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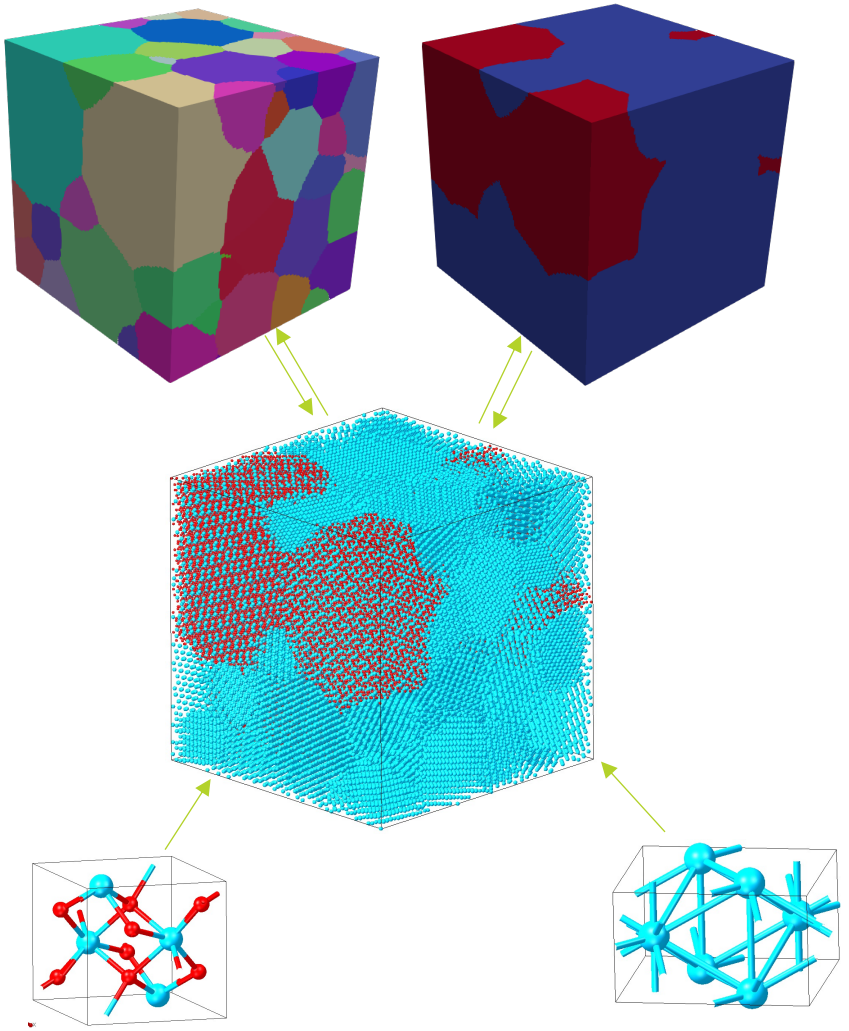
From the femtoscale to microstructures and back: an integrated multiscale approach

Kyle Starkey, **Leonid Kahle,** Clint Geller, Erich Wimmer

May 2024



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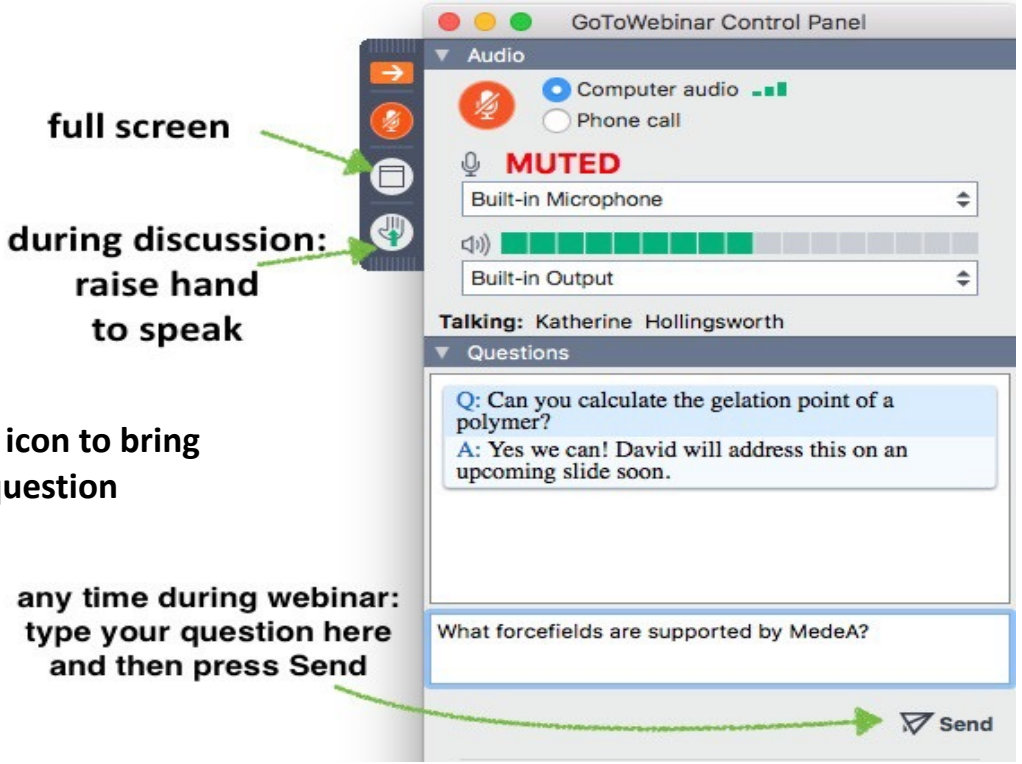
Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

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Webinar Speakers

Katherine Hollingsworth

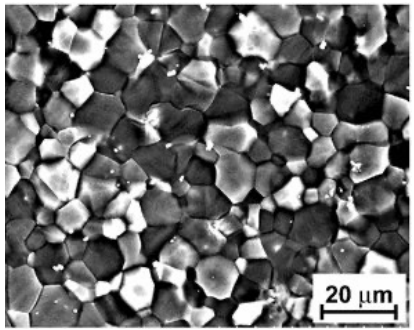
Dr. Kyle Starkey

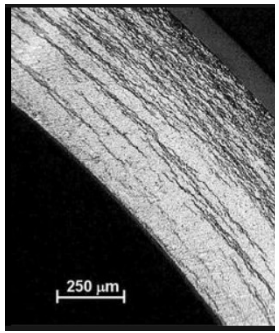
Dr. Leonid Kahle

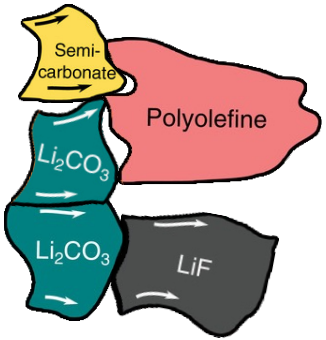
Why study materials' microstructure?

Material behavior is often determined at micrometers scale over seconds/years:

- Grain morphology/distribution when crystallizing alloys from melt.
- Hydride formation in metals and resulting component degradation.
- Buildup of solid-electrolyte interphases and effect on battery performance.
- Corrosion and cracking of metals and resulting surface passivation or cracking.







- **Bulk diffusion** • **Phase stability** • **Grain nucleation** • **Elastic deformation** • **Cracking**
- **Electrochemistry** • **Electrostatics** • **Porosity** • **Grain boundary diffusion**

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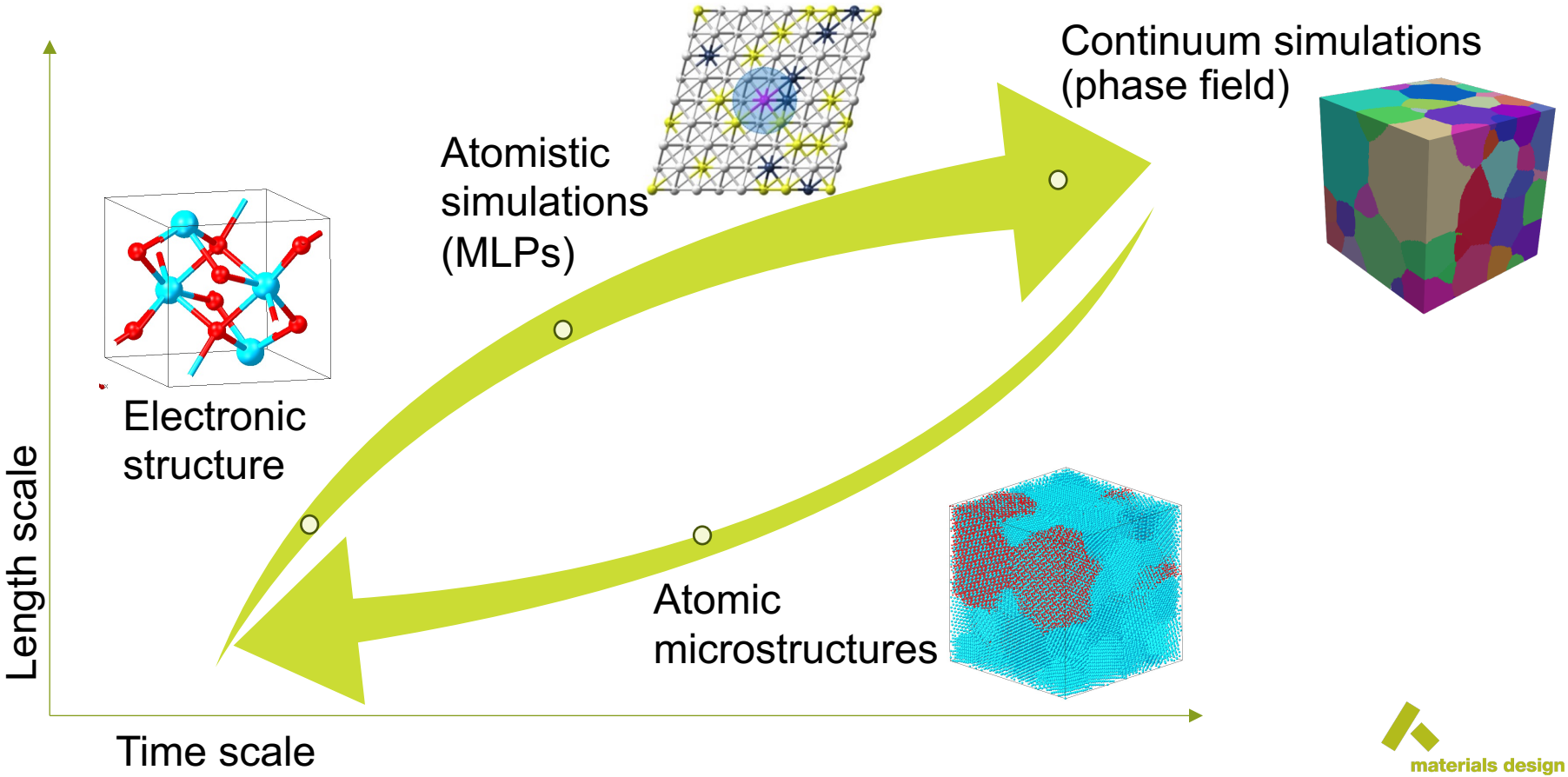
Bridging time and length scales



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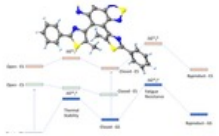
Electronic structure calculations

DFT allows for general & accurate predictions at small time and length scales:

- Up to ~100 atoms (10^{-9} m)
- DFT based MD can reach ~100 ps (10^{-10} s)
- Facilitated by *MedeA* VASP & *MedeA* Gaussian



On Demand

The Basis of Success. A Conversation with the President of Gaussian Inc., Dr. Mike Frisch

Watch On Demand

Presented by Dr. René Windiks

Medea Training: MedeA VASP and Battery Applications

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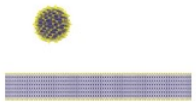
Machine-learned potentials (MLPs)

Train MLP on DFT energies and forces

- Extends time scale to ~10 ns (10^{-8} s)
- Can simulate 1000s of atoms (10^{-8} m)
- Enabled by *MedeA* MLPG & *MedeA* LAMMPS and *MedeA* VASP (MLFF)



Presented by Dr. Volker Eyert and Dr. Xiaoli Liu

Machine-Learned Potentials: Surpassing the Limits of the ab initio World without leaving it behind

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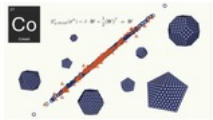

Presented by Marthe Bideault

Polyvalent Machine-Learned Potential for Cobalt: from Bulk to Nanoparticles

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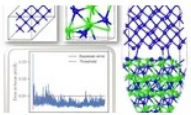

UGM 2022: Presented by Shubham Pandey and Xiaoli Liu

On-the-fly Machine Learning Forcefields with MedeA VASP

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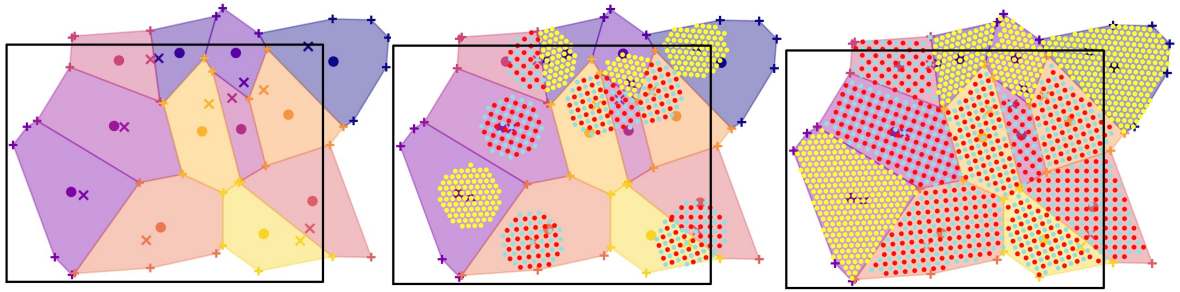
Building realistic atomic microstructures

Polycrystalline atomic systems are useful to transfer information from atomistic simulation to a continuum description (phase field) and vice versa.

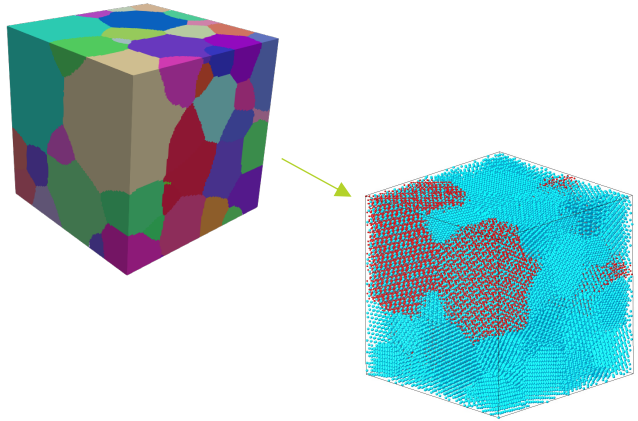
Atomic system *via* Seed & Growth algorithm:

- Define seed points where crystal growth initiates.
- Grow crystals from seed point until other grains are met.
- Constrain interatomic distance or phase stoichiometry



Transfer from continuum scale:

- Define volume for every grain
- Populate grains with atoms as in Seed & Growth



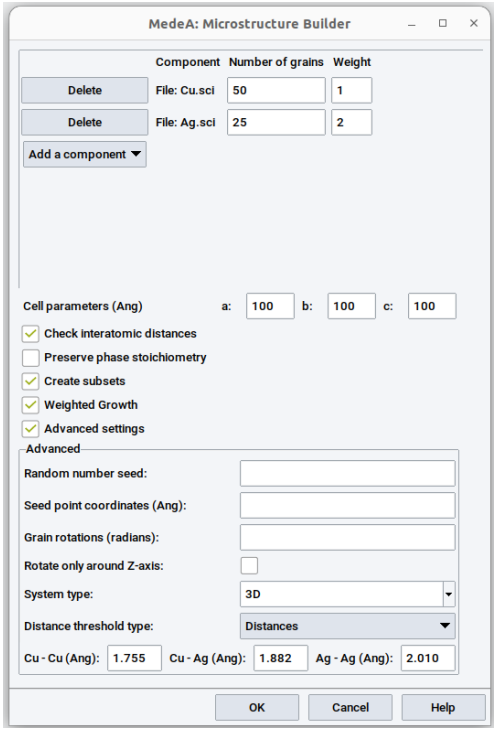
The *MedeA* Microstructure Builder for Seed & Growth

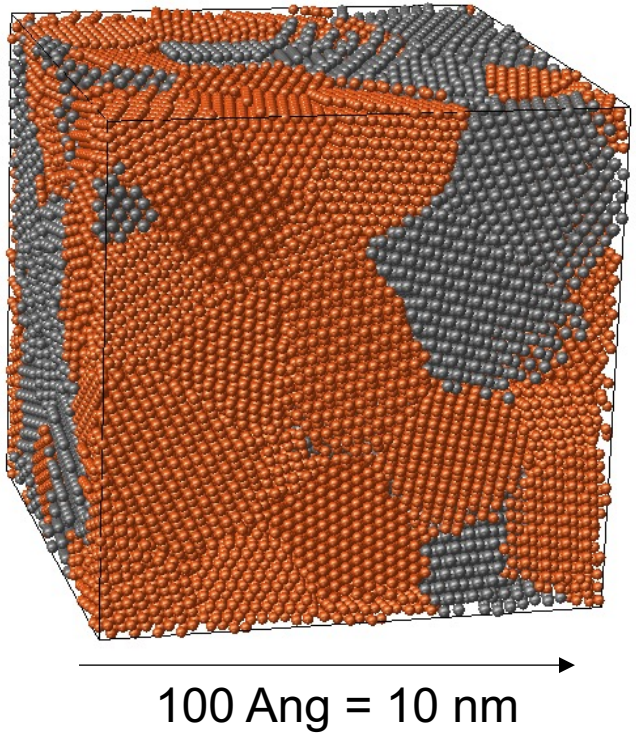
Select components
- Number of grains
- Weight (growth speed)

Set growth parameters
- Stoichiometric growth
- Interatomic distances at GB

Choose advanced settings:
- Seed points
- Grain rotations
- Distance thresholds
- Columnar or 3D-periodic

MedeA 3.8 / MedeA 3.9





100 Ang = 10 nm

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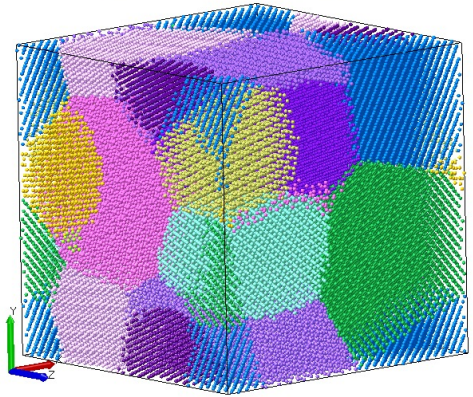
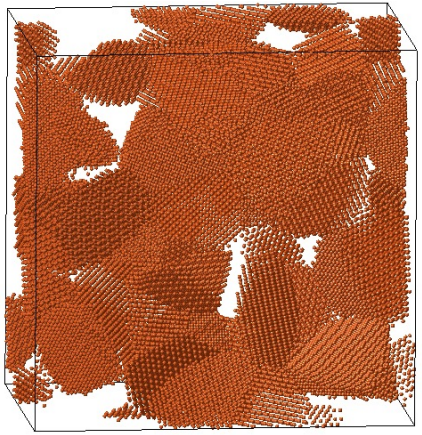
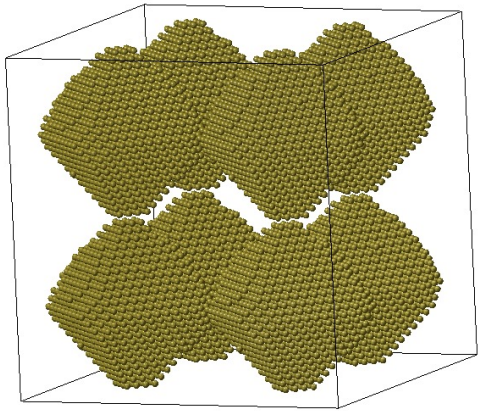
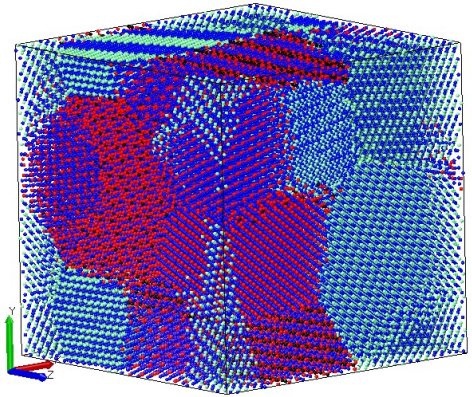
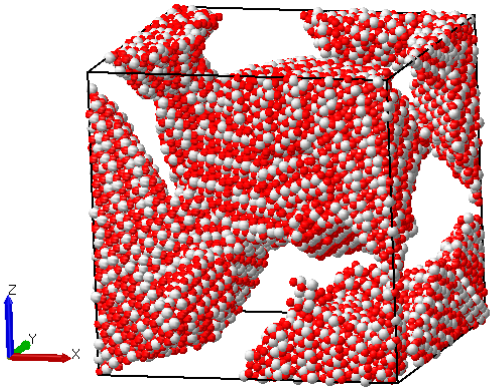
In action

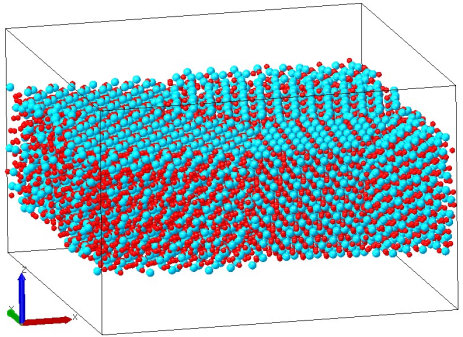












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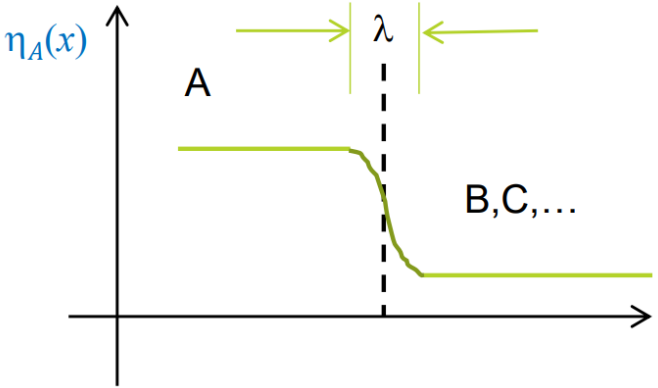
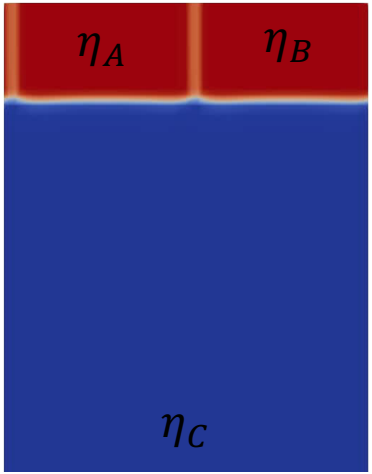
The phase field method

To move further up length and timescales, we must coarse-grain atom positions and move towards a continuum approach where phases are represented as fields

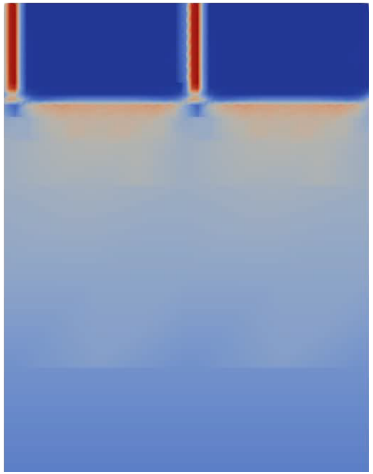
$$\eta_A = \begin{cases} 1 & \text{Phase A} \\ 0 & \text{other phases} \end{cases}$$



Order parameters



Flux



Order parameters (η_A) are used to delineate different **phases**/grains → Phase field

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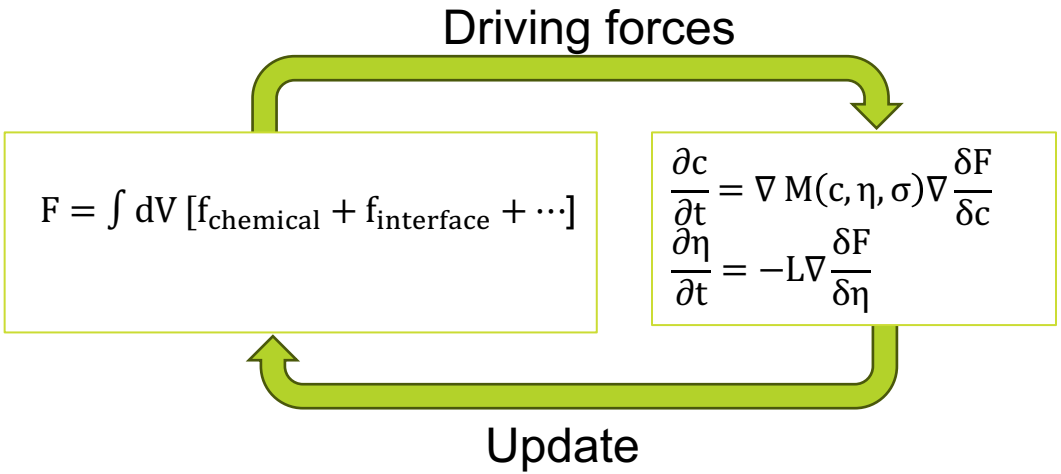
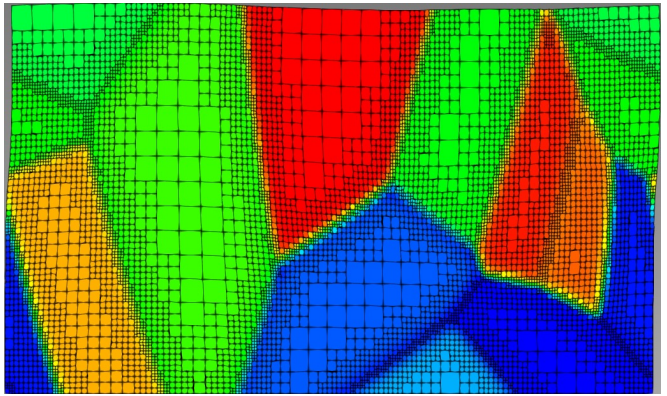
Solving the phase field equations

The energy becomes a functional of the order parameters η, concentration c, stress σ, etc.



A set of PDEs are solved iteratively and propagated in time via response functions (e.g., Fick's diffusion equation, Allen-Cahn equation, etc).

We solve the phase-field equations on an adaptive mesh using Finite Elements:



Ongoing implementation of chemo-mechanical 3D simulation software (CM3D) within *MedeA*

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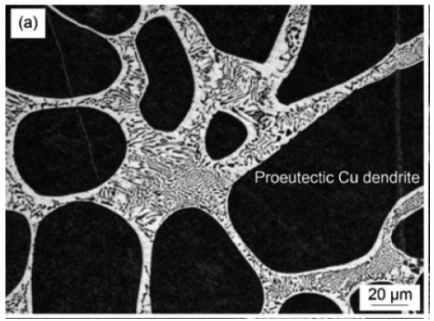
Eutectic Ag-Cu alloys

Ag-Cu industrial alloys are widely used for electrical applications:

- Microstructures of wires and magnet coils with high silver content are difficult to control.
- The low-melting eutectic in the Ag-Cu system enables good soldering alloys.

What is the effect of alloying and heat treatment on the resulting final microstructure?



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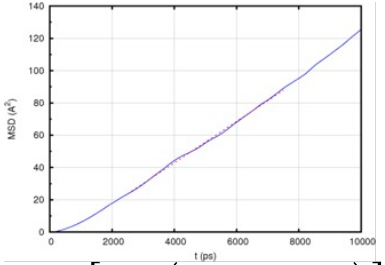
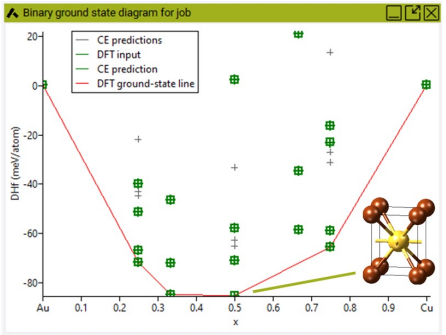
Predicting Ag-Cu microstructure

Diffusion (MedeA LAMMPS)

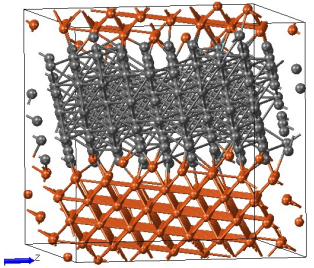


$$D = \lim_{t\to\infty}\left[\frac{1}{2dt}\left(\frac{1}{N}\sum_{i=1}\langle \mathbf{r_i}(t)^2\rangle\right)\right]$$

Bulk energies (UNCLE)



Interfaces (VASP)



$$\sigma_{ij} = \frac{E_{ij} - E_i - E_j}{2S}$$

$$\frac{\partial c}{\partial t} = \nabla M(c,\eta,\sigma)\nabla\frac{\delta F}{\delta c}$$
$$\frac{\partial \eta}{\partial t} = -L\nabla\frac{\delta F}{\delta \eta}$$

$$F = \int dV\,[f_{chemical} + f_{interface}]$$

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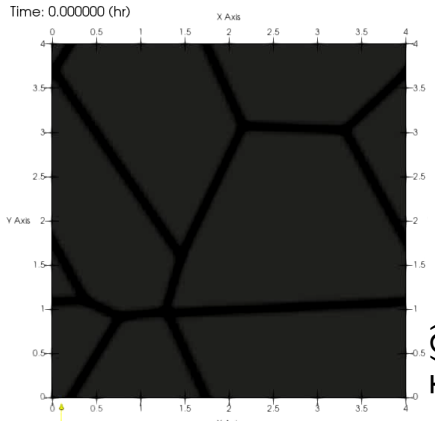
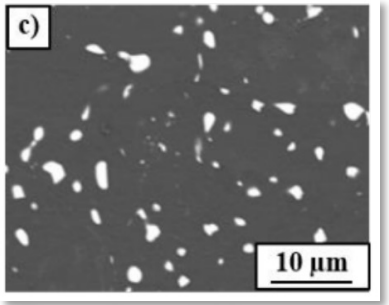
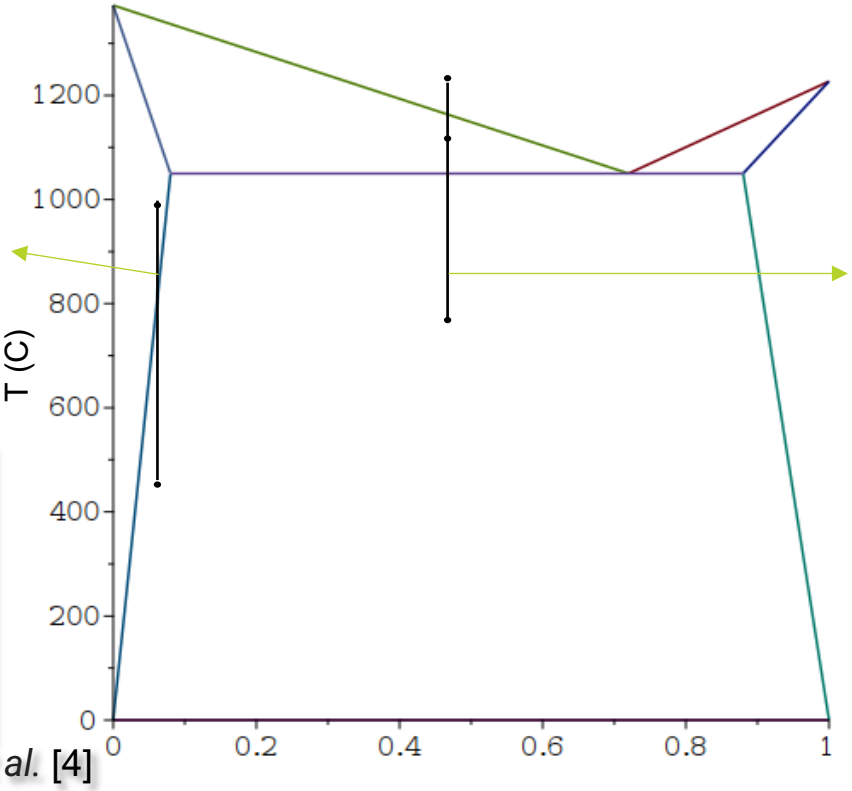
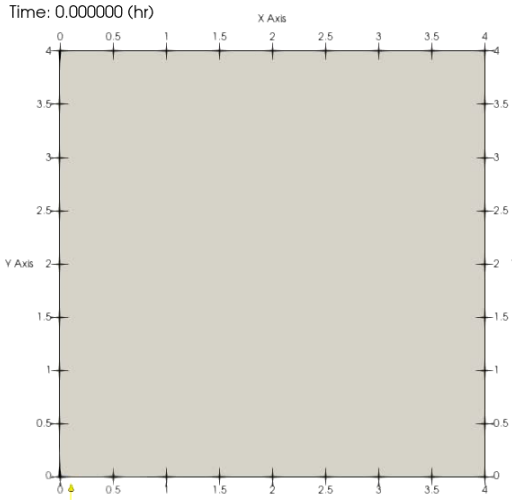
Microstructure evolution of Ag-Cu alloys

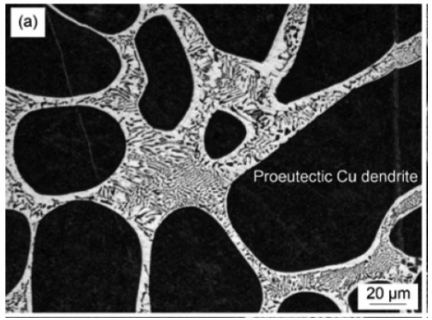




Experiment Korneva *et al.* [4]







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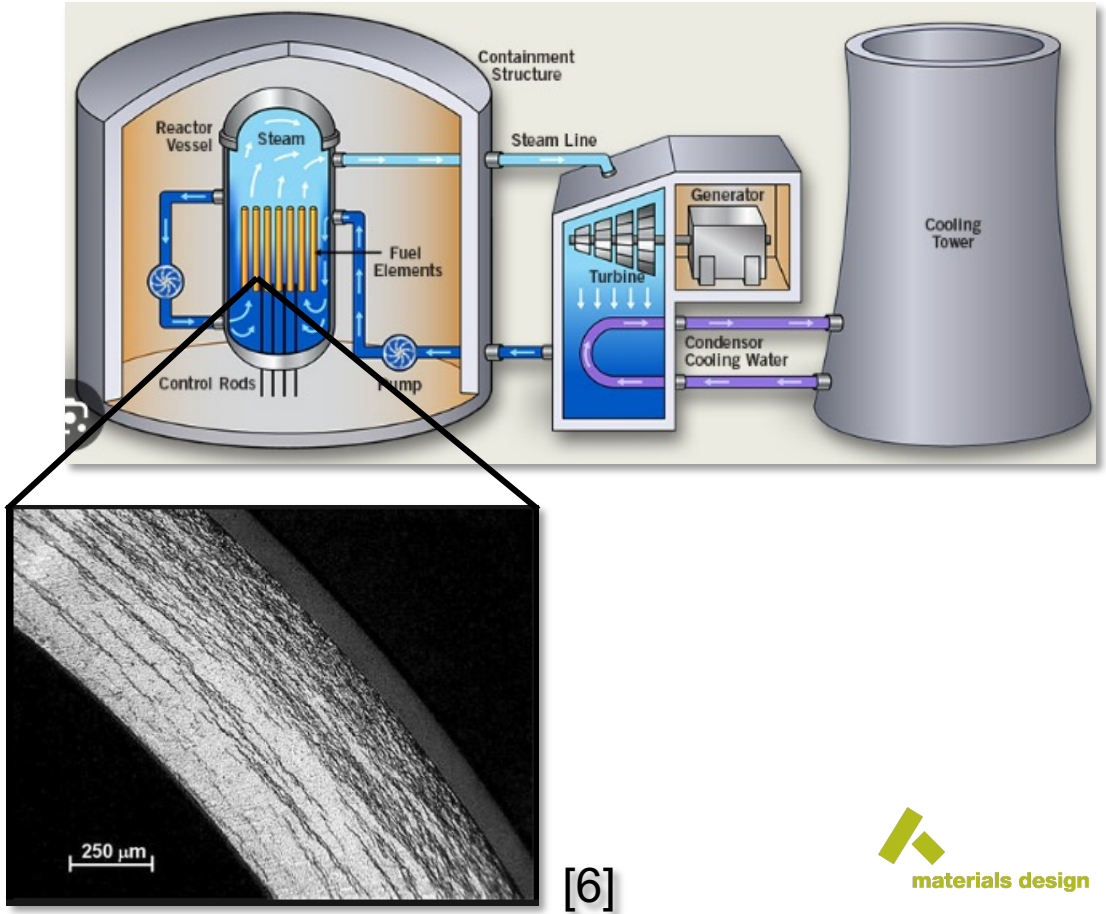
Hydride formation in water-cooled fission reactors

- Water reacts with Zr fuel element cladding, releasing hydrogen
- Formation of Zr hydride
- Hydrogen embrittlement leading to mechanical degradation

How does Zr hydride morphology evolve with H uptake, temperature, and alloy composition?



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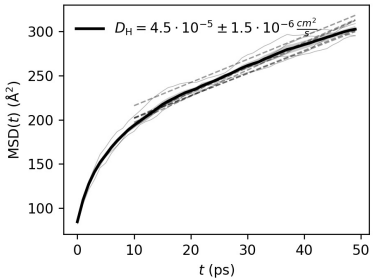
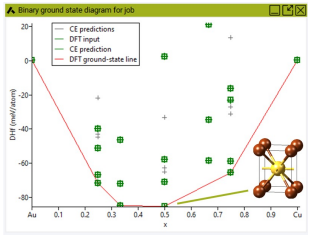
Predicting Zr-H microstructure

Diffusion

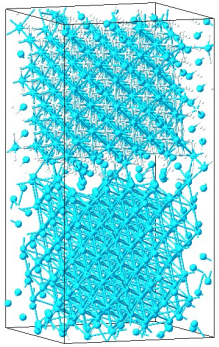


Free energy

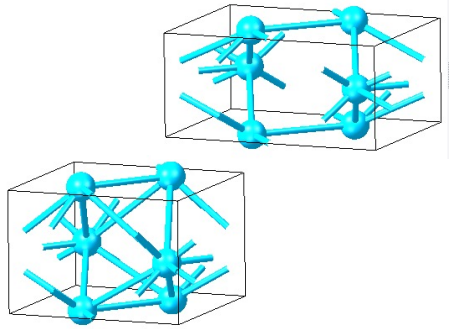


$$E = N \sum_F d_F \Pi_F(\mathbf{s})$$

Interfaces



Elastic energy



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$$\frac{\partial \eta}{\partial t} = -L\nabla\frac{\delta F}{\delta \eta}$$

$$F = \int dV\,[f_{chemical} + f_{interface} + f_{elastic}]$$

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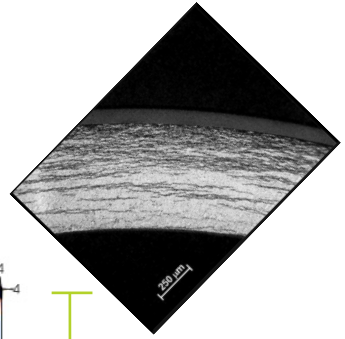
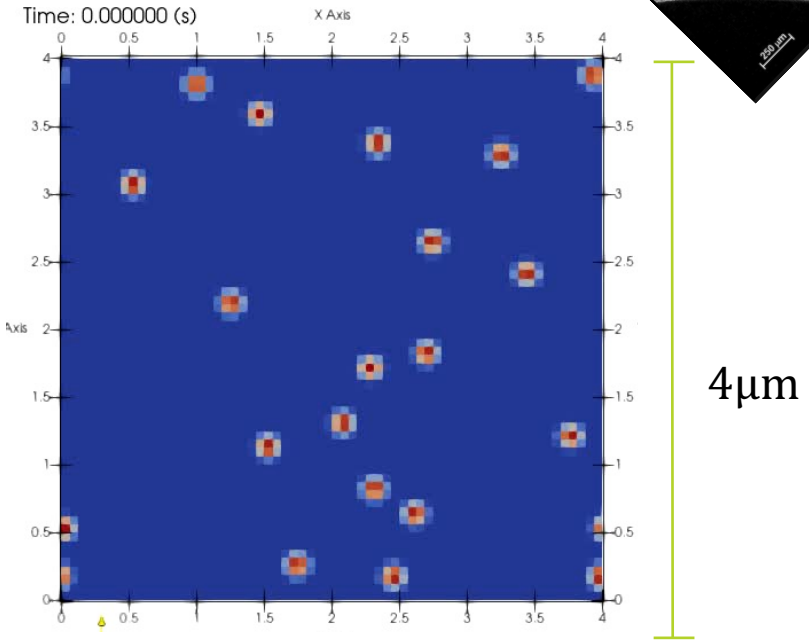
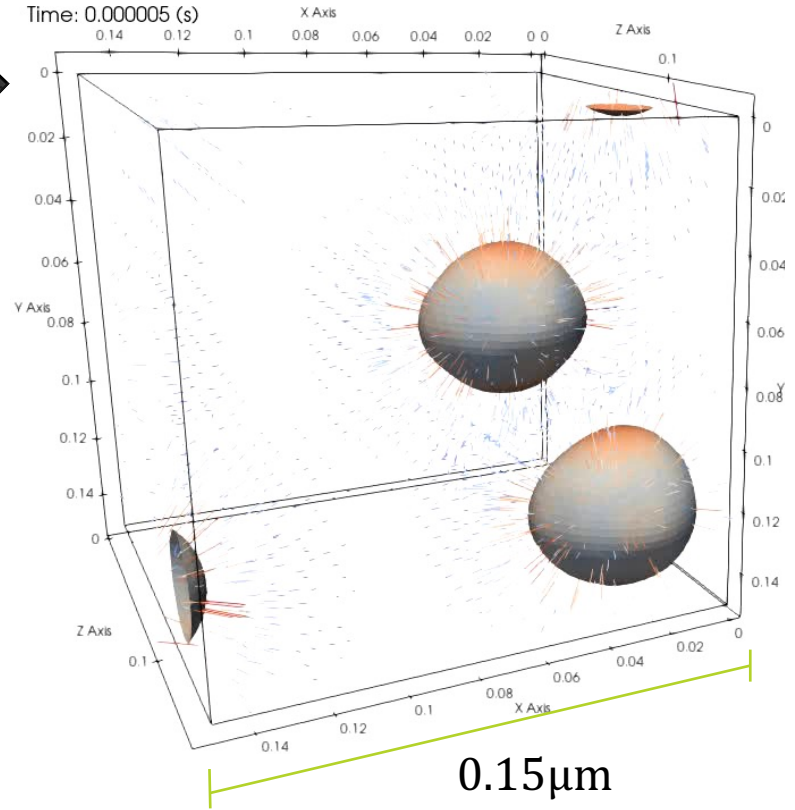
Hydride growth







Zr and hydride phase evolution (for 0.07s at 600K) shows effect of elastic anisotropy

3D simulation of hydride evolution in an H flux, with stress effects

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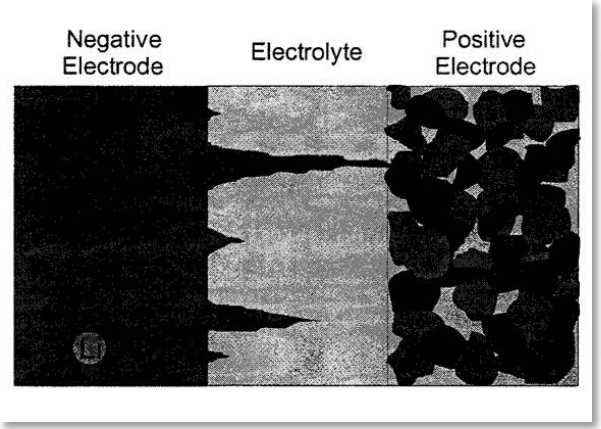
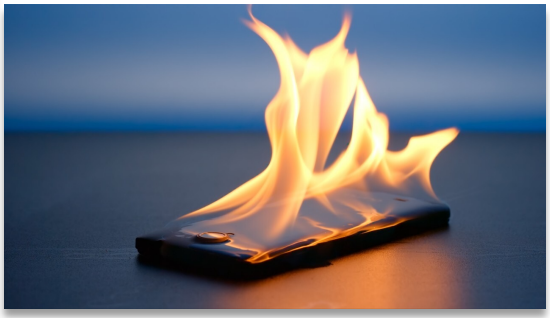
Degradation mechanisms in Li-ion batteries

Understanding and improving battery performance is essential for a transition away from fossil fuels

- Move to EV mobility (EU-wide ban of ICE in 2035)
- Need to improve capacity, lifetime, and safety
- Explore post Li-ion battery chemistry

Can we simulate the electrochemical processes in a battery and predict degradation?





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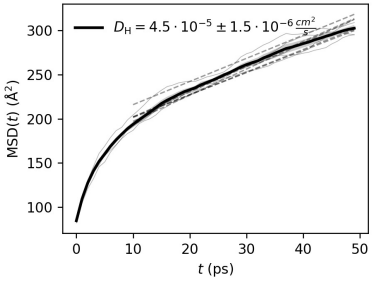
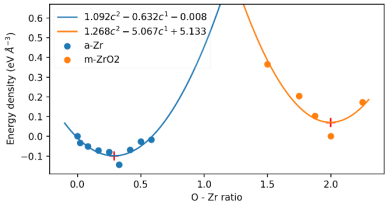
Predicting battery performance

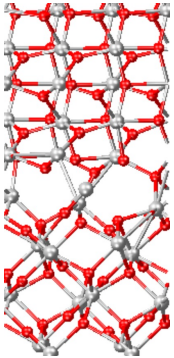
Diffusion



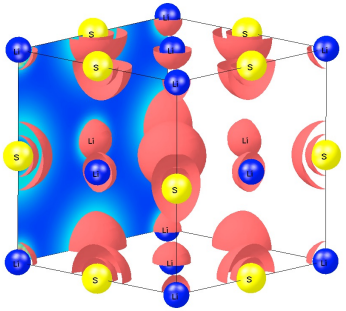
Bulk free energy



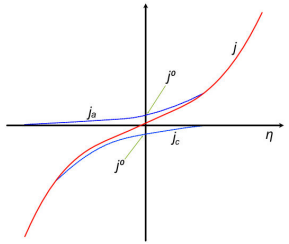
Interfaces



Electrostatics



Electrode current



$$\frac{\partial c}{\partial t} = \nabla M(c, \eta, \sigma) \nabla \frac{\delta F}{\delta c}$$

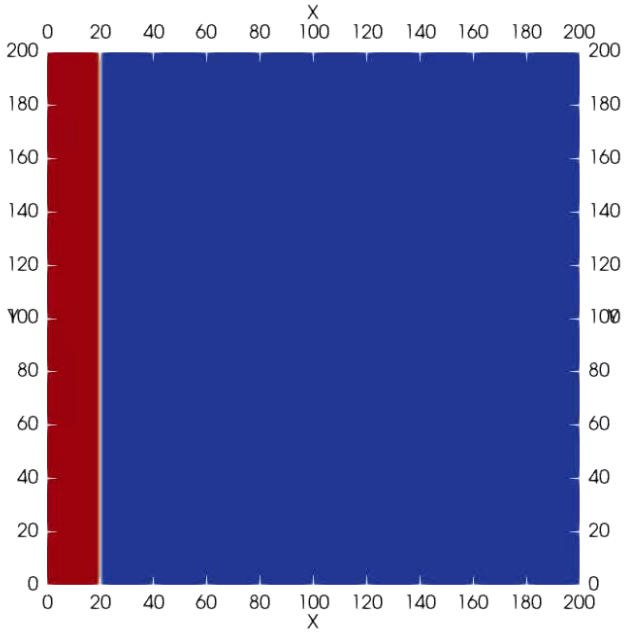
$$\frac{\partial \eta}{\partial t} = -L \nabla \frac{\delta F}{\delta \eta}$$

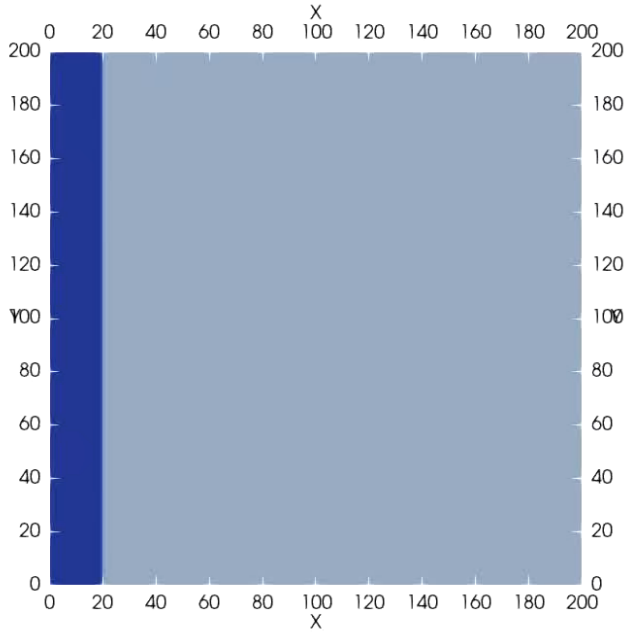
$$F = \int dV \left[f_{chemical} + f_{interface} + f_{electrostatic} \right]$$

materials design

Simulation of electrochemical reactions

- Describe Li / Li+ reaction using Butler-Volmer equation
- Simulate dendrite growth in Li-ion electrolyte





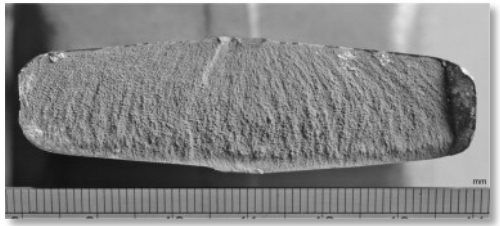
materials design

Cracking in metals and oxides

Cracks impact materials both on macro-scales and micro-scales:

- Crack nucleation and growth leads to mechanical failure in many industrial components (e.g, in transportation and oil & gas equipment)
- Corrosion kinetics instabilities
- Formation of easy H transport paths in oxide scale, leading to hydriding and embrittlement

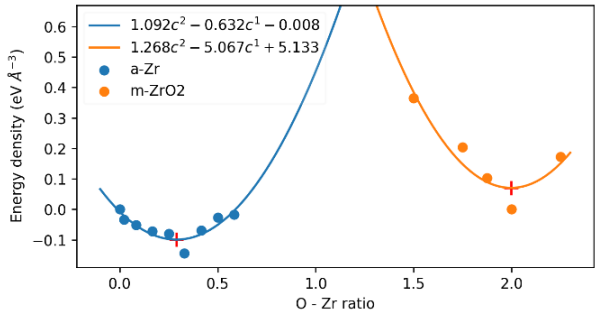
How does cracking affect microstructure evolution?



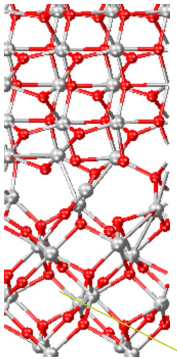
[10]

Predicting crack growth

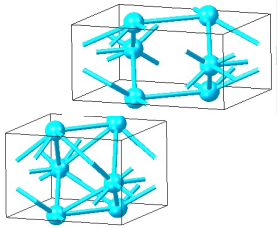
Bulk free energy



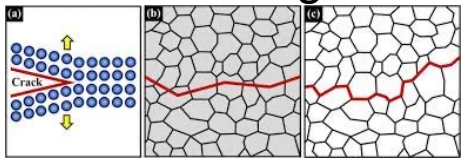
Interfaces



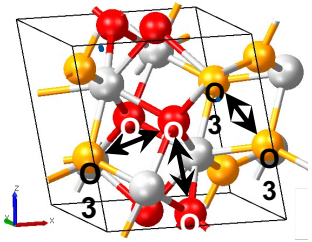
Elasticity



Cracking



Diffusion (KMC)

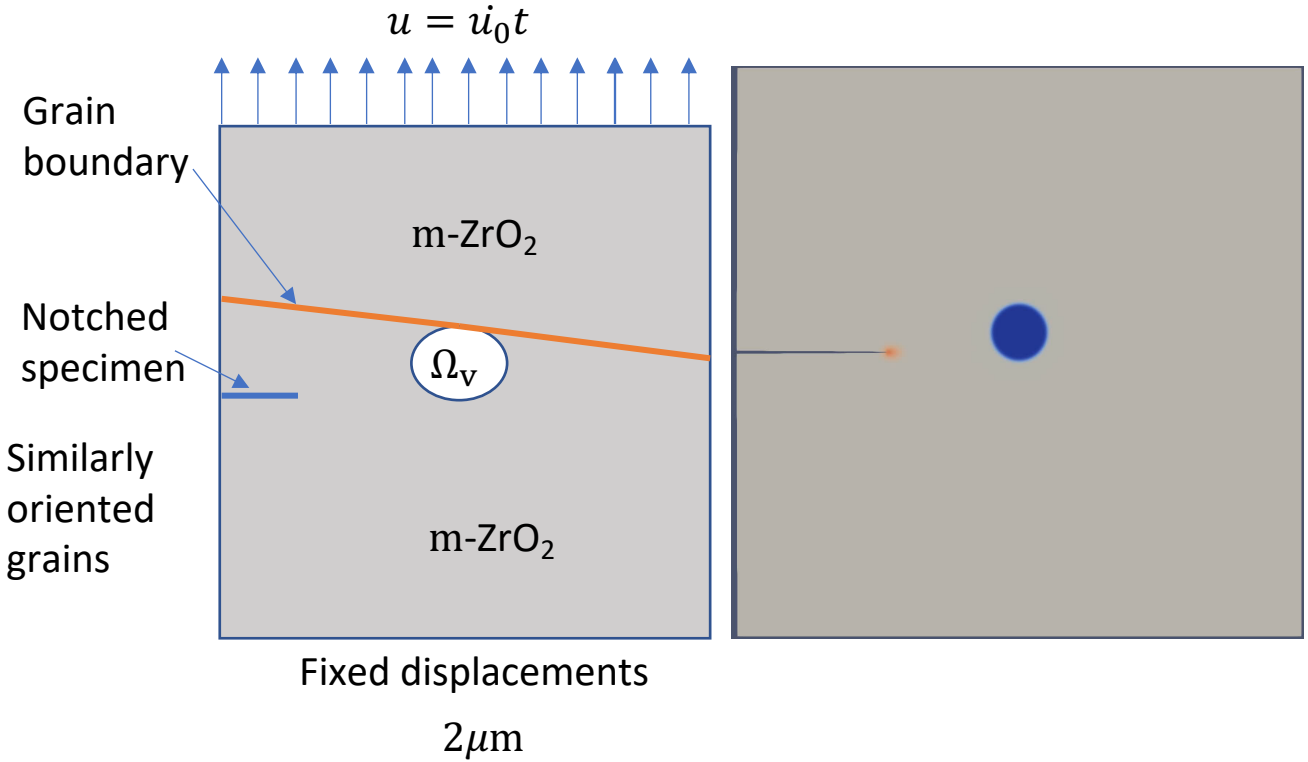


$$\frac{\partial c}{\partial t} = \nabla\, M(c,\eta,\sigma)\nabla\frac{\delta F}{\delta c}$$
$$\frac{\partial \eta}{\partial t} = -L\nabla\frac{\delta F}{\delta \eta}$$

$$F = \int dV\, [f_{chemical} + f_{interface} + f_{elastic}]$$

materials design

A moving crack interacting with a static pore and grain boundary



- Crack deflects to void so that it is perpendicular to the void surface
- Void arrests crack
- Crack nucleates at void surface
- Crack deflects along grain boundary

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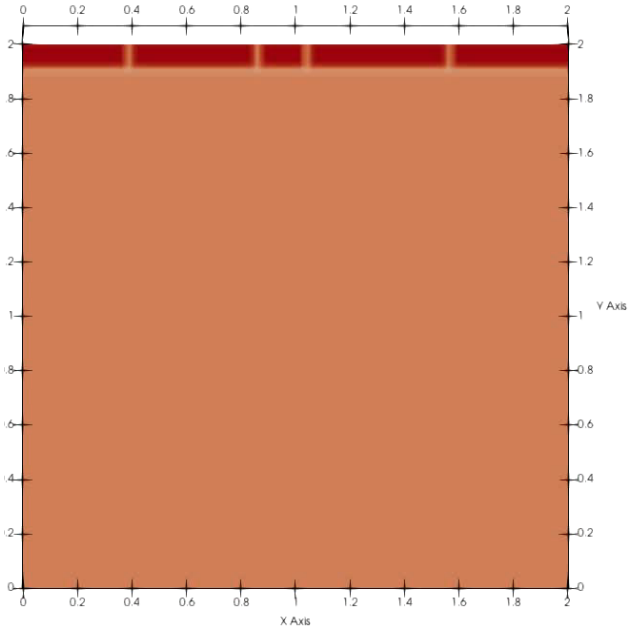
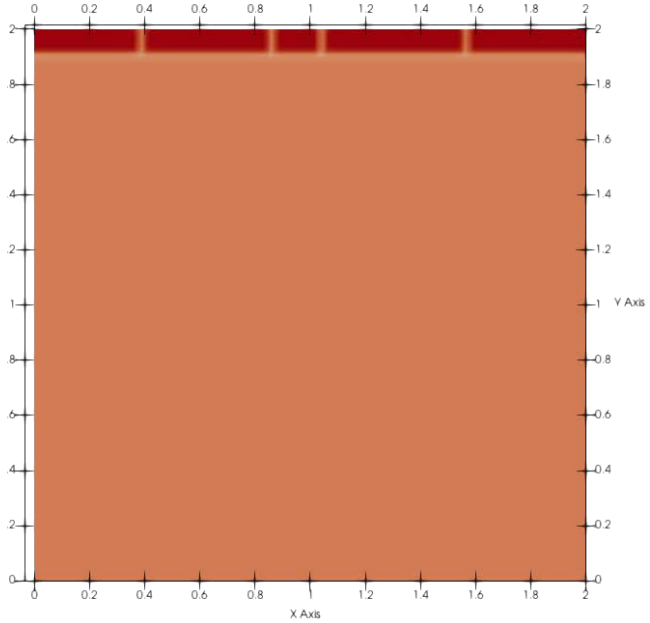
Cracking in materials with different Pilling-Bedworth ratios

Zirconium oxide PBR: 1.56



Cracks forming in a α-Zr – m-ZrO_2 multi-grain simulation at high O flux

Magnesium oxide PBR: 0.81



Cracks forming in a Mg – MgO multi-grain simulation at high O flux

$$PBR = \frac{V_{oxide}}{V_{metal}}$$

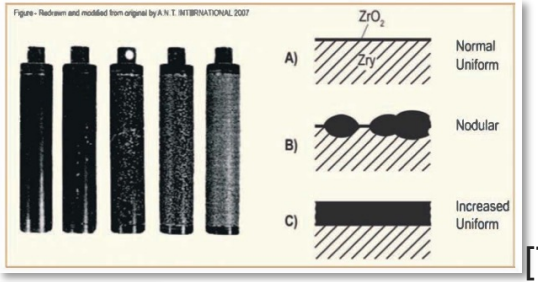
materials design

Understanding corrosion in different environments

Cost of corrosion is estimated at 3.4% of global GDP

- Water-cooled nuclear reactors: Cladding corrosion limits fuel element lifetimes and reactor power density.
- Oil & Gas: Corroding pipelines drive up costs
- Automotive: Poor corrosion resistance of magnesium alloys obstructs car industry weight reduction goals

Can we simulate corrosive processes over days/months/years, in order to make predictions?



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[8]

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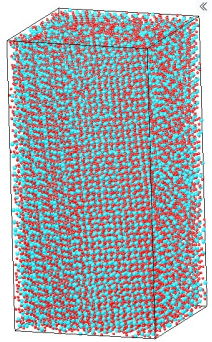
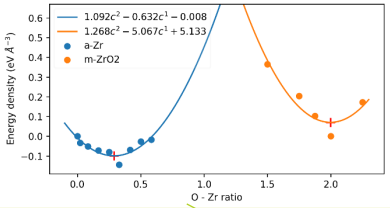
Predicting corrosion

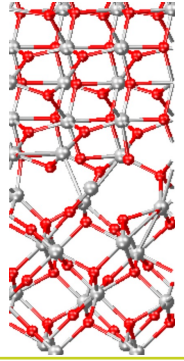
GB Diffusion



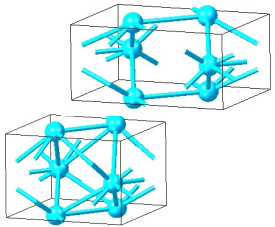
Bulk free energy



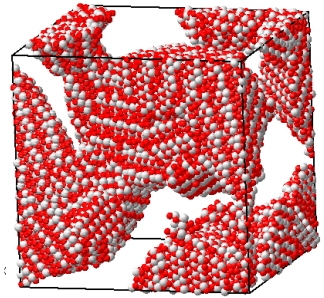
Interfaces



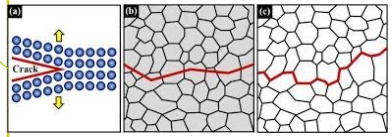
Elasticity



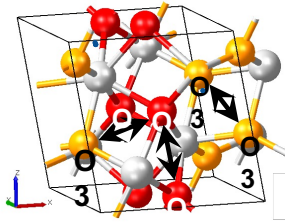
Porosity



Cracking



Bulk Diffusion



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$$\frac{\partial \eta}{\partial t} = -L\nabla\frac{\delta F}{\delta \eta}$$

$$F = \int dV\,[f_{chemical} + f_{interface} + f_{elastic}]$$

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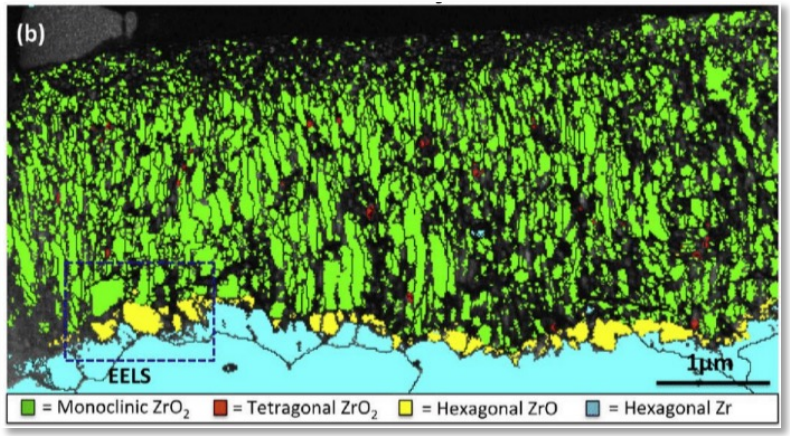
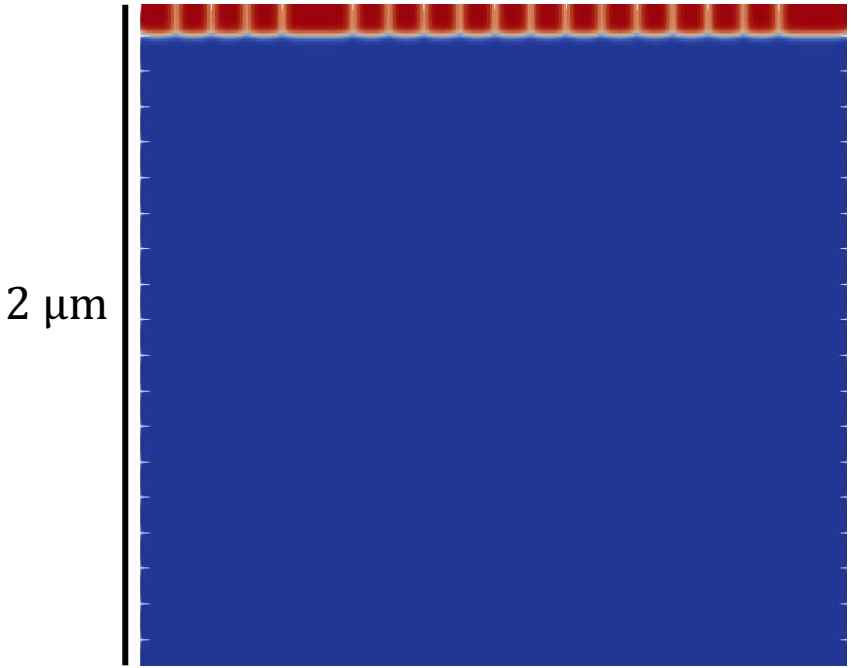
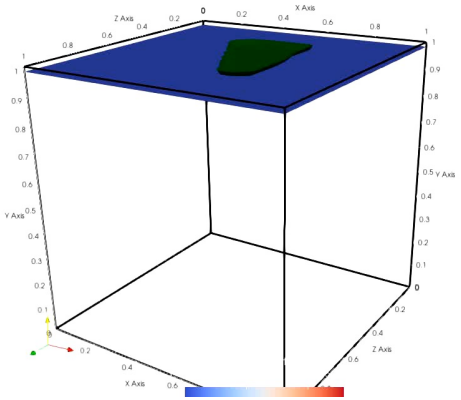
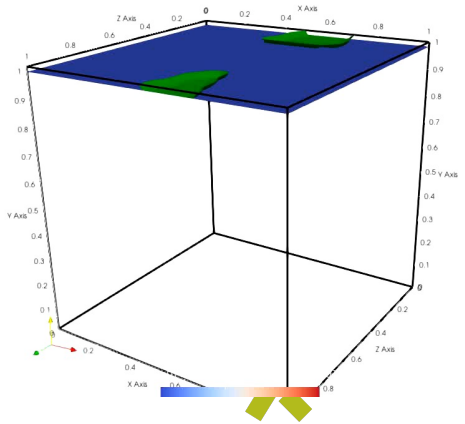
Corrosion of zirconium alloys

*Hu et al., Micron **69**, 35 (2015)*









40 simulation days of multiphase evolution of Zr – O system (no cracks)

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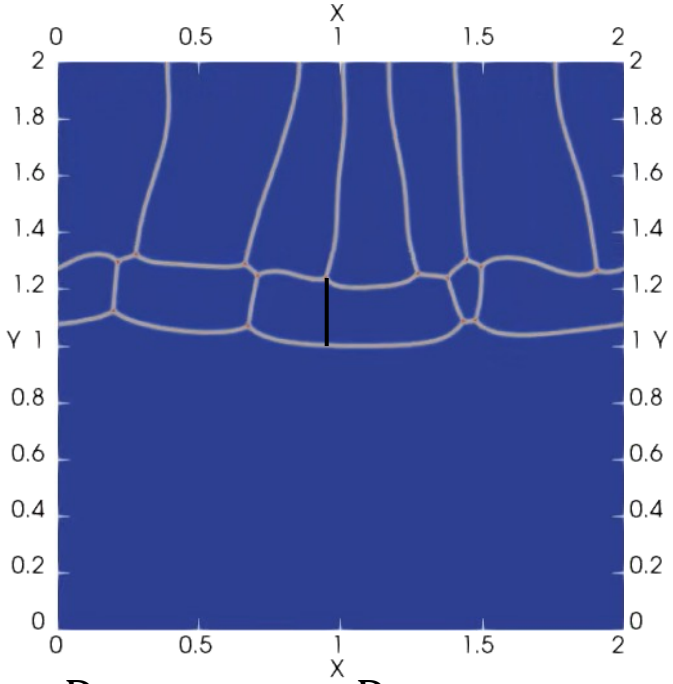
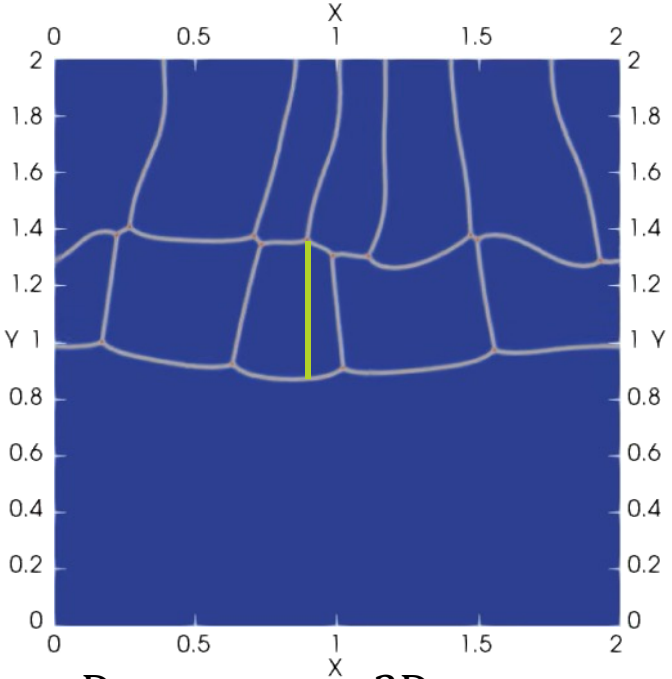
Sensitivity of grain morphology to oxygen diffusivity

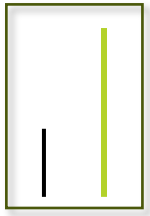


$D_{hZrO-hZrO} = D_{mZrO_2-mZrO_2}$



$D_{hZrO-hZrO} = 2D_{mZrO_2-mZrO_2}$

Doubling the GB O diffusivity roughly doubles the resulting h-ZrO thickness



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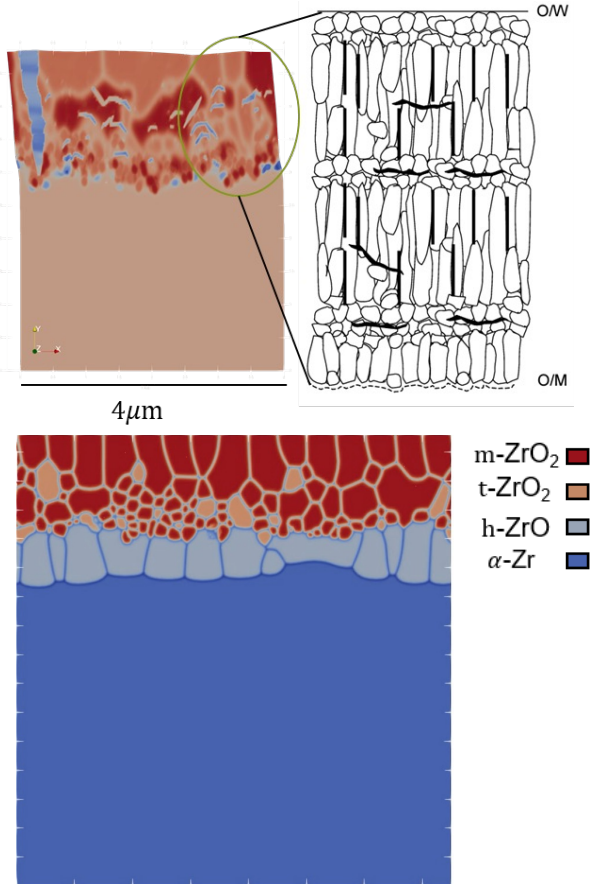
Conclusions

- We are bridging scales to solve engineering problems
  - From nanometers to micrometers ($\times 10^3$)
  - From picoseconds to … days ($\times 10^{17}$)
- Solving engineering problems requires a “multiphysics” approach: multi-grain, multi-phase, chemical (bulk) energies, interface energies, mass (bulk and GB) diffusion, elasticity (small-strain deformation), voids, cracks, nucleation, electrostatics, electrochemistry
- Coupling ab initio computations and atomistic simulations (via MLPs trained on DFT results) with phase field methods enables physics-guided and parameter-free microstructural modeling – all within the *MedeA* environment



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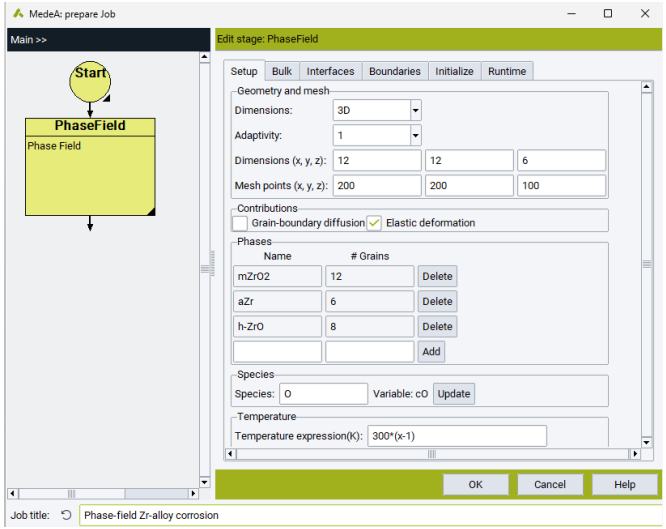
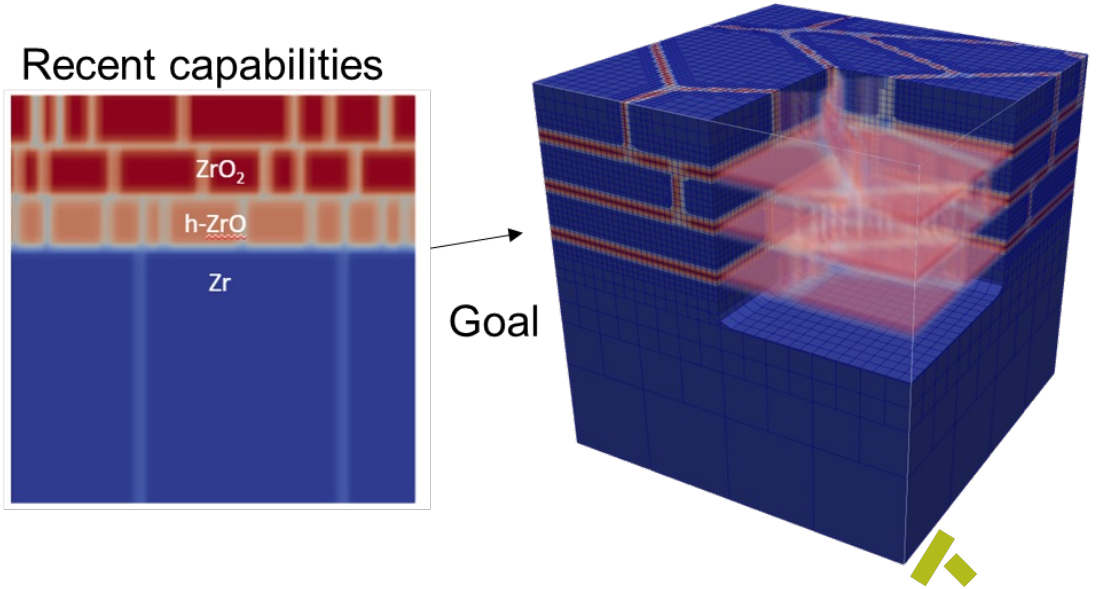
Outlook

- Microstructure and Interface Builders in *MedeA* 3.8 & ongoing improvements
- Incremental integration of new phase field modeling tool, CM3D, into *MedeA* for users.
- Applying microstructure modeling tools in several Contract Research projects.





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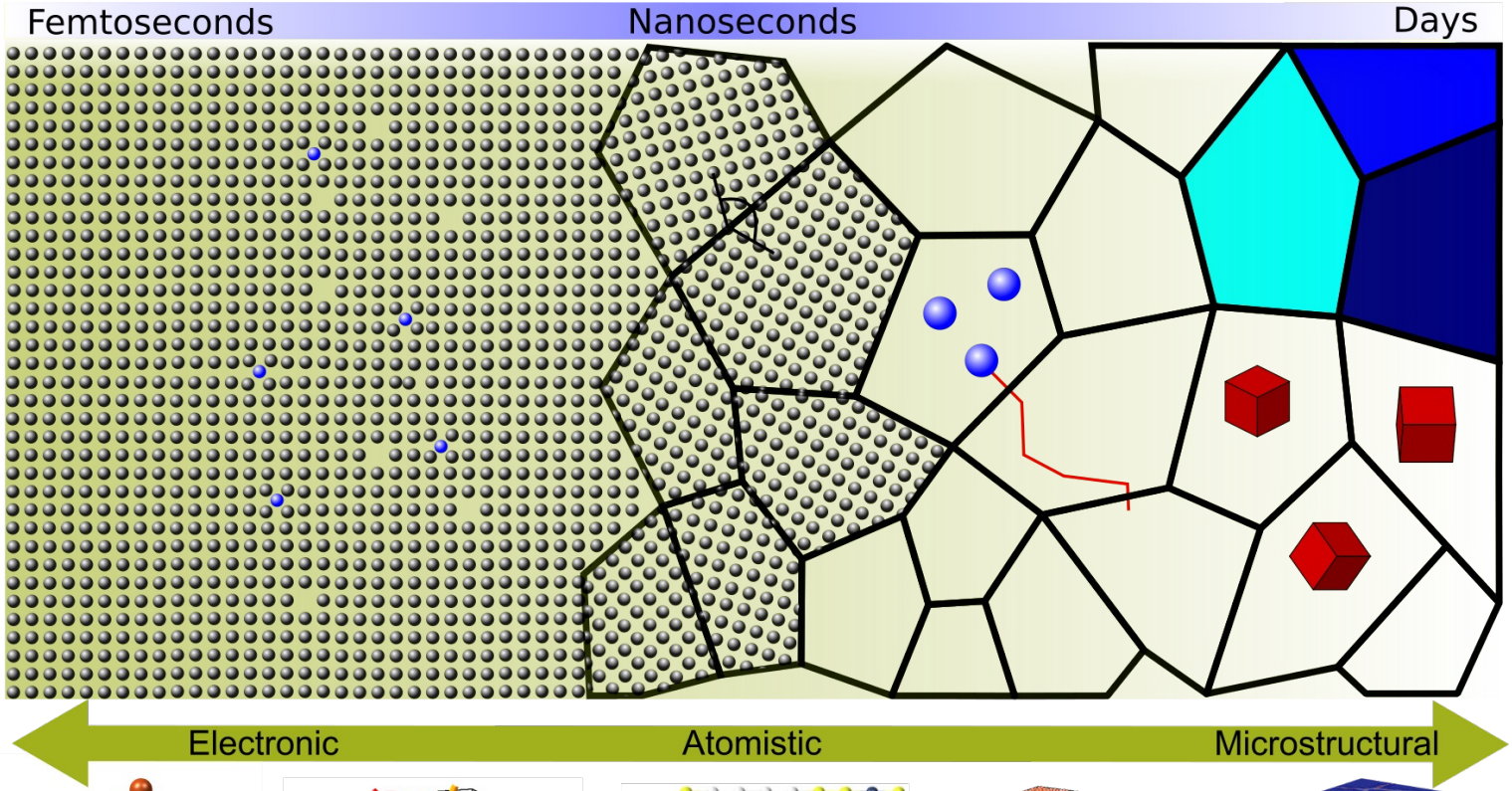
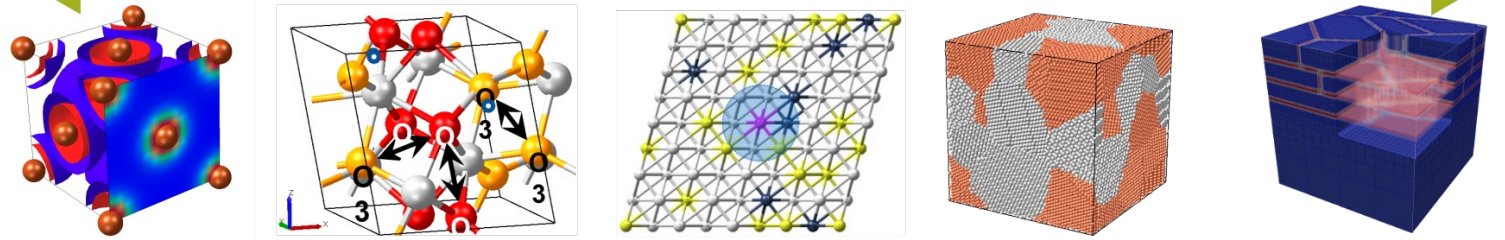


Where does your project fit?



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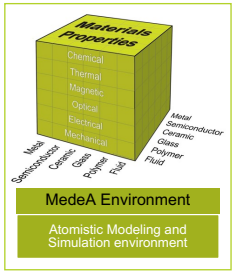
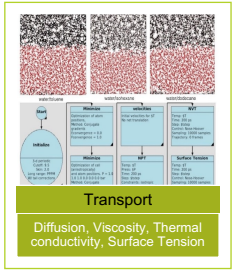
Highlighted *MedeA* Modules

MedeA Environment: The *MedeA*[1] software package is the leading environment for the atomistic simulation of materials. *MedeA* enables professional, day-to-day deployment of atomic-scale and nano-scale computations for materials engineering, materials optimization and materials discovery. In *MedeA*, world-class simulation engines are integrated with elaborate property prediction modules, experimental databases, structure builders and analysis tools, all in one user-friendly environment.

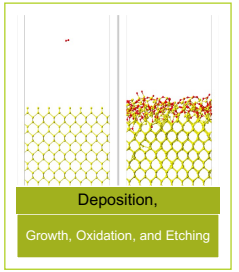


MedeA Microstructure Builder: creates microstructure models for atomistic simulations using a *Seed & Growth* algorithm with starting points either placed randomly or at user-specified coordinates within a supercell. Each such point is used as an origin to grow a crystalline grain by adding atoms from that seed point outwards, until a grain boundary is encountered.

MedeA Interface Builder: Lets you create an explicit, atomic-scale interface from two surfaces, allowing for a predefined maximum in-plane mismatch between adjoining layers. The *MedeA* Interface Builder helps to identify and build twist grain boundaries as well as coherent, and/or semi-coherent interfaces



MedeA UNCLE*:* expands access to materials and properties at the meso and micro scales. Maintaining the predictive power and accuracy of abinitio Density Functional methods, *MedeA UNCLE* lets you determine stable multi-component crystal structures and rank metastable structures by enthalpy of formation.



MedeA Phonon: allows you to explore the temperature dependence of free energies and heat capacities, the vibrational motions that lead to reactions and phase transitions, as well as Infrared and Raman spectra of structural models with ease and computational efficiency. The module can operate with VASP, LAMMPS or MOPAC as a computational engine.

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Related *MedeA* Webinars

The Basis of Success. A Conversation with the President of Gaussian Inc., Dr. Mike Frisch:
https://www.materialsdesign.com/webinars/recorded/the-basis-of-success

Medea Training: MedeA VASP and Battery Applications:
https://www.materialsdesign.com/webinars/recorded/ugm-2021-training-vasp

Machine-Learned Potentials: Surpassing the Limits of the ab initio World without leaving it behind:
https://www.materialsdesign.com/webinars/recorded/mlp-surpassing-the-limits-of-ab-initio

On-the-fly Machine Learning Forcefields with MedeA VASP:
https://www.materialsdesign.com/webinars/recorded/medea-training-on-the-fly-machine-learning-forcefields-with-medea-vasp

Polyvalent Machine-Learned Potential for Cobalt: from Bulk to Nanoparticles:
https://www.materialsdesign.com/webinars/recorded/polyvalent-machine-learned-potential-for-cobalt

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Question and Answer Session

Dr. Erich Wimmer

Materials Design

Kyle Starkey

Materials Design

Leonid Kahle

Materials Design

Questions about Materials Design Webinars

Katherine Hollingsworth

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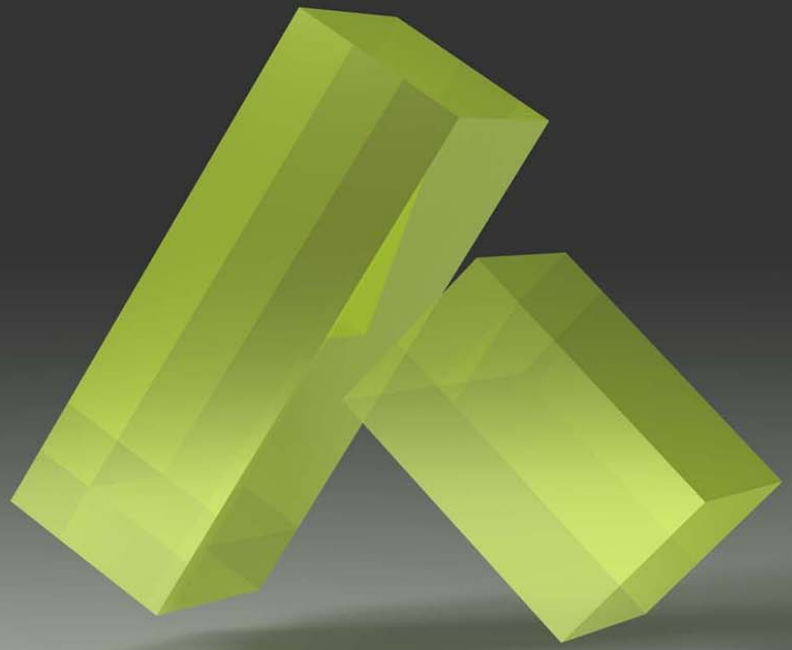

MedeA

Innovation by Simulation

Contributors

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RESEARCH INSTITUTE

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