A255-A263 (2005)

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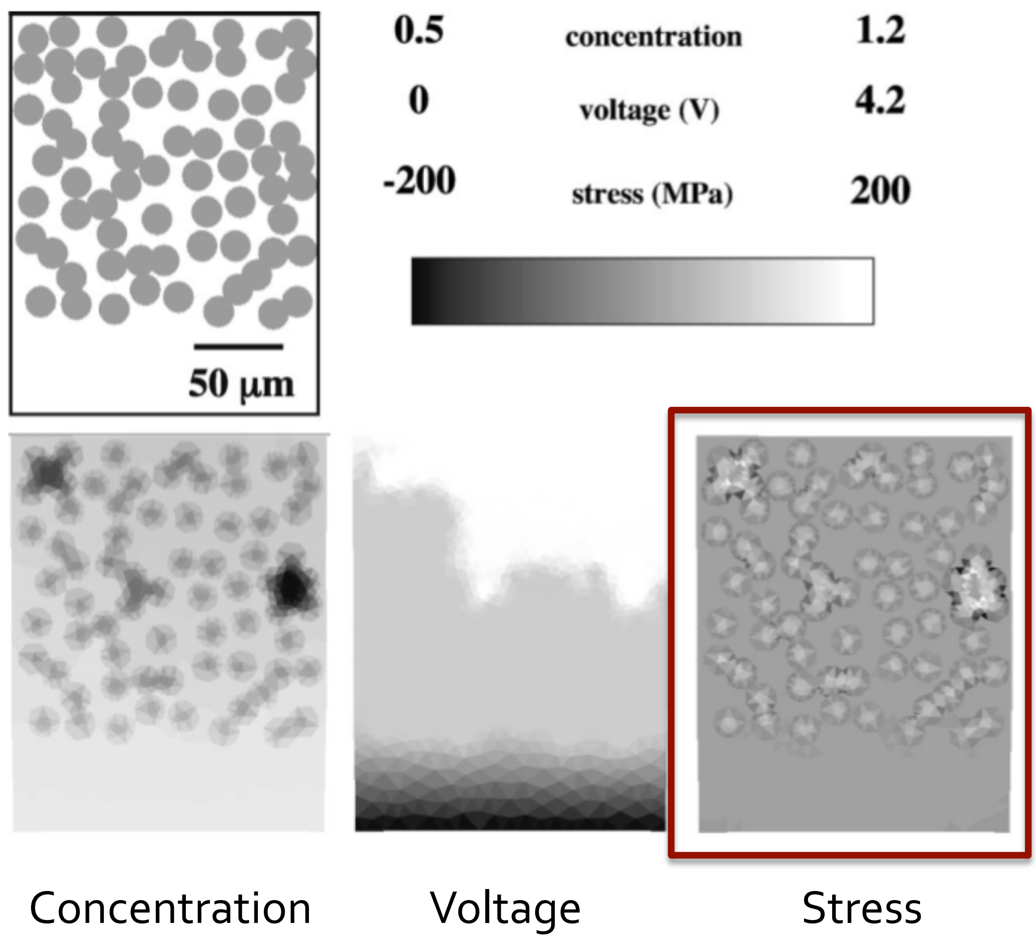

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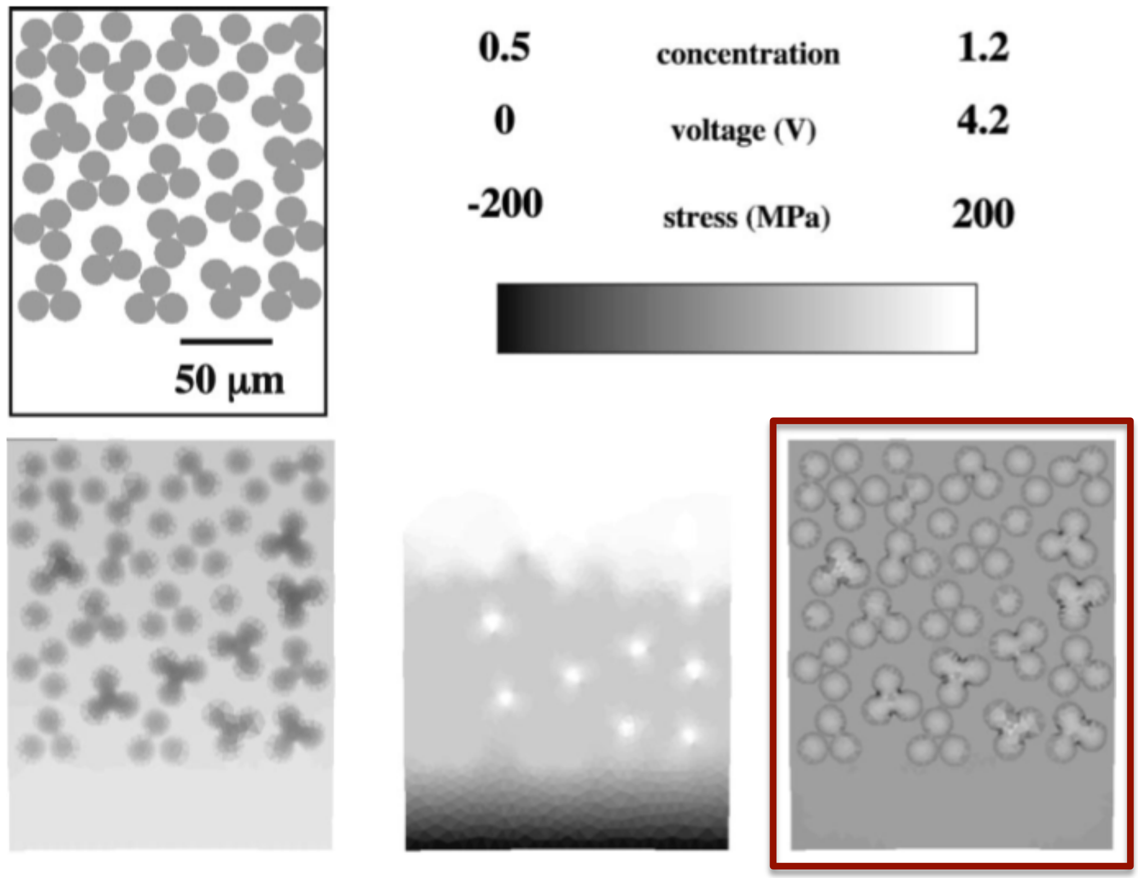

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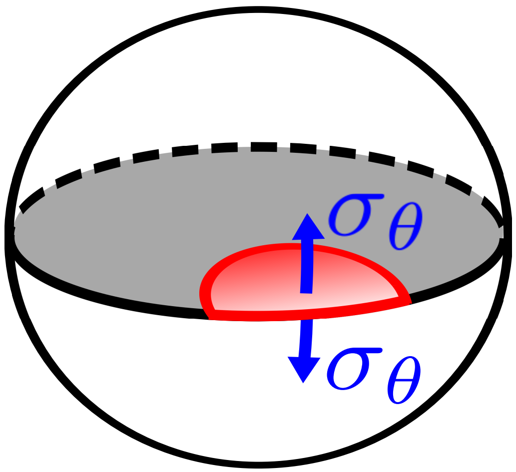
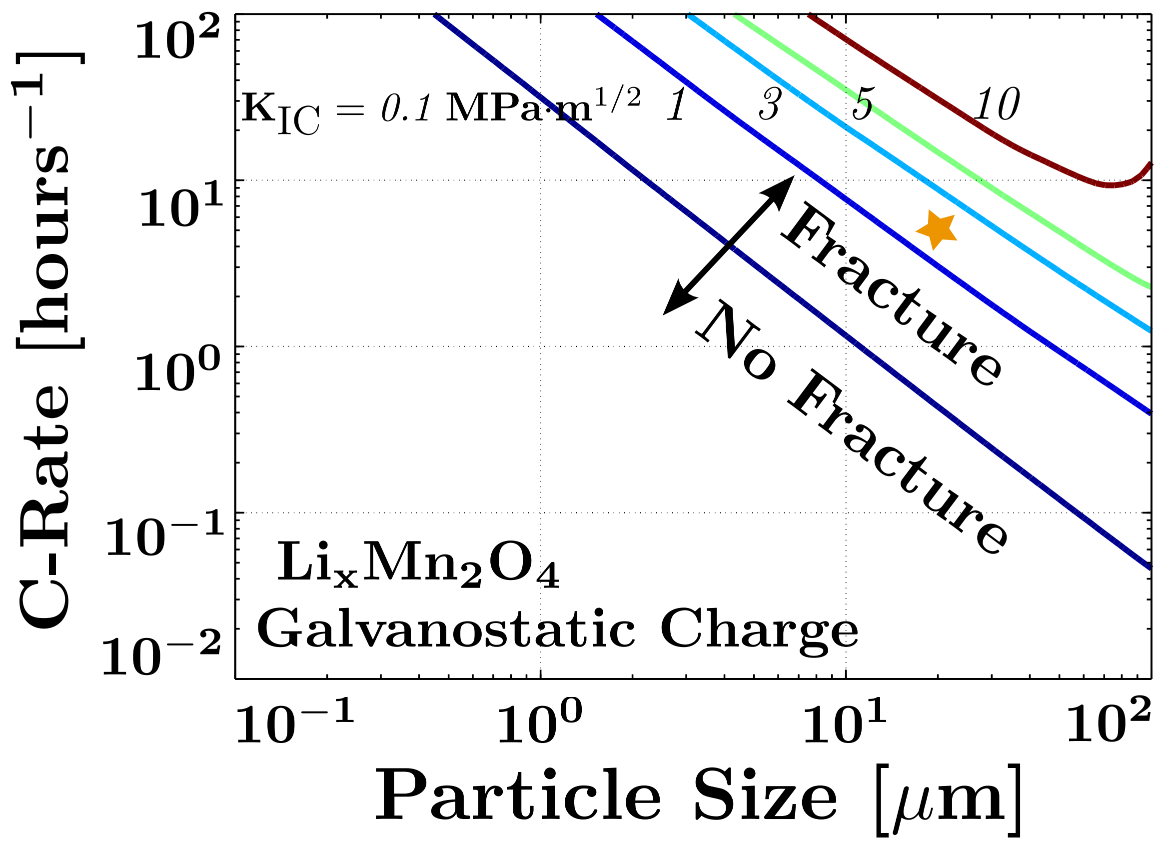
Link to Fracture Mechanics: Electrochemical Shock Map



Critical combinations of particle size and rate

Need fracture toughness measurements!



W.H. Woodford, *et al.*, *J. Electrochem. Soc.*, **157** [10] A1052-A1059 (2010)

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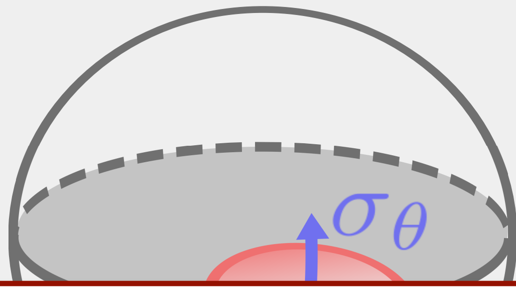
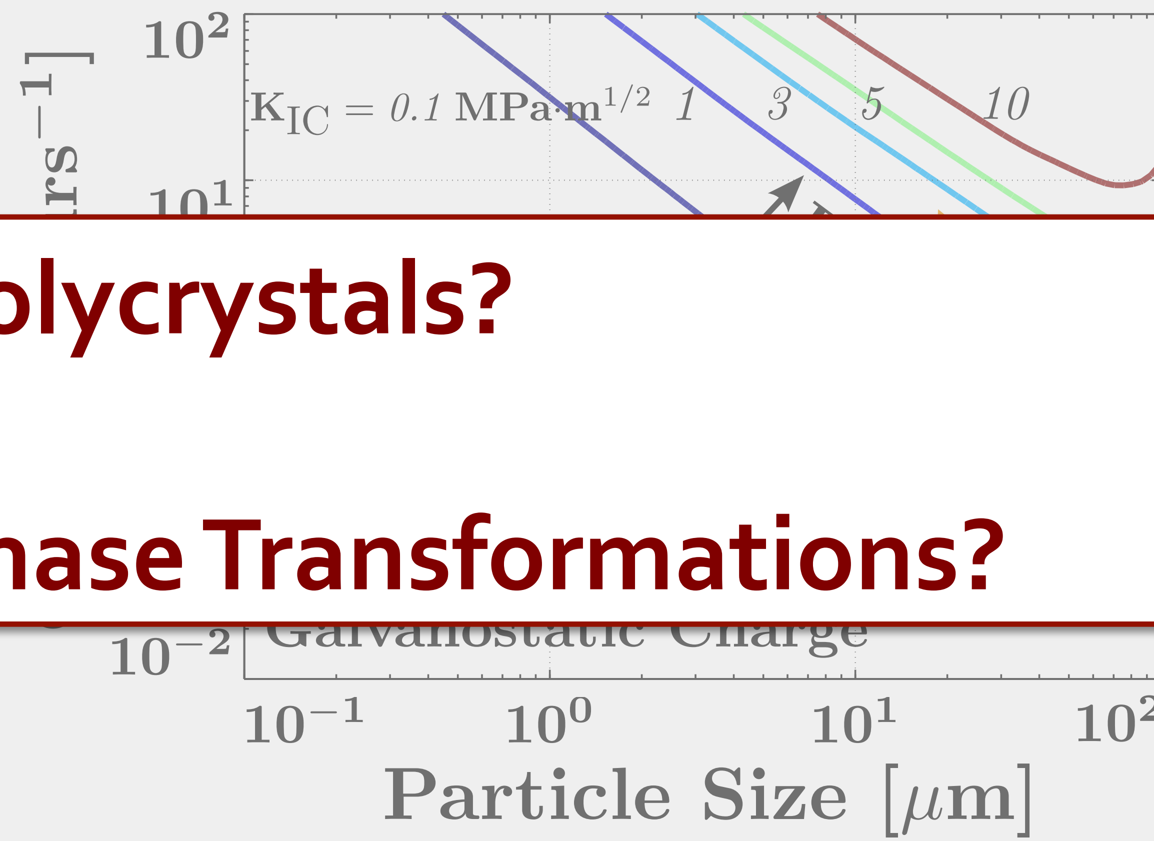




What About Polycrystals?

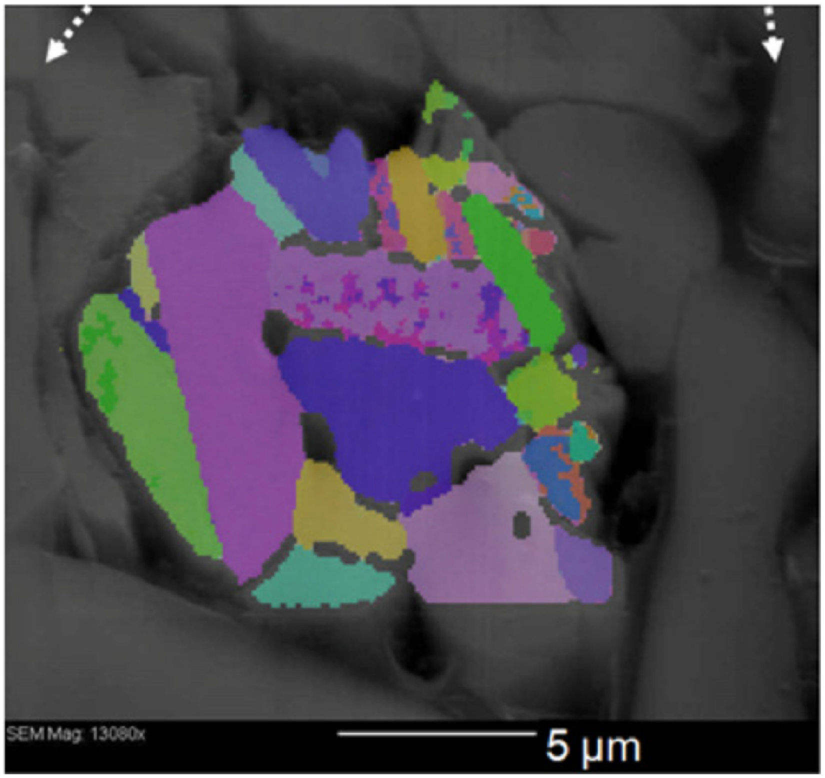
Phase Transformations?

particle size and rate

Need fracture toughness measurements!

W.H. Woodford, *et al.*, *J. Electrochem. Soc.*, **157** [10] A1052-A1059 (2010)

Microstructure Matters for Electrochemical Shock



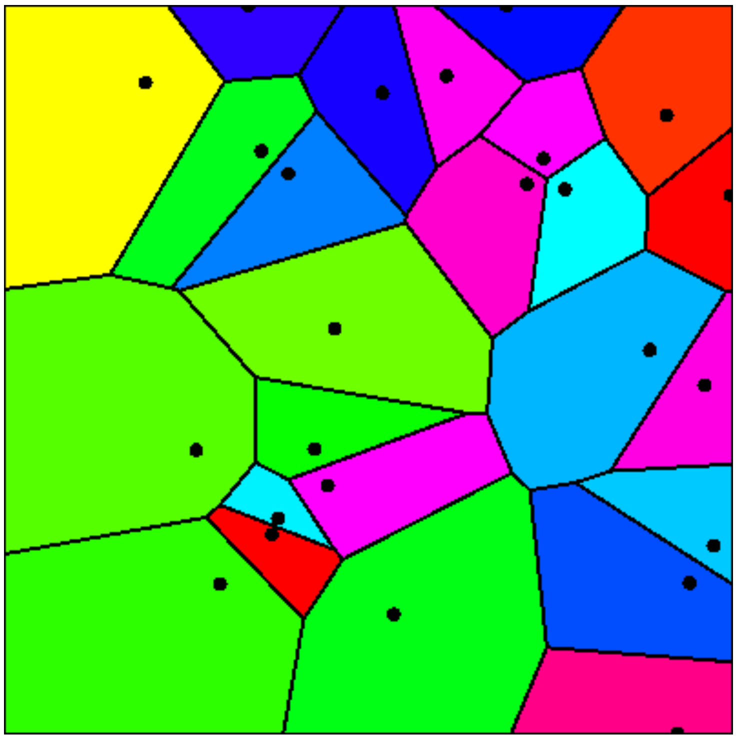
J.R. Wilson, et al., *J. Power Sources* (2010), doi: 10.1016/j.jpowsour.2010.04.066

EBSD orientation maps for $LiCoO_2$ **polycrystalline** particles in composite (Lishen) electrodes

Microstructure Matters for Electrochemical Shock

Goal: Develop Models for Electrochemical Shock that incorporate this microstructural complexity and address (anisotropic) phase transformations

Microstructure Generation



2D Voronoi Construction

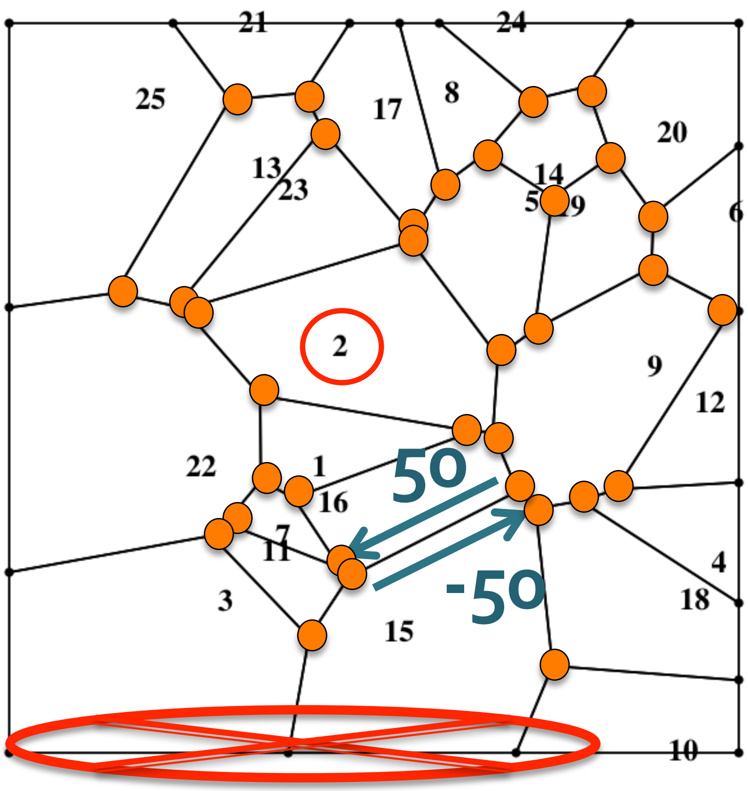
- 2N Random numbers per grain (x_i,y_i)

Random Grain Orientations

- Use OOF2's EulerABG Convention
- 3 Random numbers per grain for (α_i,β_i,γ_i)

- All done in *Mathematica*

Microstructure Information



Each grain is numbered

Each boundary is numbered and we know which grains it separates

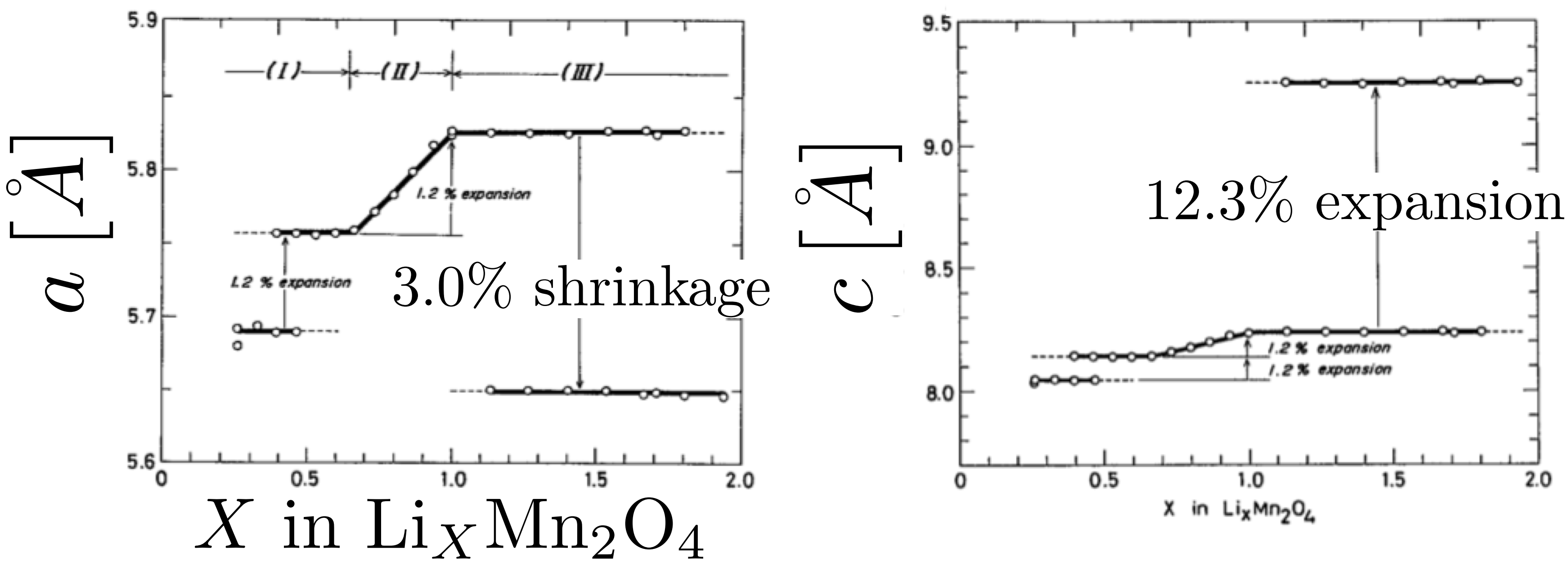
- $n \longrightarrow -n$ for opposite direction along same edge
- Exclude Boundary Edges from Analysis

We know the location of each triple point

LiMn$_2$O$_4$: A Model System

$$\text{LiMn}_2\text{O}_4 + \text{Li}^+ + e^- \rightarrow \text{Li}_2\text{Mn}_2\text{O}_4$$

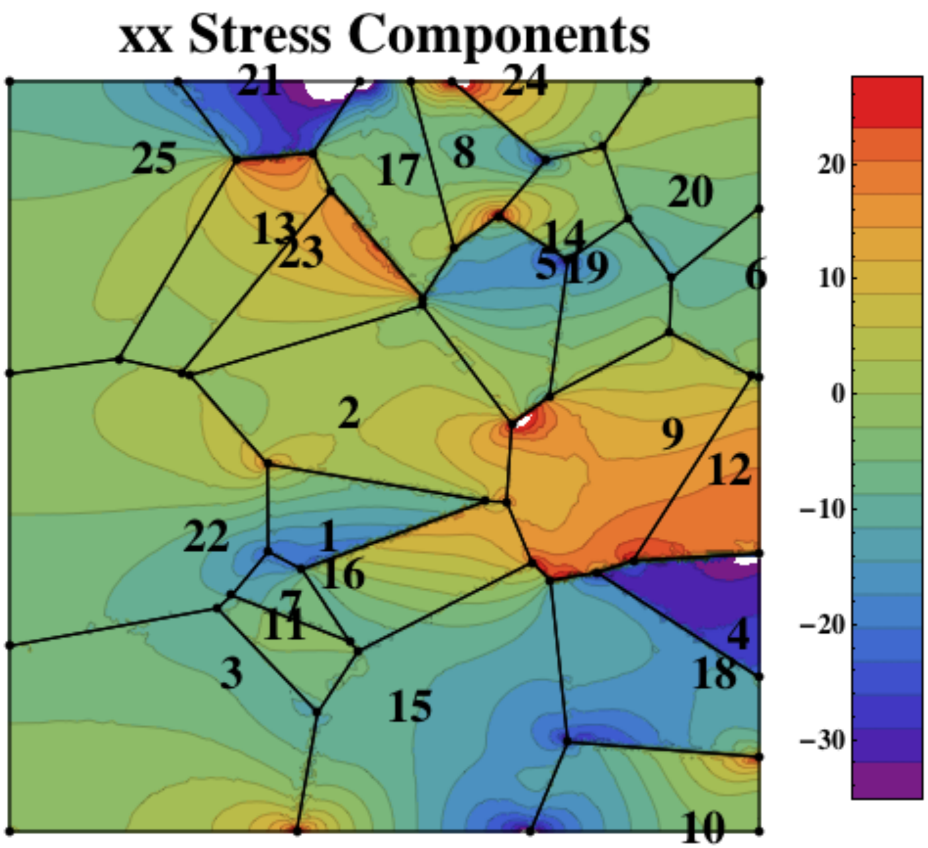
cubic *tetragonal*

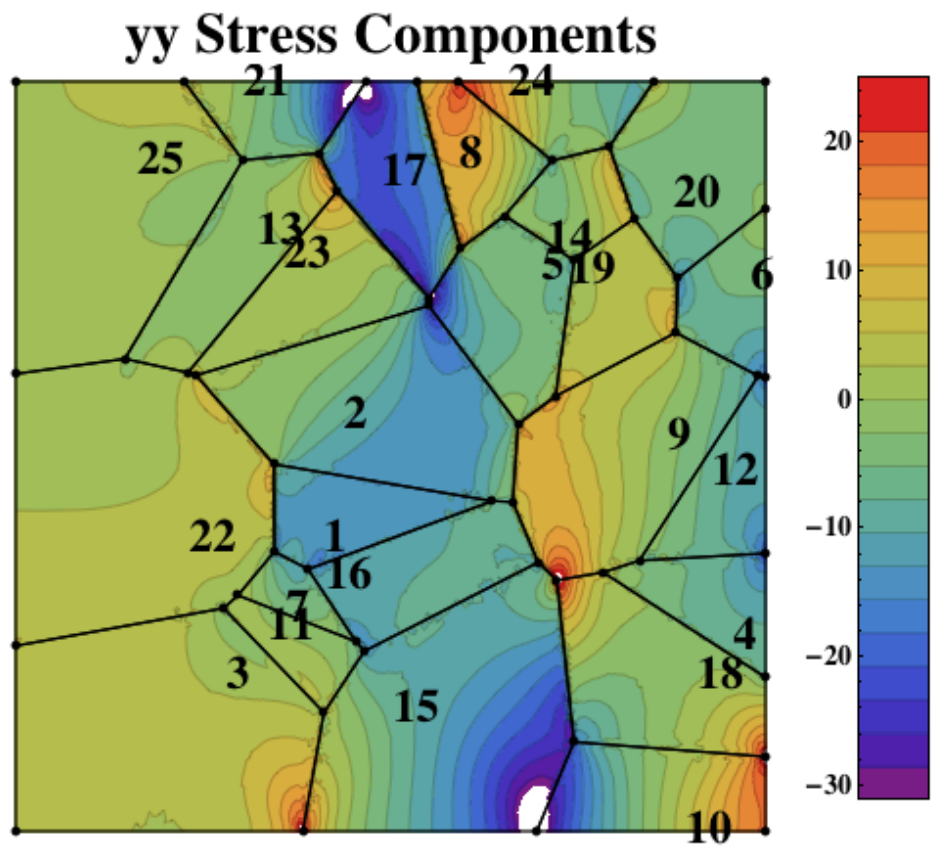


Start with end point analysis… (Analogies to thermal shock)

T. Ohzuku, M. Kitagawa, and T. Hirai, *J. Electrochem. Soc*. **137**[3] 769–775 (1990)

Cartesian Stress Components

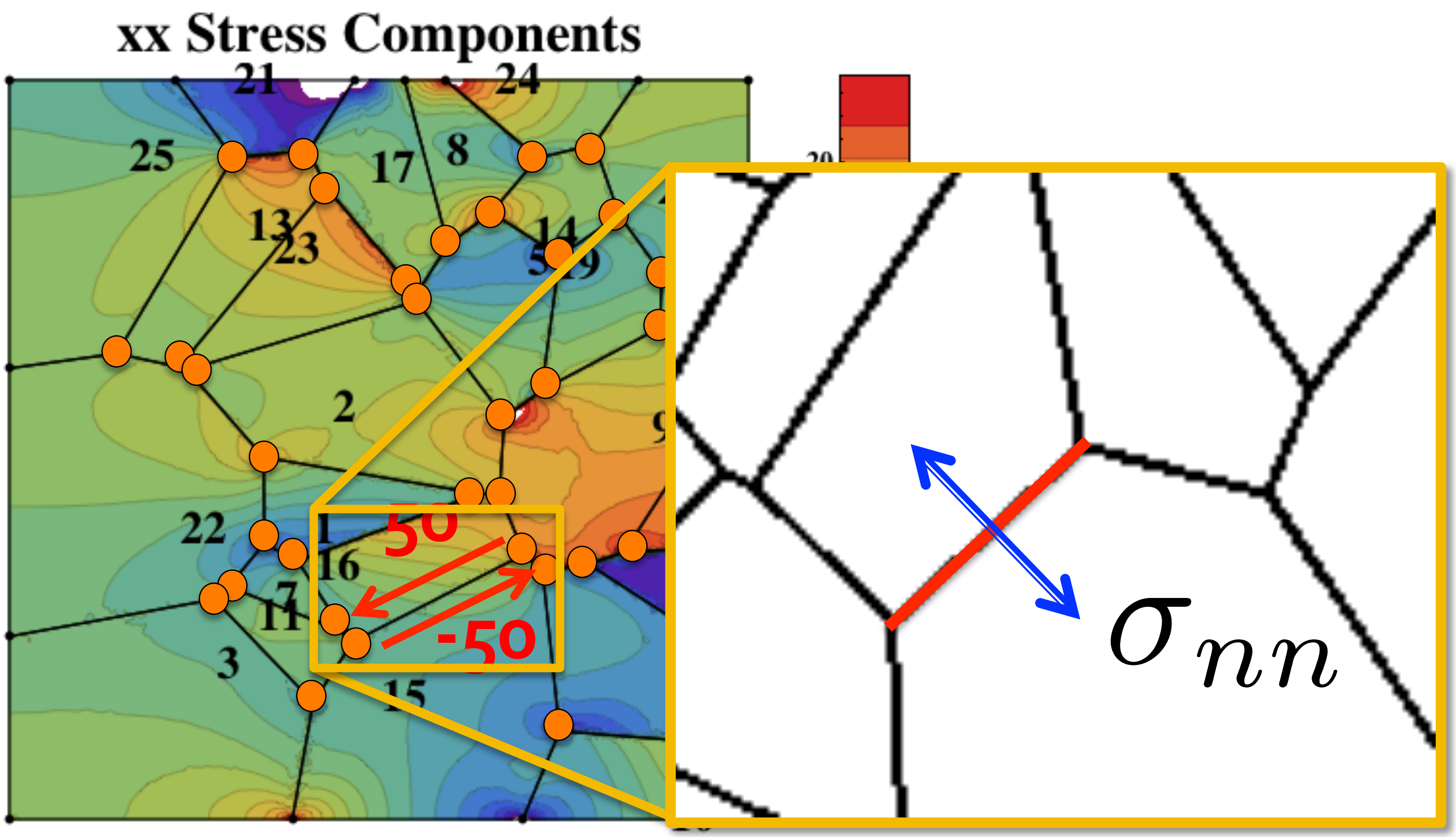




Assumptions: Plane Stress Condition; Zero-Displacement normal to external boundaries

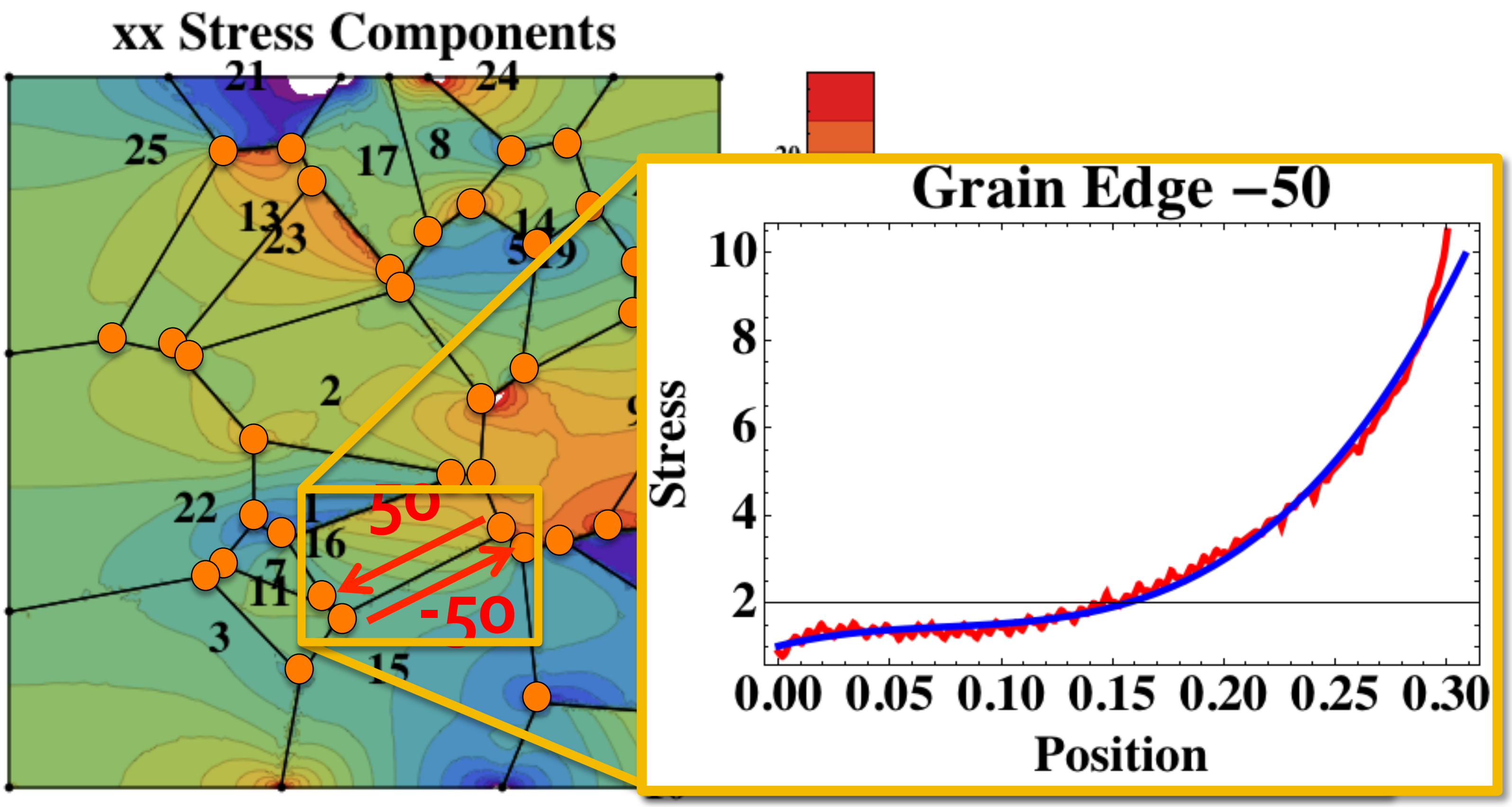
Note: Stresses here are referred to the the OOF/Lab frame coordinates

Extracting Local Stress Information



Use tensor transformation to extract grain boundary normal stress

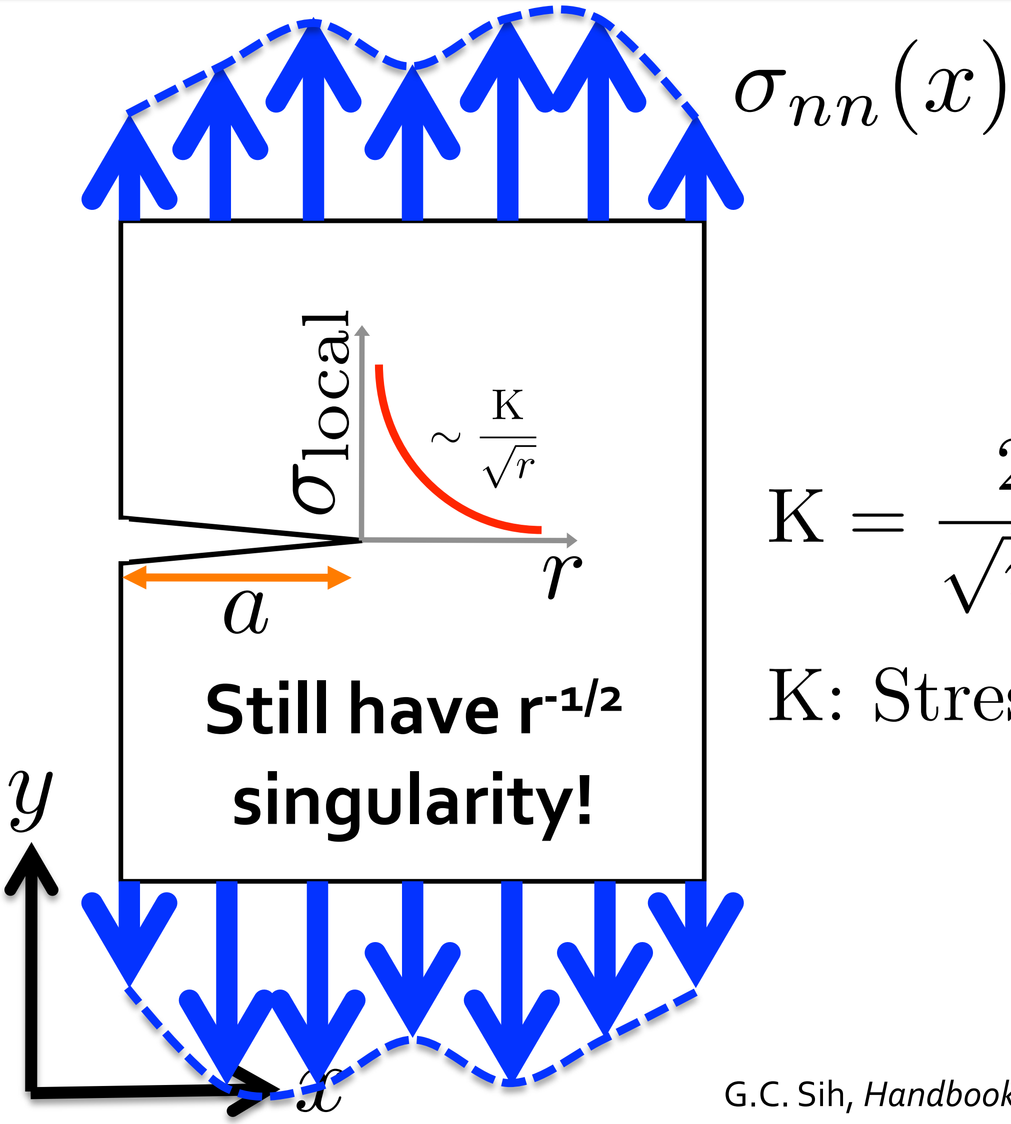
Extracting Local Stress Information



Red line: Linear interpolation of raw data from OOF2
Blue line: Calculated with cubic polynomial fit (fast!)

$$\sigma(x) = a + bx + cx^2 + dx^3$$

Stress-Intensity Factor – Nonuniform Loading



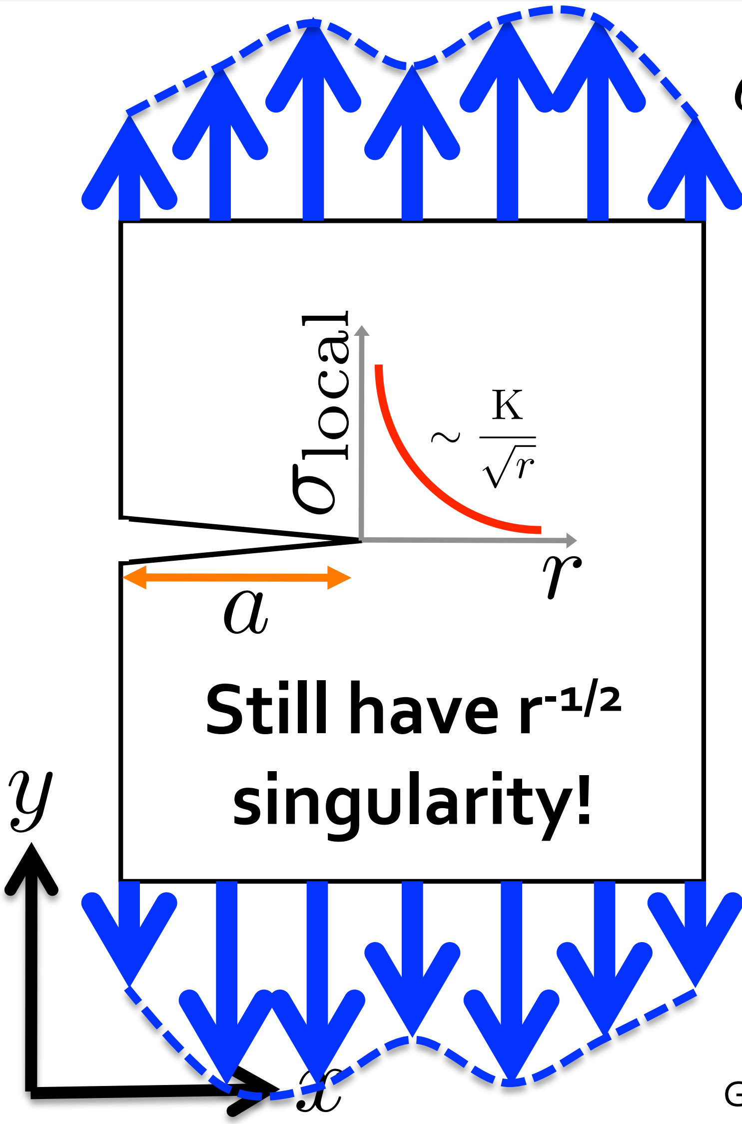
$$\text{K} = \frac{2}{\sqrt{\pi a}} \int_0^a \sigma_{nn}(x') \sqrt{\frac{x'}{a - x'}} \mathrm{d}x'$$

K: Stress-Intensity Factor

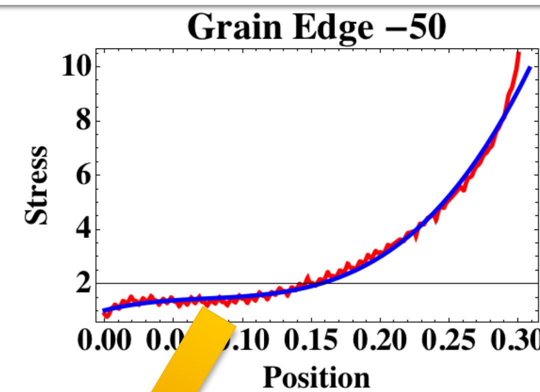
$$\text{K} > \text{K}_{\text{IC}}$$

G.C. Sih, *Handbook of Stress Intensity Factors*, Lehigh University Press (1973)

Stress-Intensity Factor – Nonuniform Loading



$\sigma_{nn}(x)$



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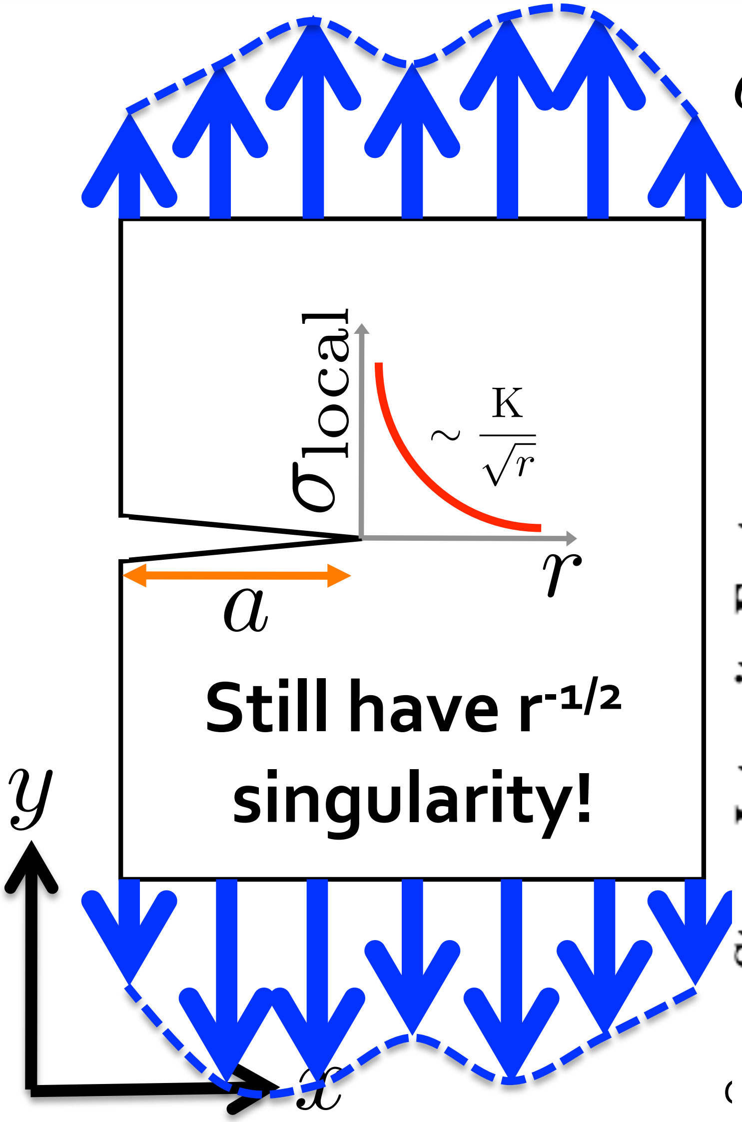
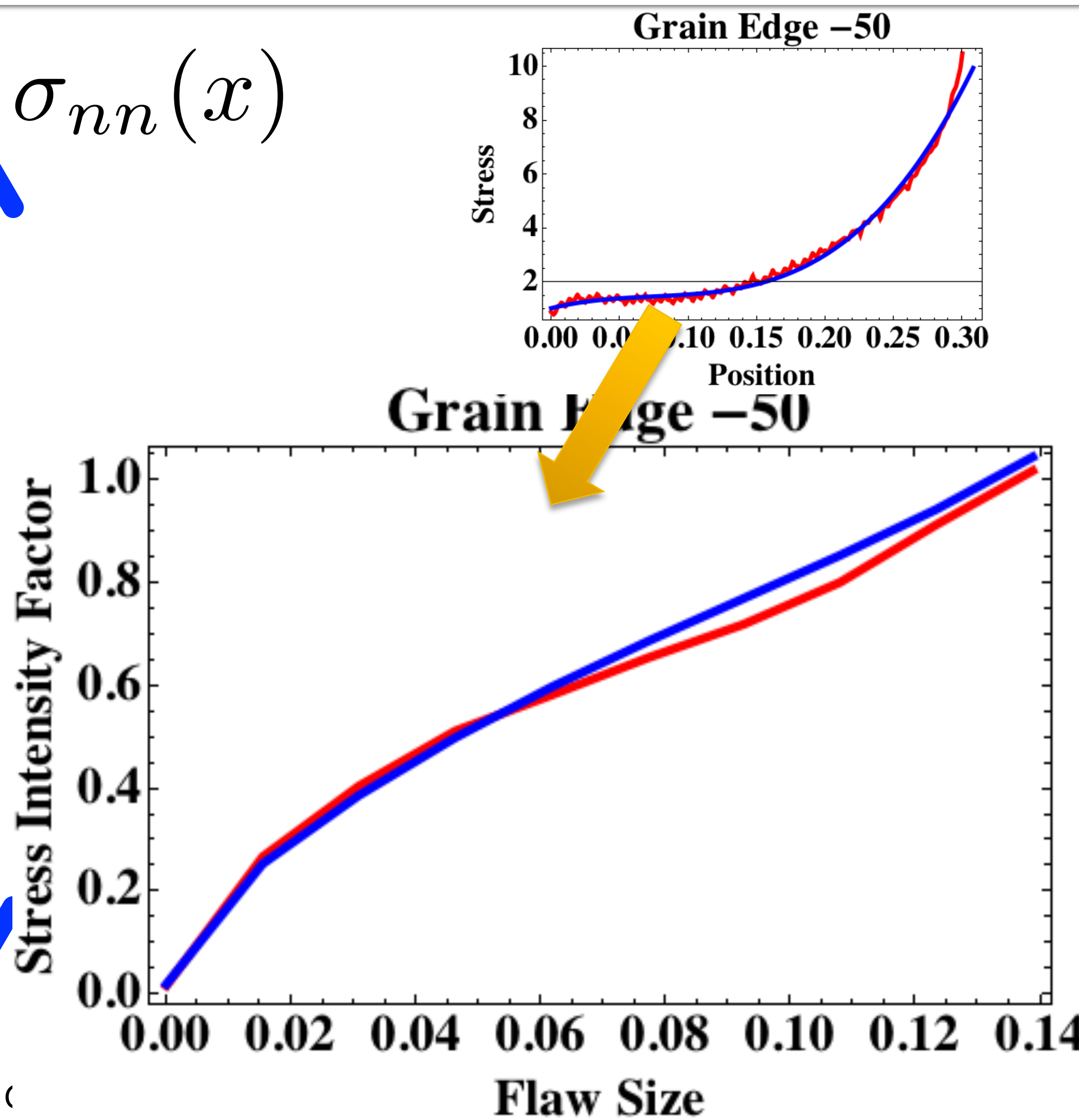
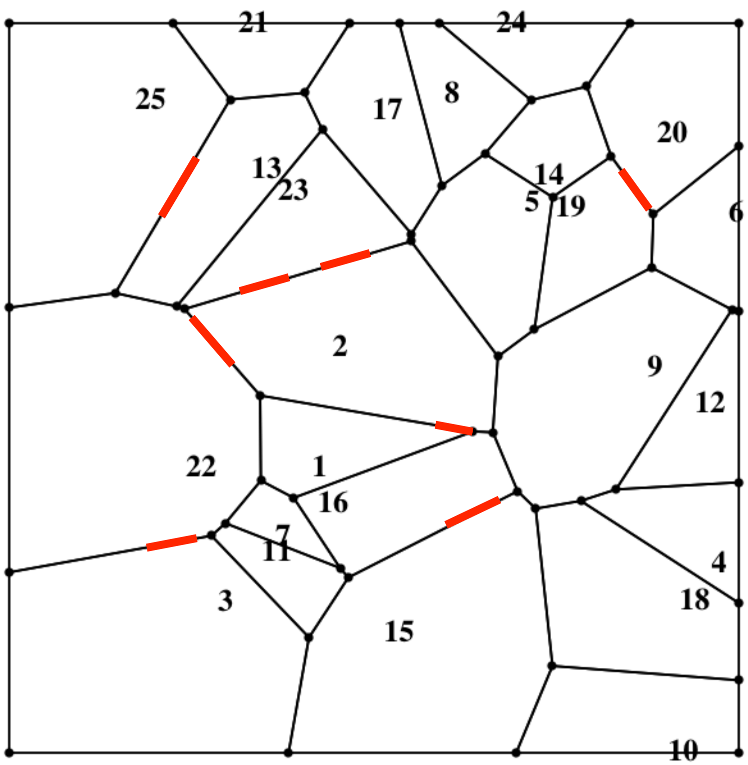




x'

973)

Introducing Random Flaws



Method:

1) Choose an edge

   Remember, they have been numbered…

2) Choose a random flaw size from a flaw size distribution

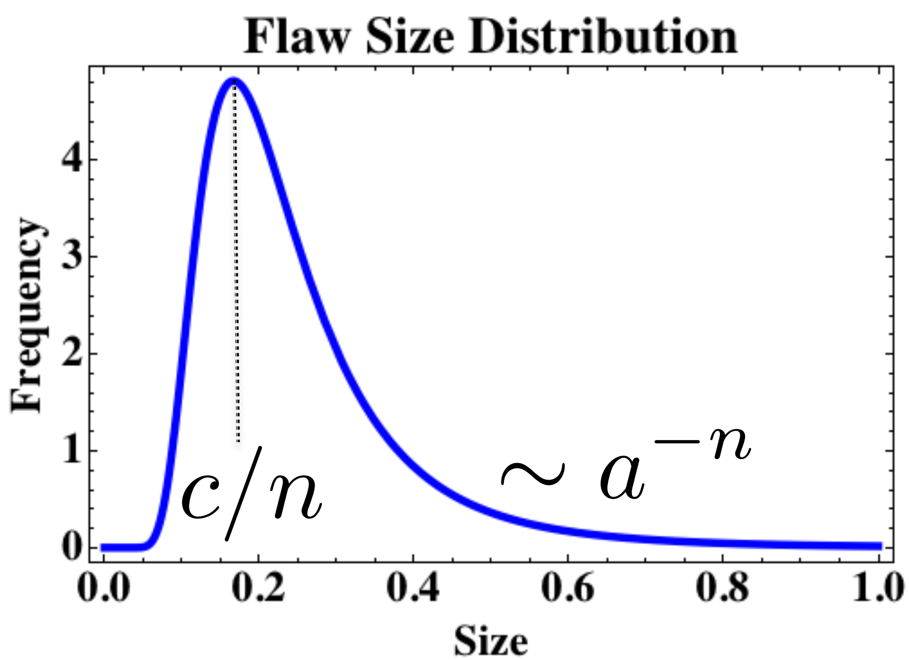
   Need flaw distribution information!

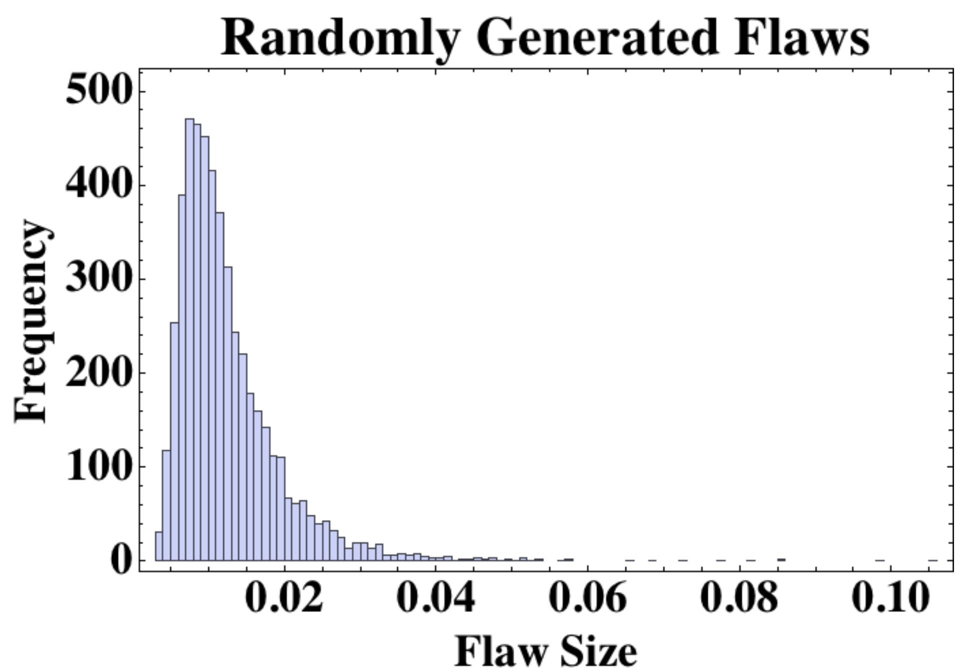
3) Choose a random position along the edge

4) Calculate K using polynomial model for stress distribution

Flaw Size Distributions

- Flaws are ***not*** Weibull distributed



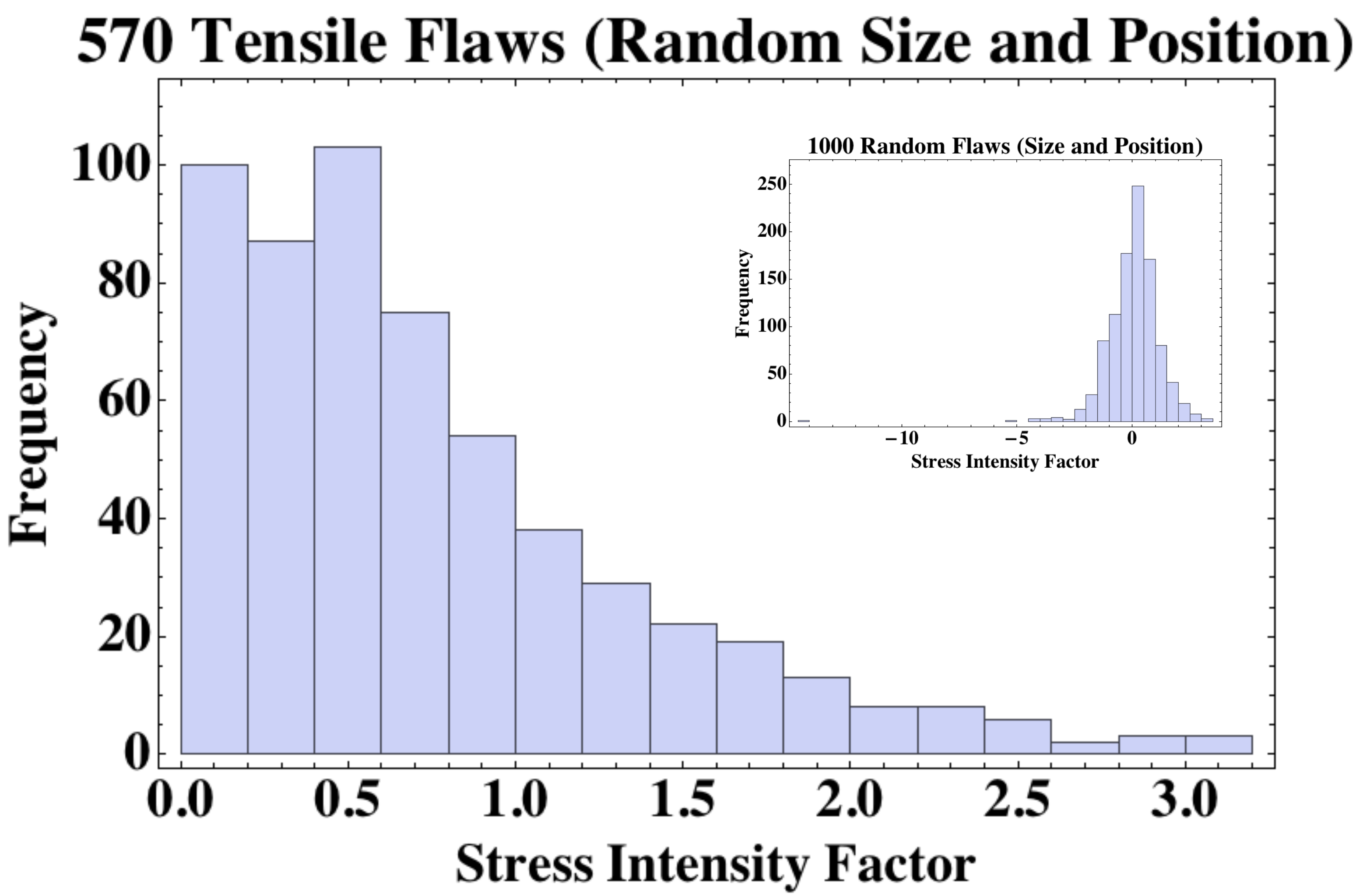


$$f(a) = \frac{c^{n-1}}{(n-2)!} a^{-n} e^{-c/a}$$

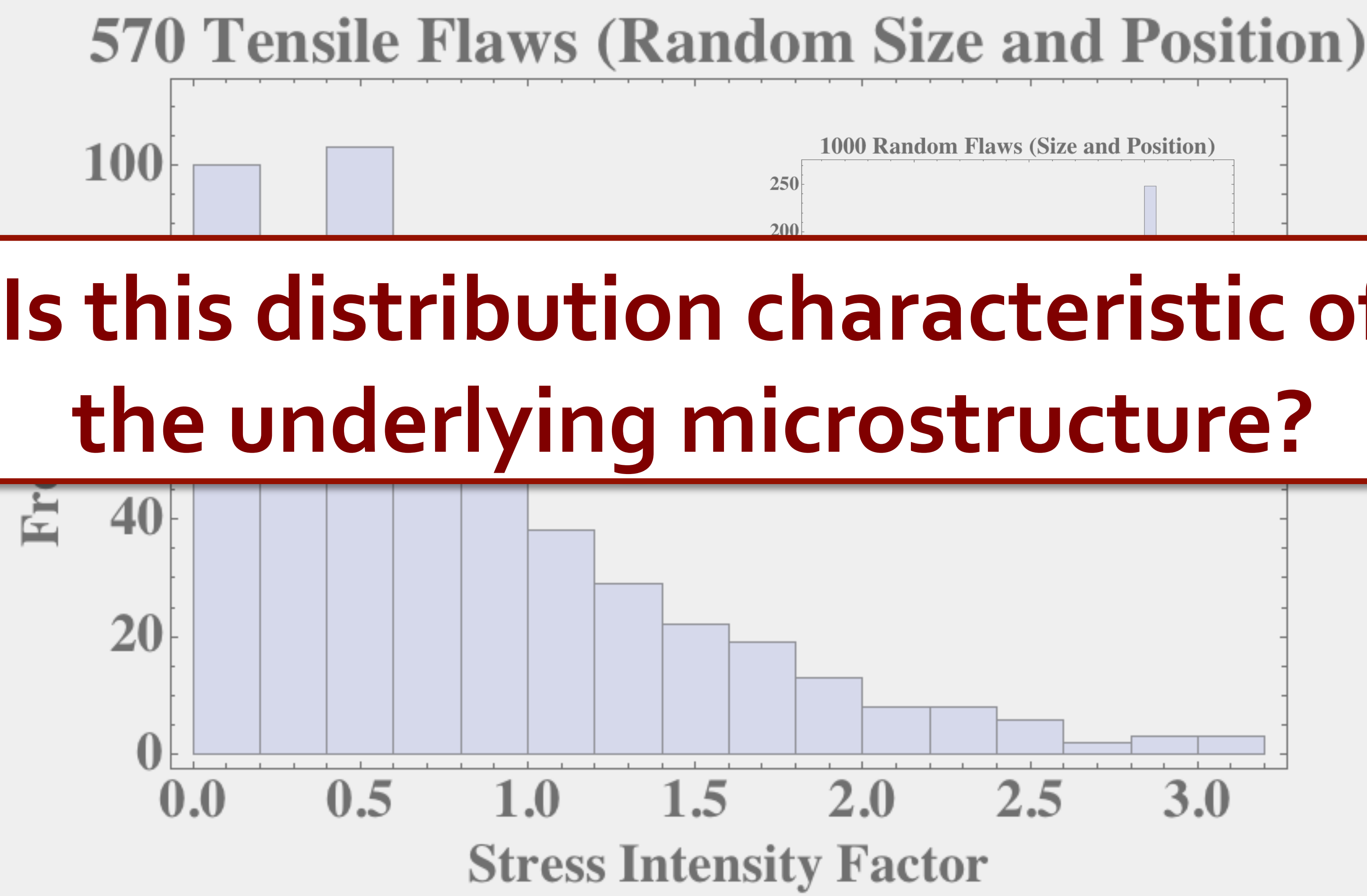
f: probability density
a: flaw size
c: scale parameter
n: width parameter

J. D. Poloniecki and T. R. Wilshaw, *Nature*, **229** 226-227 (1971) & A. De S. Jayatilaka and K. Trustrum, *J. Mater. Sci.*, **12** 1426-1430 (1977)

K Distribution from Random Flaws

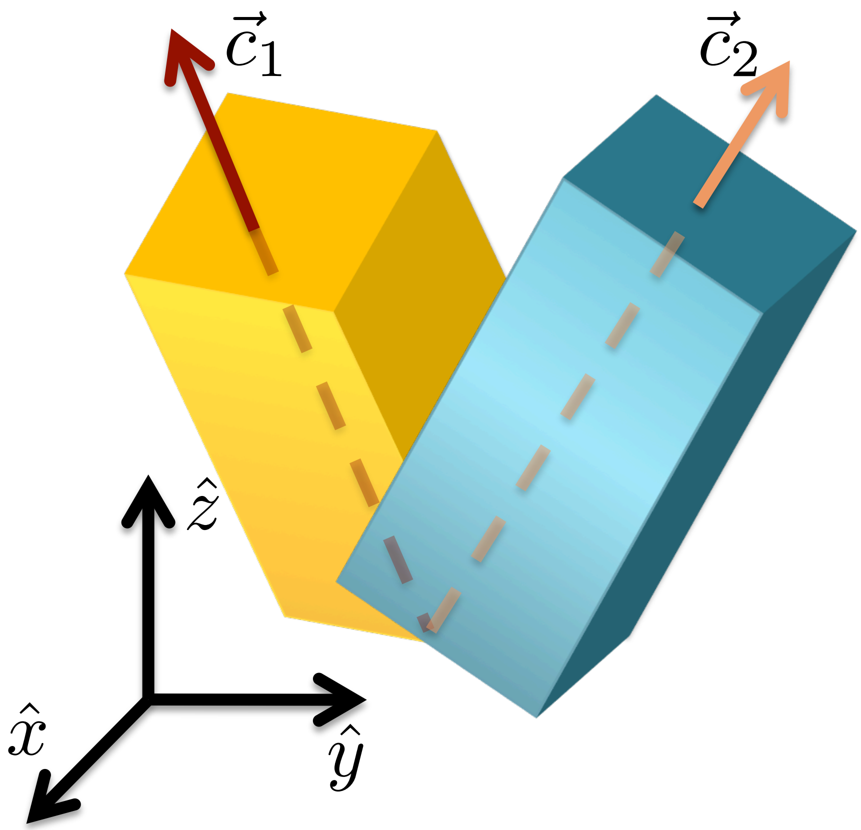


K Distribution from Random Flaws



Is this distribution characteristic of the underlying microstructure?

Other Potentially Interesting Microstructure Variables



Grain Orientation

Triple Points

Grain Size

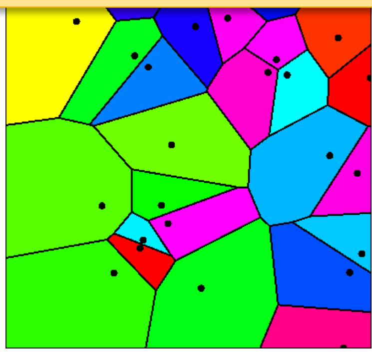
Porosity

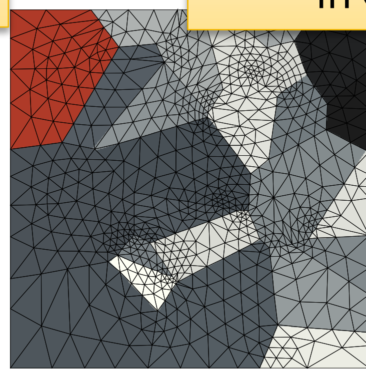
Summary

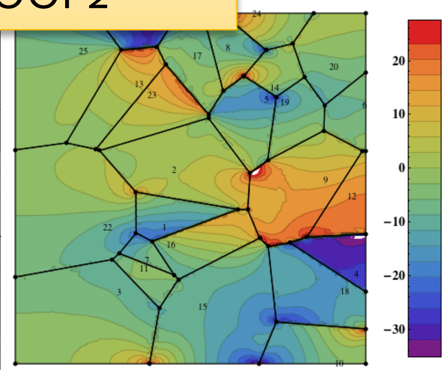
Generate Random Voronoi Microstructure in Mathematica

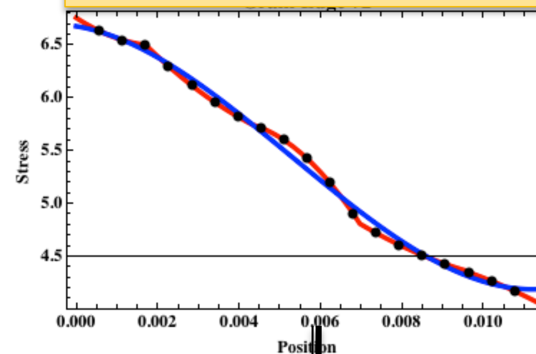
Finite Element Stress Calculations in OOF2

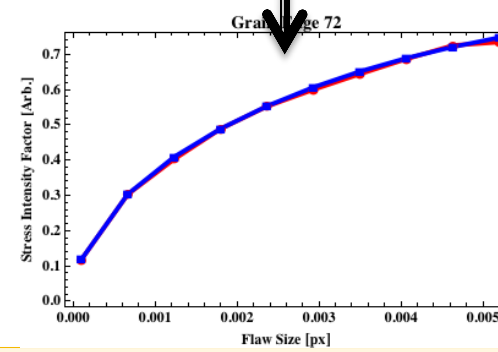
Extract Local Stresses Along Each Grain Boundary



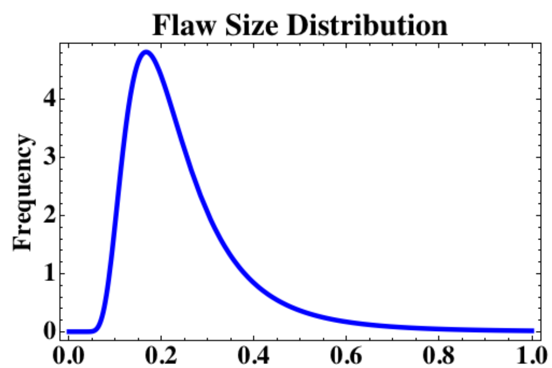




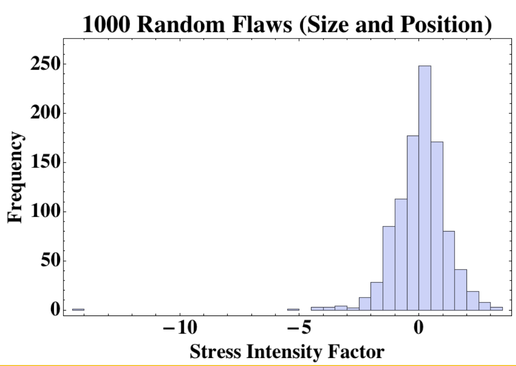




Calculate Stress Intensity Flaw-Size Relations for All Grain Boundaries



Populate the Microstructure with Random Flaws



Extract Failure Probabilities and Extreme Values Statistics

Conclusions and Future Directions

Microstructure matters for electrochemical shock – *opportunity for design*

- Mathematica + OOF2 is a convenient, powerful tool set

This is a snapshot of current development

Potential Future Directions:

- Introducing **Second Phases** (or porosity)
- Electrochemical **Kinetics**

Experiments – X-Ray Tomography?

Acknowledgements

- National Science Foundation Graduate Research Fellowship
- Dept. of Energy, Basic Energy Science, Award No. DE-SC0002633

Questions?