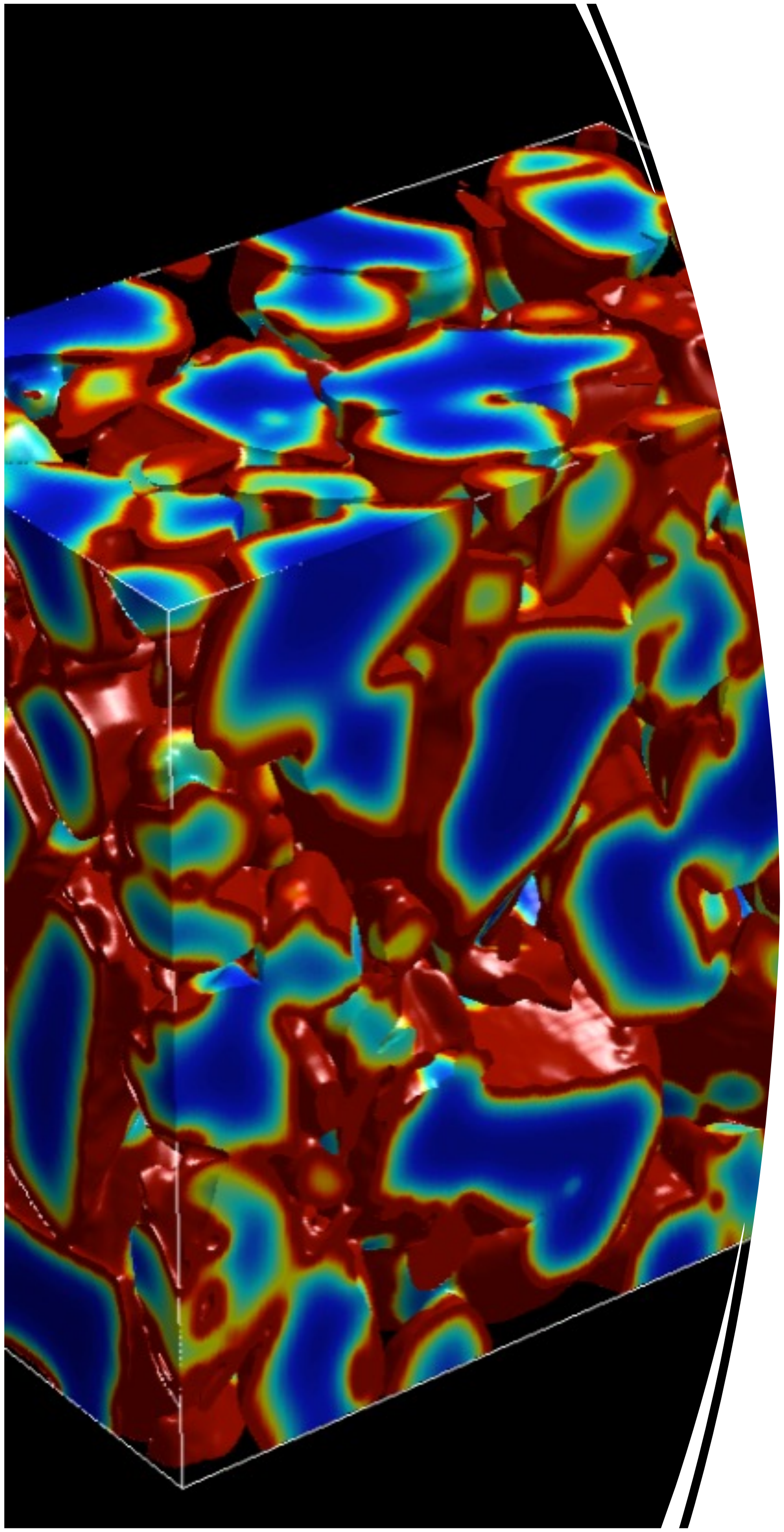

# IPAM Tutorial:
## The Role of Materials and Microstructures in Electrochemical Energy Storage
## Part 2

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# Any questions from last time?

# The Role of Materials and Microstructures in Electrochemical Energy Storage

- **Lesson Plans**

Part 1: Electrochemical Dynamics in Batteries

- How batteries work
- Different components of batteries
- Governing equation for electrochemical dynamics
- Key material properties & how they are measured/calculated

Part 2: Electrochemical Dynamics in Batteries

- How microstructure affects electrochemical dynamics
- Additional highlights from simulation results
- Examples of stochasticity

Hands-On Session (next Tuesday)

# Where we left off: How are parameters measured?

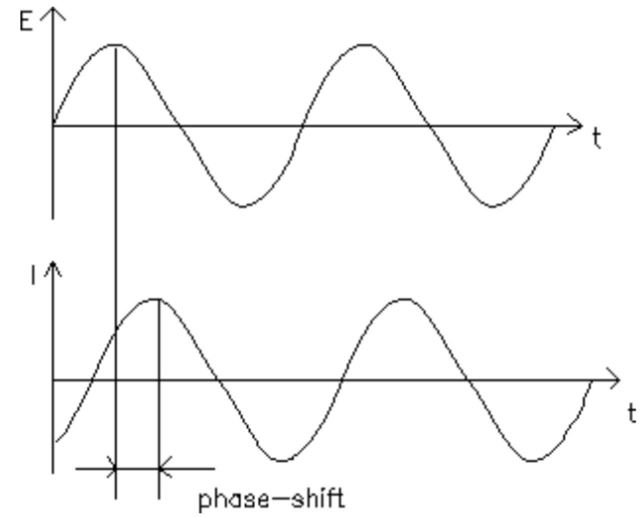
- **Open circuit voltage**: Charge/discharge a battery, ideally with a reference electrode, VERY SLOWLY (~C/30).
- **Diffusivity in the active materials**: PITT (potentiostatic intermittent titration technique), GITT (galvanostatic intermittent titration technique), or EIS (electrochemical impedance spectroscopy) and fit. But different techniques often give contradictory values.
- **Exchange current density**: Potential sweep to obtain I-V curves to obtain a Tafel plot, and then extrapolate to the equilibrium potential. Challenge: not the entire electrode is active; the active area is not known.
- **Conductivity**: I-V curve on individual component.

# Various electrochemical characterization techniques

- Potential sweep
- EIS

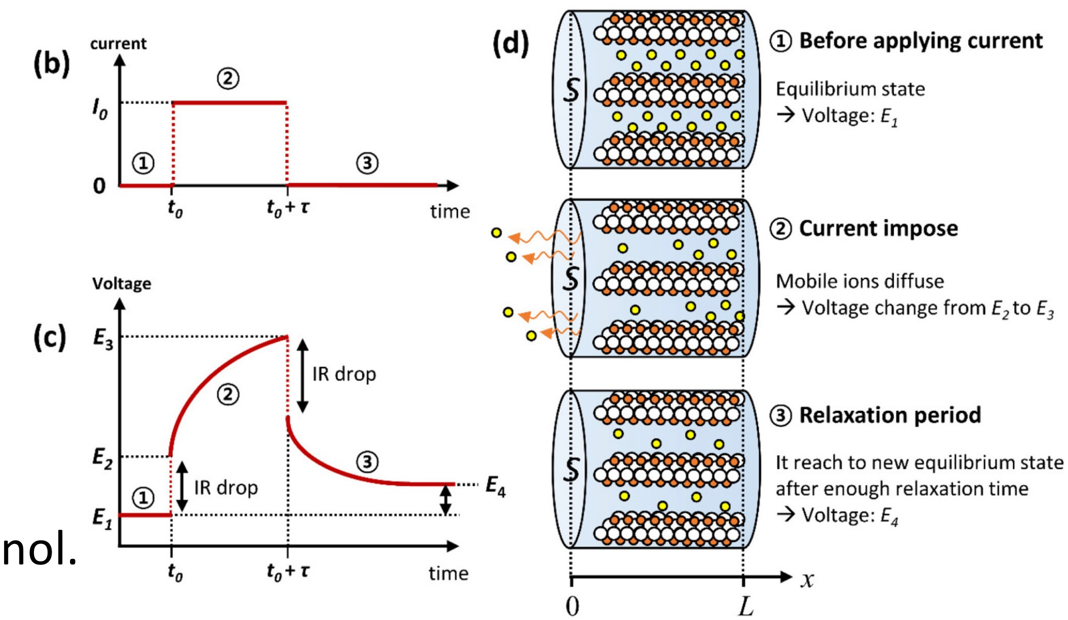
Ohm's Law: R=E/I

Generalized for AC: Z=E/I




https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/

- PITT/GITT: step change in applied potential or current




J. Kim, et al. J. Electrochem. Sci. Technol. 2022;13(1):19-31

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- **Open circuit voltage**: Charge/discharge a battery, ideally with a reference electrode, VERY SLOWLY (~C/30).
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- **Exchange current density**: Potential sweep to obtain I-V curves to obtain a Tafel plot, and then extrapolate to the equilibrium potential. Challenge: not the entire electrode is active; the active area is not known.
- **Conductivity**: I-V curve on individual component.

- **But sometimes these quantities can be obtained via lower-scale (e.g., atomistic) simulations!**

# Example of multiscale model coupling

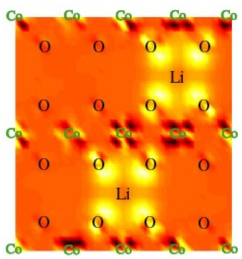
Thermodynamics: Open circuit voltage
Diffusion kinetics: Diffusivity or mobility
Electrochemistry: Reaction rate

Figure credit: Anton Van der Ven (UCSB)

# Example of multiscale model coupling

**Thermodynamics: Open circuit voltage**
**Diffusion kinetics: Diffusivity or mobility**
Electrochemistry: Reaction rate

First-principles energies of a "few" excitations

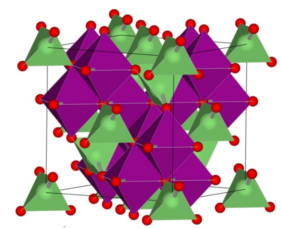



$$H = \sum_{i=1}^{N_e}\left(-\nabla_i^2 + V_{nuc}(r_i)\right) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|r_i - r_j|} + E_{nuc}(\{R\})$$

$$E(\vec{\sigma}) = V_o + \sum_i V_i\sigma_i + \sum_{i,j} V_{i,j}\sigma_i\sigma_j + \sum_{i,j,k} V_{i,j,k}\sigma_i\sigma_j\sigma_k + \ldots$$

Lattice Model Hamiltonian

Van der Ven, Gerd Ceder



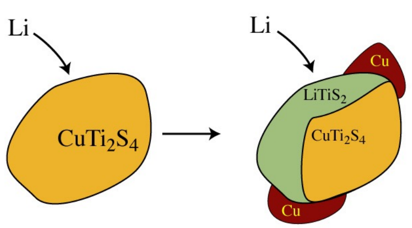
$$Z = \sum_{\vec{\sigma}} \exp\left(-\frac{E(\vec{\sigma})}{k_B T}\right)$$

Monte Carlo

Thermodynamics

Kinetics

$$J = -L\nabla\mu \qquad \dot{C} = \nabla\cdot L\nabla\mu$$




Micro-Scale (Phase-Field) Simulations

Thornton

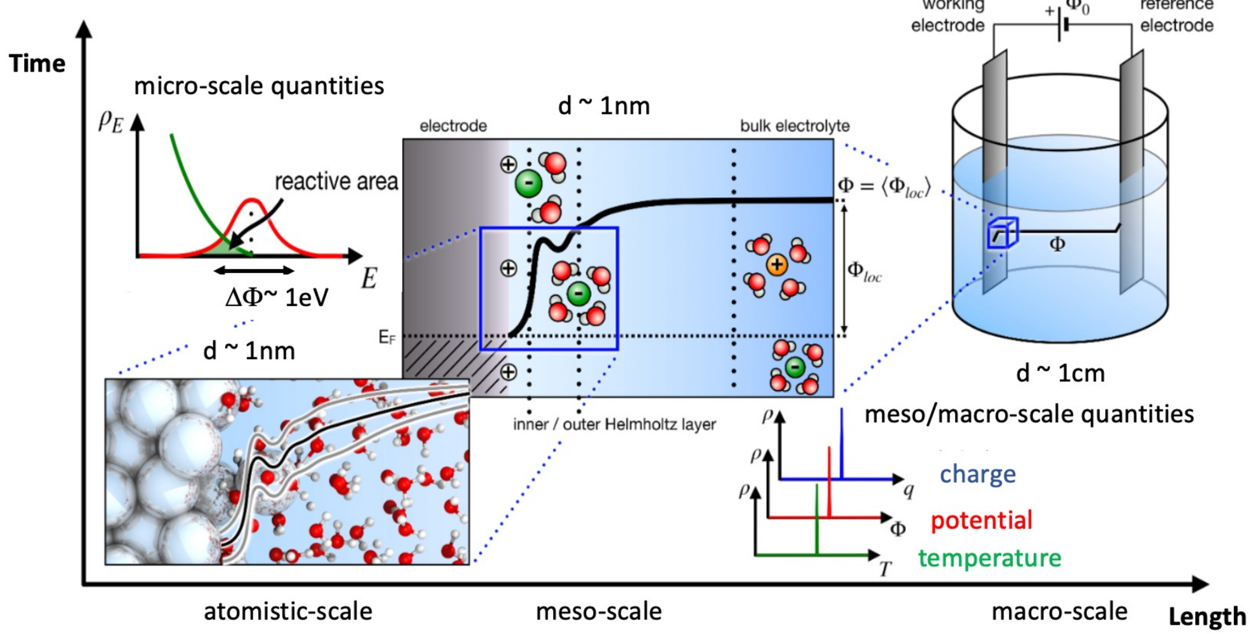
Figure credit: Anton Van der Ven (UCSB)

# An IPAM focus & impact

Thermodynamics: Open circuit voltage
Diffusion kinetics: Diffusivity or mobility
**Electrochemistry: Reaction rate**

From Jörg’s talk

Revised picture




Realistic atomic scale simulations need to include stochastic fluctuations in charge, density, potential, etc.

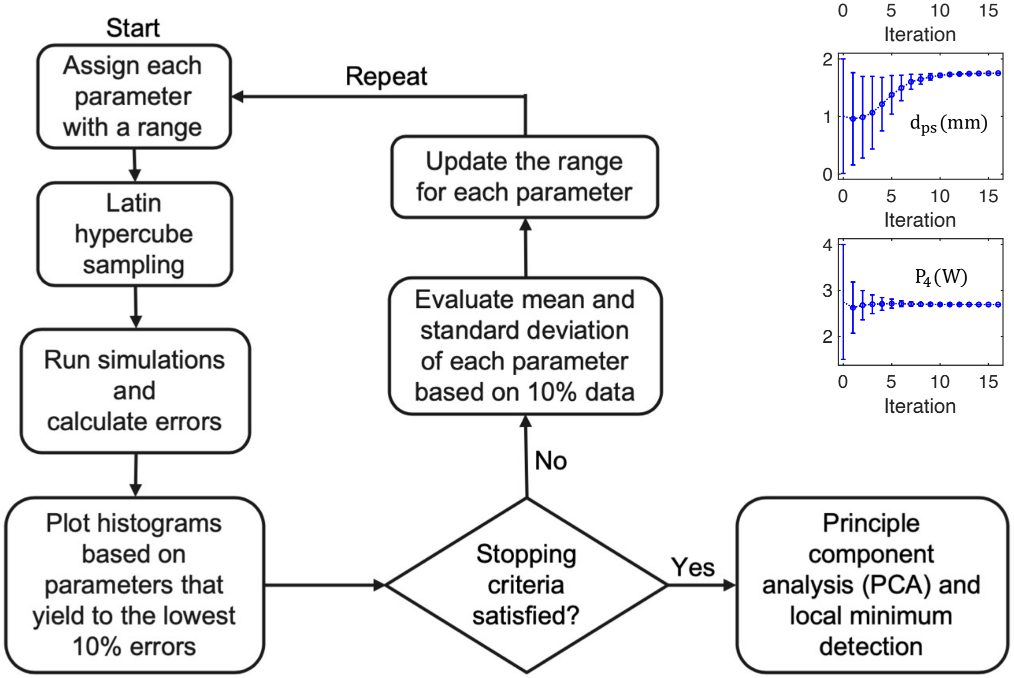
Wippermann, Todorova, JN, Nature Review Chemistry (2025)

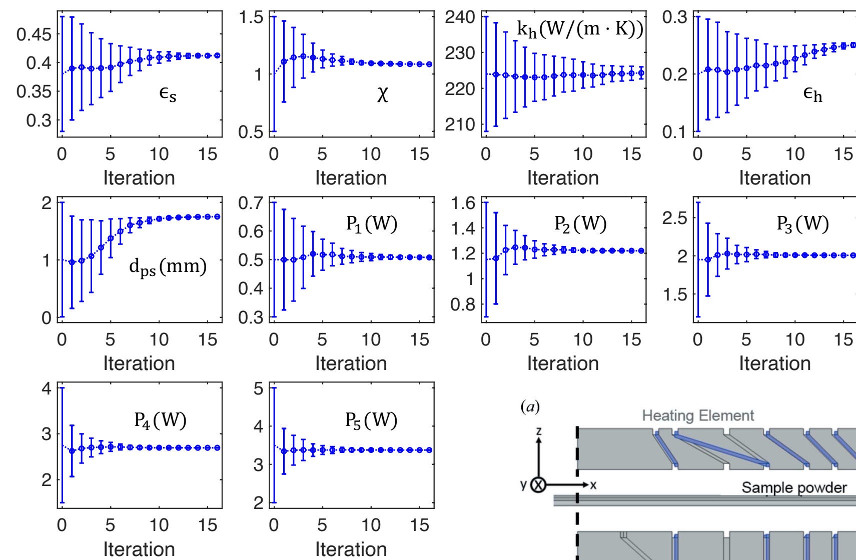
Reaction rate

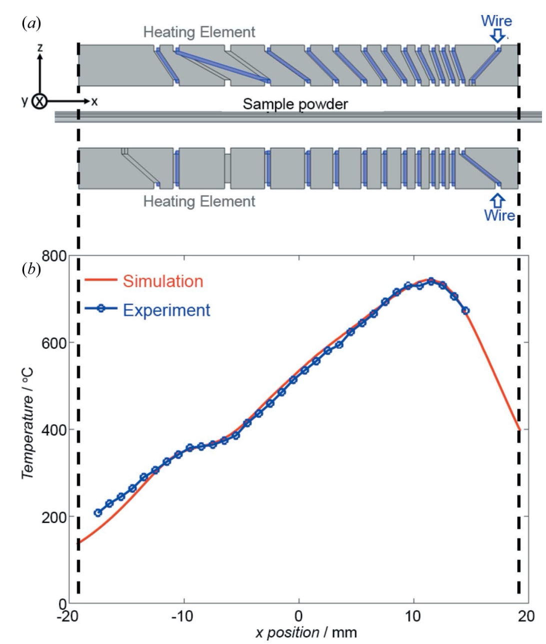
# When all fails: Parameter optimization

- Selected experiments + ML can be used to “determine” the likely value of missing/uncertain material parameters.

Example: Thermal profile of a sample in a thermal gradient furnace



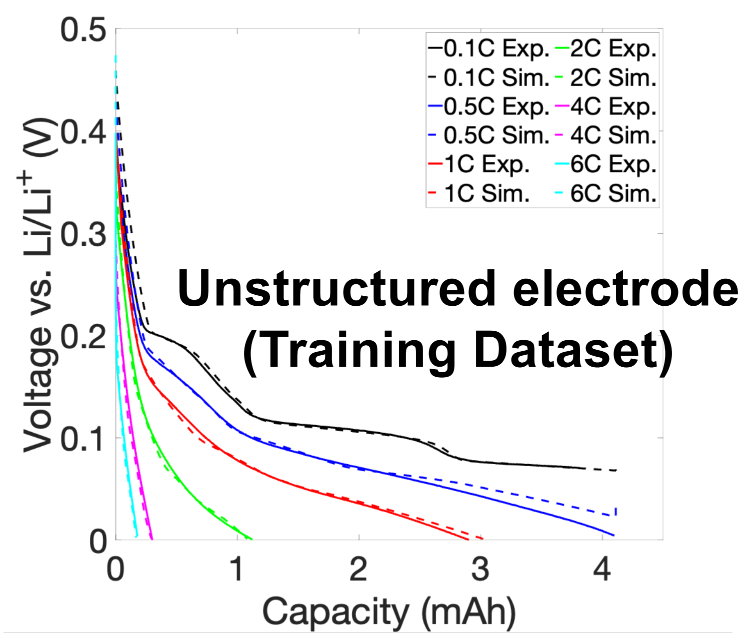



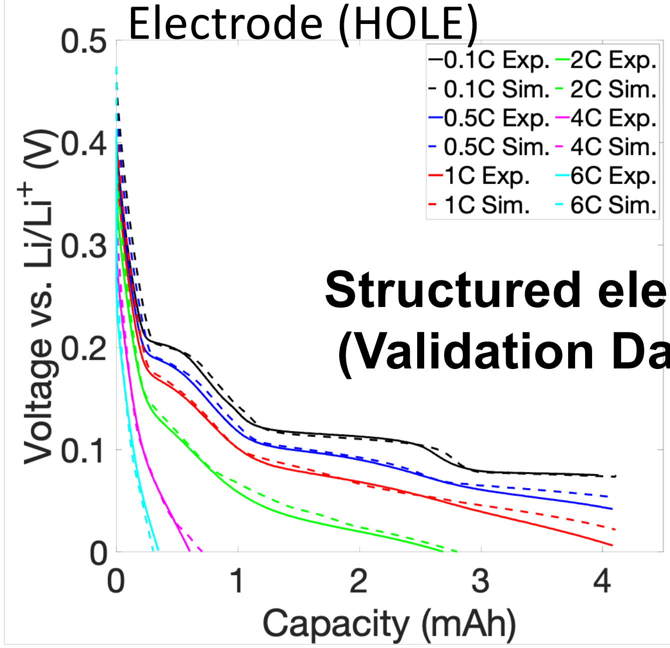

Huang … Thornton, Comp. Mat. Sci. (2021)

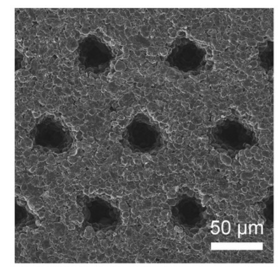
# ML-based model parameterization for battery modeling

- For coarse-grained (device scale) models, there are several parameters that are difficult to determine
  - Intrinsic properties modified by (implicit) microstructure
- **Three-electrode measurements** can be used to parameterize the model via particle swarm optimization
- Excellent agreement across the range of rates examined




Highly Ordered Laser-Patterned Electrode (HOLE)




Goel ... Thornton, Energy Storage Mat. (2023)

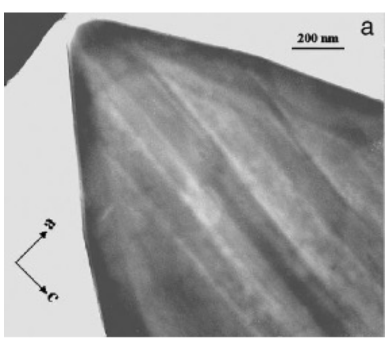
# A quick review & question break

- Material properties needed for electrochemical dynamics modeling
- Parameterization via lower-scale modeling
  - DFT + Monte Carlo
  - Ab initio MD, etc. for interfacial phenomena
- Parameterization optimization (ML)
- Questions?

Up next: Microstructure effect (ex. LFP)

# Role of microstructure: $LiFePO_4$ (LFP)

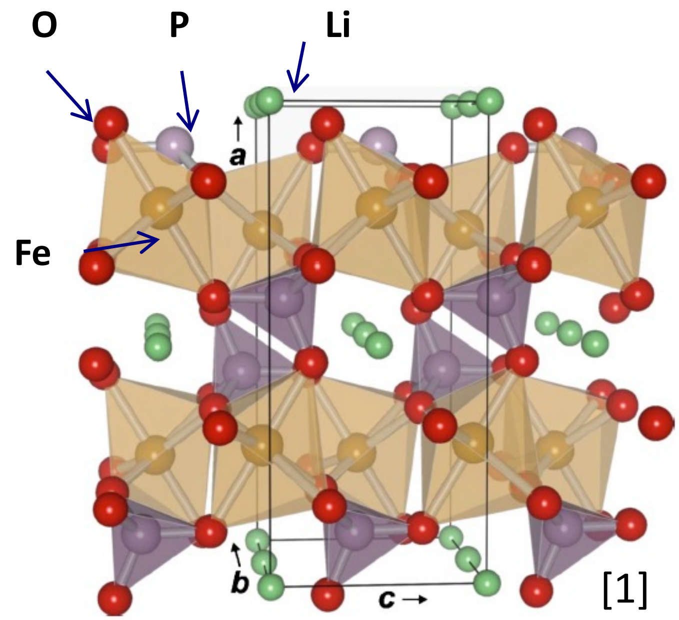
- Li intercalation compound
- $FePO_4$ is **earth abundant** (unlike cobalt)
- Considered not a promising candidate due to low electronic conductivity
- After nanosizing and coating with carbon, it was shown to be practical
- Olivine structure – highly anisotropic properties




**Two-phase reaction (Chen G, et al. 2006)**

**Highly anisotropic crystal**

Li intercalation along b channels




Olivine structure

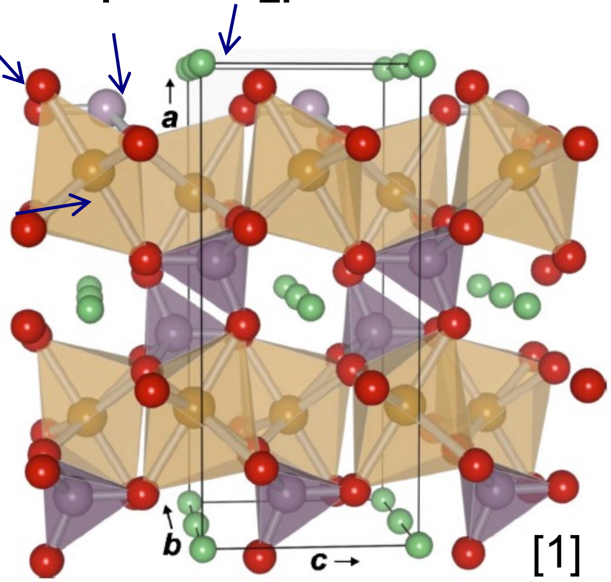
[1] T. Maxisch & G Ceder, *Phys Rev B* (2006)

- **Anisotropic mobility**
- **Anisotropic interfacial energy**
- **Anisotropic mechanical properties**
- **Anisotropic electron conduction**

# Role of microstructure: $LiFePO_4$ (LFP) DFT+ MC

**Highly anisotropic crystal**

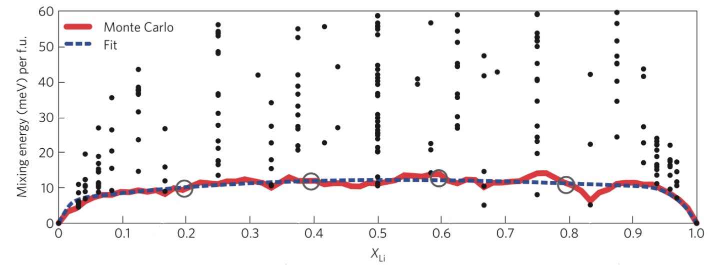
Li intercalation along b channels




Olivine structure

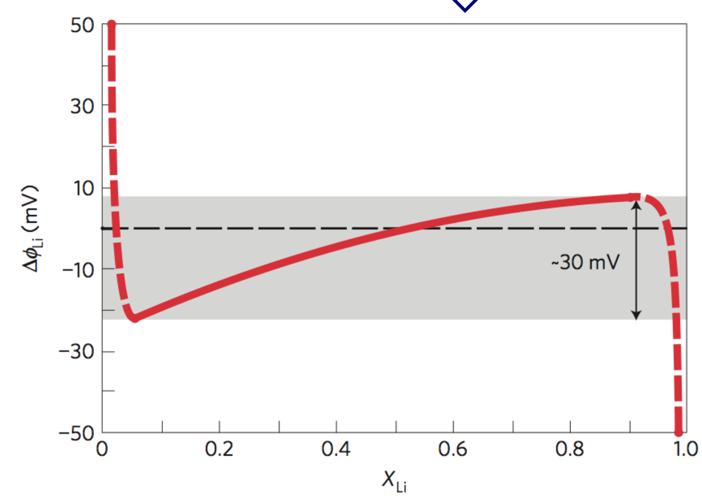
- **Anisotropic mobility**
- **Anisotropic interfacial energy**
- **Anisotropic mechanical properties**
- **Anisotropic electronic conductivity**

[1] T. Maxisch & G Ceder, *Phys Rev B* (2006)




Free energy of LFP

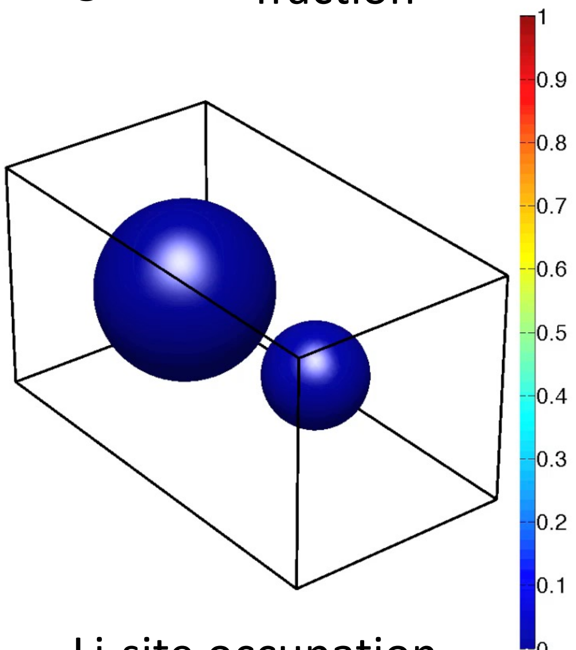
M. Malik *et al.*, Nat Mater (2011) – Ceder's group



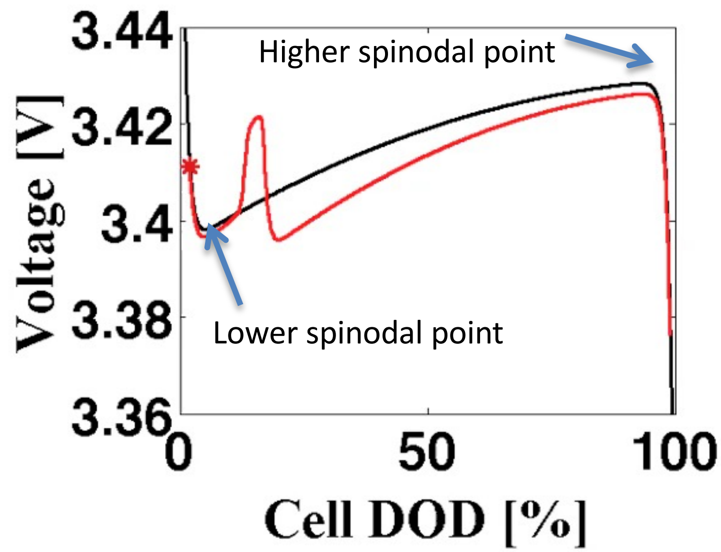

**Nonmonotonic Li chemical potential amplifies the stochasticity!**

# Particles with different sizes: sequential transformation

DOD: Depth of Discharge = Li-site occupation fraction

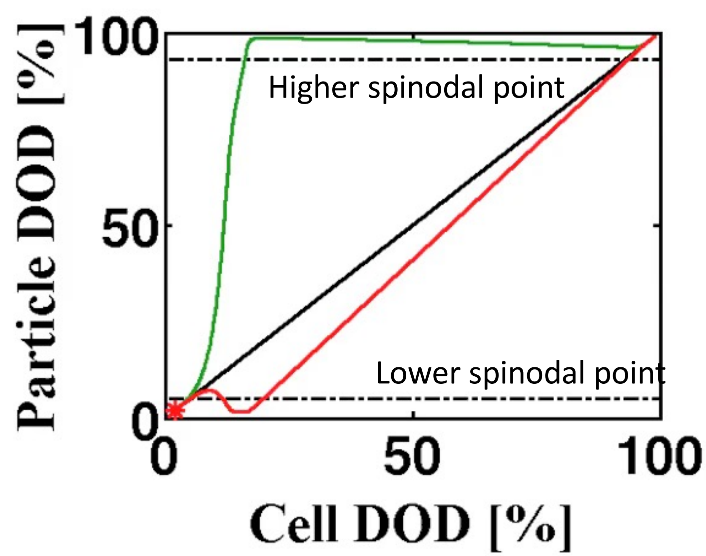



Li-site occupation fraction in the particles [x in $Li_xFePO_4$]




Equilibrium potential

Applied voltage




Smaller particle DOD

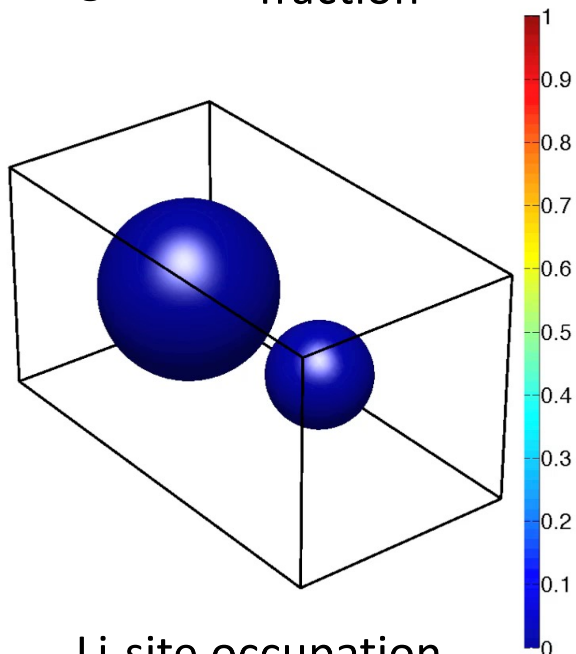
Cell DOD

Larger particle DOD

Orvananos … Thornton, 2015, J. Electrochem. Soc. 162 A965.

# Particles with different sizes: sequential transformation

DOD: Depth of Discharge = Li-site occupation fraction

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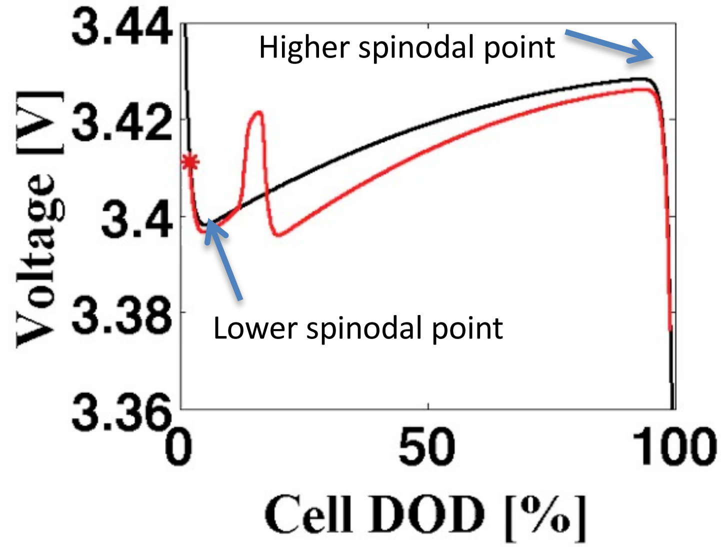
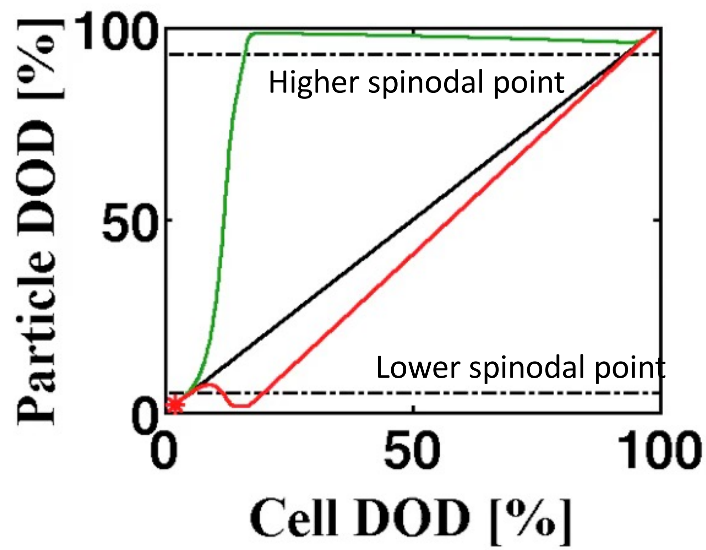



Equilibrium potential

Applied voltage




Smaller particle DOD

Cell DOD

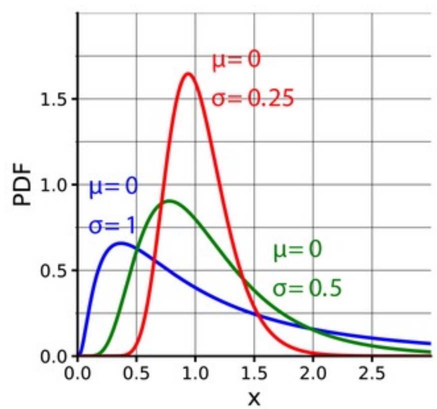
Larger particle DOD

Orv

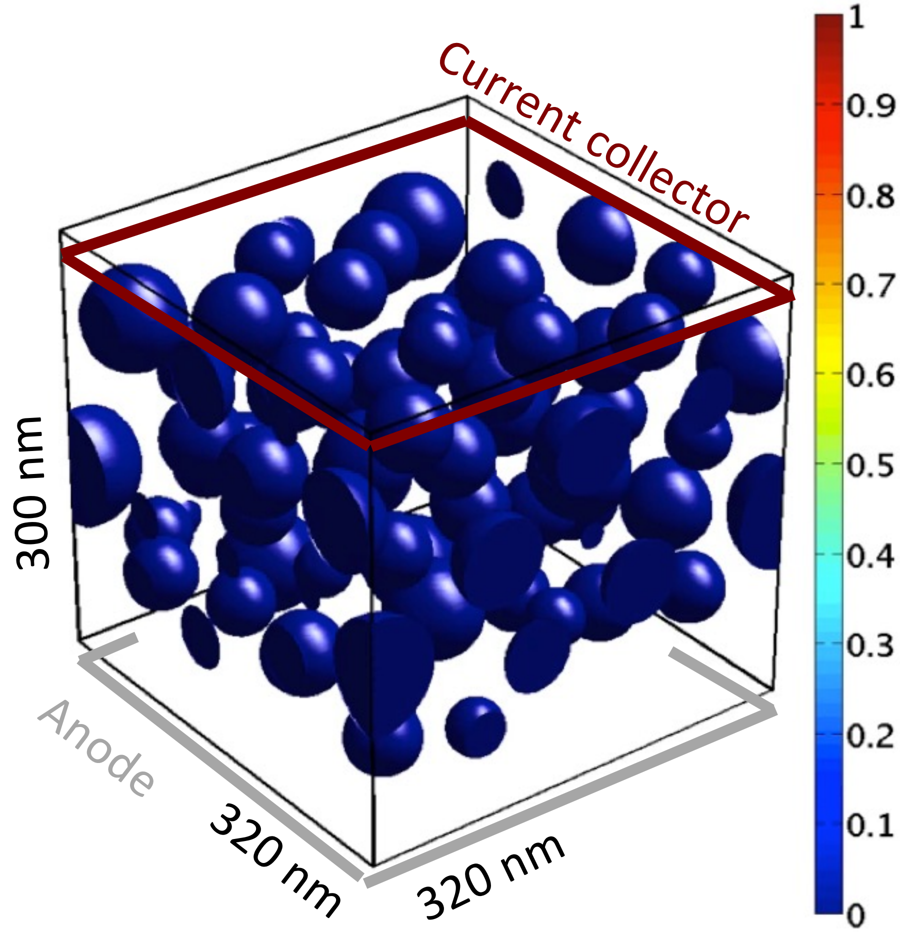
**Voltage fluctuation & nonmonotonic concentration evolution!**

# Insights gained applies for many particles

- 65 spherical particles with a log-normal size distribution, randomly positioned in a 300nm×320nm×320nm domain



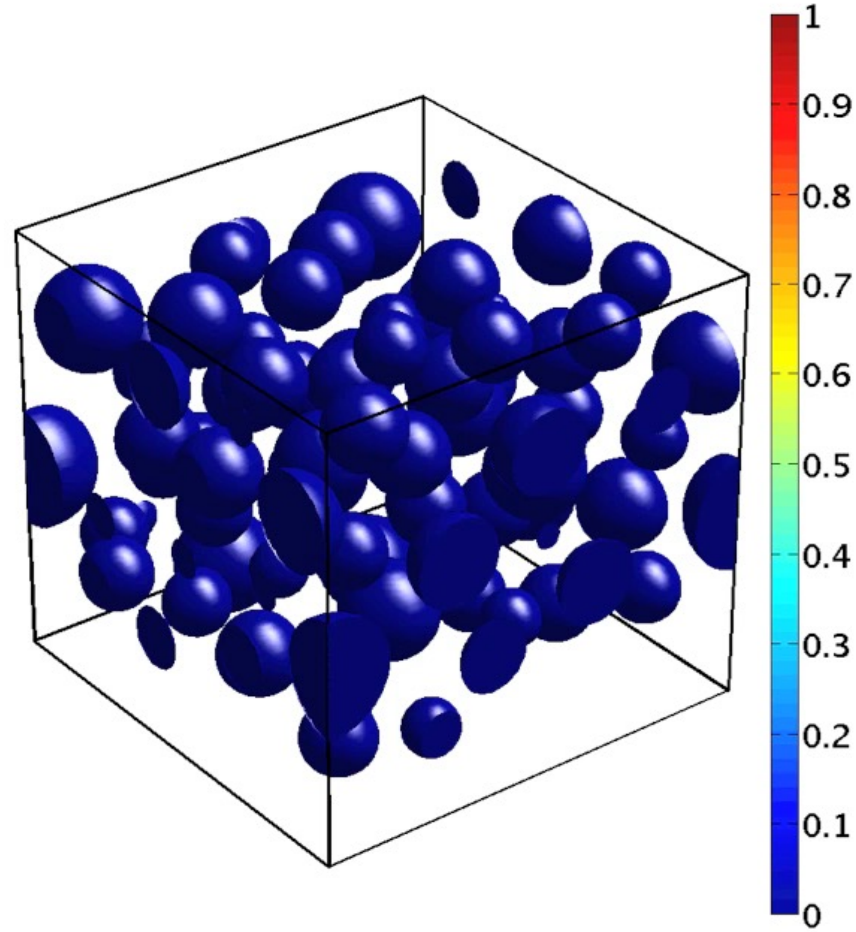

Log-normal distribution




Orvananos, B., … Thornton, 2014, Electrochimica Acta, 137, 245.

# Insights gained applies for many particles

- "Cell" discharged at C/11.1 rate
- Particles lithiate in groups
- Four sequential lithiation groups observed

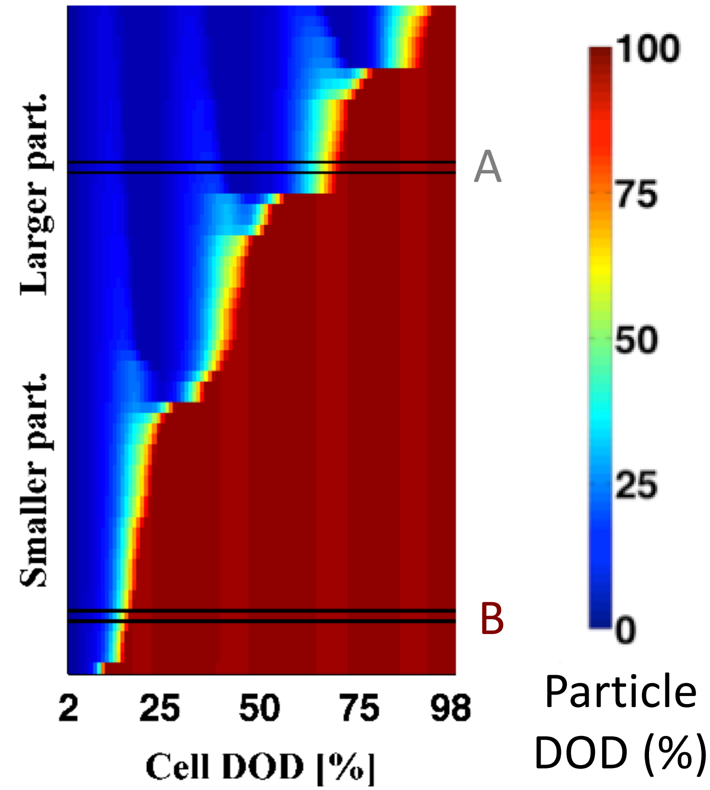


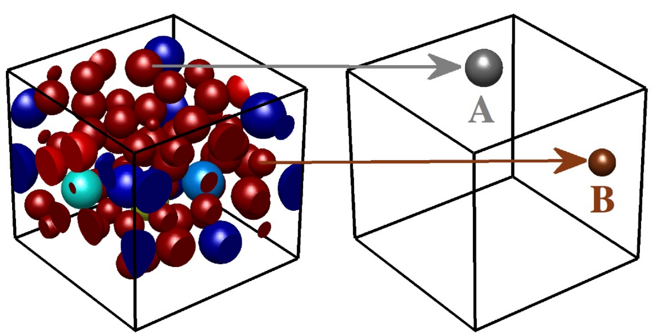

Li site fraction $Li_xFePO_4$

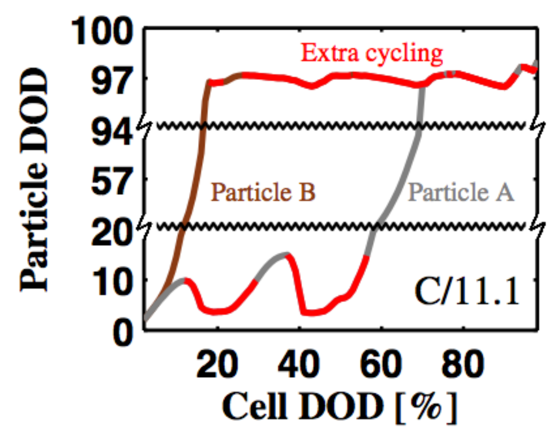
Orvananos, B., … Thornton, 2014, Electrochimica Acta, 137, 245.

# DOD of the particles ordered by particle size

- When the smaller particles undergo rapid lithiation, they extract lithium from the larger particles
- When the larger particles phase transform, they extract lithium from the smaller ones, but to a lesser degree



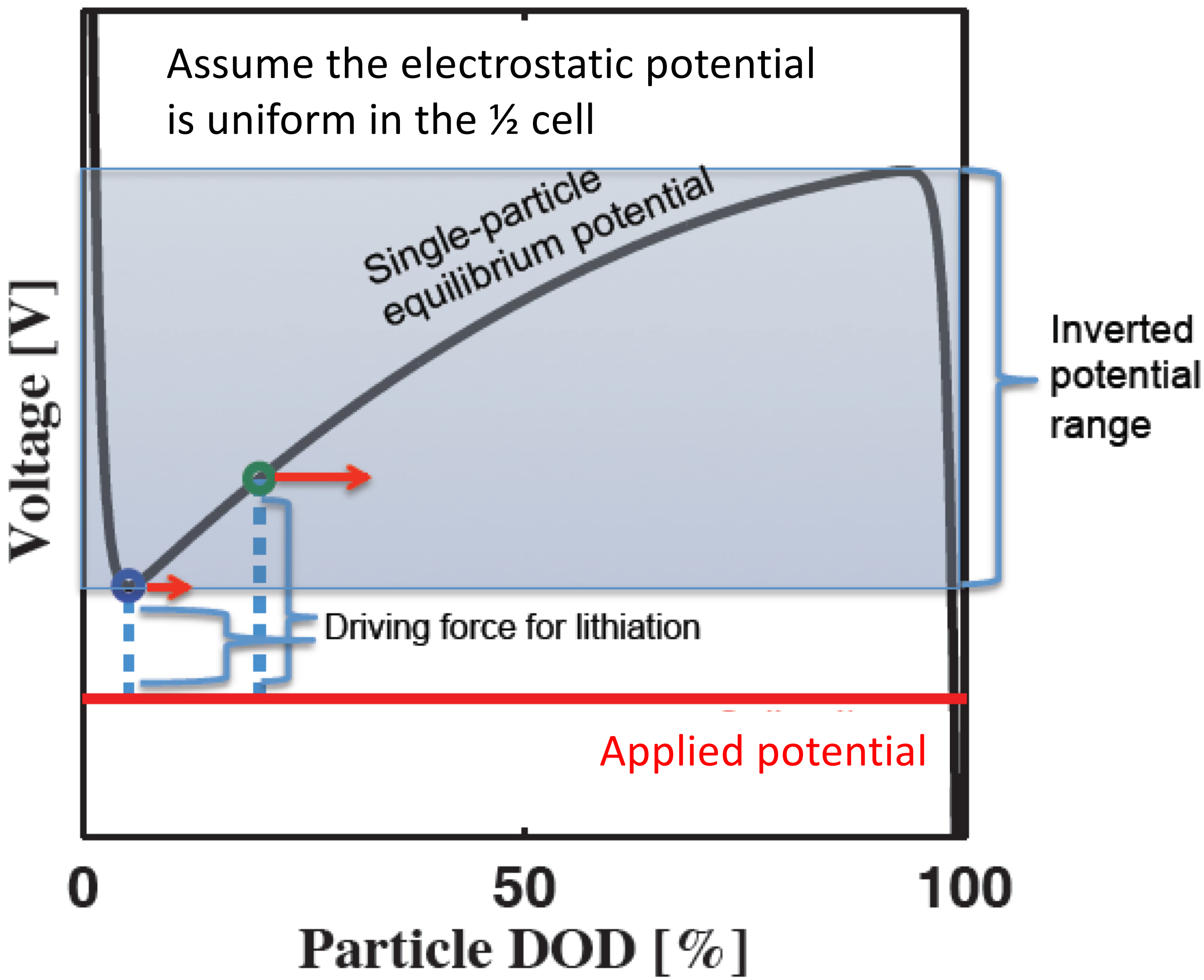




Orvananos, B., … Thornton, 2014, Electrochimica Acta, 137, 245.

# What's the mechanism behind this behavior?

- Driving force for lithiation




DOD:
Depth of
Discharge
=
Li occupation
fraction

DOD varies from particle to particle

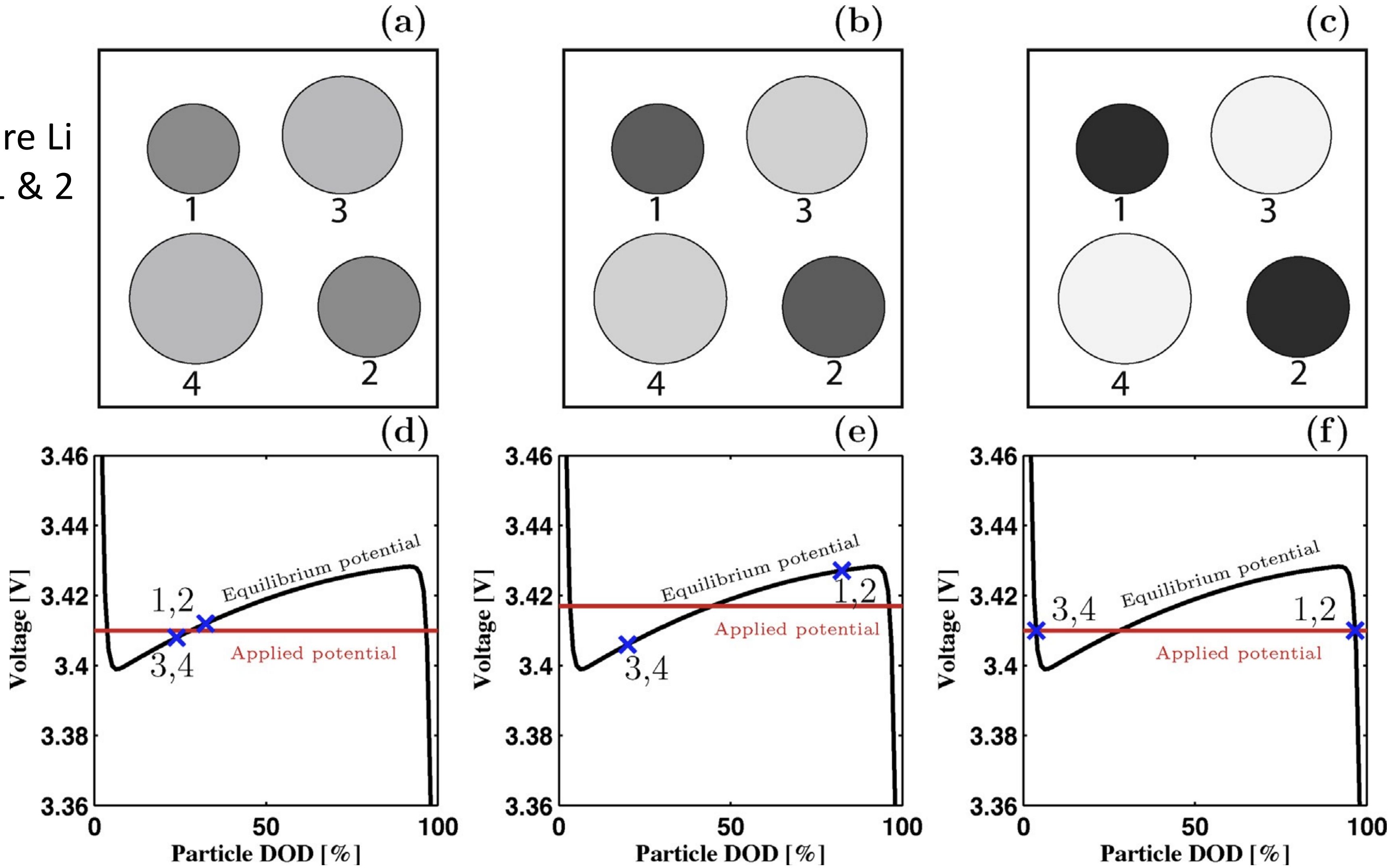
Size dependence due to different surface area per volume

# What's the mechanism behind this behavior?

Orvananos, B., … Thornton, 2014, Electrochimica Acta, 137, 245.

- Redistribution

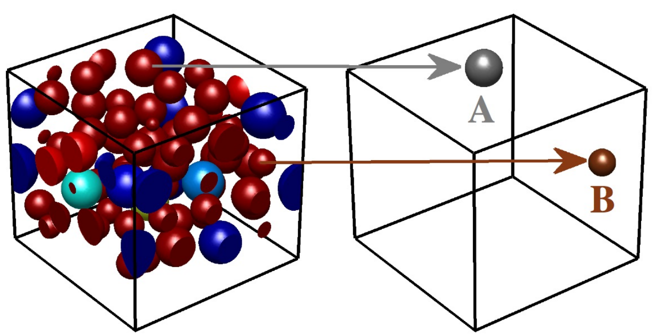
More Li
in 1 & 2




(Li occupation fraction)

# Consequence of interpaticle phase separation

- When the smaller particles undergo rapid lithiation, they extract lithium from the larger particles
- When the larger particles phase transform, they extract lithium from the smaller ones, but to a lesser degree

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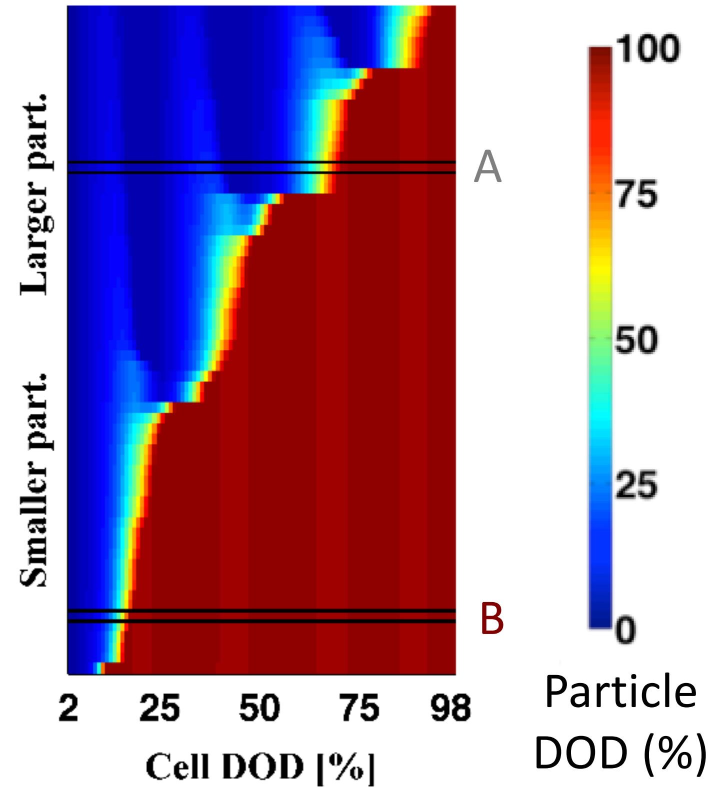
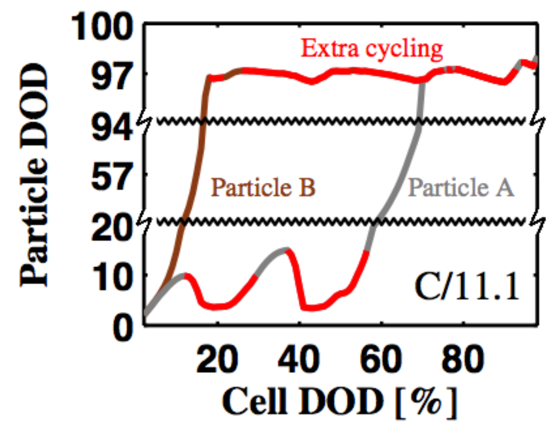
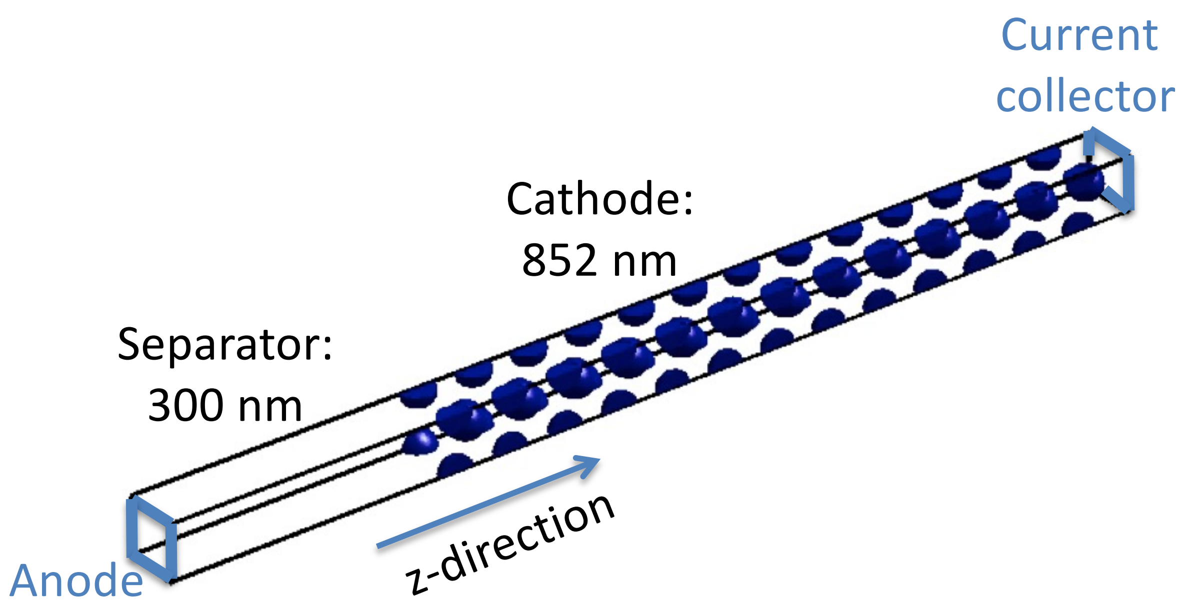


# How about the potential gradient over the cell?

- 26 particles with a 40 nm diameter in BCC arrangement
- Periodic boundary conditions in x-z and y-z planes
- Minimum distance between particles: 15.43 nm

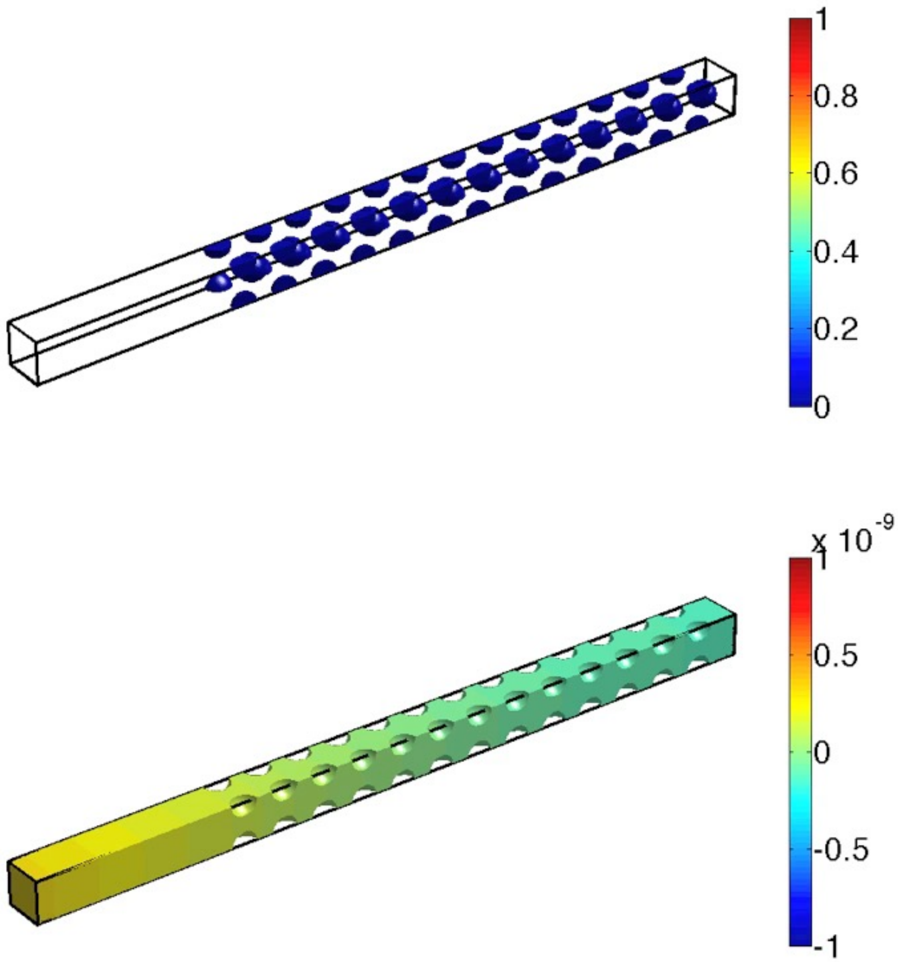



Orvananos, … Thornton, J. Electrochem. Soc., 161, A535-A546 (2014)

# Discharge (Li intercalation) at C/12 Rate

Li-site fraction in the particles [x in $Li_xFePO_4$]

Salt concentration diff. from avg. conc. [mol/cm3]

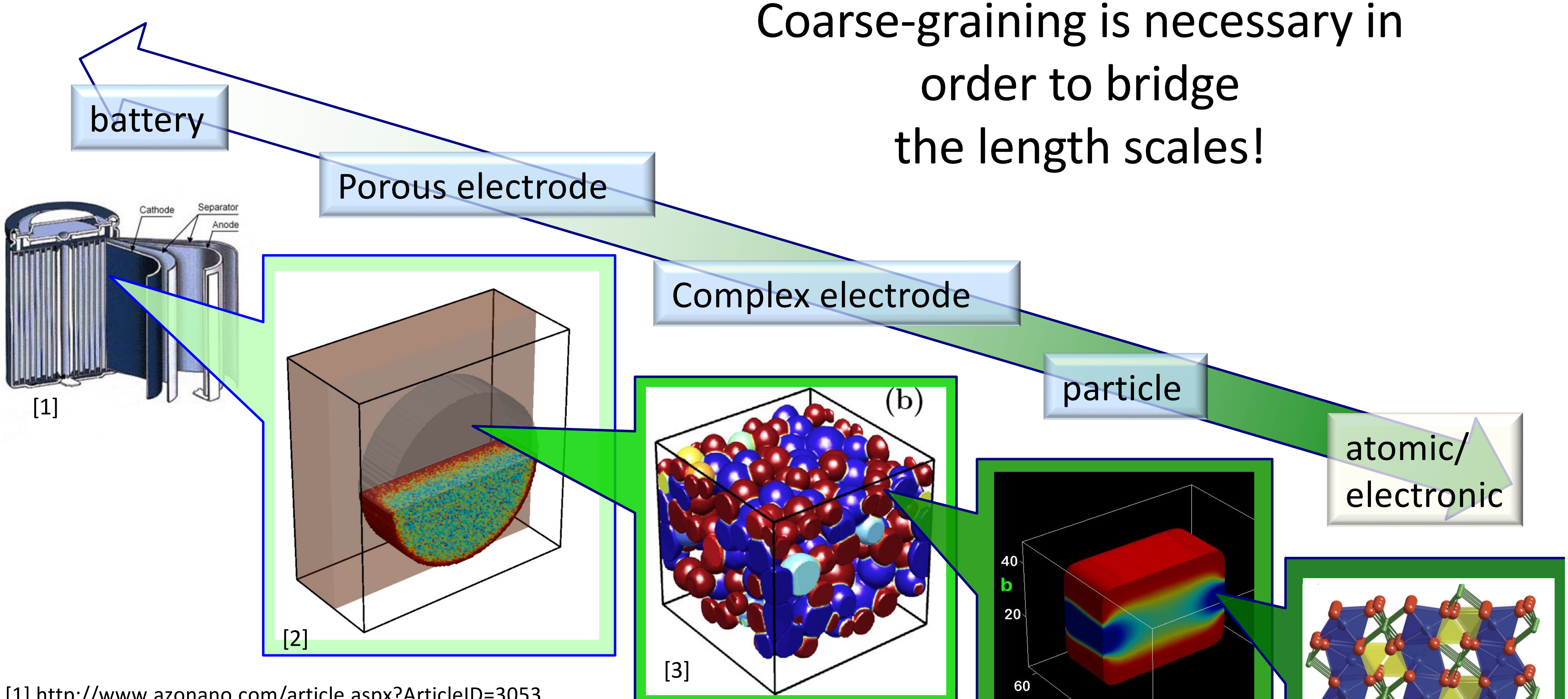


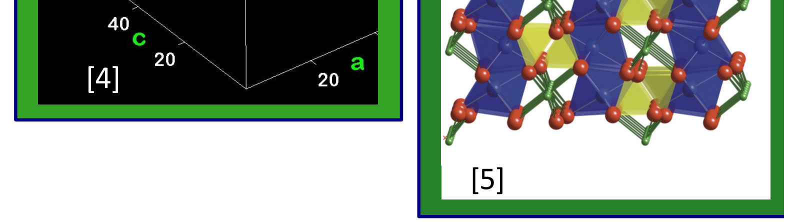

- Initial uniform concentration buildup
- Followed by a rapid lithiation closer to the separator
- The reaction front moves in an intermittent manner
- ~5 waves

Orvananos, … Thornton, J. Electrochem. Soc., 161, A535-A546 (2014)

# Electrochemical Simulations at Multiple Scales

Coarse-graining is necessary in order to bridge the length scales!




[1] http://www.azonano.com/article.aspx?ArticleID=3053
[2] F. C. Strobridge, B. Orvananos, M. Croft, H.-C. Yu, R. Robert, H. Liu, Z. Zhong, T. Connolley, M. Drakopoulos, K. Thornton, and C. P. Grey, Chemistry of Materials, 27, 2374–2386 (2015)
[3] B. Orvananos, R. Malik, H.-C. Yu, A. Abdellahi, C. P. Grey, G. Ceder, and K. Thornton, Electrochimica Acta 137, 245-247 (2014)
[4] H.C. Yu and Thornton
[5] Y.S. Meng and M. E. Arroyo-de Dompablob, Energy Environ. Sci., 2, 589–609 (2009)

# Approach: Coarse-Graining

1. Develop tools for accurate prediction with direct simulation

- Can be used to develop understanding of the effect of microstructures
- Complex phenomena such as anisotropy can be captured

2. Develop accurate mean-field description

- Examples
  - Effective properties based on the geometric features of the complex microstructures
  - Tortuosity expression
  - Dimensionless parameter that correlates with performance

3. Application to electrode/cell performance simulations

# Coarse-grained governing equations – Parameters "accounting for" microstructures

**Mass transport in the active material:**

$$\frac{\partial c_{p,\psi}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{p,\psi} r^2 \frac{\partial c_{p,\psi}}{\partial r}\right)$$

**Mass transport in the electrolyte:**

$$\varepsilon_\psi \frac{\partial c_{e,\psi}}{\partial t} = \nabla \cdot \left(D_{eff,\psi} \nabla c_{e,\psi}\right) + \left(1 - t^0_{+,\psi}\right) a^p_\psi J_\psi - \frac{i_{e,\psi} \cdot \nabla t^0_{+,\psi}}{F}$$

**Electrostatic potential of electrolyte:**

$$-\nabla \cdot \left(\kappa_{eff,\psi} \nabla \phi_{e,\psi} + \frac{2RT}{F} \kappa_{eff,\psi} \left(1 + \frac{\partial \ln\left(f_{\pm,\psi}\right)}{\partial \ln\left(c_{e,\psi}\right)}\right)\left(1 - t^0_{+,\psi}\right) \nabla \ln c_{e,\psi}\right) = a^p_\psi F J_\psi$$

**Electrostatic potential of solid:**

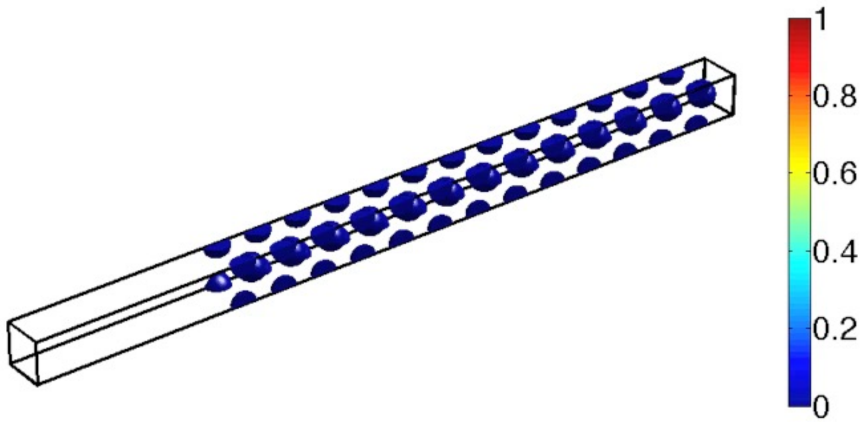
$$\nabla \cdot \left(\sigma_{eff,\psi} \nabla \phi_{sp,\psi}\right) = a^p_\psi F J_\psi$$

**Electrochemical reaction:**

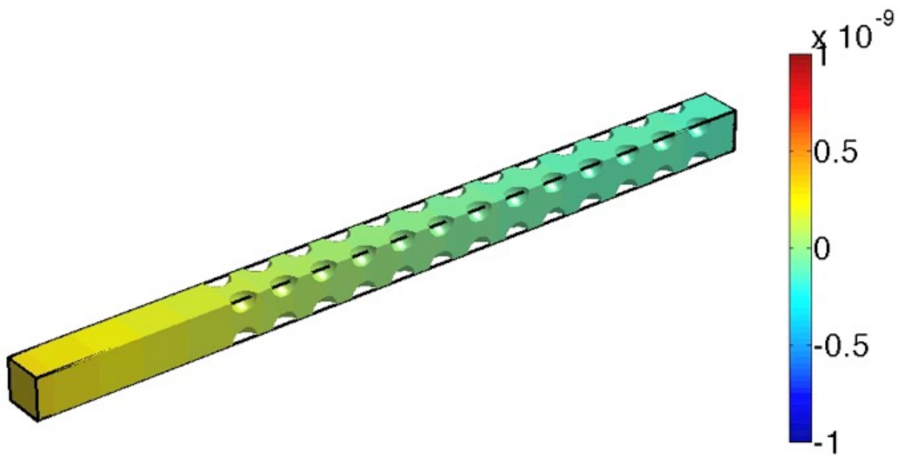
$$J_\psi = k_\psi \left(c^{max}_{p,\psi} - c^{surf}_{p,\psi}\right)^{1/2} \left(c^{surf}_{p,\psi}\right)^{1/2} \left(\frac{c_{e,\psi}}{c_{e,ref}}\right)^{1/2} \left(\exp\left(\frac{0.5F}{RT}\eta_\psi\right) - \exp\left(\frac{-0.5F}{RT}\eta_\psi\right)\right)$$

# Discharge (Li intercalation) at C/12 Rate

Li-site fraction
in the particles
[x in $Li_xFePO_4$]



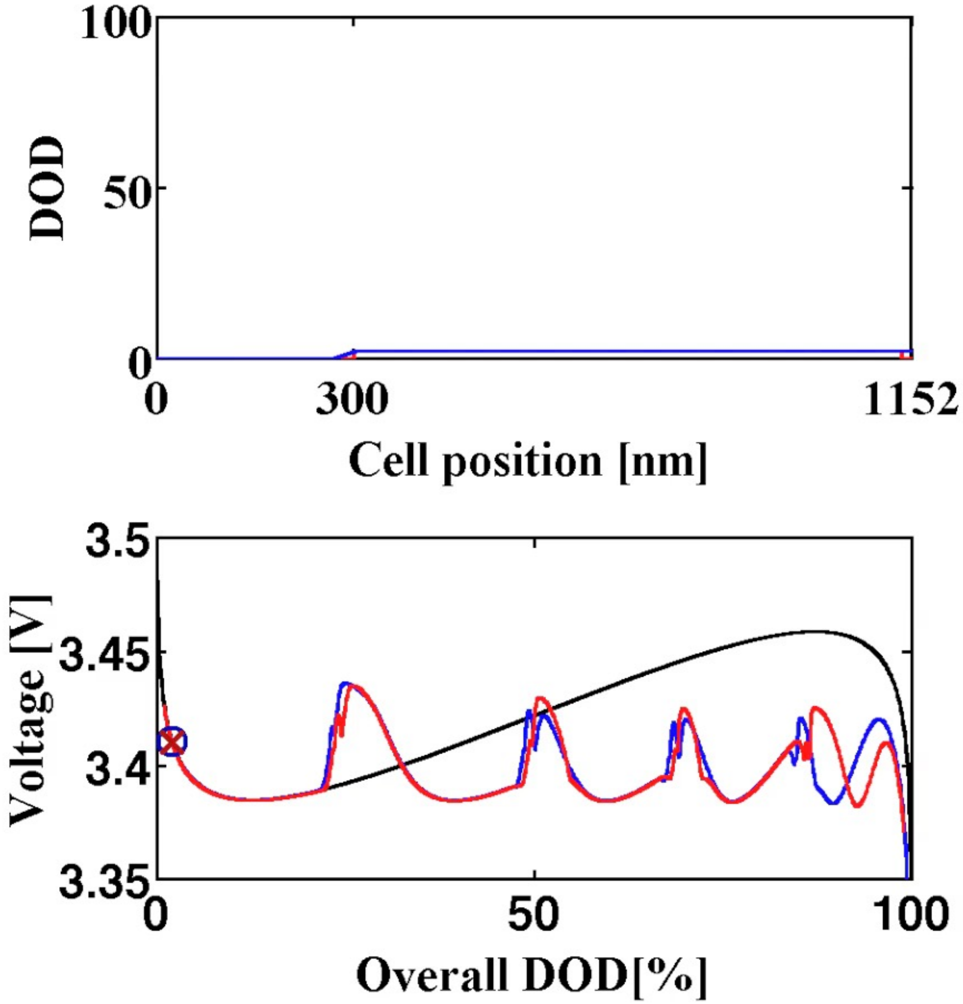

Salt concentration diff.
from avg. conc.
[mol/cm3]




- Initial uniform concentration buildup
- Followed by a rapid lithiation closer to the separator
- The reaction front moves in an intermittent manner

Orvananos, … Thornton, J. Electrochem. Soc., 161, A535-A546 (2014)

# Comparison to porous electrode simulations




Red curve: Particle-level simulation

Blue curve: Porous electrode simulation

Black curve: Single particle equilibrium potential

Particle size distribution not included

Orvananos, … Thornton, J. Electrochem. Soc., 161, A535-A546 (2014)

# A quick review & question break

- Intro to LFP
  - Highly anisotropic
  - Tendency for phase separation

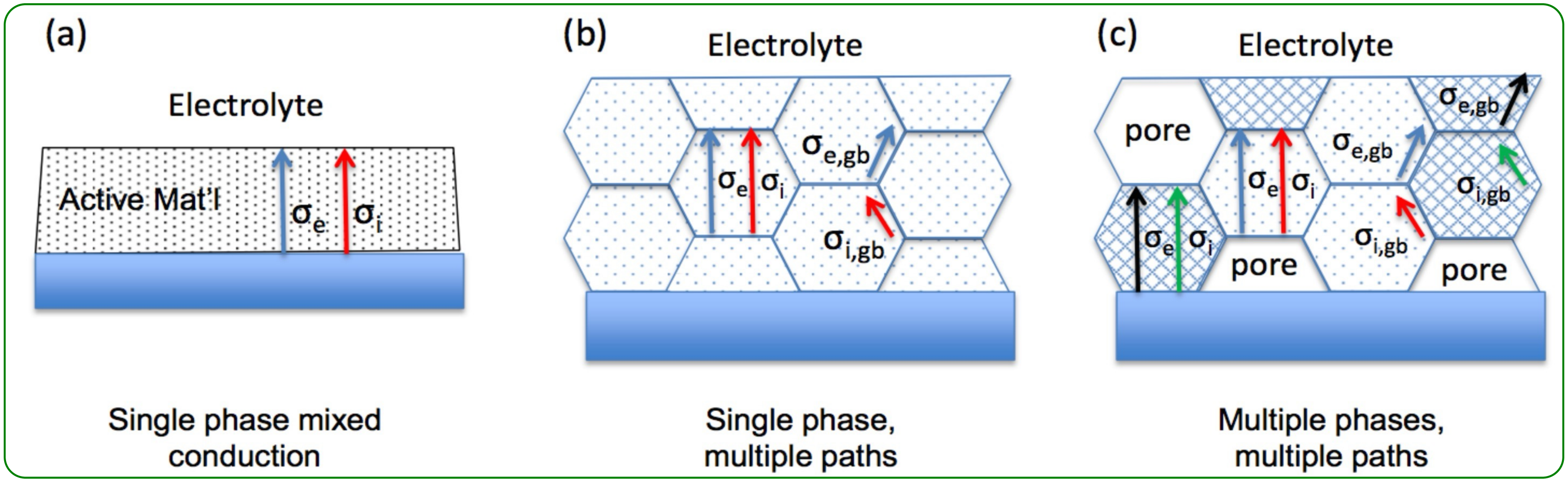
- Interpaticle phase separation
  - Due to their size distribution
  - Due to spatial position (electrostatic potential difference)

- Questions?

Up next: Microstructure effect on transport

# Transport in Electrode: Mesoscale to Microscale

**Focus:** To examine the impact of mesoscale transport on macroscale performance of battery electrodes

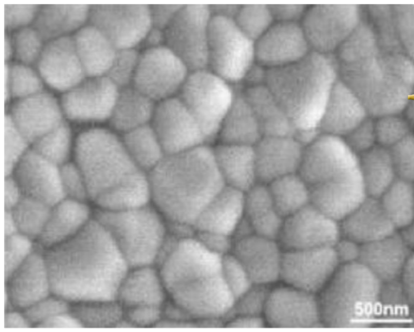



- Establish **the relationship between morphological features and effective transport behavior.**
- **Elucidate the impact of tortuous grain boundary transport** in electrode structures.
- **Develop design rules** for transport of ions and electrons in complex electrode structures (multiple phases and paths) to enable synthesis of electrode particles and fabrication of electrodes with **optimal performance**.

# Enhanced/Hindered Grain Boundary Diffusion

## Solid Oxide Fuel Cells

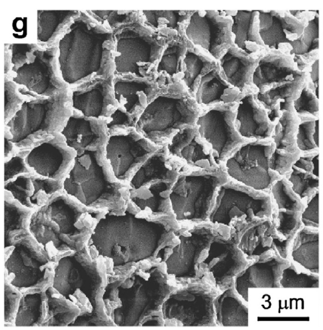
Yttria-Stabilized Zirconia (YSZ)




J. Obare, et al. *Scr. Mater.* **2013**, 68, 111

## Solid State Battery Electrolyte

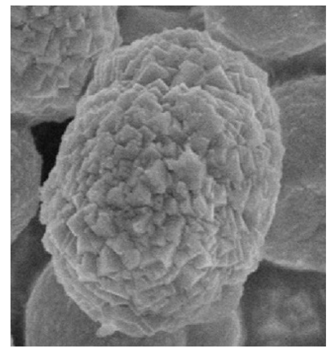
$Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZO)



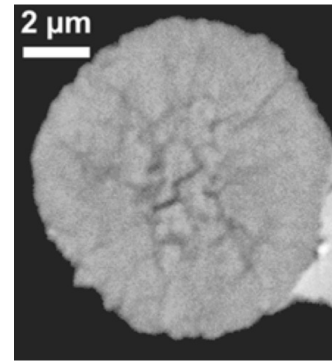

E.J. Cheng, et al. *Electrochem. Acta* **2017**, 223, 85

## Battery Cathode Particles

Nickel Mangenese Cobalt oxide (NMC)
Nickel Cobalt Aluminum oxide (NCA)



Y. Fang, et al. *J. Alloys Compd.* **2018**, 743, 707




Courtesy of Ping-Chun Tsai, Bohua Wen, Yet-Ming Chiang MIT

**Other applications:**

- Impurities in solar cells (e.g., CdTe)
- Structural materials (change in GB characteristics

NECCES
A DOE Energy Frontier Research Center

# Approaches

1. Develop tools for accurate prediction with direct simulation

- Can be used to develop understanding of the effect of microstructures on transport.
- Complex cases such as orientation-dependence can be captured.

2. Develop accurate mean-field description

- An expression capable of universally predicting the transport behavior based on the **geometric features** of the complex microstructures.
- Enable better prediction of the transport behavior in microstructures with varying degrees of anisotropy without the use of computationally intensive simulations.

3. Application to electrode/cell performance simulations

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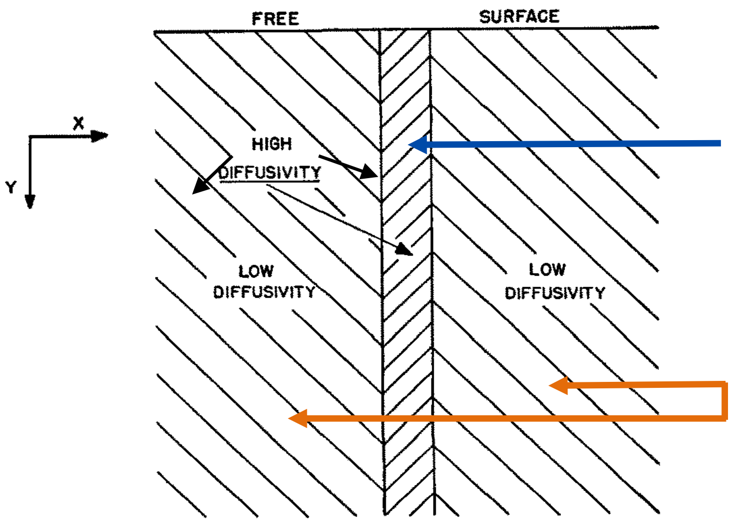
# Modeling GB Diffusion: Sharp Interface Description



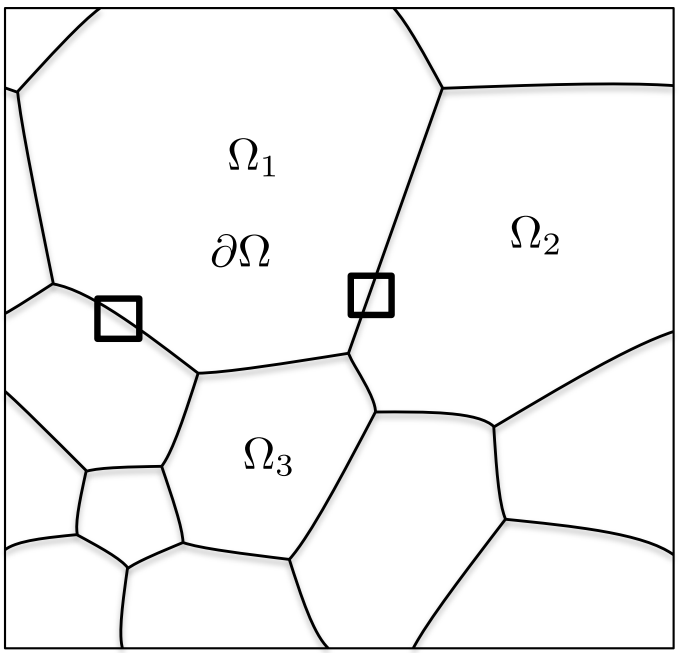

## Grain Boundary Diffusion (1D)

$$\frac{\partial C}{\partial t} = D_{gb}\left(\frac{\partial^2 C}{\partial y^2}\right) + \left(\frac{2}{\xi}\right) D_b \left(\frac{\partial C}{\partial x}\right)_0$$

## Bulk Diffusion

$$\frac{\partial C}{\partial t} = D_b \nabla^2 C$$

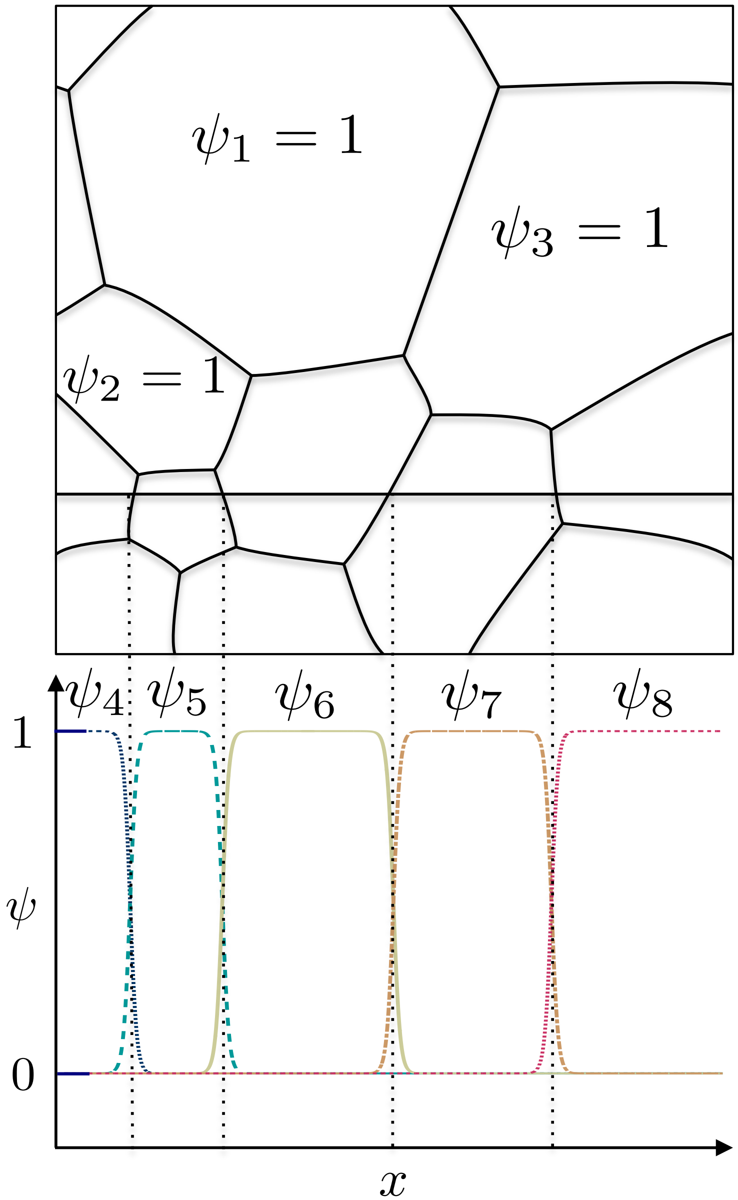
J. C. Fisher, J. Appl. Phys. **22**, 74 (1951).




## Grain Boundary Diffusion (2D/3D)

- The bulk of the domain (i.e. grains) are defined by $\Omega$
- The domain boundaries (i.e. grain boundaries) are denoted by $\partial\Omega$, where the interface has zero thickness
- Meshing can become cumbersome

# Modeling GB Diffusion: Diffuse Interface Description



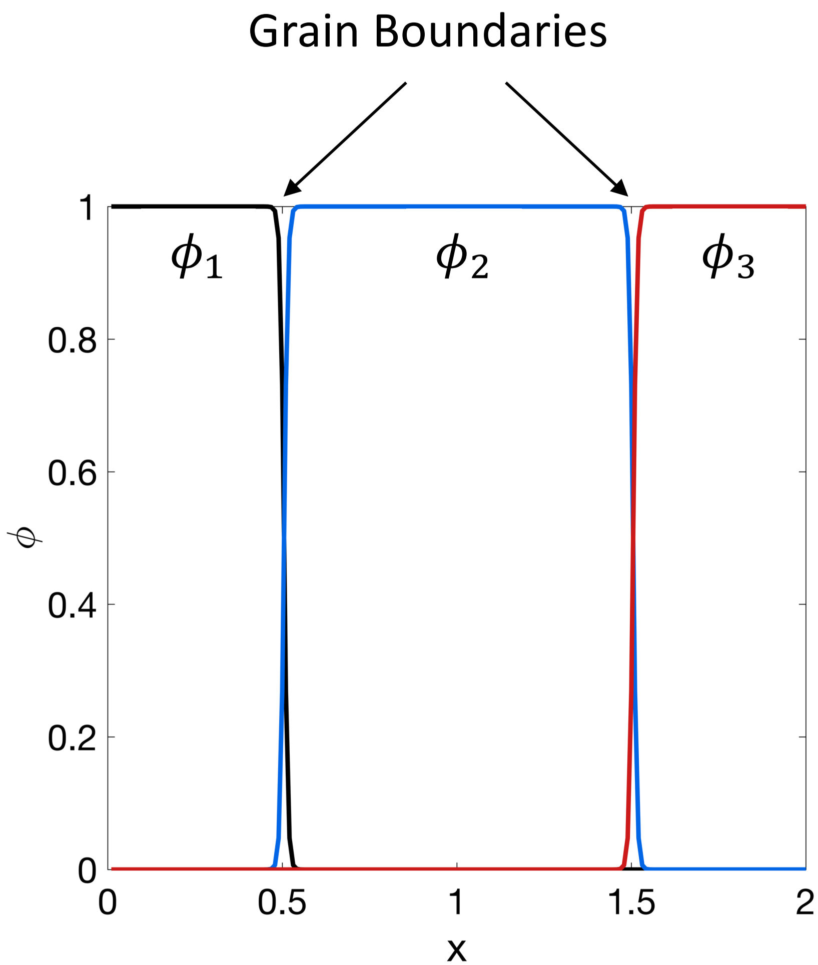

- A continuous domain parameter $\psi(x)$ is used to distinguish the different grains and boundaries
- The bulk of the grains are defined in regions which $\psi = 1$
- The domain of one grain smoothly transitions from zero to one at the boundary so that $0 < \psi < 1$
- Easily extendable to 3D

**SBM Coupled Bulk and Boundary Diffusion:**

$$\frac{\partial C}{\partial t} = \frac{1}{1 + \frac{\lambda_g}{2}\sum_{q=1}^{Q} |\nabla \psi_q|}\left[\nabla \cdot D_b \nabla C - \frac{1}{2}\left(\sum_{q=1}^{Q} |\nabla \psi_q| \lambda_g D_g \nabla_\Gamma^2 C\right)\right]$$

SBM converges to the conventional equations ✓

# Hindered Grain Boundary Diffusion




$\kappa$: Degree of hindrance

$\delta$ : Interface thickness

$D_{bulk}$ : Bulk diffusivity

$D_{gb}$ : Grain boundary diffusivity

Sharp Interface

$$\frac{\partial C}{\partial t} = D_{bulk} \frac{\partial^2 C}{\partial x^2}$$

$$J_{gb} = -\frac{1}{\kappa} \Delta C_{gb}$$

Diffuse Interface (SBM)

$$\frac{\partial C_q}{\partial t} = D_{bulk} \frac{1}{\phi_q} \frac{\partial}{\partial x} \phi_q \frac{\partial C_q}{\partial x} + \boxed{\frac{1}{\phi_q} \left| \frac{\partial \phi_q}{\partial x} \right| \left[ -\frac{1}{\kappa} \Delta C_{gb} \right]}$$

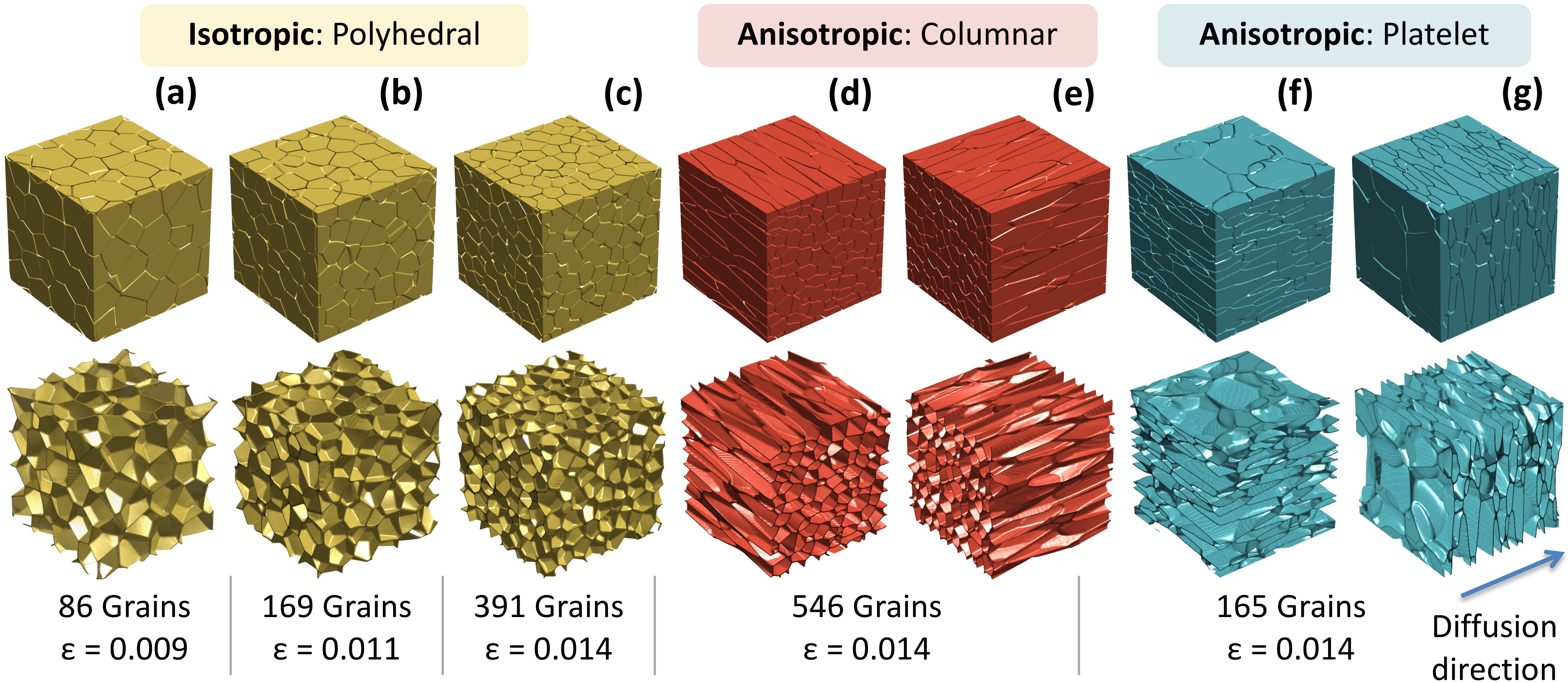
$$\Delta C_{gb} = C_q - \frac{\sum_{i \neq q}^{Q} \phi_i C_i}{\sum_{i \neq q}^{Q} \phi_i}$$

SBM Term

$$\kappa = \delta \left( \frac{1}{D_{gb}} - \frac{1}{D_{bulk}} \right)$$

# Polycrystalline Microstructures

## Varying Degrees of Anisotropy in Grain Morphologies




Renderings, using DREAM.3D, of the bulk and grain boundary network of **(a-g)** various microstructures with isotropic (polyhedral grains; **yellow**) and anisotropic grain morphologies (columnar and platelet grains; **red** and **teal**). The grain boundary volume fraction is denoted as ε.

DREAM.3D: http://dream3d.bluequartz.net

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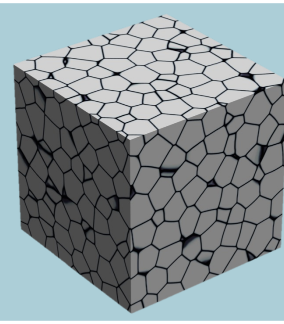
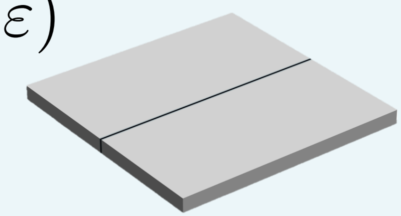
# Effective Diffusivities

$$D_{eff}^{Flux} = -J_{avg}\frac{L}{\Delta C}$$



Calculated from steady-state solutions from polycrystalline simulations.

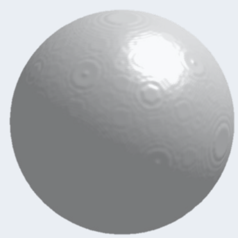
$$D_{eff}^{Hart} = D_g\varepsilon + D_b(1-\varepsilon)$$



Hart's prediction of effective diffusivity assumes uniformly oriented grains parallel to main diffusion direction.

Hart, Acta Metallurgica, 5, 597 (1957)

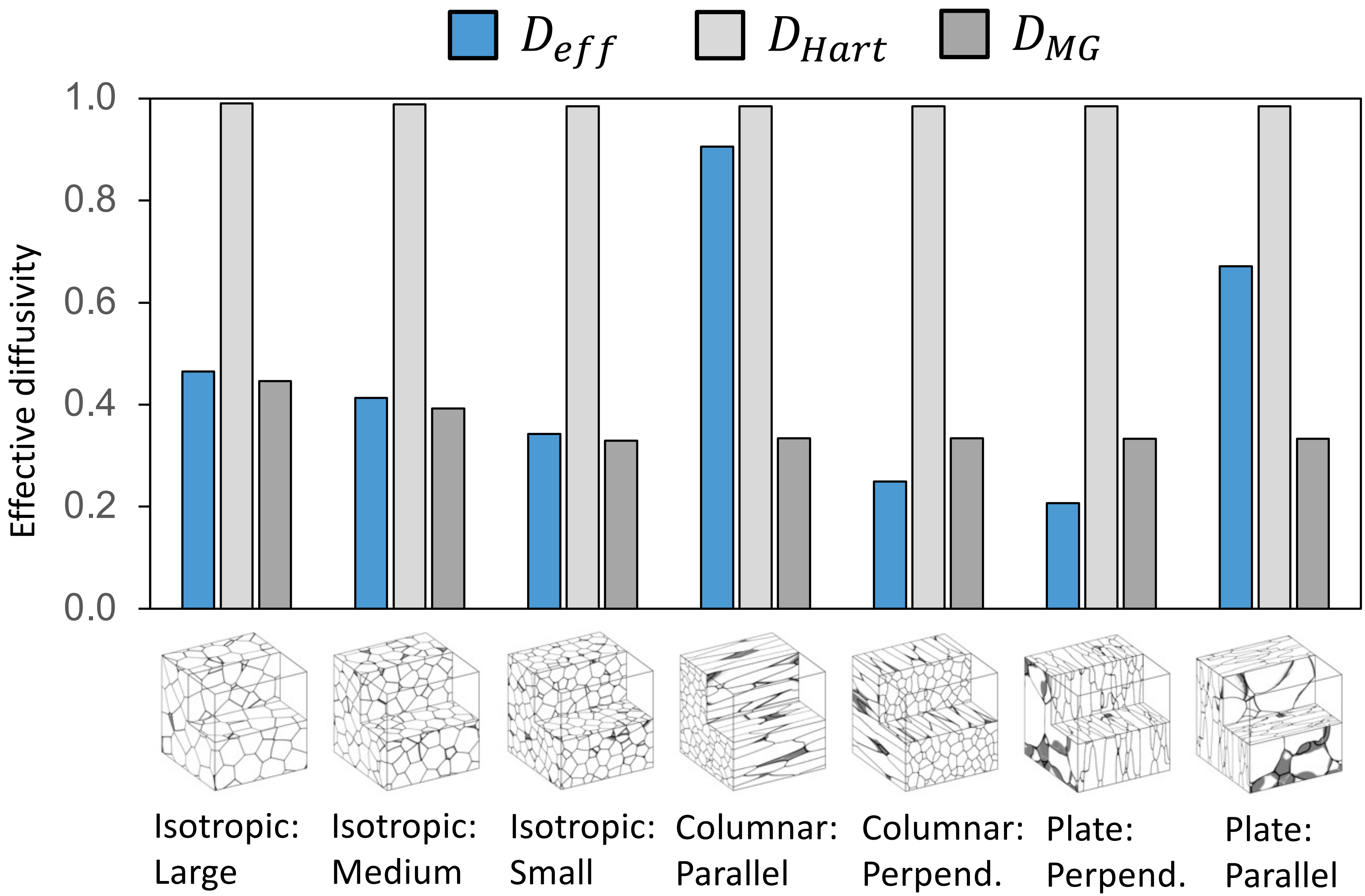
$$D_{eff}^{MG} = \frac{D_g\Big((3-2\varepsilon)D_b + 2\varepsilon D_g\Big)}{\varepsilon D_b + (3-\varepsilon)D_g}$$



Maxwell Garnett's prediction of effective diffusivity assumes isotropic spherical grains.

Garnett, Philos. Trans. R. Soc. 205, 397 (1905); Jamnik, et al. Phys. Chem. Chem. Phys. 8, 1310 (2006)

# Hindered GB Diffusion: Comparisons to Mean Field Approximations



# Predicting Transport Behavior from Geometric Features of the Microstructure

$$f_{act} = \frac{\sum_i A_i \left(\hat{t}_i \cdot \hat{d}\right)^2}{\sum_i A_i}$$

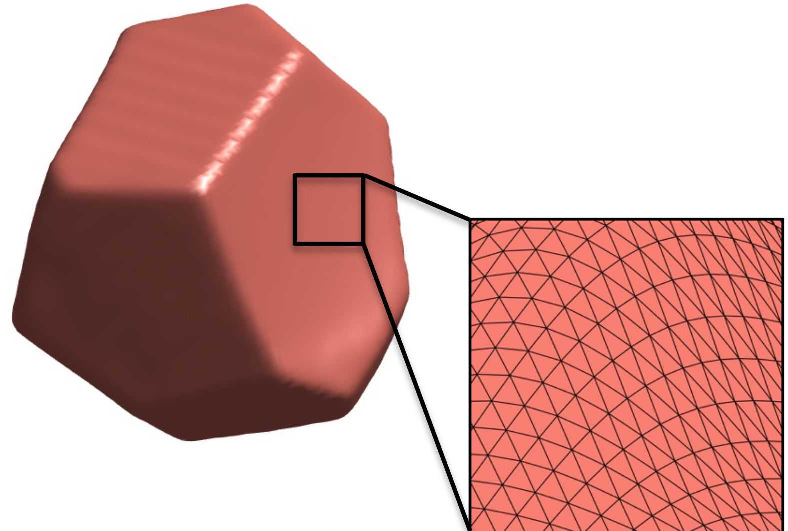
**Fraction of active area**

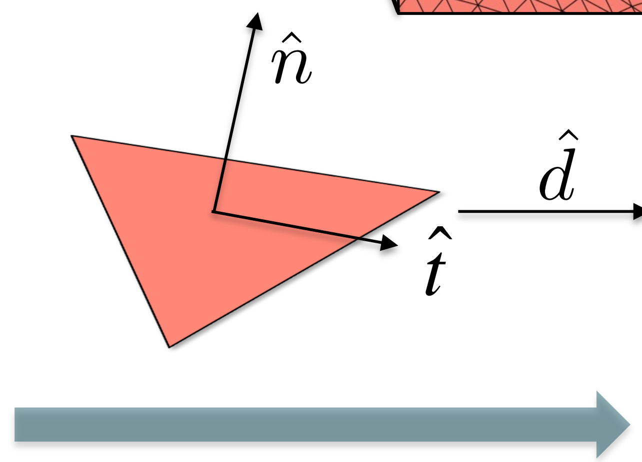
The grain boundary network can be projected in the main diffusion direction to yield the active fraction of the grain boundary network that enhances transport.

$$\varepsilon_{act} = \varepsilon f_{act}$$

$$D_{eff}^{proj} = D_g \varepsilon_{act} + D_b (1 - \varepsilon_{act})$$

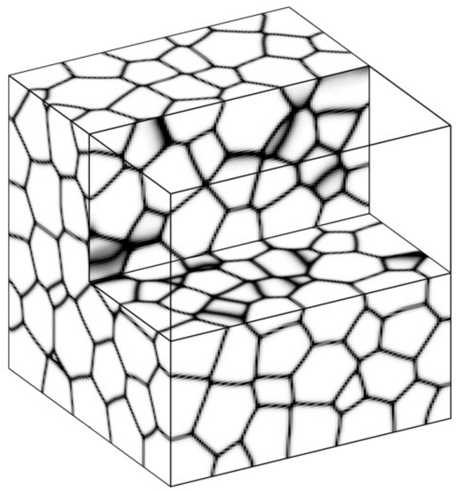
Hart's original equation can be rewritten to account for the active grain boundary fraction.

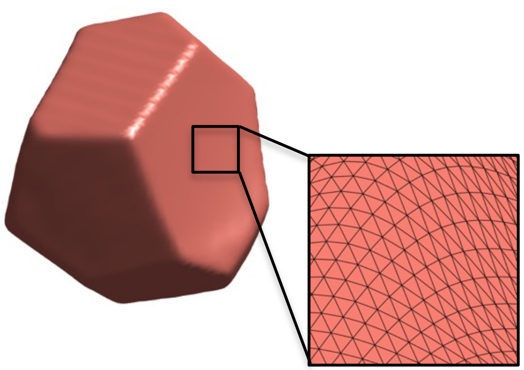


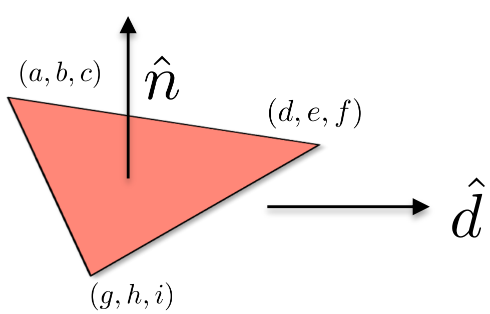



Principal Diffusion Direction

# Coarse-Grained Effective Diffusivity
## (Enhanced & Hindered)



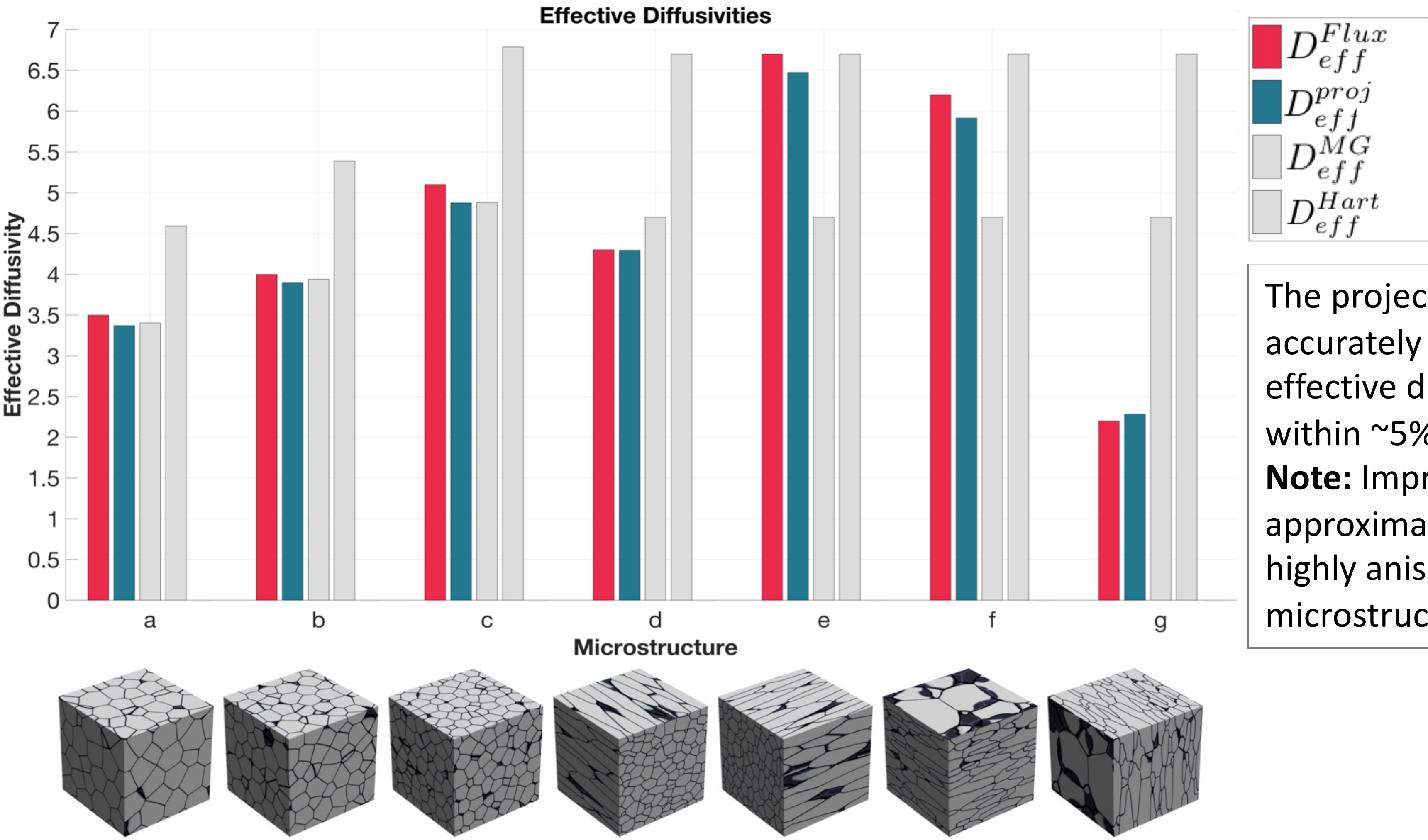





| | |
|---|---|
| $f_\perp = \dfrac{\sum_i A_i (\hat{n}_i \cdot \hat{d})^2}{\sum_i A_i}$<br>$f_\parallel = 1 - f_\perp$ | "Fraction of area" perpendicular to diffusion direction |
| $D_\parallel = \dfrac{f_\parallel \varepsilon D_{gb} + (1-\varepsilon) D_{bulk}}{f_\parallel \varepsilon + (1-\varepsilon)}$ | Parallel contribution |
| $D_{proj} = \dfrac{1}{\dfrac{f_\perp \varepsilon}{D_{gb}} + \dfrac{f_\parallel \varepsilon + (1-\varepsilon)}{D_\parallel}}$ | Harmonic mean of hindering and parallel contributions |

$V_{gb}$: grain boundary volume fraction

# Enhanced GB Diffusion: Comparisons




The projection method accurately predicts the effective diffusivities within ~5%.
**Note:** Improved approximations for highly anisotropic microstructures

Effective diffusivities calculated from **Simulations**, **Grain Boundary Projection**, **Maxwell-Garnett**, and **Hart** predictions, respectively. This illustrates the shortcomings of classical mean field approaches, which inadequately capture the complexity of microstructures.

# Extending the Model: Diffusivity Tensors

$$f_{act} = \frac{\sum_i A_i \left(\hat{t}_i \cdot \hat{d}\right)^2}{\sum_i A_i}$$

$$\overleftrightarrow{P}_i = \overleftrightarrow{I} - \hat{n} \otimes \hat{n} = \begin{pmatrix} 1 - n_1 n_1 & -n_1 n_2 & -n_1 n_3 \\ -n_2 n_1 & 1 - n_2 n_2 & -n_2 n_3 \\ -n_3 n_1 & -n_3 n_2 & 1 - n_3 n_3 \end{pmatrix}_i$$

Geometric factor corresponds to diagonal term of projection matrix P

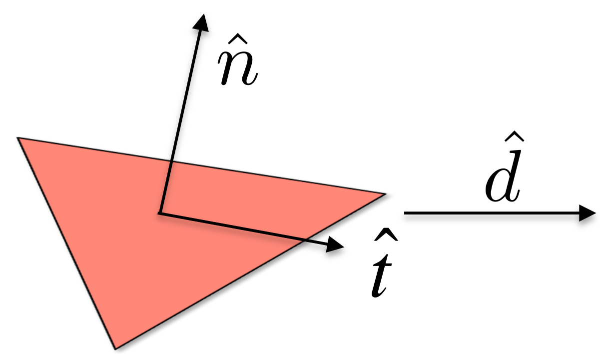
$$\overleftrightarrow{f}_{act} = \frac{\sum_i A_i \overleftrightarrow{P}_i}{\sum_i A_i}$$

$$\overleftrightarrow{\varepsilon}_{act} = \varepsilon \overleftrightarrow{f}_{act}$$

$$\overleftrightarrow{D}^{proj}_{eff} = D_g \overleftrightarrow{\varepsilon}_{act} + D_b (\overleftrightarrow{I} - \overleftrightarrow{\varepsilon}_{act})$$

(For enhanced GB diffusion)

Using the entire projection matrix, we can predict the entire diffusivity tensor




Principal Diffusion Direction

# A quick review & question break

- General approach
- Transport in polycrystalline materials
  - Sharp interface model for simple geometries
  - Diffuse interface model for complex morphologies (SBM)
  - Comparisons
- Projection method
- Questions?

Up next: Final thoughts

# Example: an electrochemical dynamics model of an electrode (part of a ½ cell)

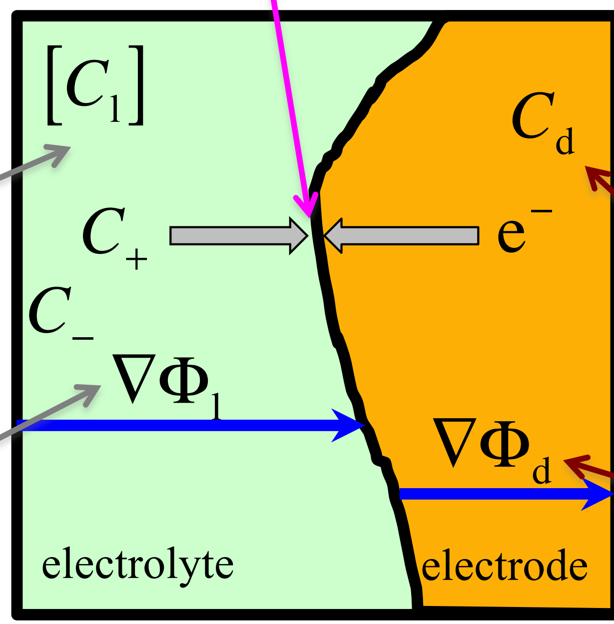
- **Five equations:** 1) diffusion in solid, 2) transport in liquid, 3) current continuity in solid, 4) current continuity in liquid, and 5) reaction at solid-liquid interface

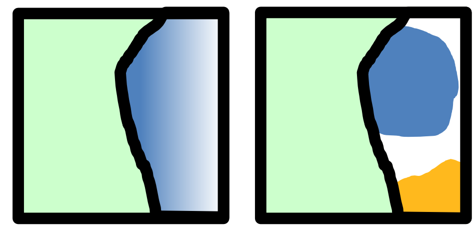
$$\boxed{C_+ + \mathrm{e}^- + X \rightarrow C_\mathrm{d} X}$$

Butler-Volmer $$R_{rxn} = \mathbf{n}\cdot\frac{\mathbf{i}}{z_+ F} = \frac{i_0\sqrt{a_l}}{F}\left[\exp\left(\frac{-\alpha F}{RT}(\phi_d - \phi_l - \phi_{eq})\right) - \exp\left(\frac{(1-\alpha)F}{RT}(\phi_d - \phi_l - \phi_{eq})\right)\right]$$

$$\frac{\partial C_\mathrm{l}}{\partial t} = \nabla\cdot\left(D_\mathrm{l}\nabla C_\mathrm{l}\right) - \frac{\mathbf{i}\cdot\nabla t_+}{z_+ \nu_+ F}$$

$$F\nabla\cdot\left[\left(z_+ u_+ - z_- u_-\right)C_\mathrm{l}\nabla\Phi_\mathrm{l}\right] = \nabla\cdot\left[\left(D_- - D_+\right)\nabla C_\mathrm{l}\right]$$



$$\frac{\partial C_\mathrm{d}}{\partial t} = \nabla\cdot\left(D_\mathrm{d}\nabla C_\mathrm{d}\right)$$

$$\nabla\cdot\left(\kappa_\mathrm{s}\nabla\Phi_\mathrm{s}\right) = 0$$

John Newman and Karen E. Thomas-Alyea. Electrochemical Systems. Wiley Inter-Science, third edition, 2004.

# Phase Field Model for Localized Corrosion

Kinetics at the interface: reaction current

$$\frac{i_{rxn}}{i_{corr}} = \left(1 - \frac{i_{rxn}}{i_{max,c}}\right) \exp\left(\frac{z_M\,(1-\beta)\,F}{RT}\eta\right)$$

$$\eta = V_s - Ecorr - \Phi$$

Ionic transport within the electrolyte (smooth boundary method)

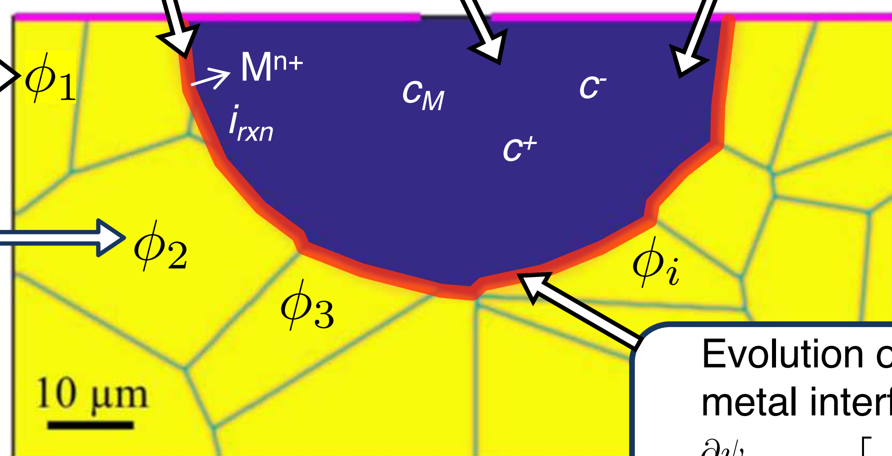
$$\frac{\partial c_i}{\partial t} = \frac{1}{\psi}\nabla\cdot(\psi D_i \nabla c_i) + \frac{1}{\psi}\left(\frac{z_i F}{RT}\nabla\cdot(\psi D_i c_i \nabla\Phi)\right) + \frac{|\nabla\psi|}{\psi}\left(\frac{i_{rxn}}{z_i F}\right)$$

Electrostatic potential

$$\nabla\cdot(\psi\kappa\nabla\Phi) = F\nabla\cdot\left(\psi\sum_{j=1}^{n-1} z_j(D_n - D_j)\nabla c_j\right) - |\nabla\psi| i_{rxn}$$

Evolution of phases in the metal (grains or intermetallic particles)

$$\frac{\partial\phi_i}{\partial t} = \nabla\cdot\left[M(\psi)\nabla\frac{\delta\mathcal{F}}{\delta\phi_i}\right] - \frac{V_M i_{rxn}}{z_M F}|\nabla\psi|$$




Evolution of the electrolyte-metal interface

$$\frac{\partial\psi}{\partial t} = \nabla\cdot\left[M(\psi)\nabla\frac{\delta\mathcal{F}}{\delta\psi}\right] + \frac{V_M i_{rxn}}{z_M F}|\nabla\psi|$$

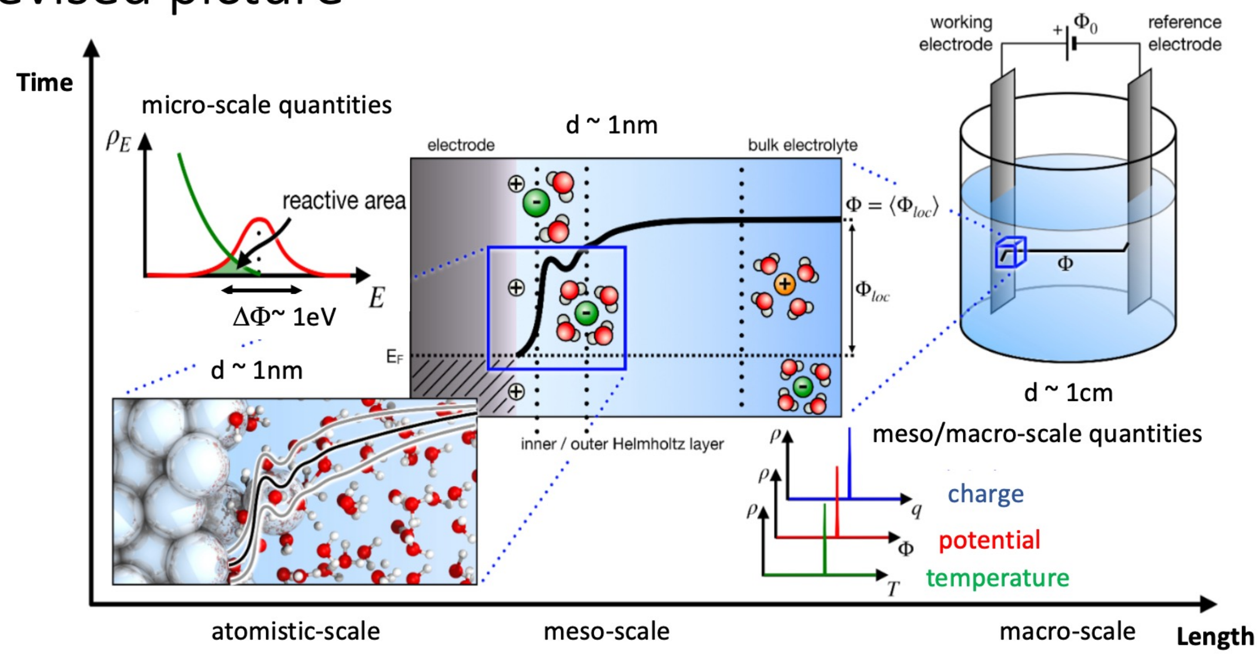

[1] A. Chadwick, J. Stewart, R. A. Enrique, S. Du, and K. Thornton, *J. Electrochem. Soc.*, 165 (10) C633 (2018).

# An IPAM focus & impact

Thermodynamics: Open circuit voltage
Diffusion kinetics: Diffusivity or mobility
**Electrochemistry: Reaction rate**

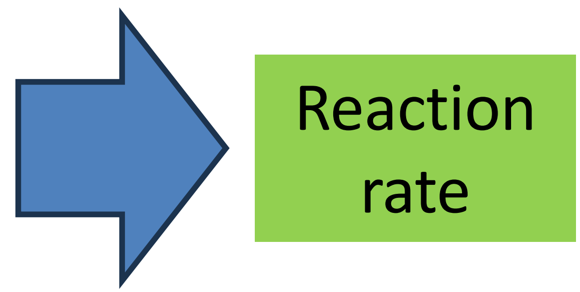
From Jörg's talk

Revised picture




Realistic atomic scale simulations need to include stochastic fluctuations in charge, density, potential, etc.

Wippermann, Todorova, JN, Nature Review Chemistry (2025)



# Summary

- It is important to connect models at different length scales!
- Electrochemistry can amplify the stochastic nature of microstructures
- Transport properties depend strongly on the microstructure
- Accurate electrochemical dynamics simulations require either explicit or implicit account of the microstructure and properties of the individual components
- The governing equations and concepts are similar for other electrochemical phenomena, including corrosion