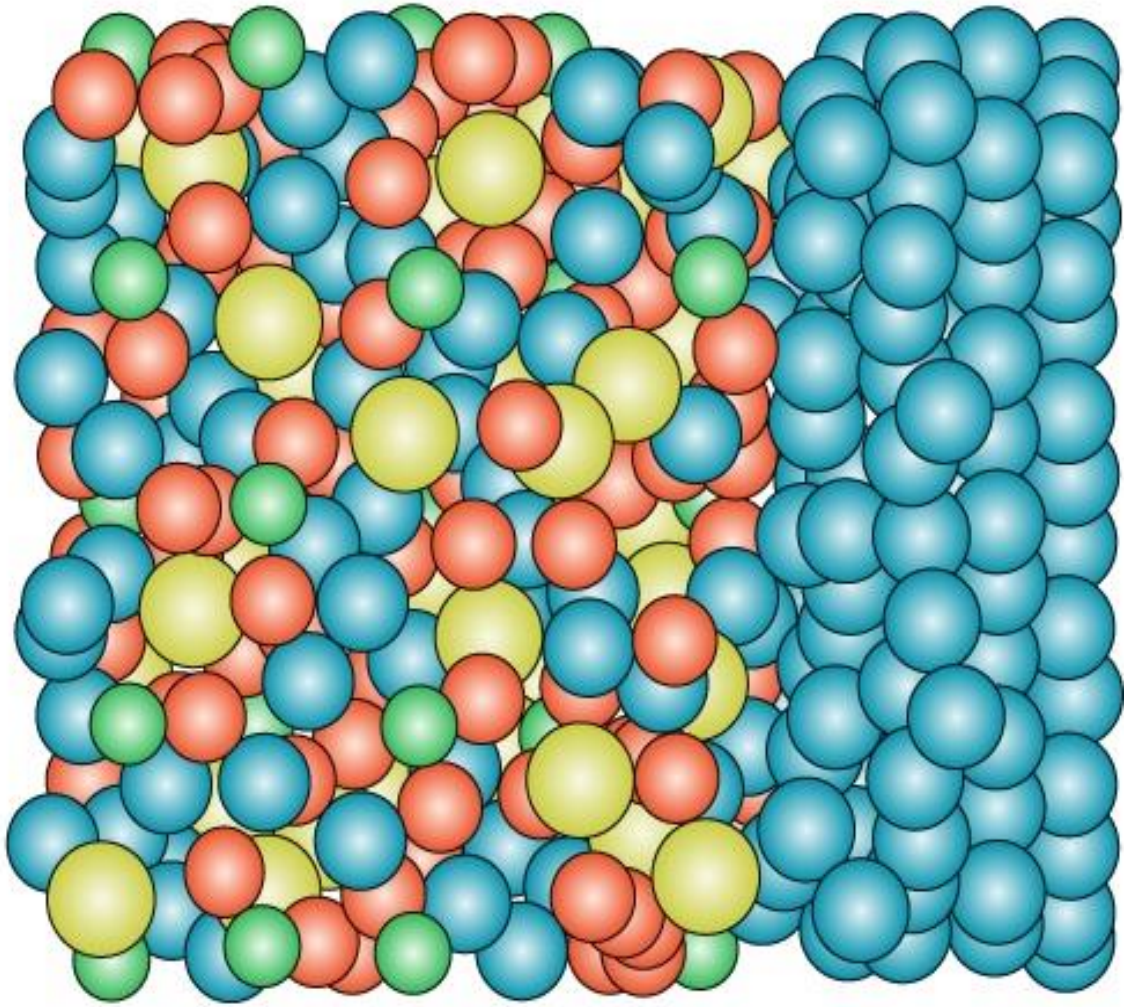
Understanding Interfaces in Solid Electrolytes Through Atomistic Modelling



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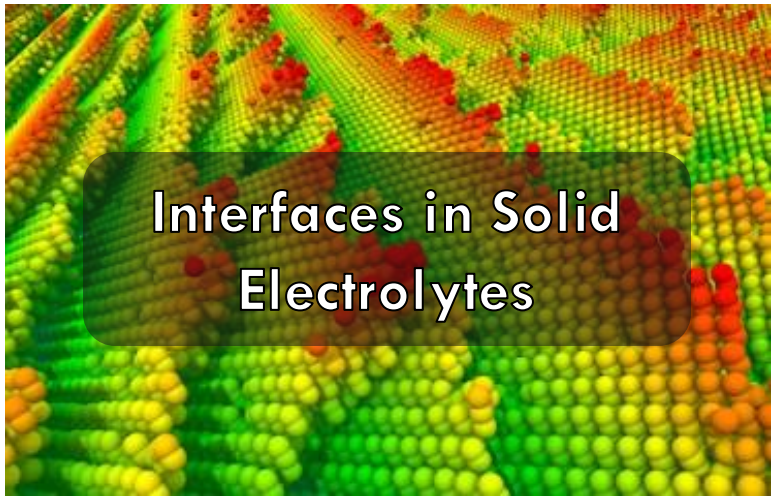
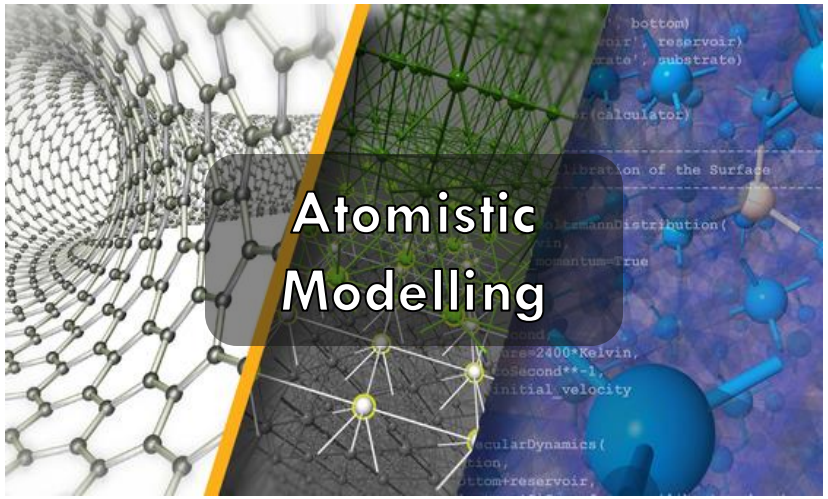
2025 MRS Fall Meeting, Boston, November 30th

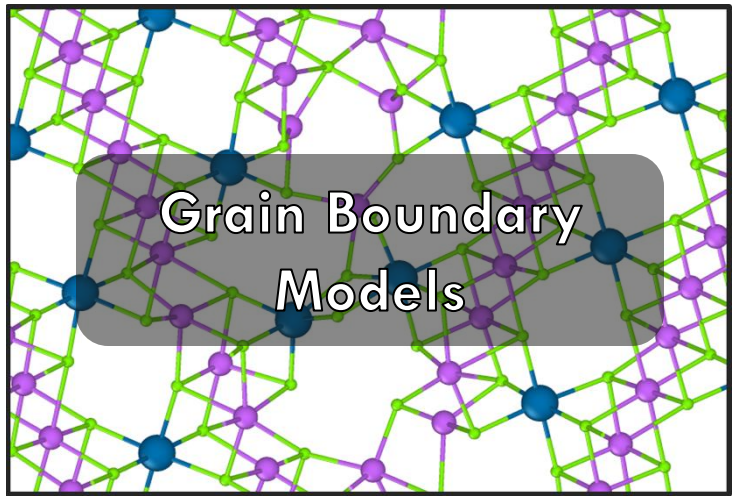
Newcastle University

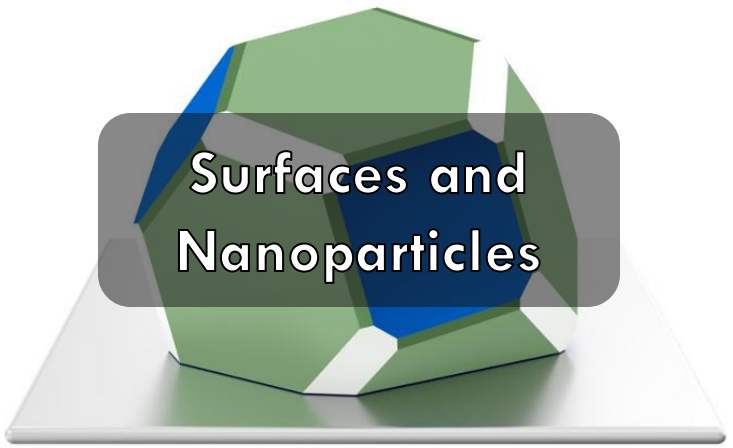
Northumbria University NEWCASTLE

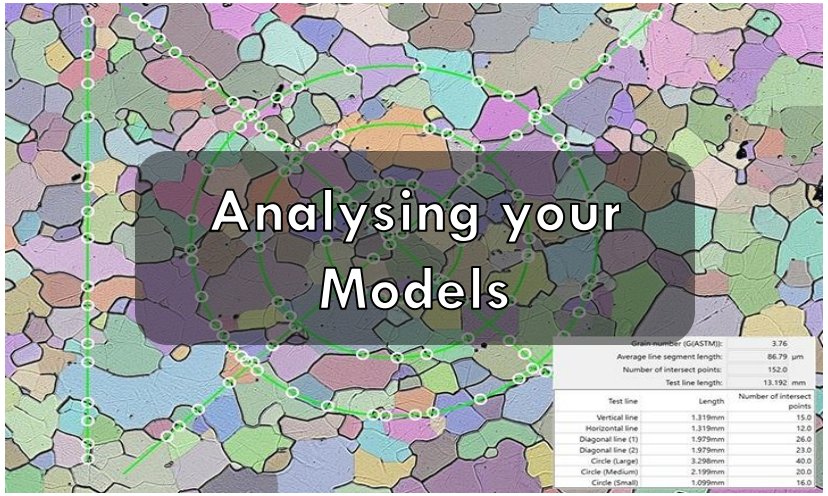
A Taste of Things to Come …

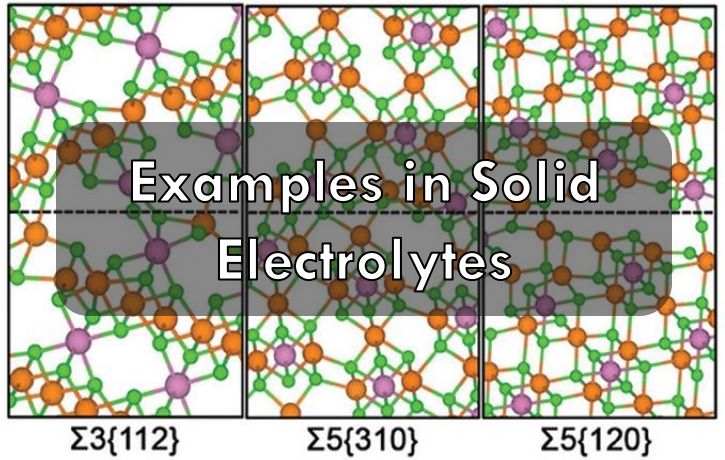




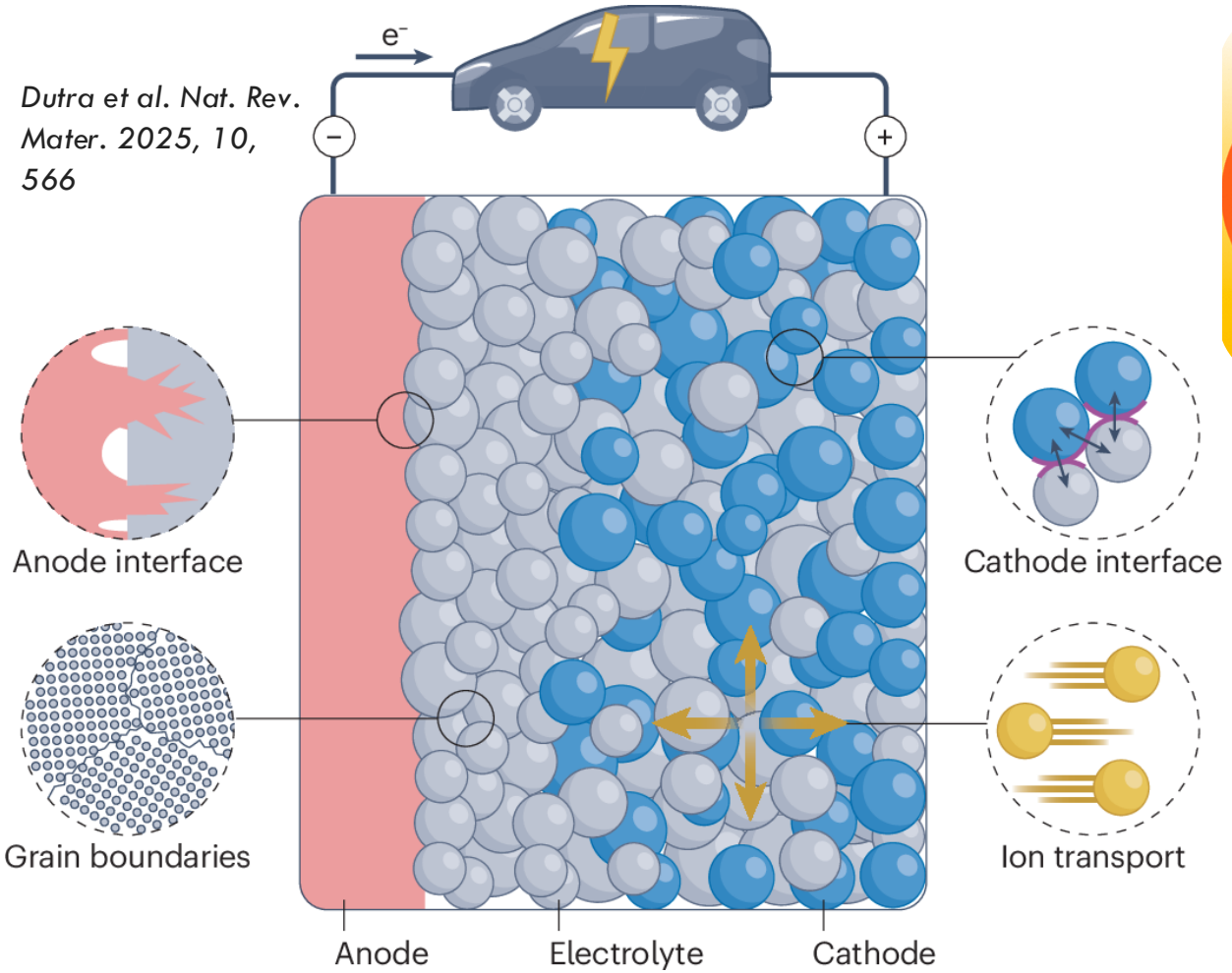




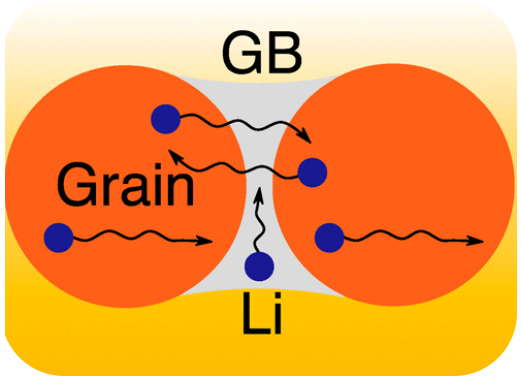




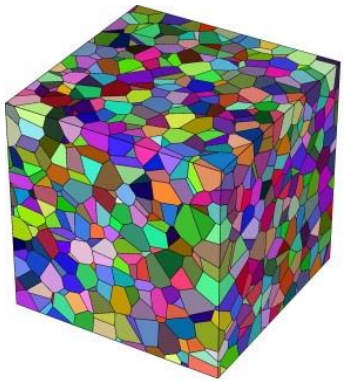
Interfaces in Solid Electrolytes



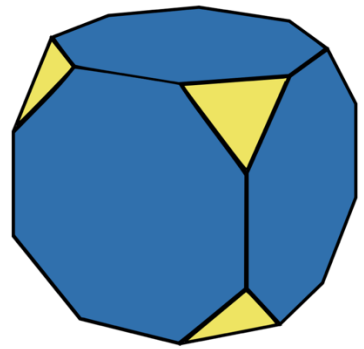
Dutra et al. Nat. Rev. Mater. 2025, 10, 566



Grain boundaries

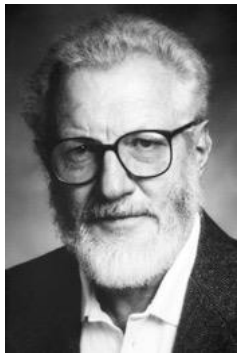


Polycrystals



Nanoparticles

'The interface is the device'

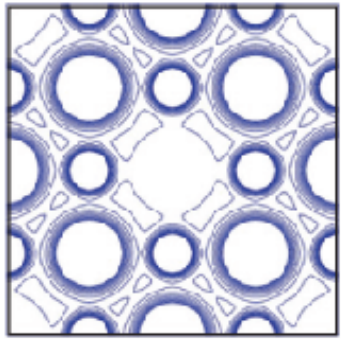


Herbert Kroemer
Nobel Laureate in Physics 2000

Modelling Methods

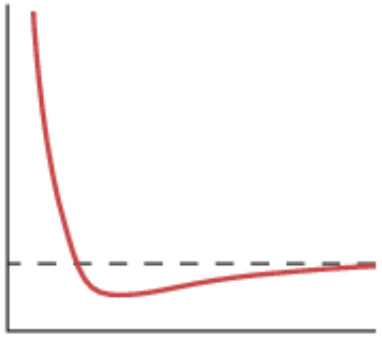
Quantum Mechanics

- Less approximations but computationally expensive
- DFT and AIMD
- Electrons and nuclei treated explicitly



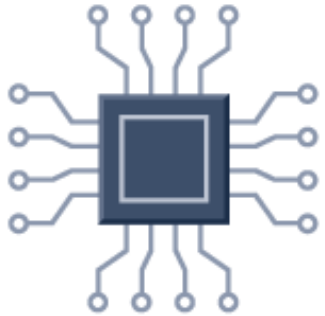
Classical

- More approximations but computationally cheaper
- MD and Monte Carlo
- No electronic degrees of freedom/fixed charges



Machine Learning

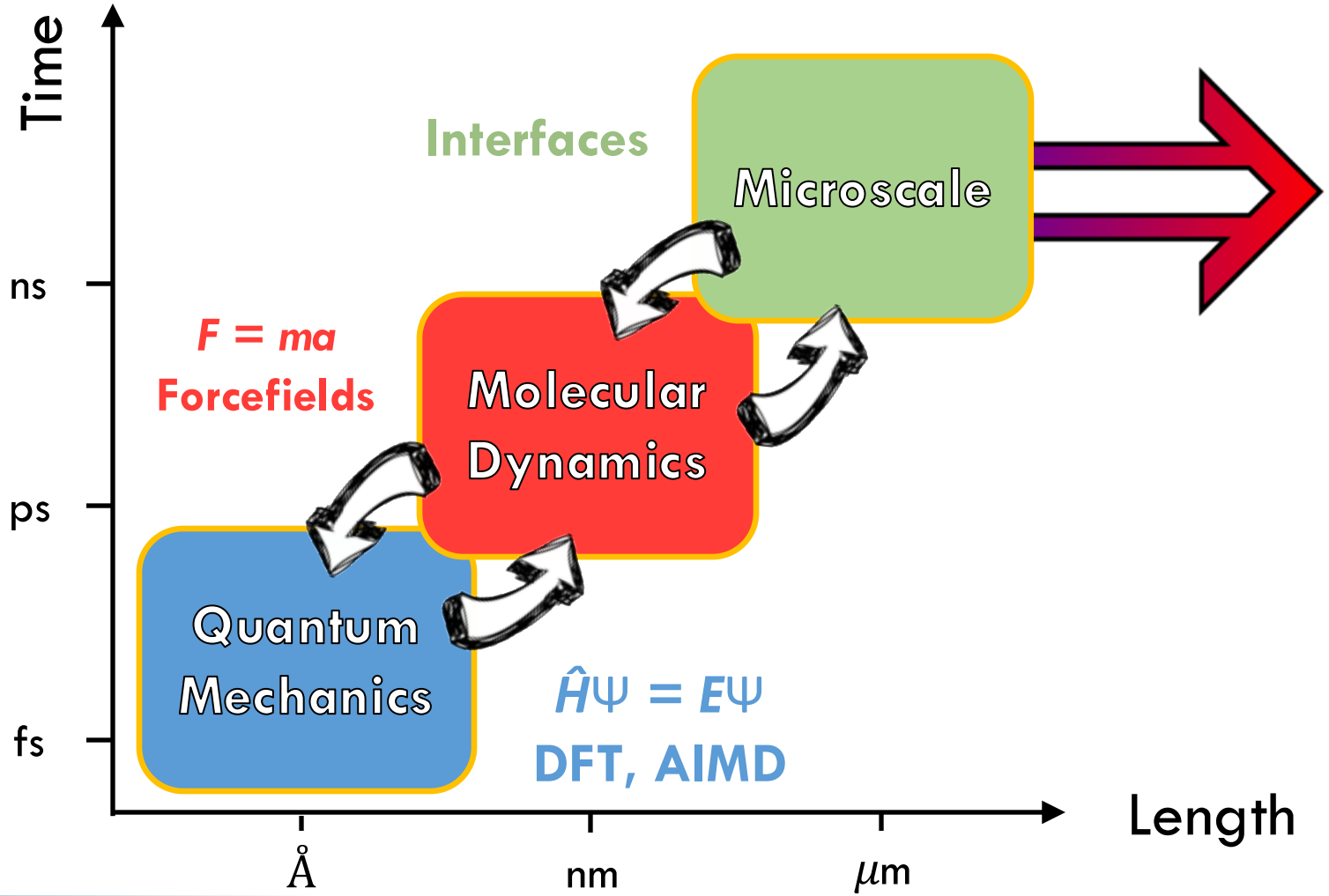
- ML forcefields
- Screening and discovery
- Requires reliable training data

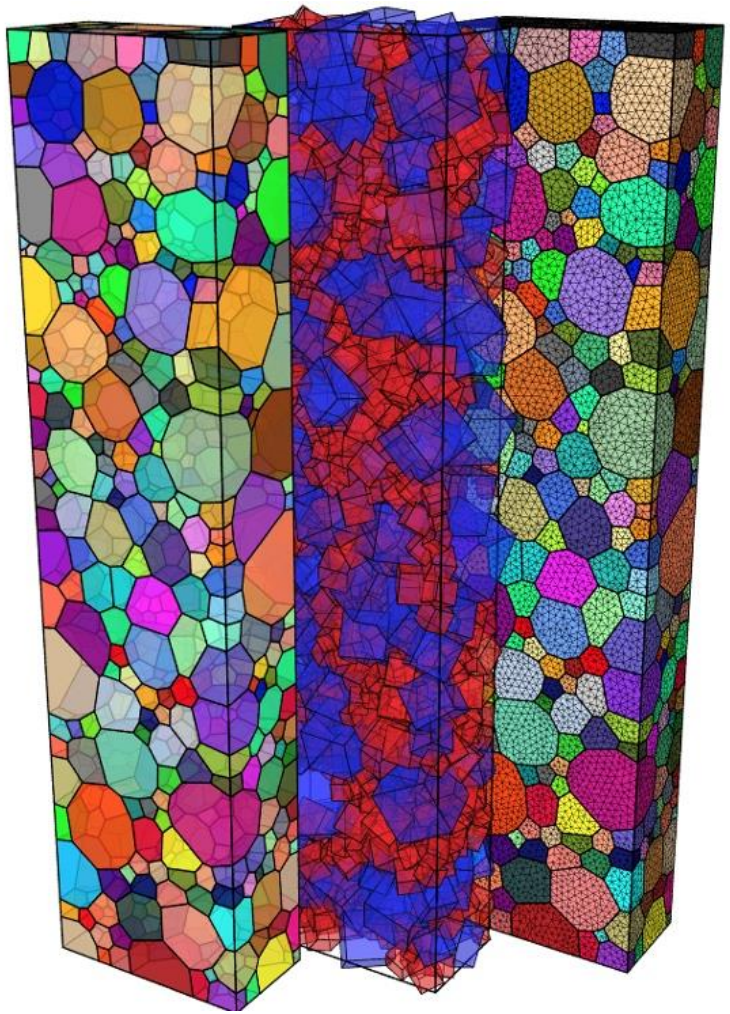


Continuum

- No atomistic details
- Larger length and timescales

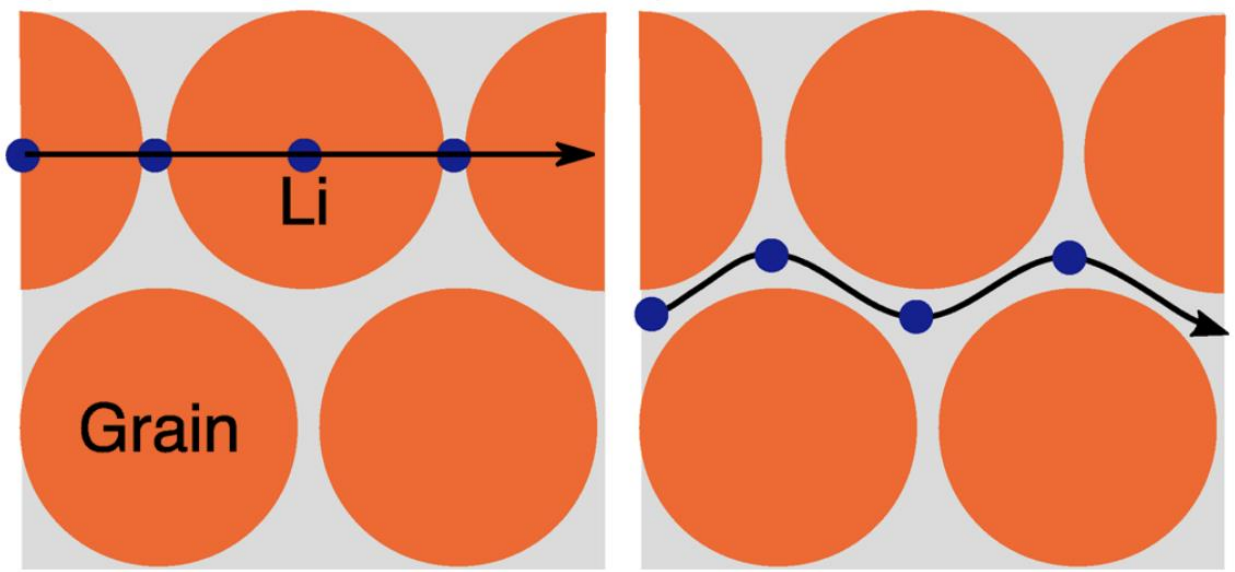
Multiscale Modelling of Interfaces





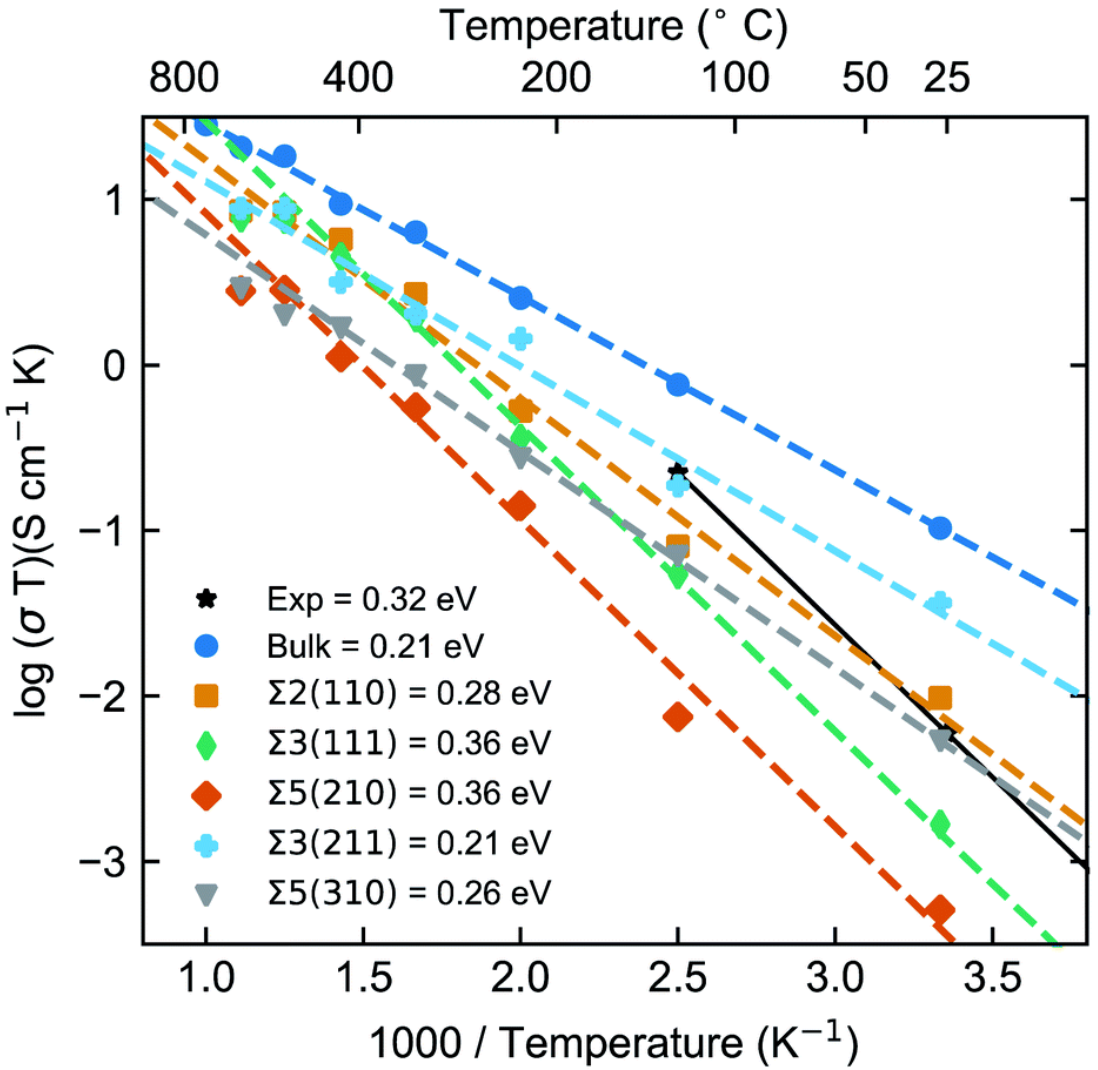
Why Bother Modelling Grain Boundaries?

Impact on Conductivity



Dawson et al., J. Am. Chem. Soc. 2018, 140, 362

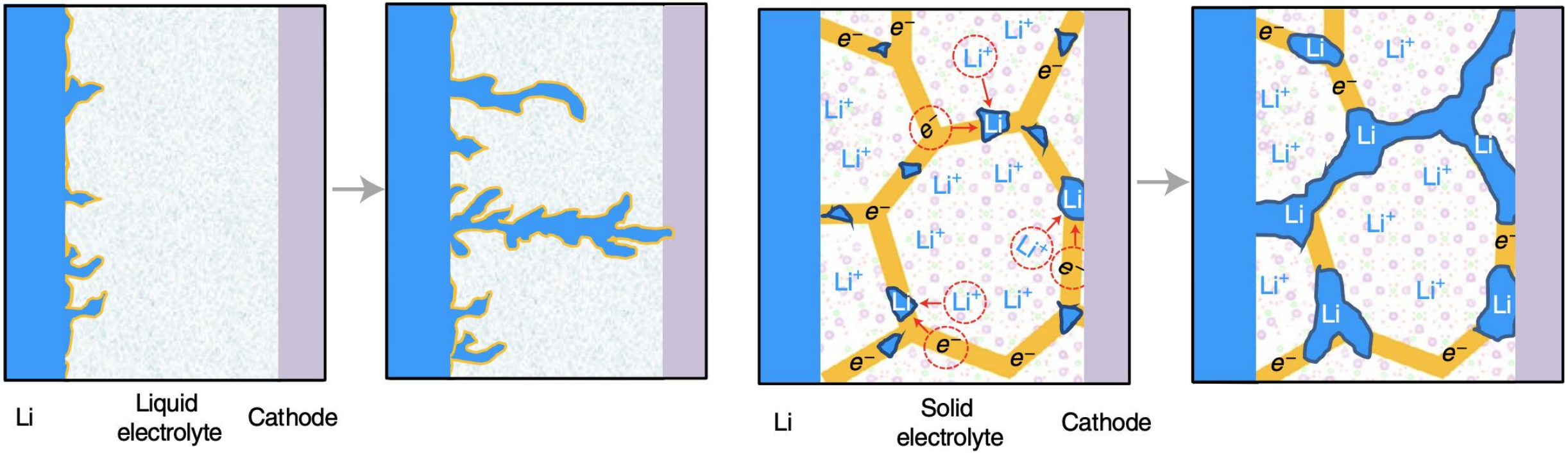
- Bottlenecks to Li-ion conductivity or Li-ion highways?
- Poorly understood at atomic scale



Symington et al., J. Mater. Chem. A 2021, 9, 6487

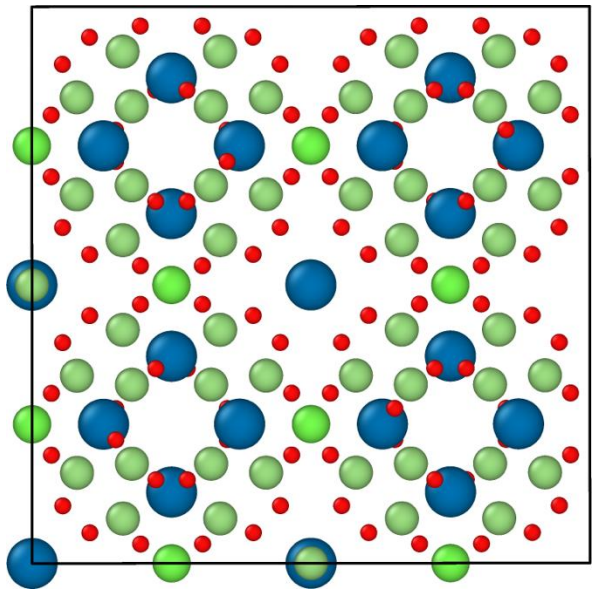
Impact on Dendrites

Liu et al., Nat. Mater. 2021, 20, 1485



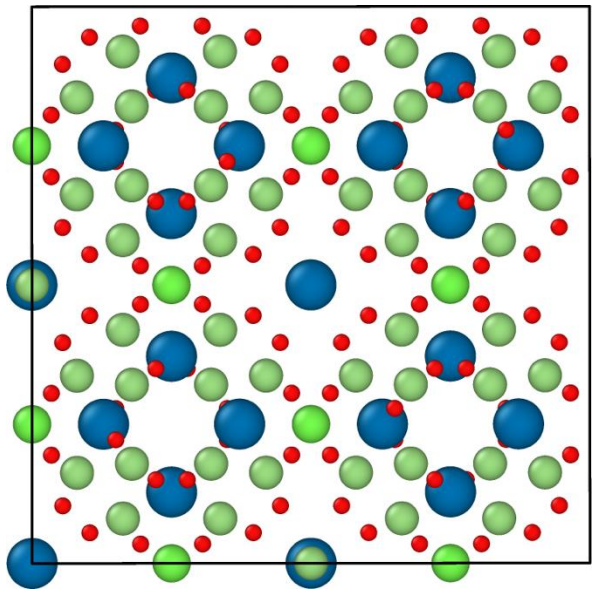
- Li infiltration strongly linked with local electronic structure
- Li ions reduced at grain boundaries to form Li dendrites

The Problem With Models



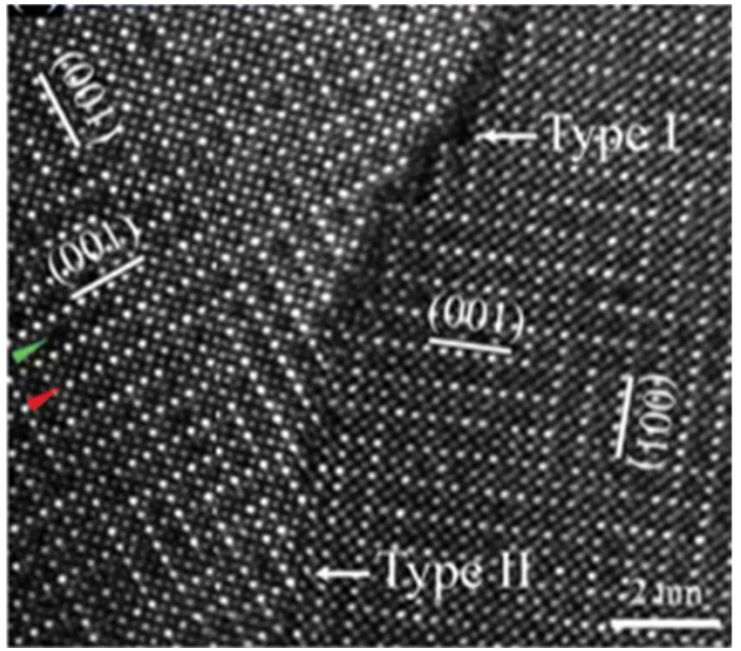
- Pretend we knew the exact quantum mechanical solution.
- Would we get exact results?
- Would we even get good results?

The Problem With Models



This material doesn't exist!

Hood ZD, Chi M. J.Mater Sci. 2019 15;54(15):10571-94.

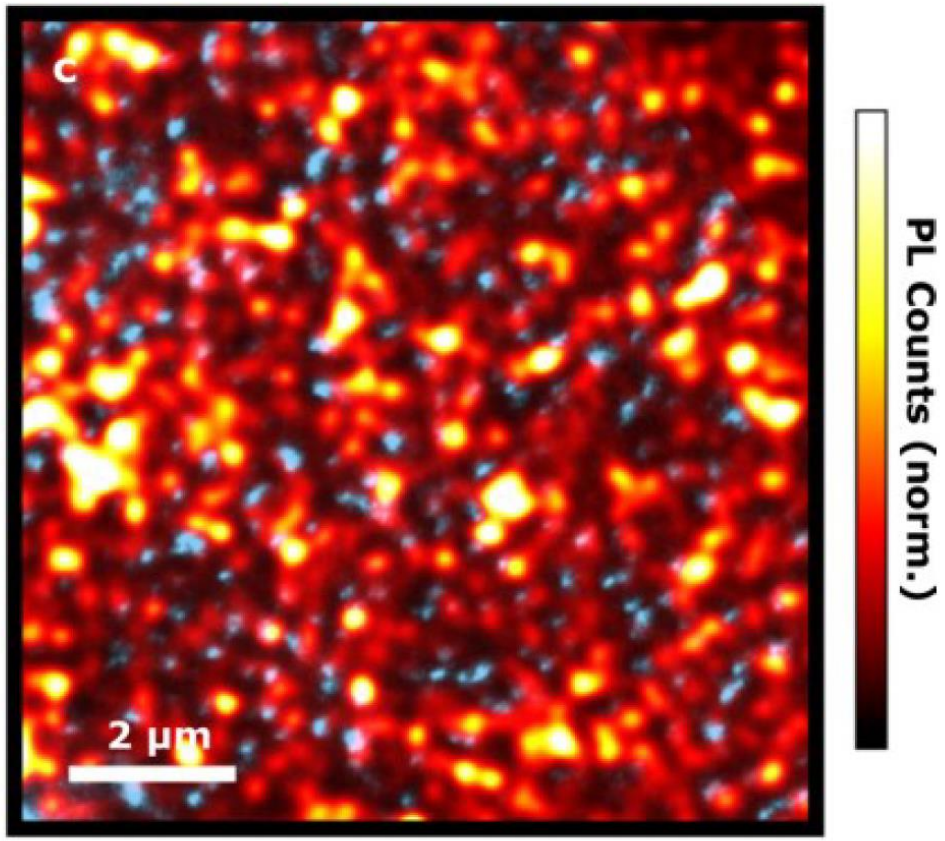


Real materials are messy.

Density functional theory isn't wrong. Your model is wrong.

What Can Experiment Tell Us?

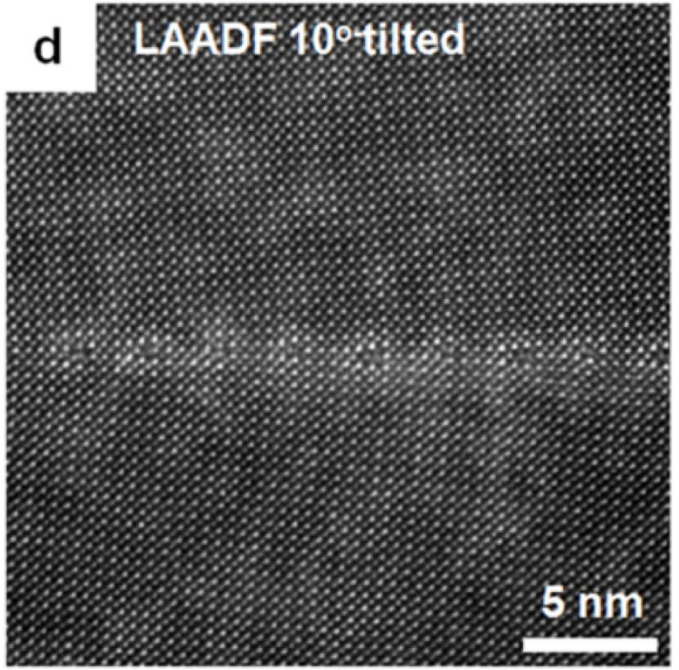
- Some space-resolved techniques give insight.
- Limited resolution and difficult to interpret.



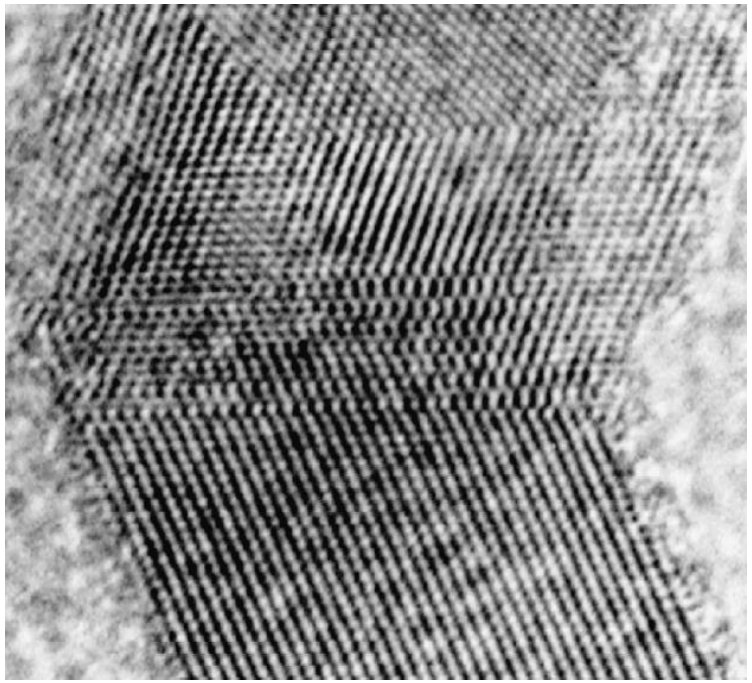
Doherty TA, Winchester AJ, et. al. Nature. 2020 16;580(7803):360-6.

Experiments Are Hard

- Nice experiments require nice samples.
- Can you grow nice films?
- If not, are you lucky enough to see a boundary?



Choi SY, Kim SD, et al. Nano Lett. 2015 10;15(6):4129-34.

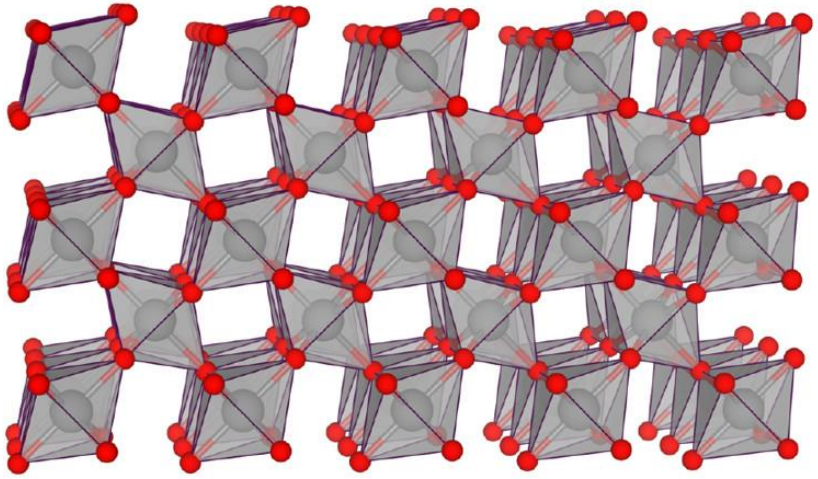


Penn RL, Banfield JF. Amer. Mineral. 1999 1;84(5-6):871-6.

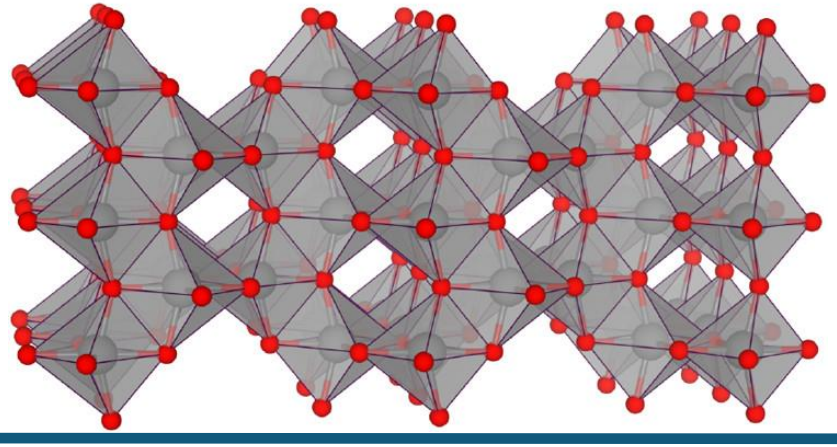
Case Study: Titanium Dioxide

- Everyone's favourite oxide.
- Pure anatase does not form large crystals, but shows better performance as an optoelectronic.
- Only recently that decent TEM was possible.

Rutile

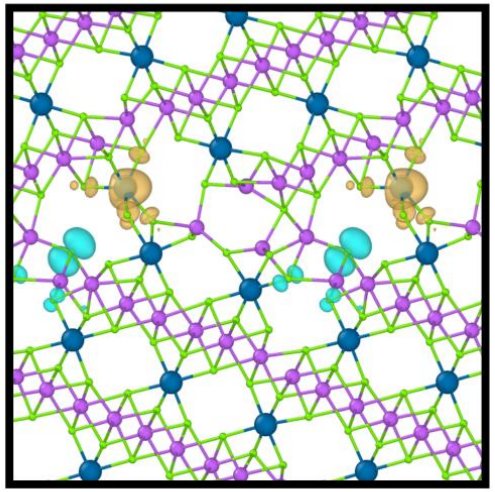


Anatase



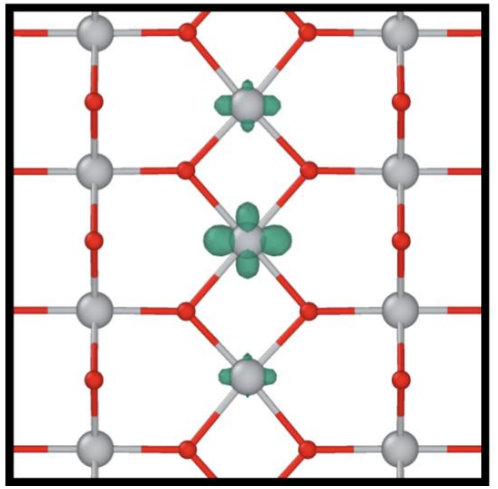
Case Study: Titanium Dioxide

- People assume grain boundaries harm performance by introducing electron traps.

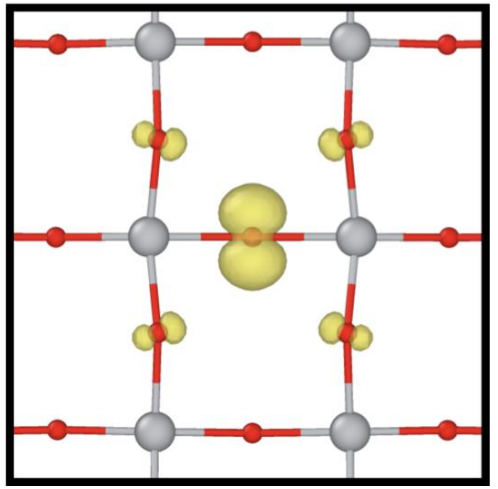


- If grain boundaries are killer, why does anatase perform so well?

Rutile Electron Polaron



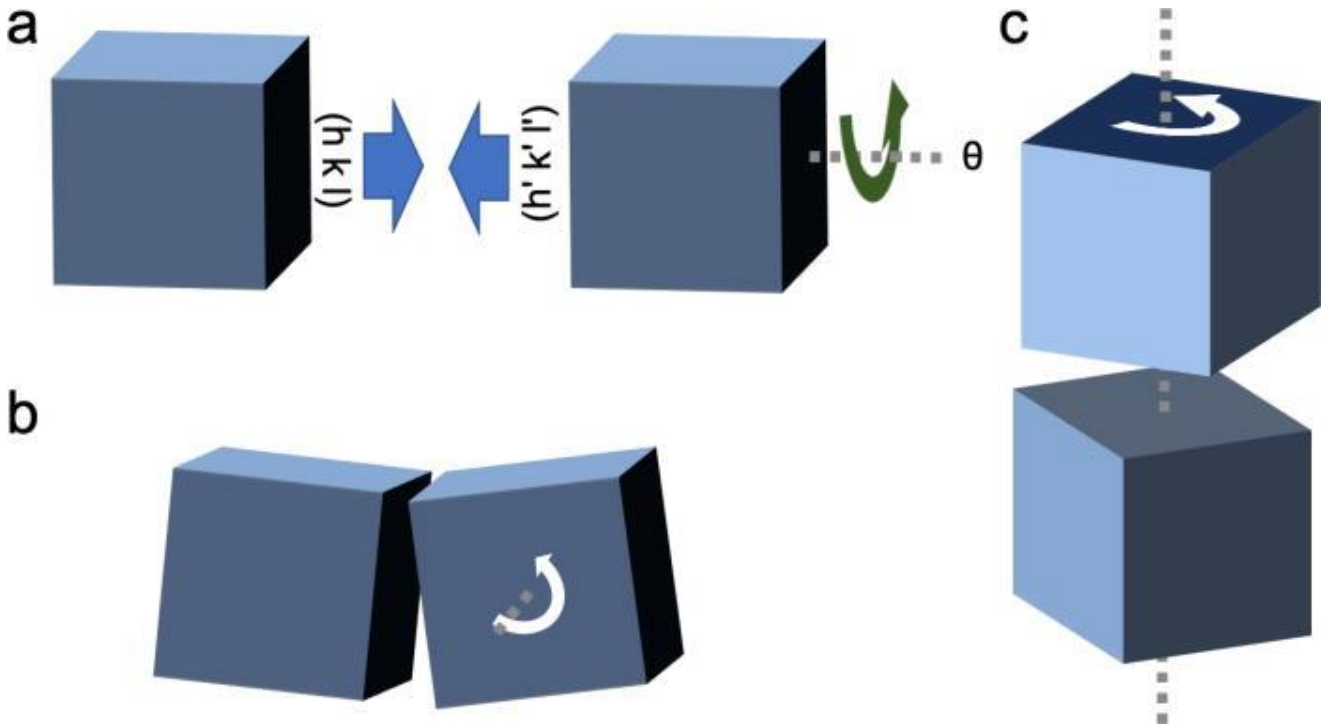
Anatase Hole Polaron



Building Models

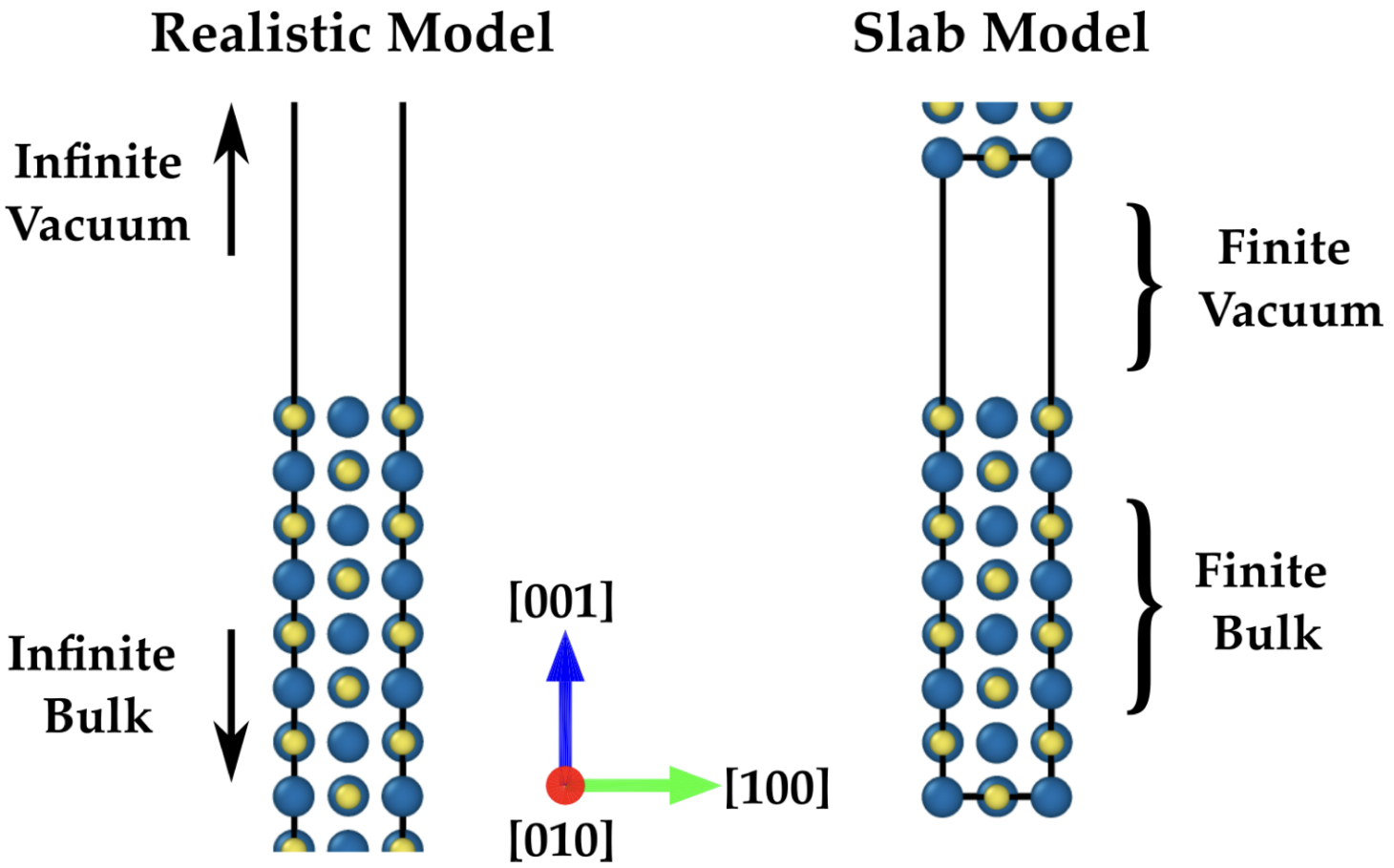
What is a Grain Boundary?

- Two crystals coming into contact.
- The crystals have different orientations defined by (h,k,l).



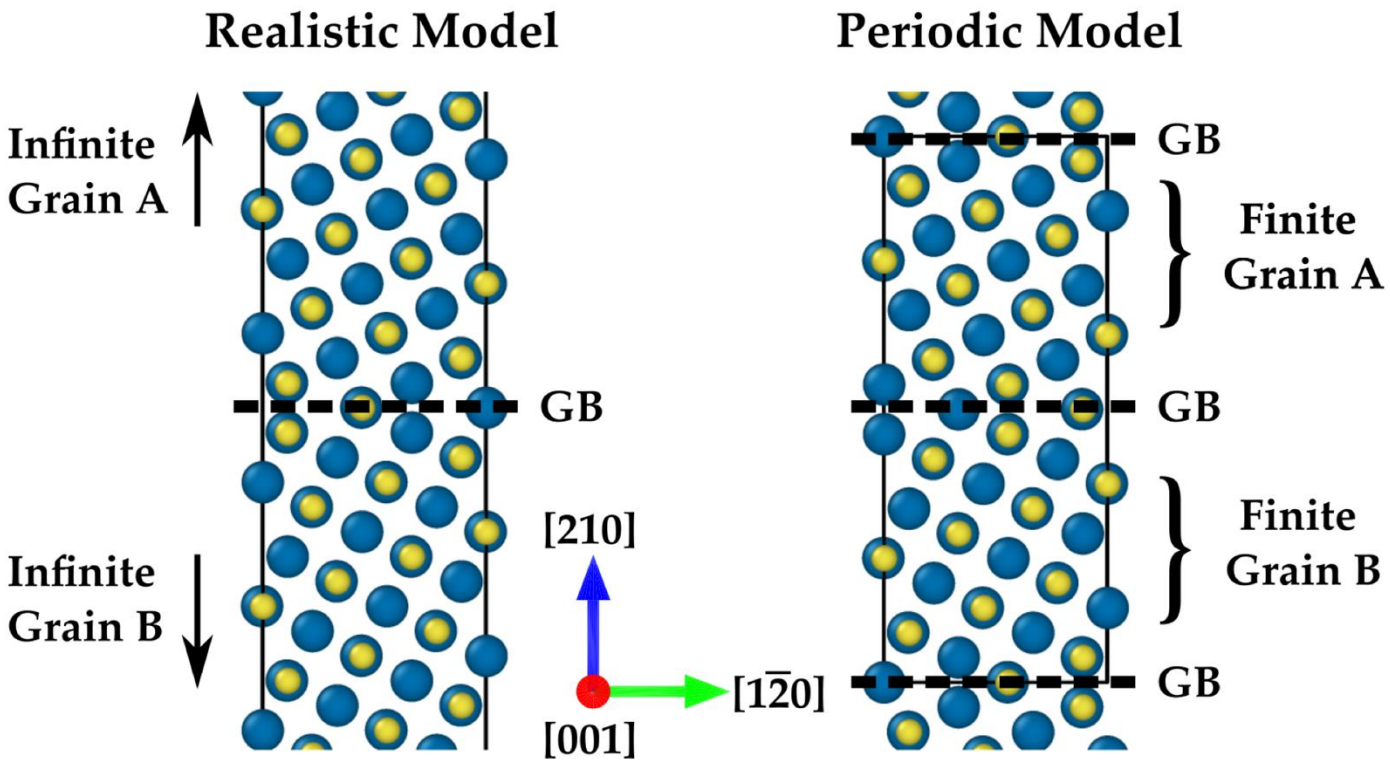
Periodic Supercells

- Simulations have periodic boundary conditions.
- Large cells are approximately ‘infinite’ cells.



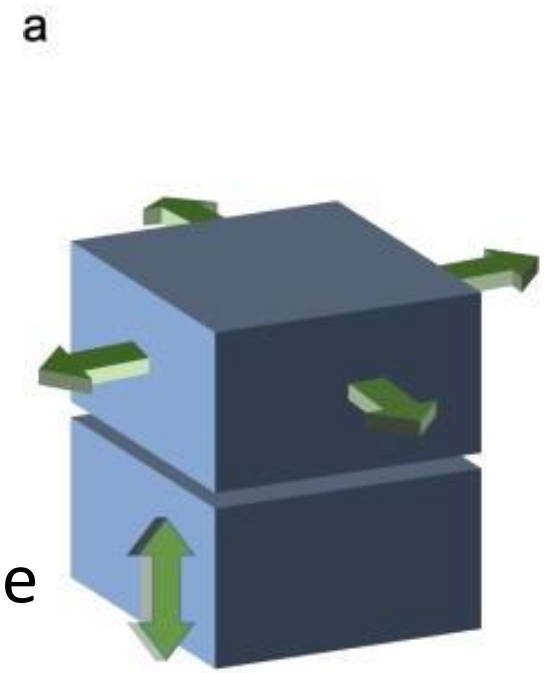
Periodic Supercells

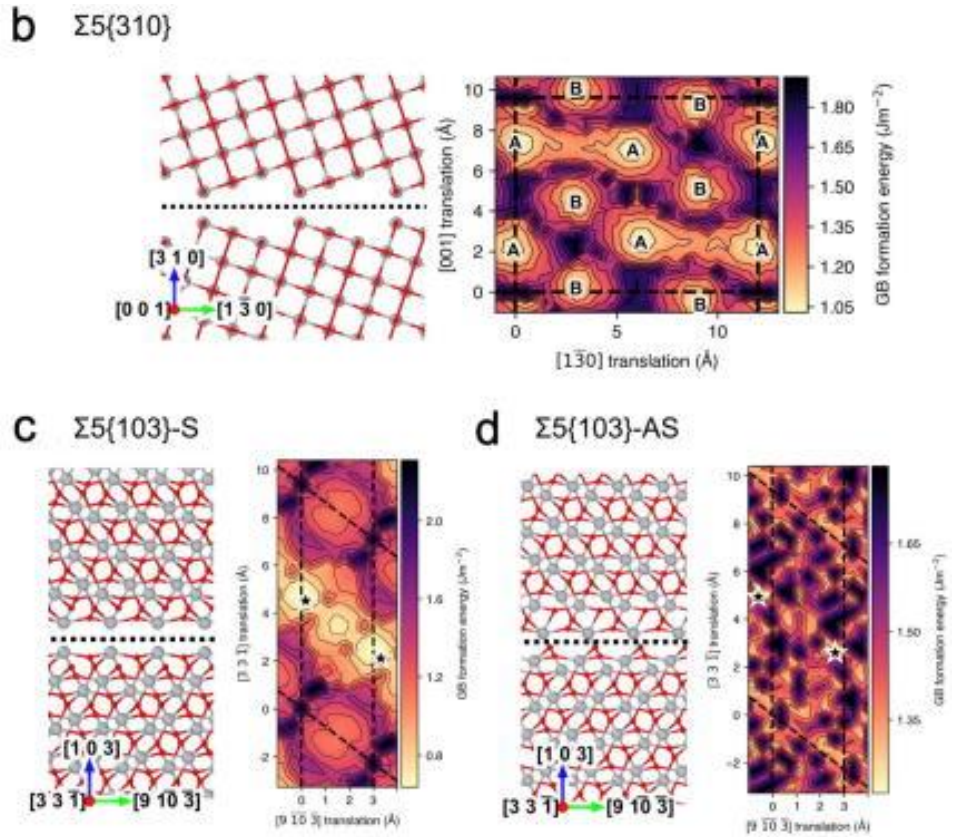
- Two grain boundaries per simulation cell.
- Thick grains required to prevent interactions between images.



Optimising Boundary Structures

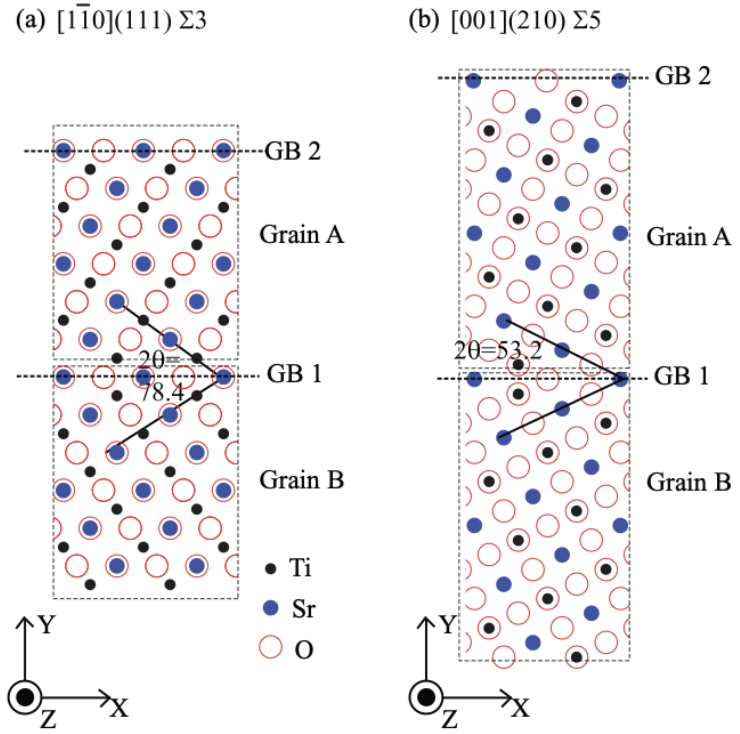
- Mirror-symmetric boundaries are often local minima, but not global minima.
- Test different translations between the grains.

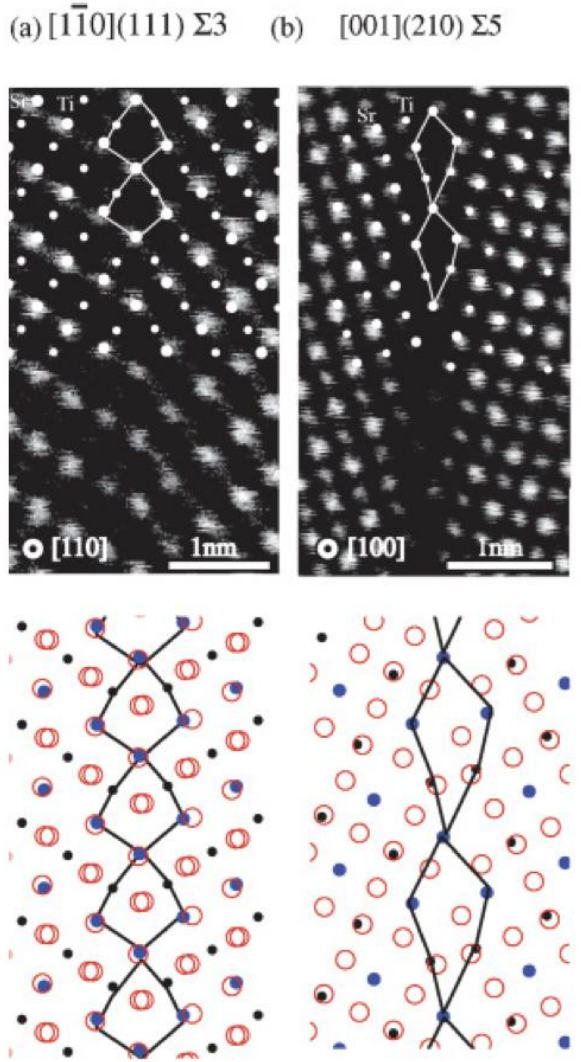




Experimentalists Build Models Too!

- Idealised samples known as bicrystals are constructed.
- Cut two crystals and stick them together.
- Rigid-body translation agrees very well!

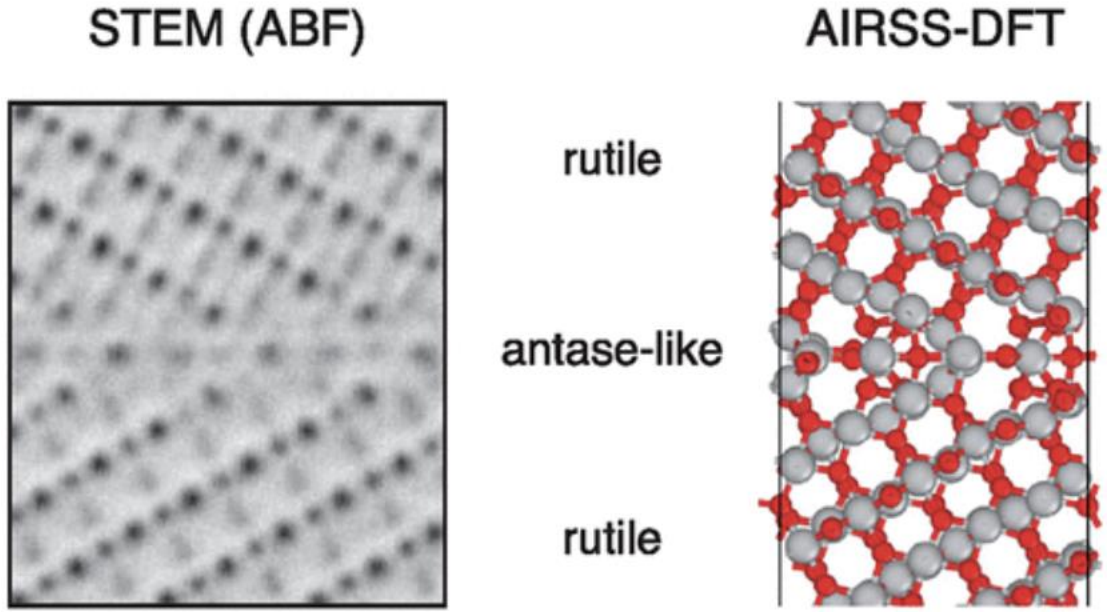




Lee HS, Mizoguchi T, et al. Phys. Rev. B. 2011 1;83(10):104110.

Experimentalists Build Models Too!

- Genetic algorithms, structure searching, etc. also a good choice.
- Boundaries often mimic competing phases.
- Constrain your search to systems with reasonable bonding.



Schusteritsch G, Ishikawa R, et al. Nano Lett. 2021 31;21(7):2745-51.

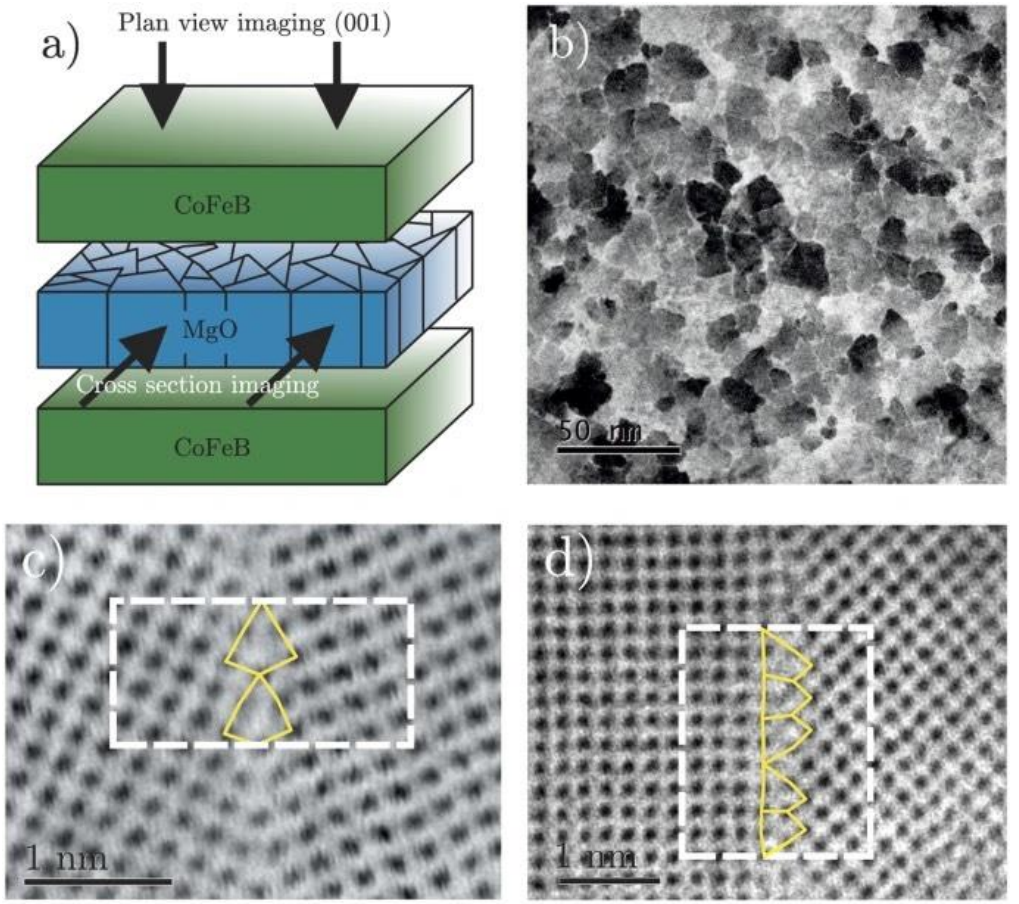
Recap: Building Models

- Two grains give two boundaries in a periodic supercell.
- Consider all translations between the two grains.
- Also worth considering global optimisation schemes for each translation.
- Constrain search to systems with sensible bonding.

Which Boundaries Should We Study?

Low Energy Boundaries Make Sense

- Low energy boundaries occur more frequently.
- In the absence of experimental data, trial and error is reliable but slow.
- Substrate may constrain film orientations.

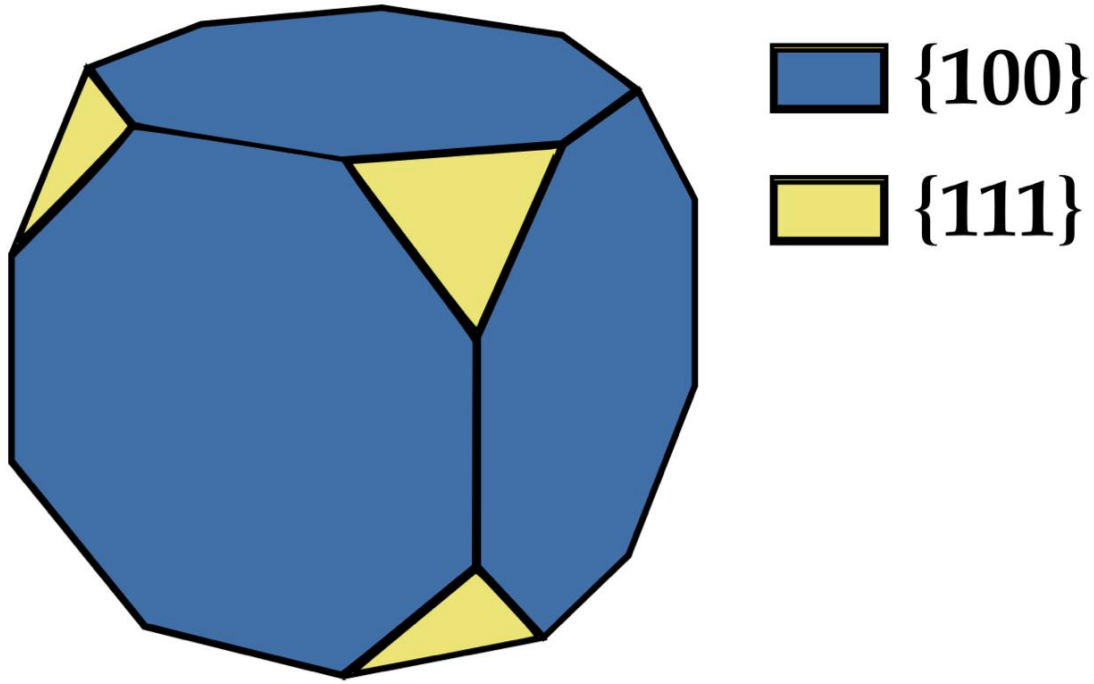


Bean JJ, Saito M, et al. Scientific reports. 2017 4;7(1):45594.

What About Nanoparticles?

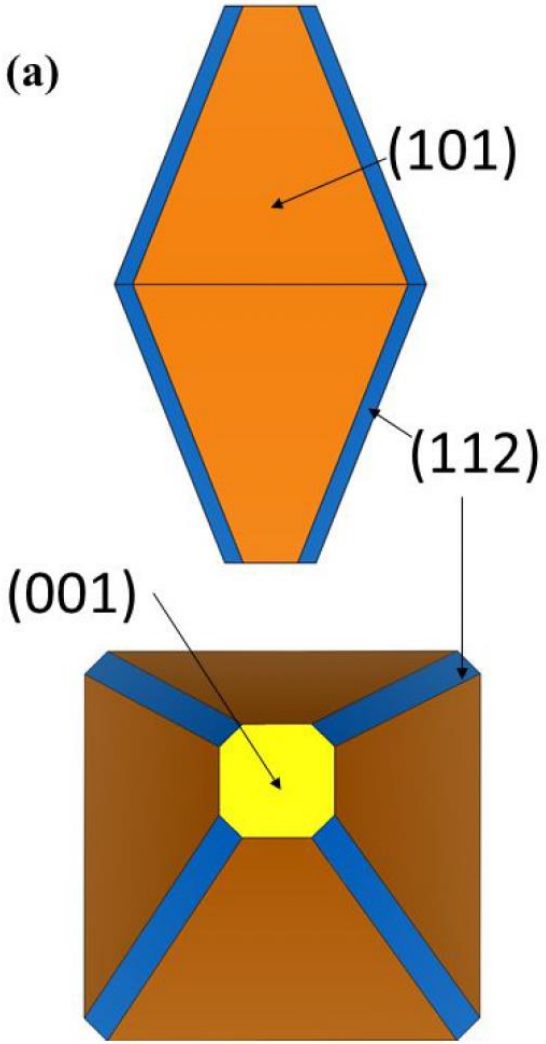
- Low energy surfaces sound most relevant.

- The lower energy means a greater surface area.



What About Nanoparticles?

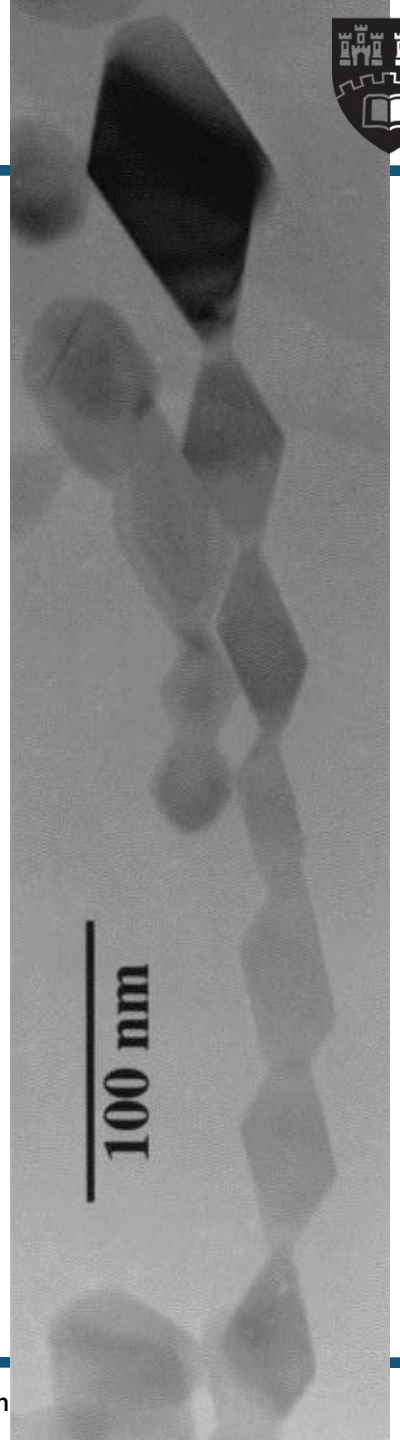
- But high energy surfaces appear on crystals in small amounts.
- High energy surfaces want to bond to something.



Oriented Attachment

- Crystals attach along high energy surfaces.

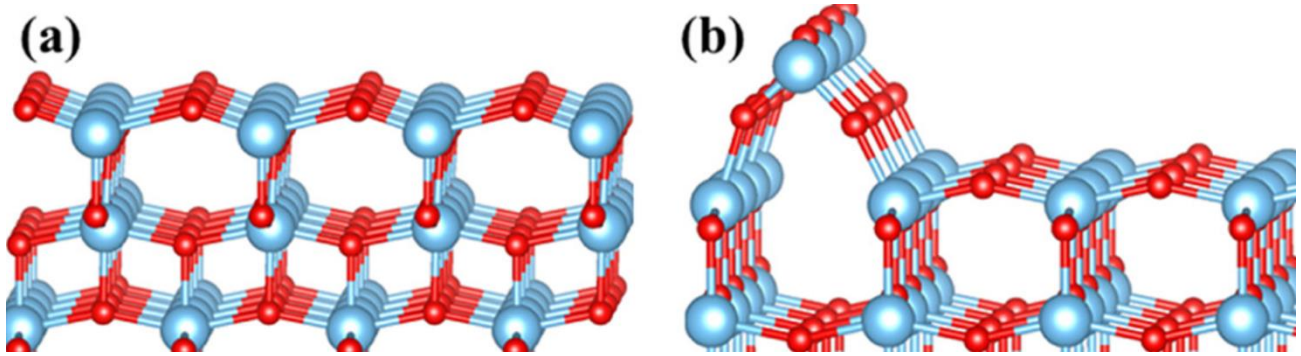
- If your material is hydrothermally coarsened, consider oriented attachment when building models.

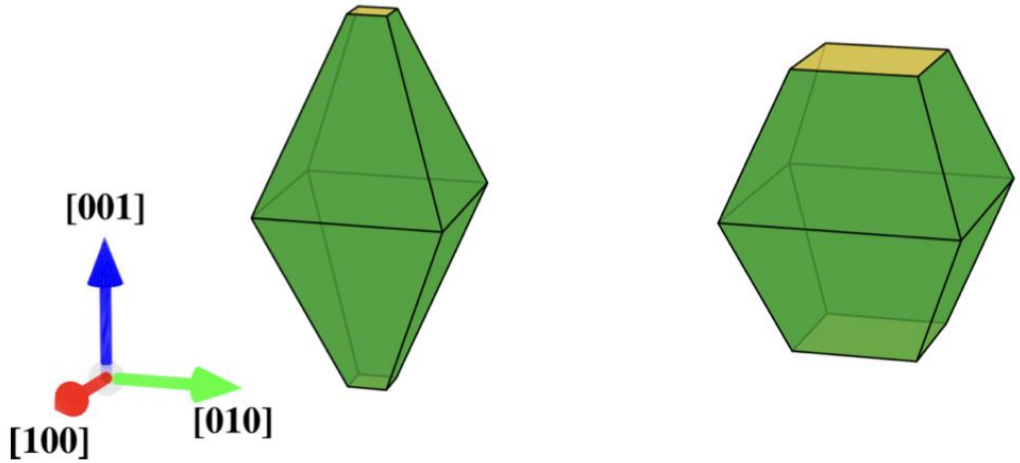


Oriented Attachment

- Different growth conditions cause surface reconstructions that affect crystal shape.

- Think carefully about what sort of system you're trying to model.





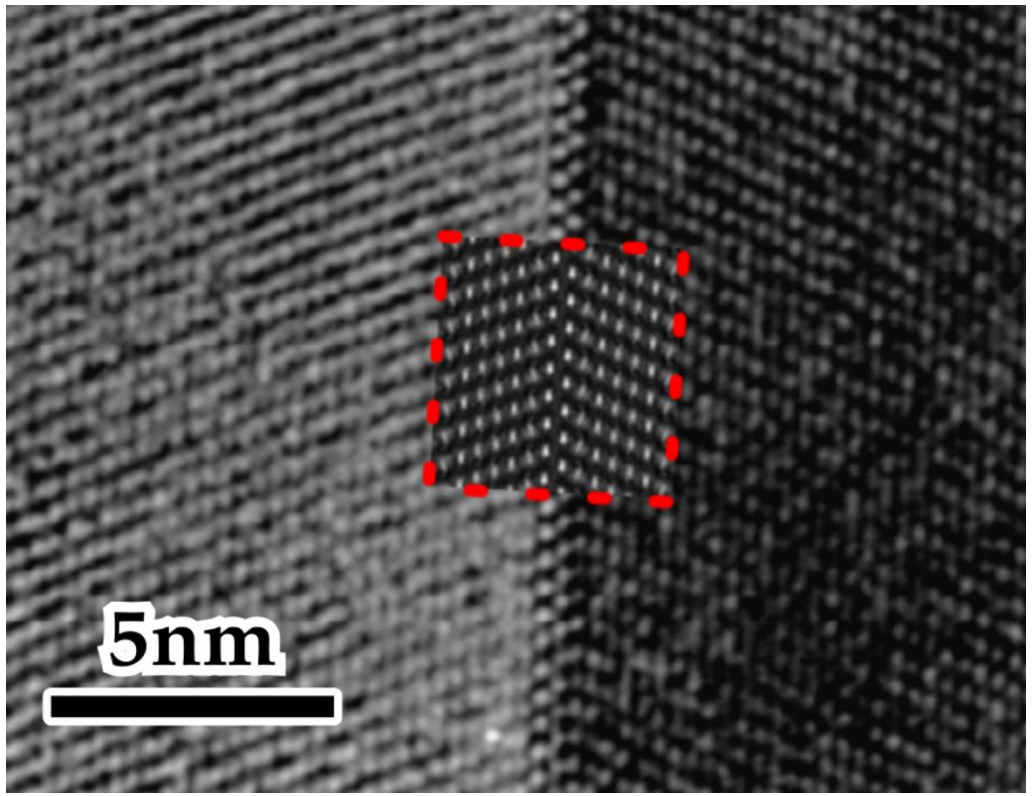
Recap: Which Boundaries Should We Study?

- General rule is that low energy boundaries are realistic.
- The synthesis of a material affects which boundaries you expect to see. Substrates are important.
- Nanoparticles will attach along certain facets, making certain boundaries more common.

Analysing Your Models

Comparisons With Experiment

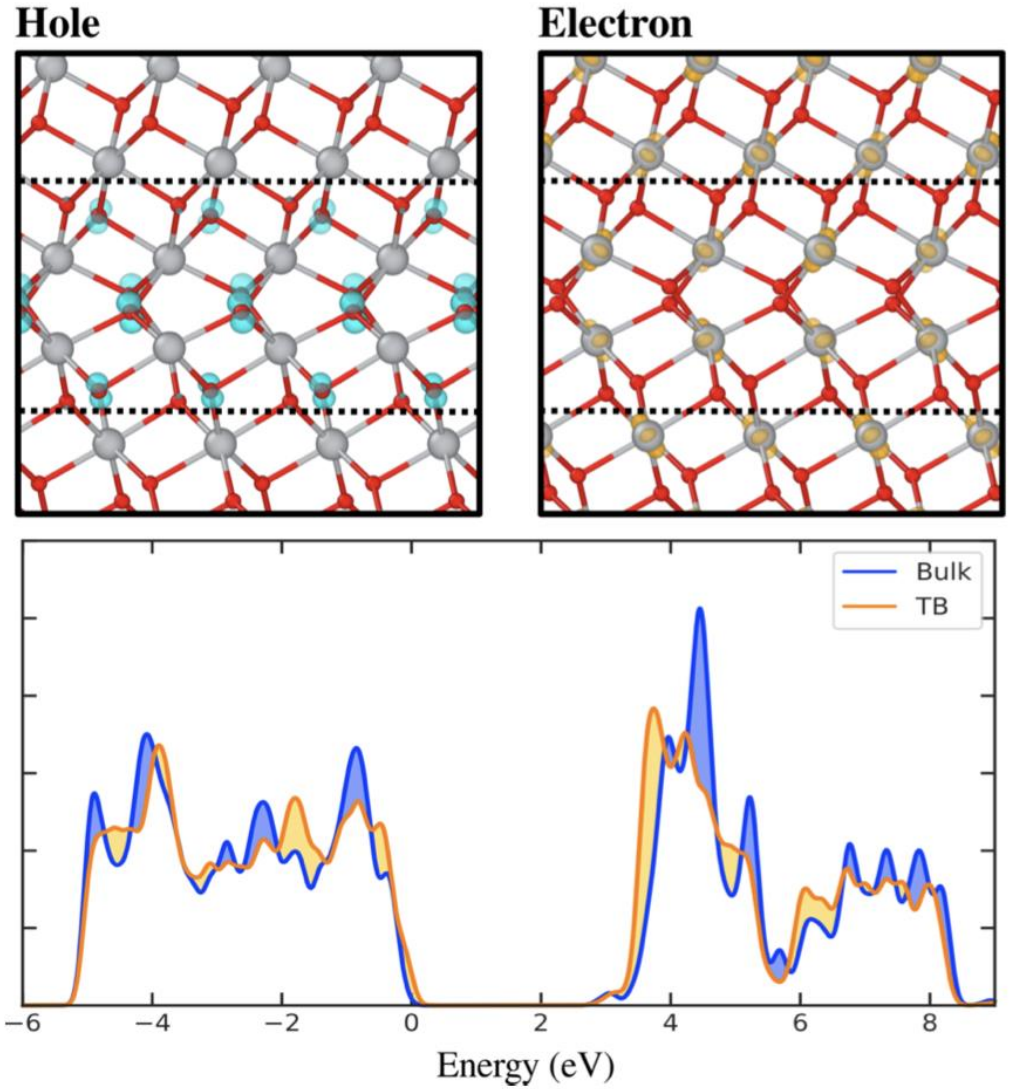
- Possible to simulate electron microscopy.
- Our model of the {112} twin matches experiment very well!



Quirk JA, Lazarov VK, McKenna KP. Adv. Theory Simul. 2019; 2(12):1900157.

It's All Relative

- The most important thing is how the boundary is different from the bulk.
- Be qualitative instead of quantitative. Let someone else do the hard work!

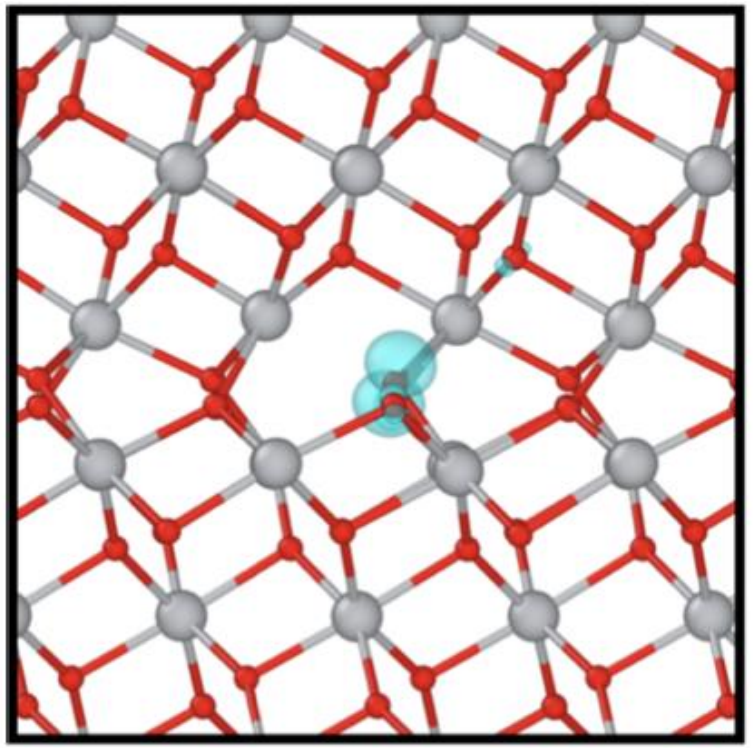


Don't Forget About Point Defects

- Point defects (vacancies, interstitials, etc.) will have different formation energies at the boundary.

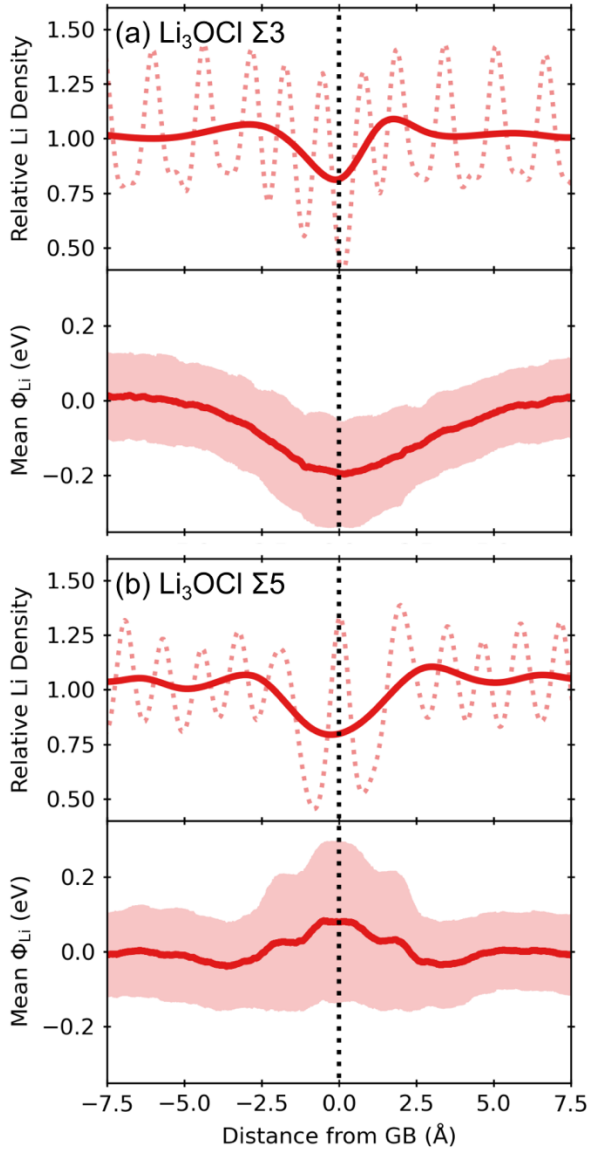
- For charged defects, this causes a space charge region to develop.

-0.18eV



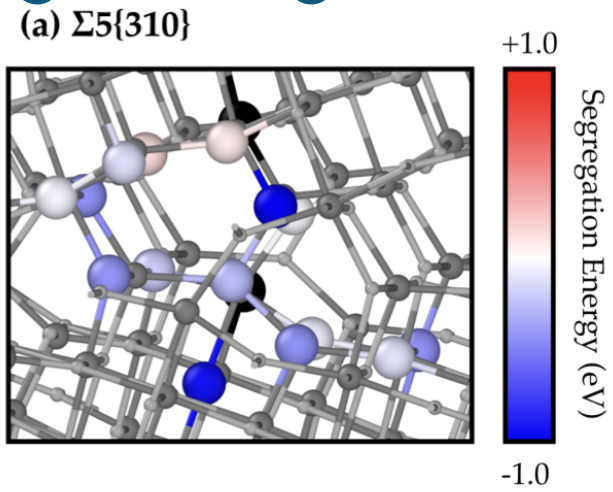
Segregation During Dynamics

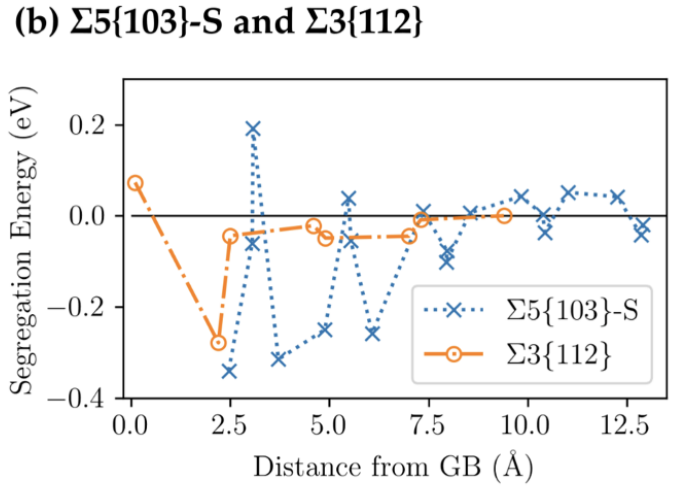
- Defects may segregate during dynamics.
- Space charge region develops naturally during simulation.
- May take some time to equilibrate.



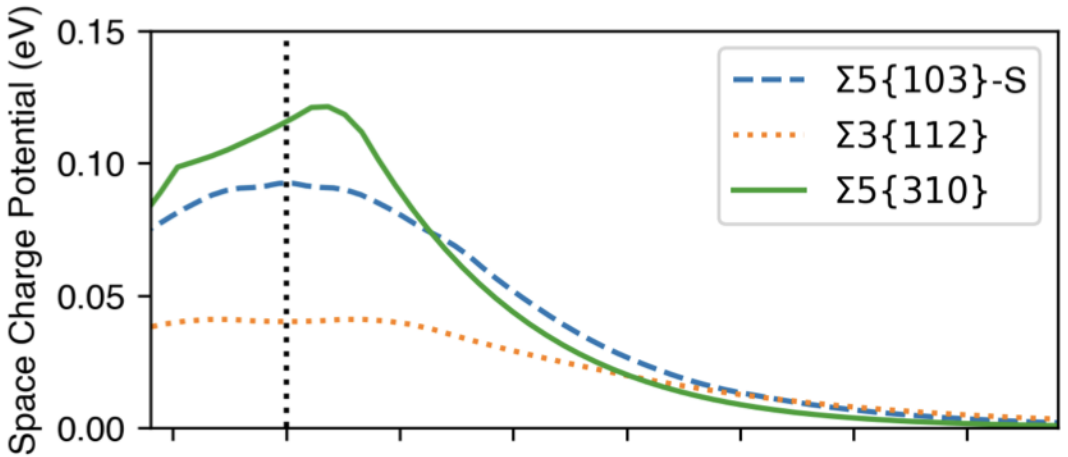
Estimating Space Charge Regions

- Segregation energies can be obtained from static calculations.
- Plug these into PYSCSES to estimate the size of the space charge.

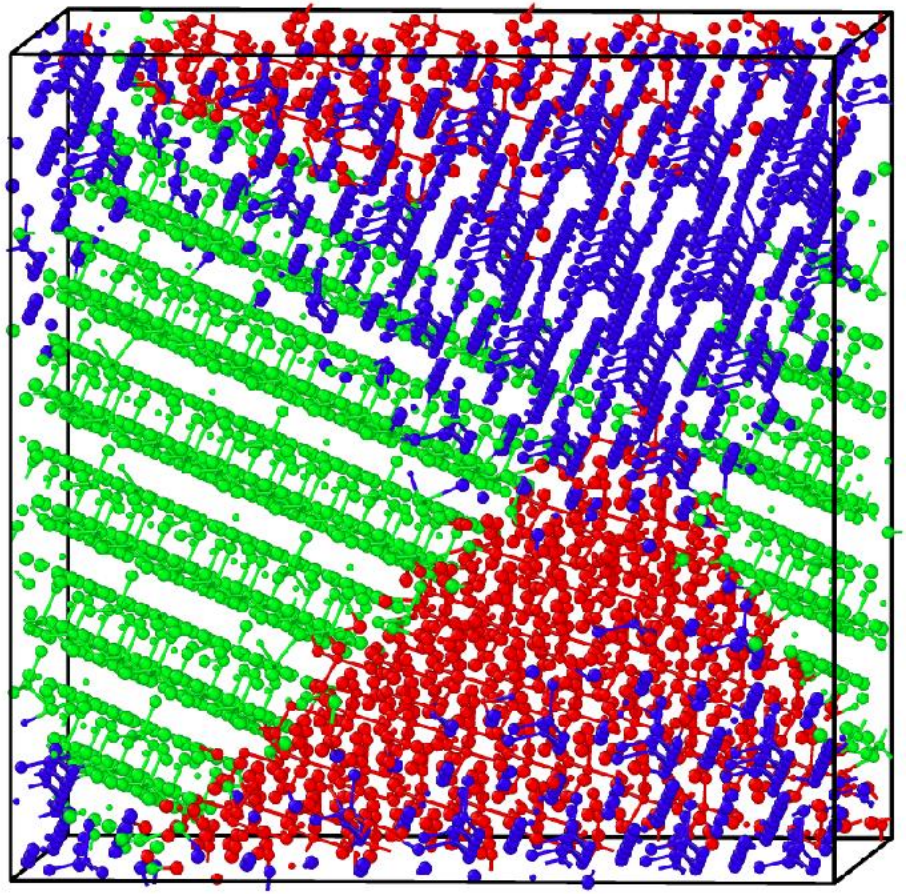




PYSCSES

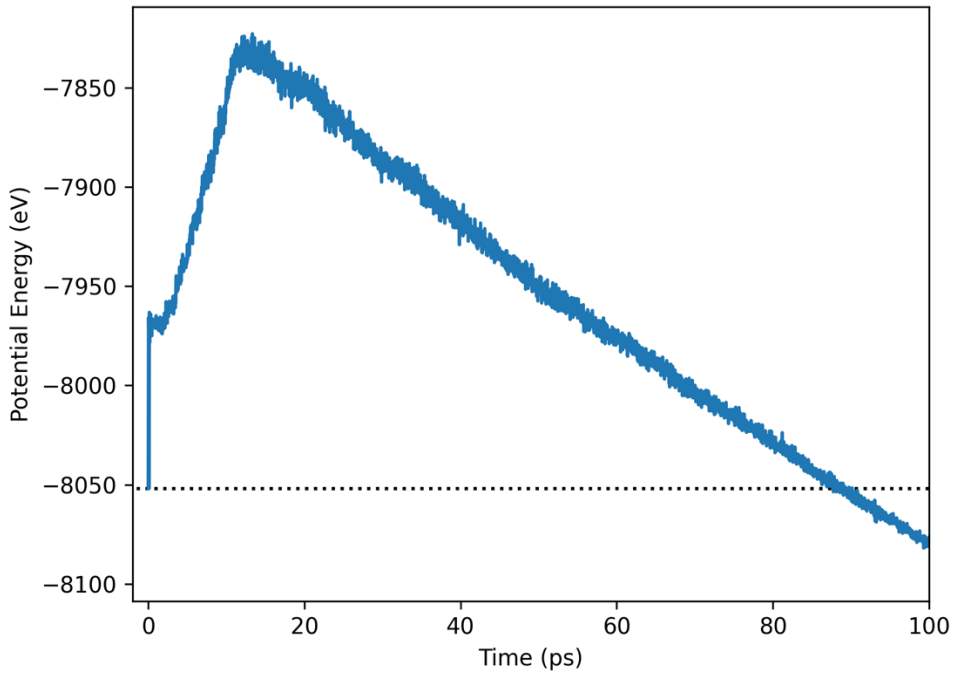


Beyond Simple Models



ATOMSK

The Swiss-army knife of atomic simulations



Recap: Analysing Grain Boundaries

- Qualitative over quantitative. The interesting thing is how boundaries differ.
- Choose your quantity and see how the boundary perturbs it.
- Consider the interaction of point defects with extended defects.

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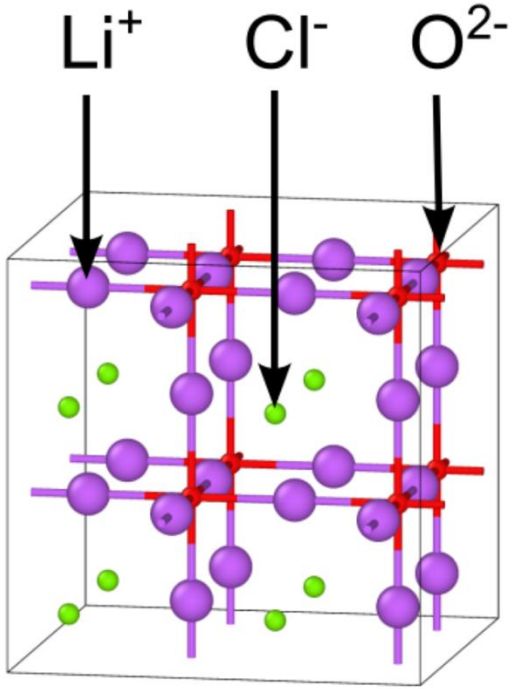
Grain Boundaries in Solid Electrolytes

Design Principles for Grain Boundaries

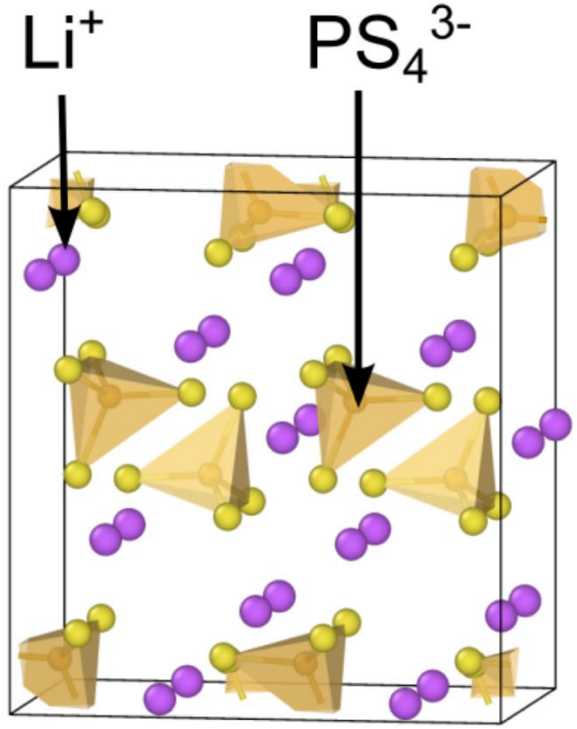
Bulk

Li_3OCl



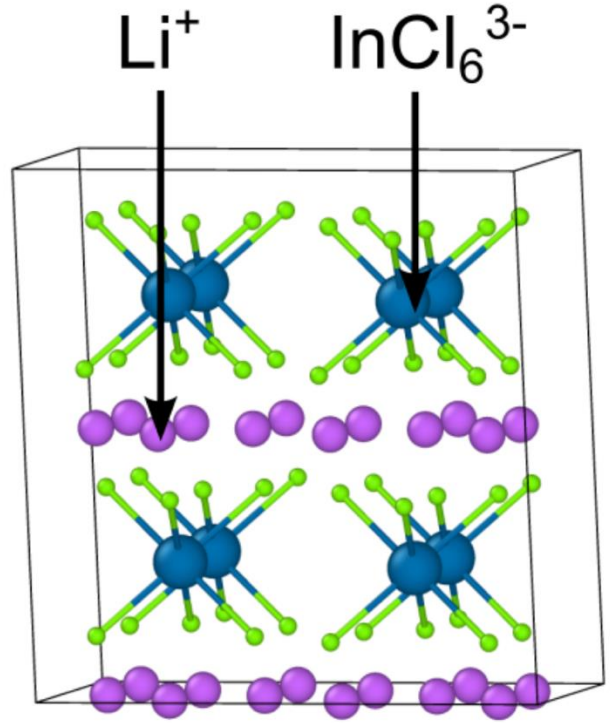
High GB resistance

Li_3PS_4



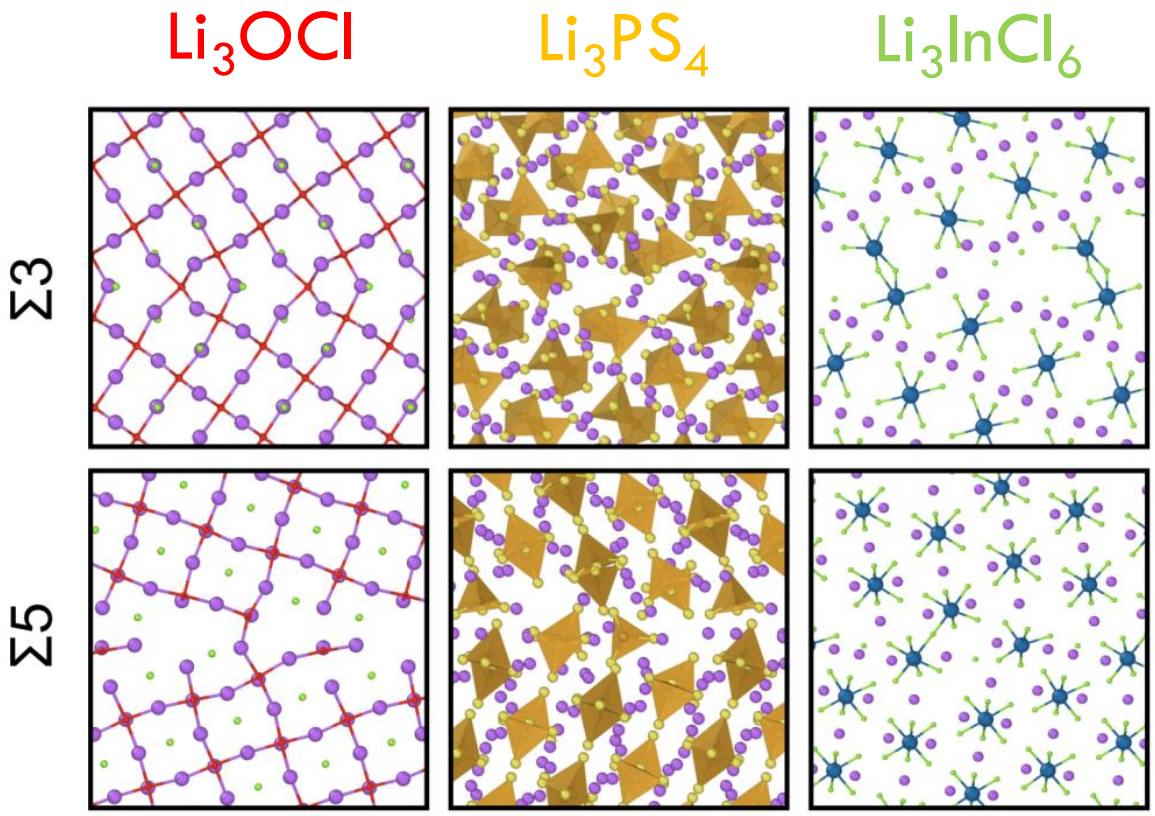
Low GB resistance

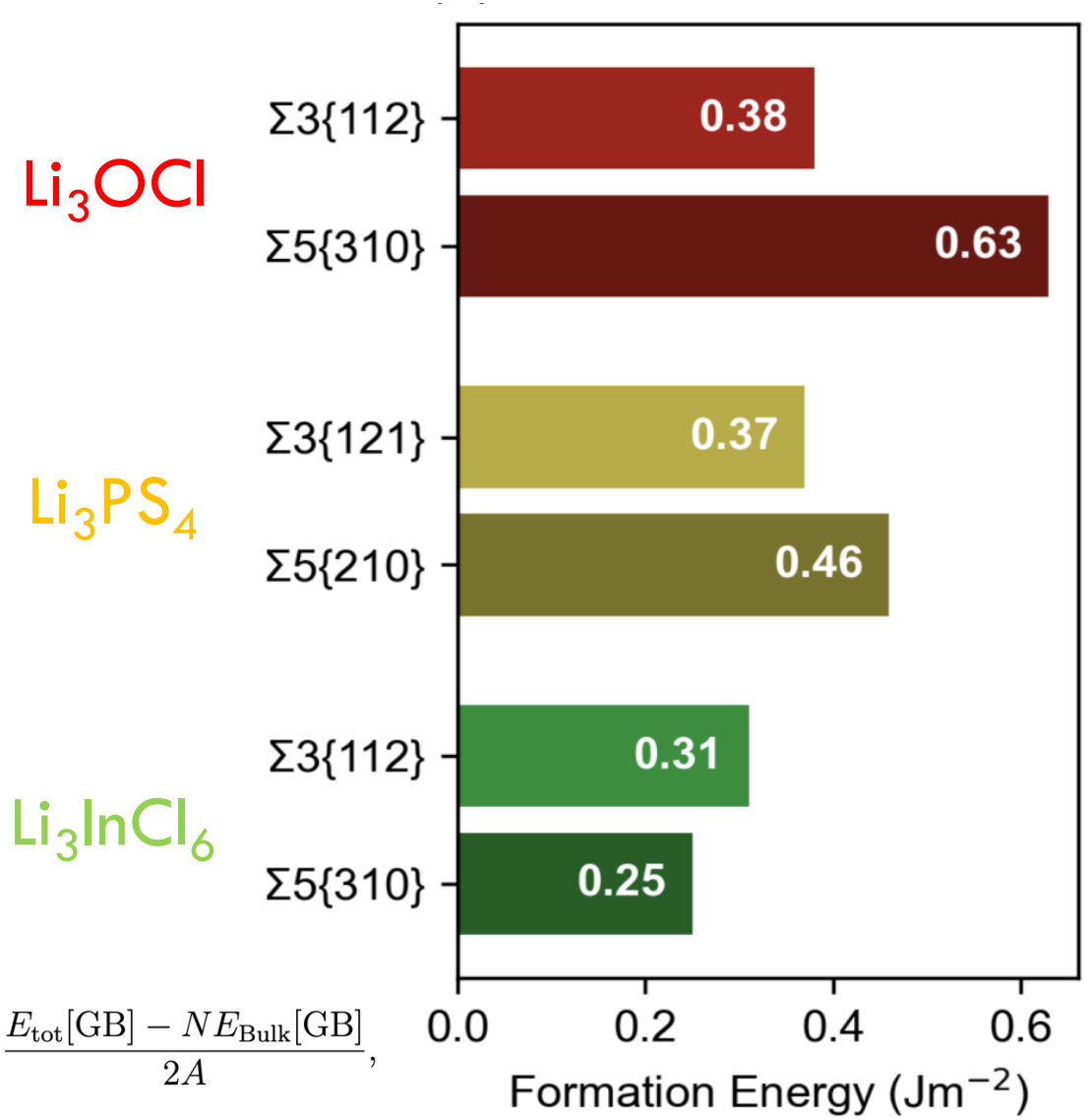
Li_3InCl_6



???

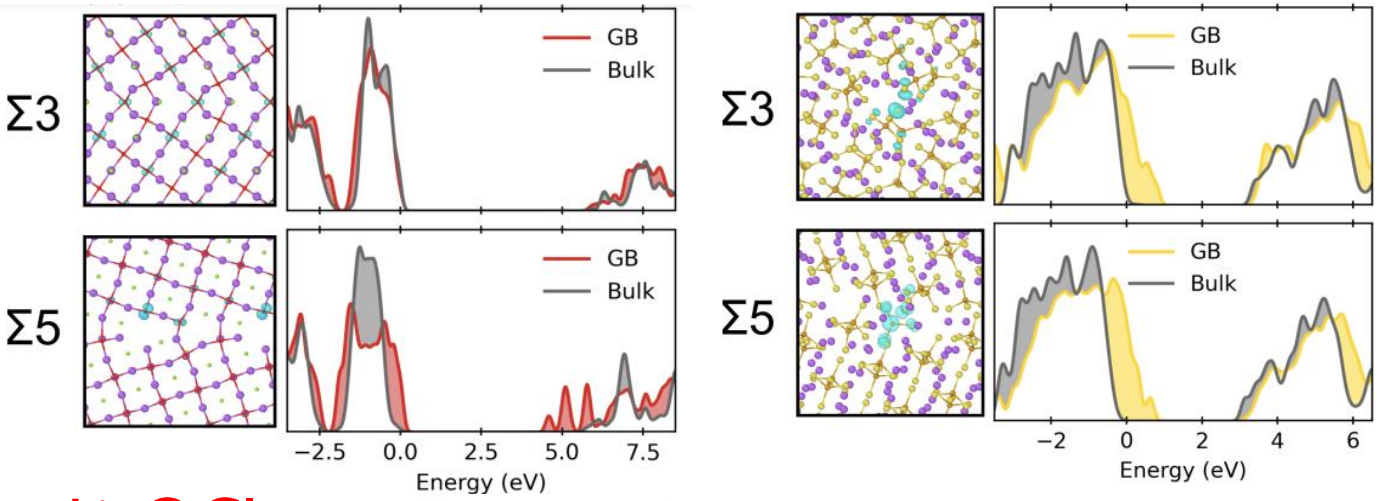
Structures and Energies





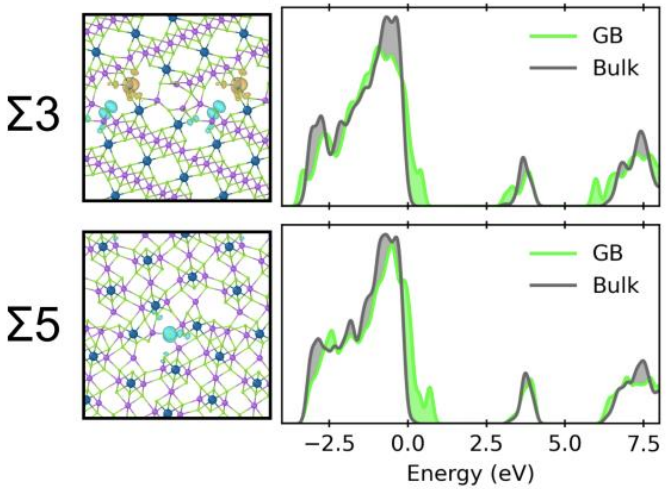
$$\gamma = \frac{E_{\mathrm{tot}}[\mathrm{GB}] - N E_{\mathrm{Bulk}}[\mathrm{GB}]}{2A},$$

Electronic Structures

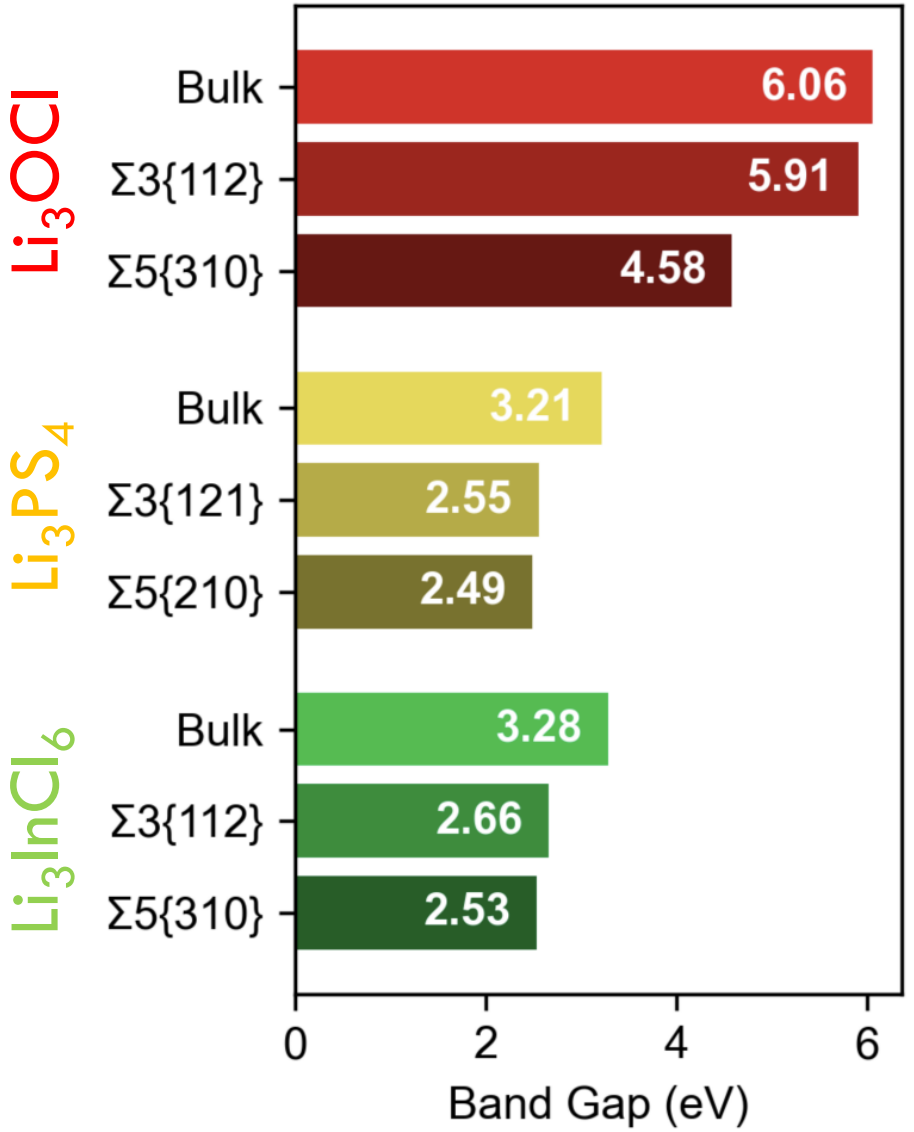


Li_3OCl

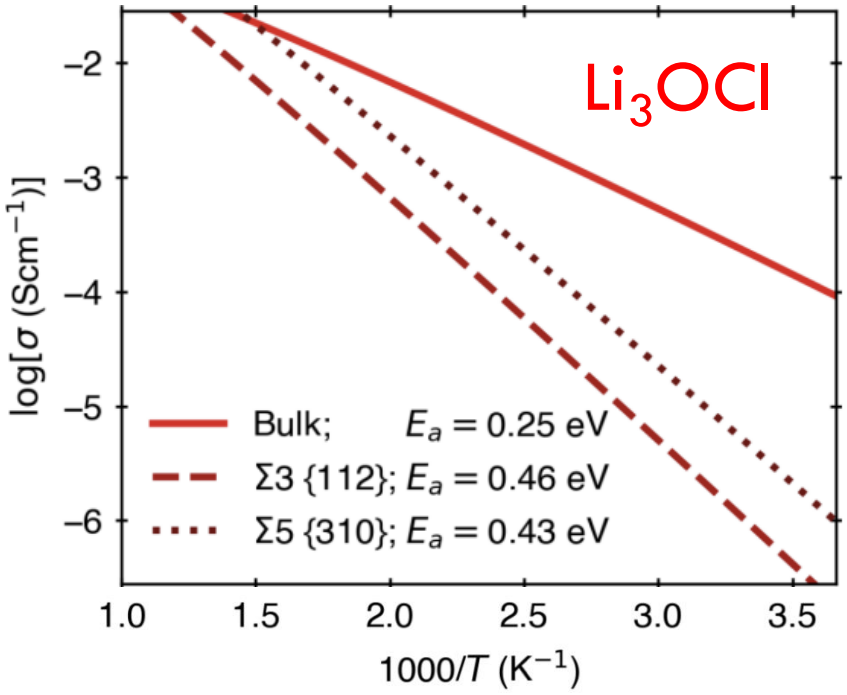
Li_3PS_4

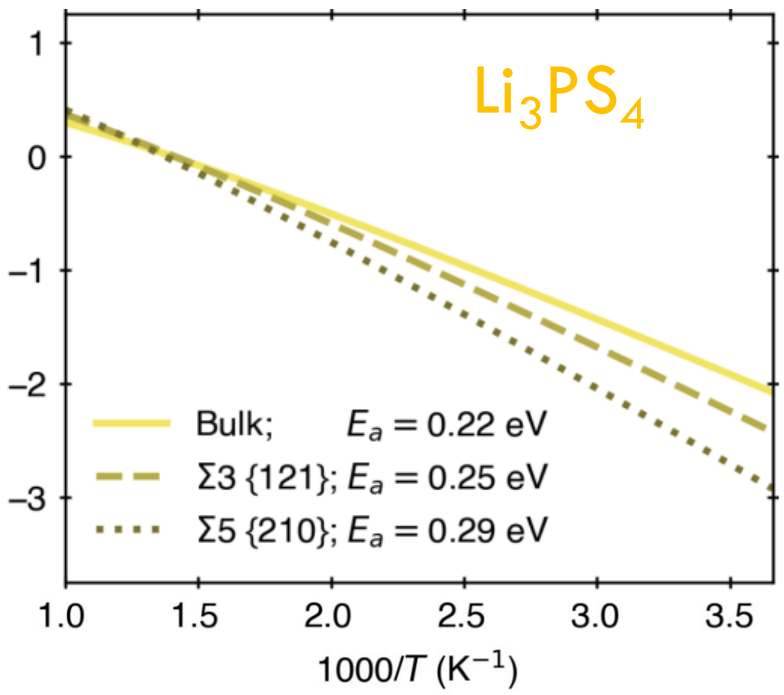


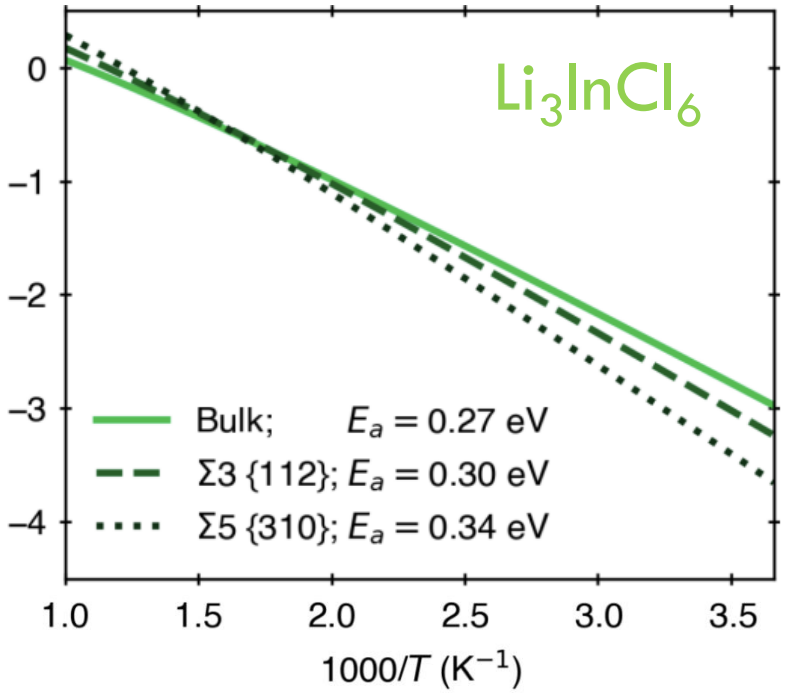
Li_3InCl_6



Li-Ion Conductivity

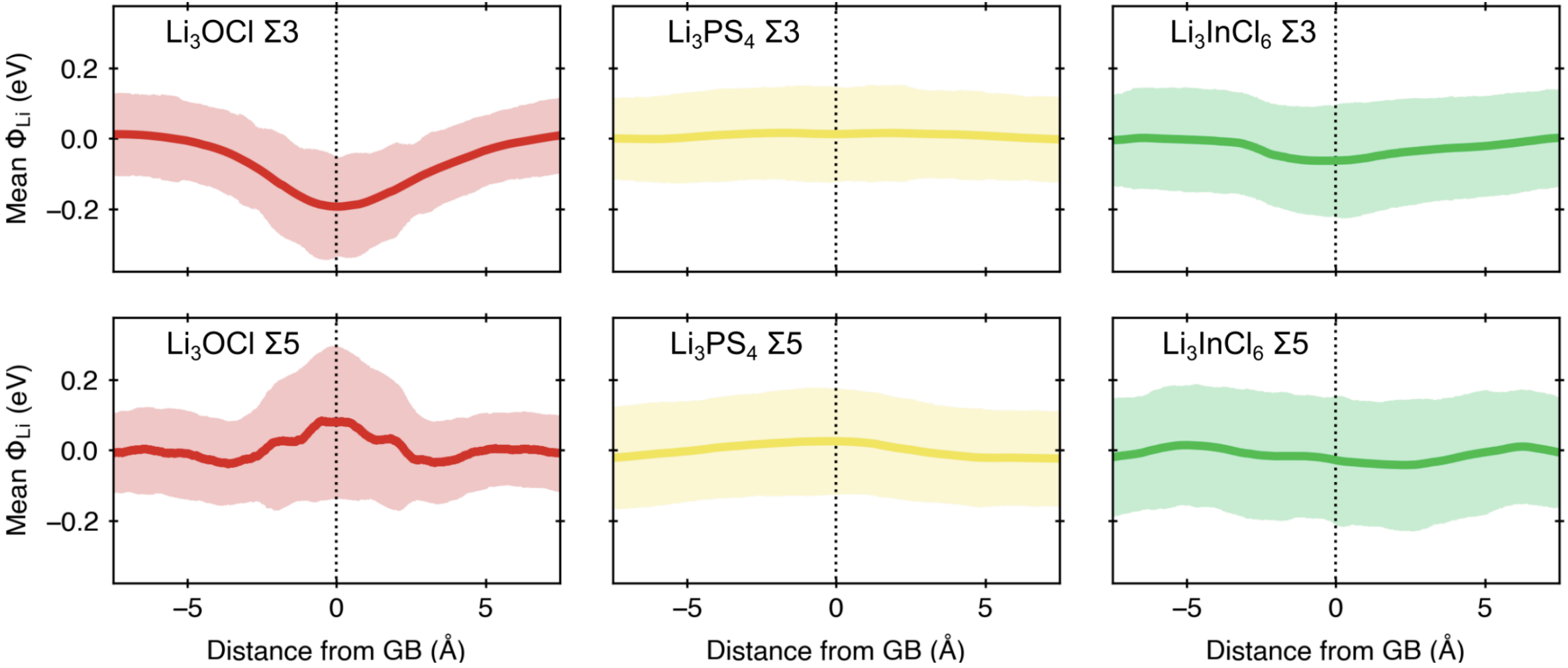




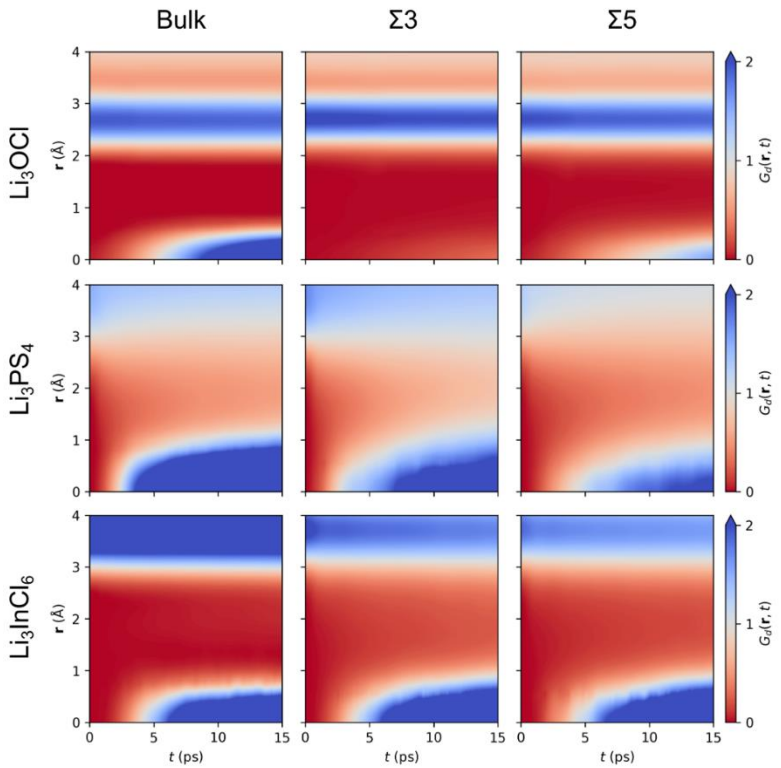


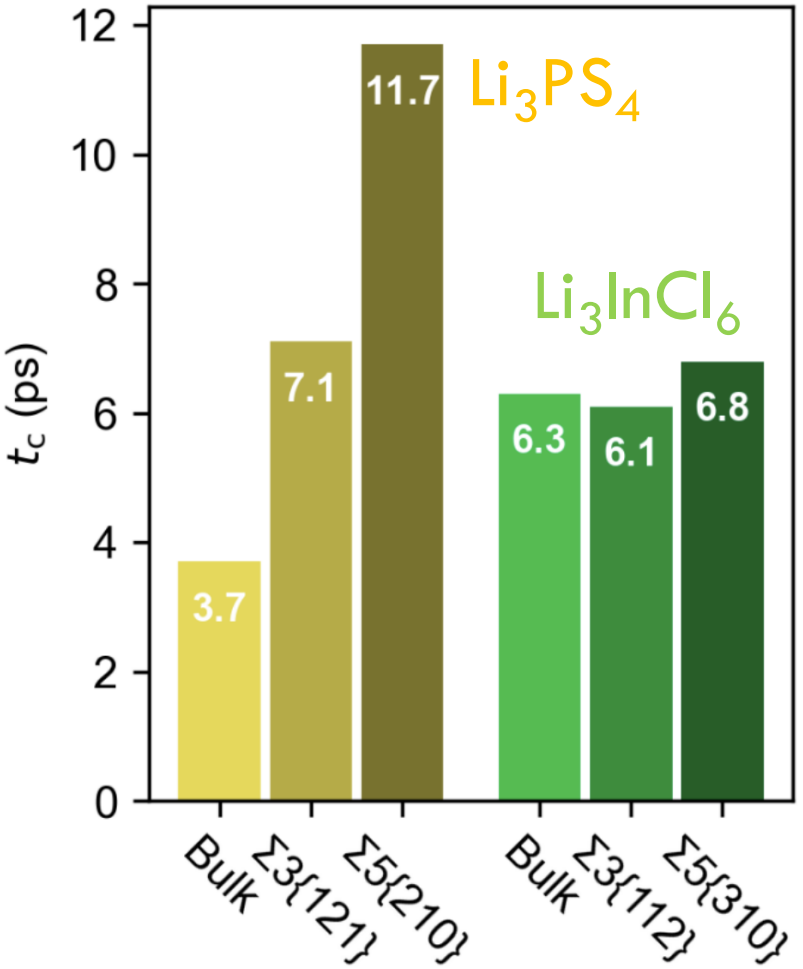
- Large grain boundary resistance in oxide Li_3OCl
- Weak grain boundary resistance in sulfide and halide

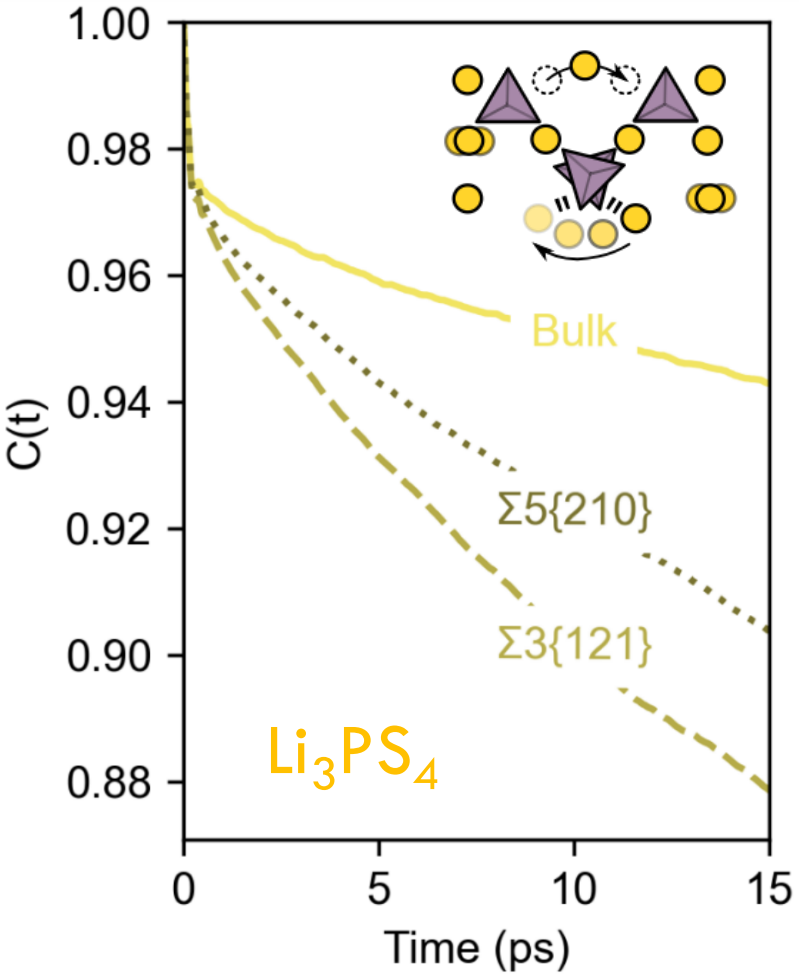
Electrostatic Potentials



Correlated Motion







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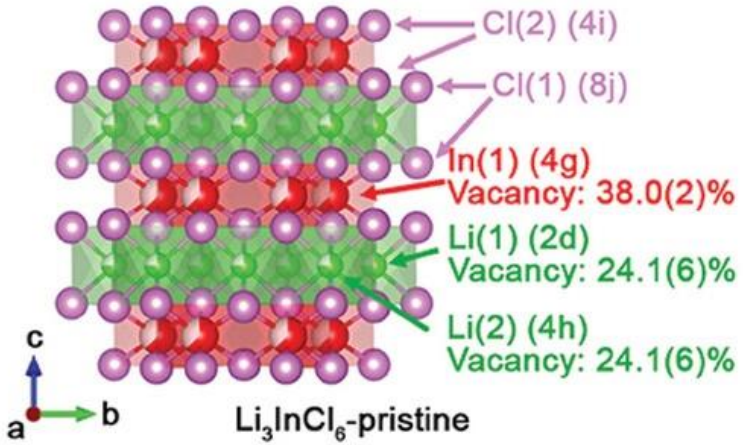
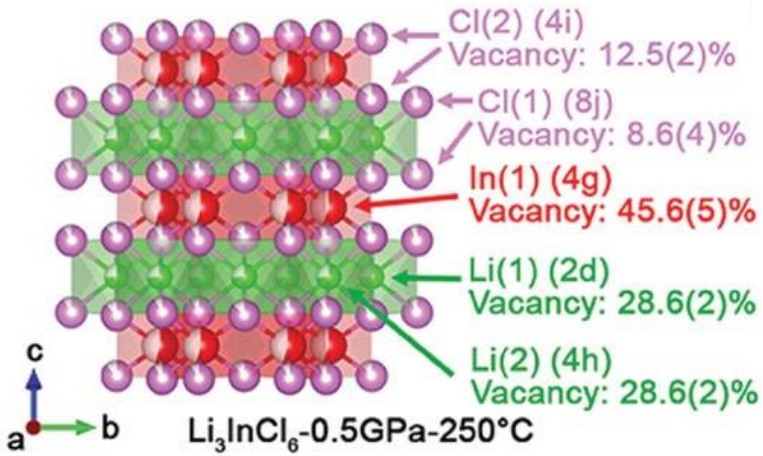
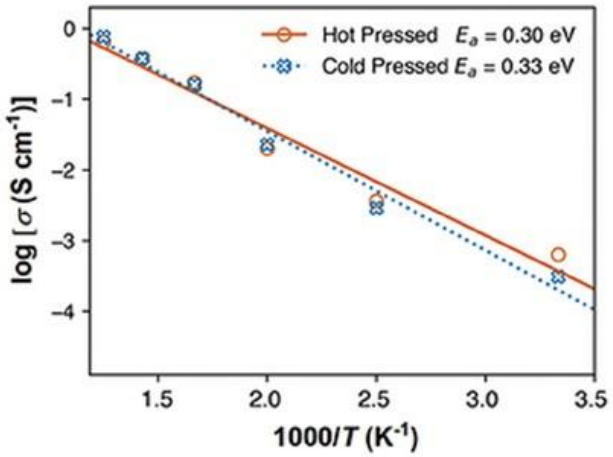
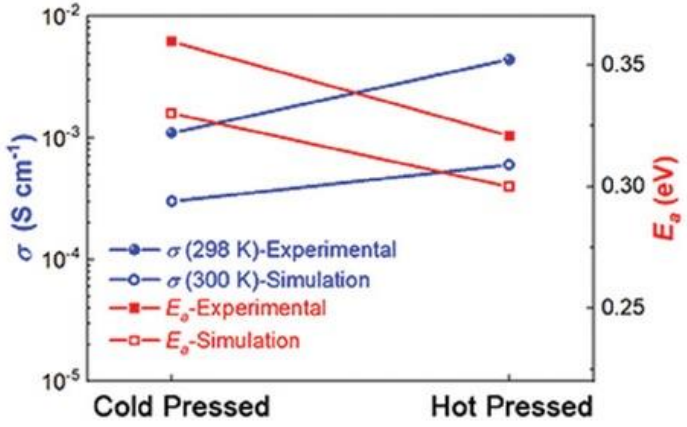
Nanocrystalline Disorder in Li_3InCl_6









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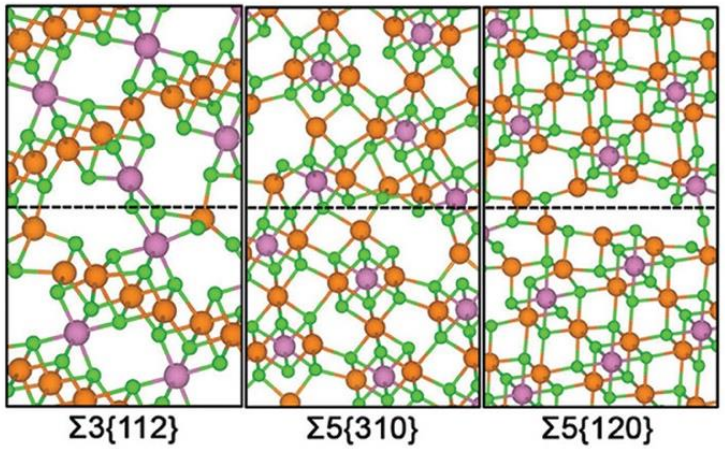
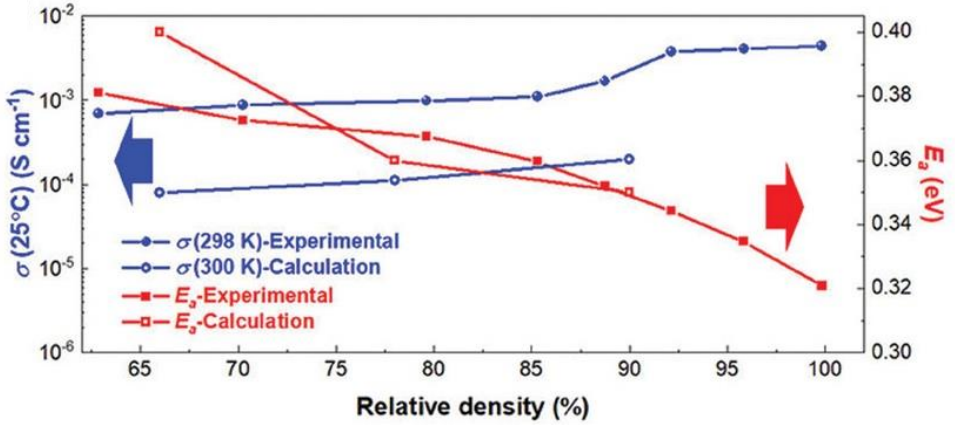
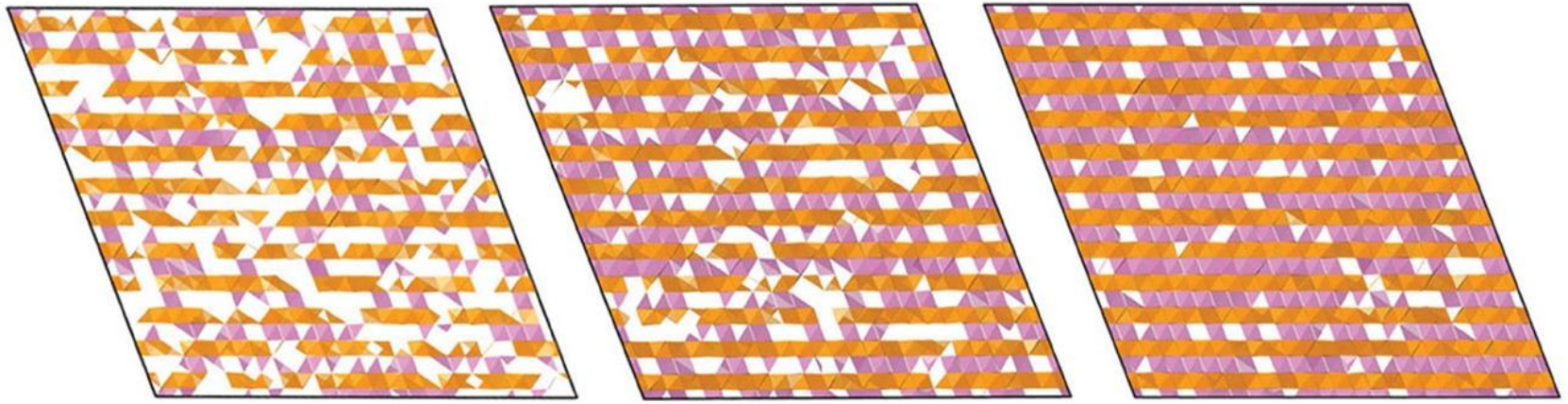
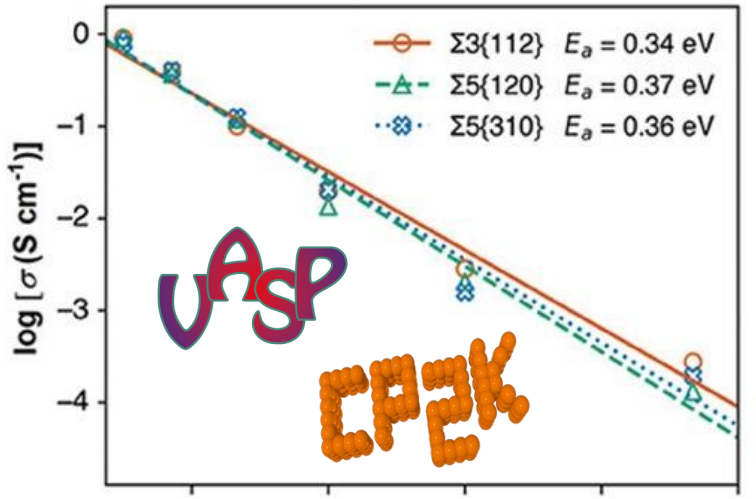
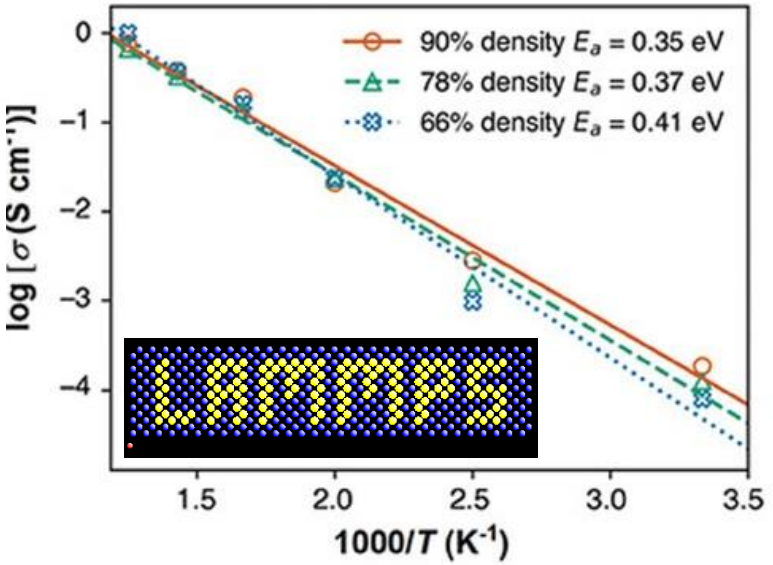
Grain Boundaries and Porosity



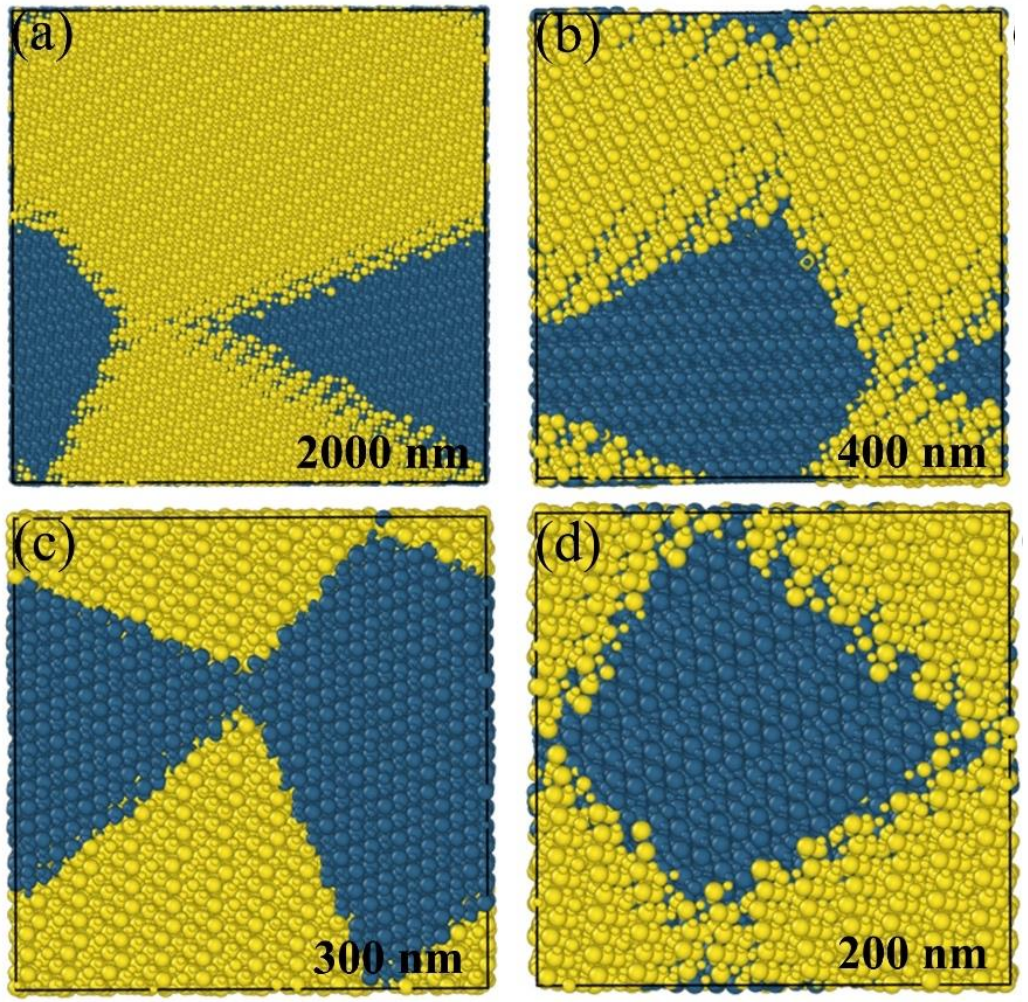


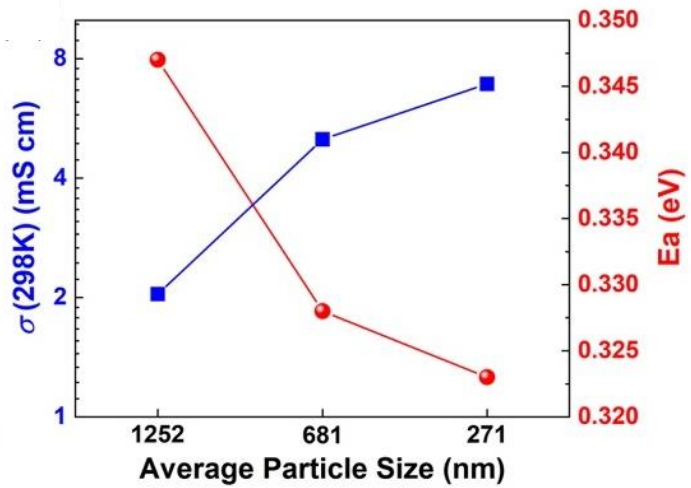


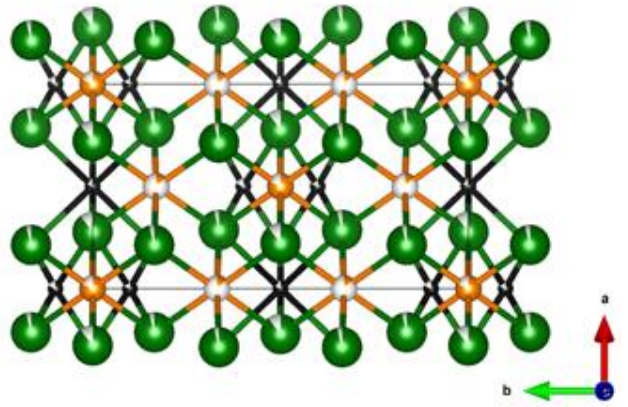


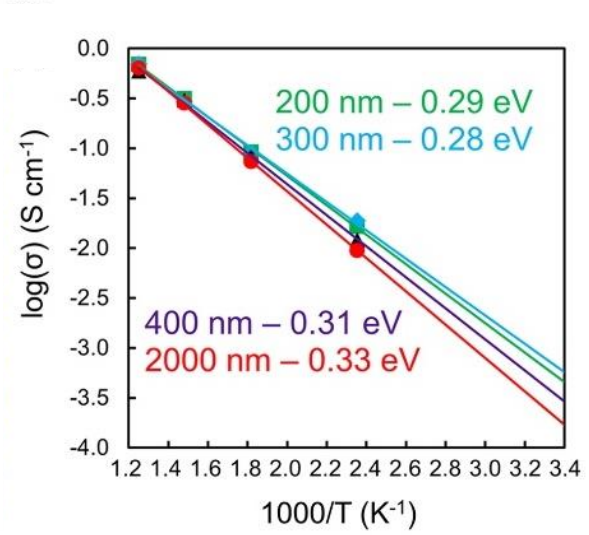


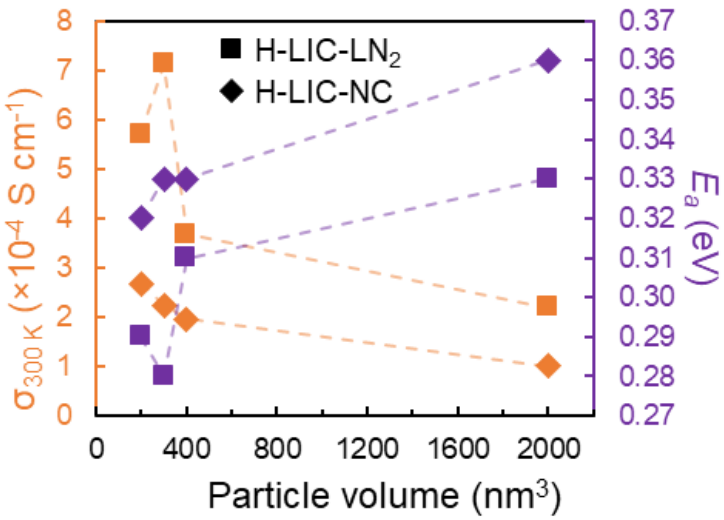
Polycrystals











Recap: Grain Boundaries in Solid Electrolytes

- Atomistic modelling of grain boundaries and nanosizing can give lots of useful information
- Synergy between simulation and experiment is vital
- Without experimental validation modelling will always be partly guesswork

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Further Reading

REVIEW ARTICLE
https://doi.org/10.1038/s41563-019-0431-3
nature materials

Fundamentals of inorganic solid-state electrolytes for batteries

Theodosios Famprikis[1,2,3*], Pieremanuele Canepa[2,3,5], James A. Dawson[2,3], M. Saiful Islam[2,3*] and Christian Masquelier[1,3,4*]

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Perspective

Going against the Grain: Atomistic Modeling of Grain Boundaries in Solid Electrolytes for Solid-State Batteries

Published as part of the ACS Materials Au virtual special issue "2023 Rising Stars".

James A. Dawson*

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Applied Physics Reviews REVIEW pubs.aip.org/aip/are

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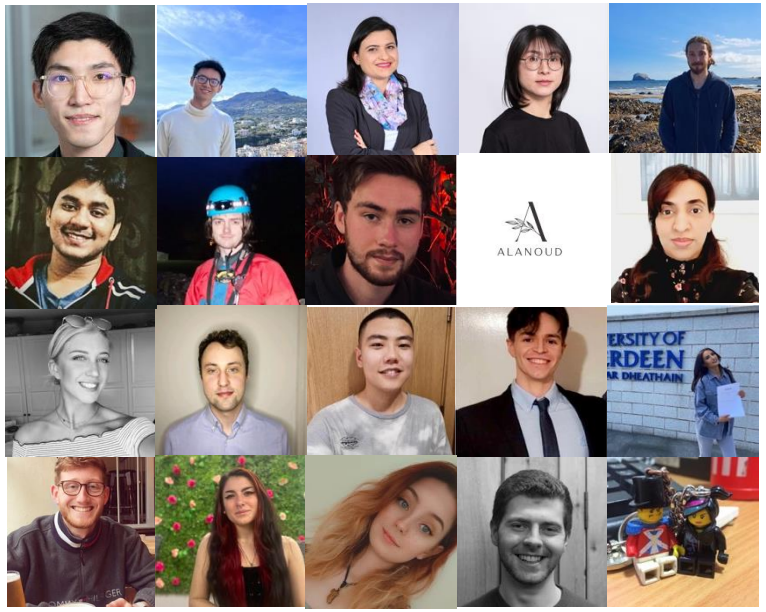

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