UCLA

From thermodynamic to kinetic selectivity in solid-state energy materials & interfaces

Nathan Szymanski

USNC-TAM 2026

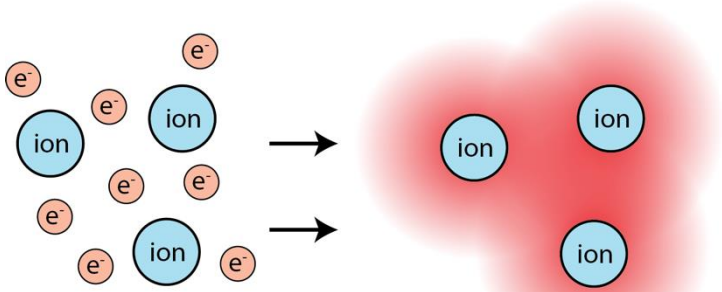
June 23rd

MD² LAB
MATERIALS DESIGN THROUGH DYNAMICS

Samueli School of Engineering

Computational design of energy storage materials

Density functional theory (DFT) and Machine Learning (ML)



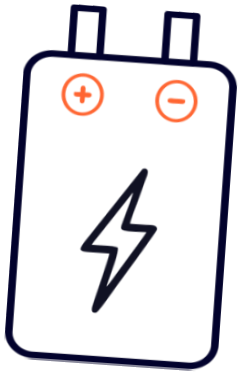
$$H\psi(r_i) = E\psi(r_i)$$

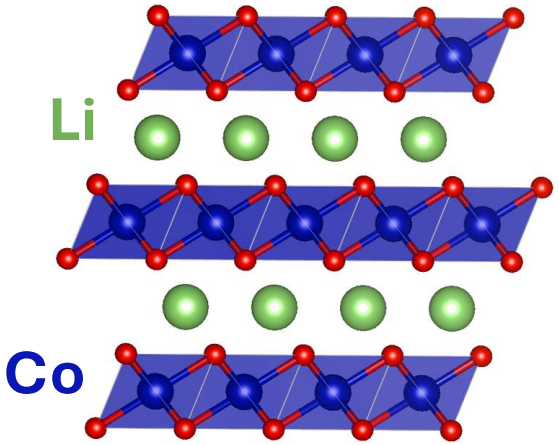
Energies and forces
Electronic properties
Response functions

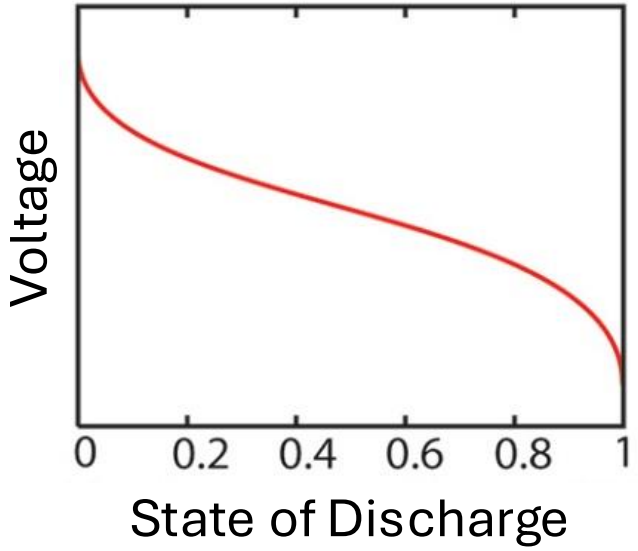
Provide answers to the questions:

Are its equilibrium properties suitable?

Does it maintain those properties in a realistic, multi-phase system?







He *et al.*, Energy Env. Mater. (2019).

Computational design of energy storage materials

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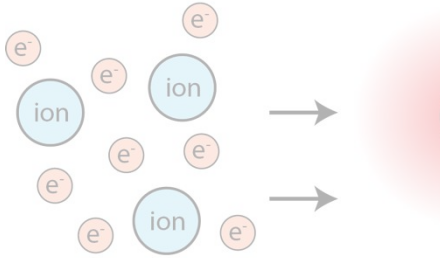

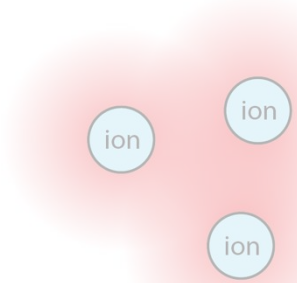

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ASSBs:

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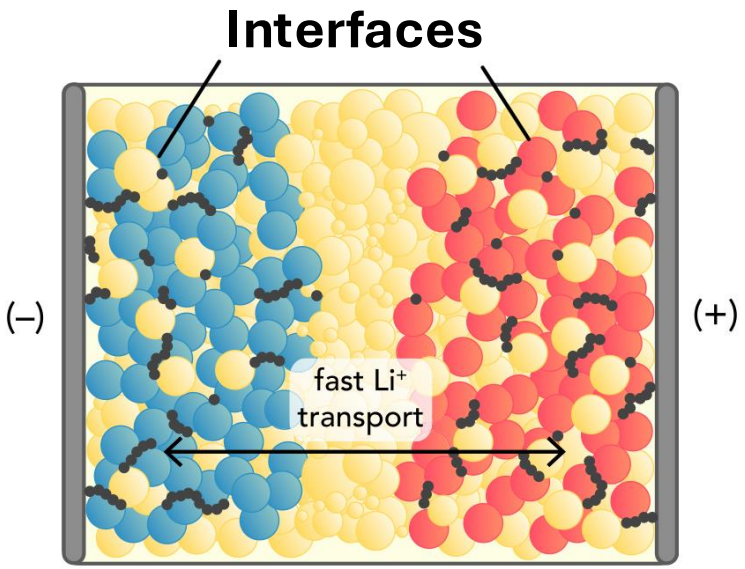
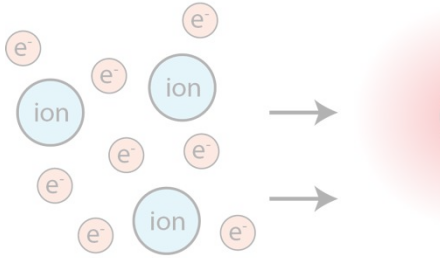
- Cathode
- Additive



Computational design of energy storage materials

Density functional theory (DFT) and Machine Learning (ML)



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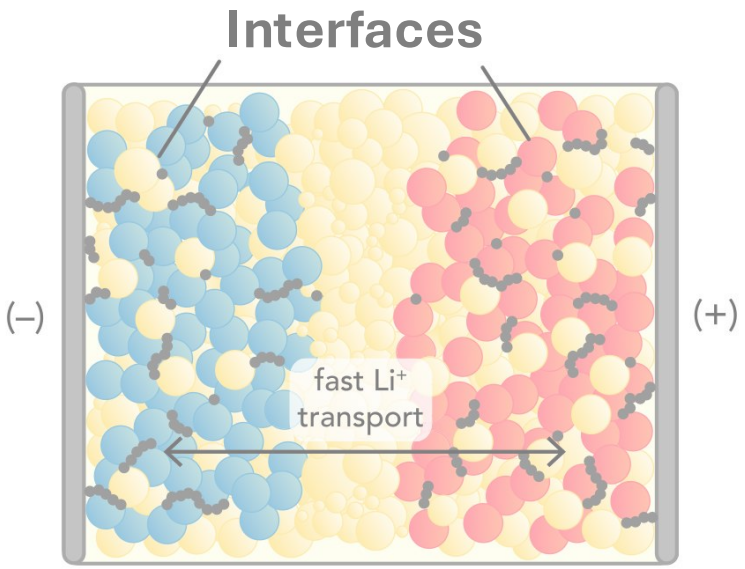

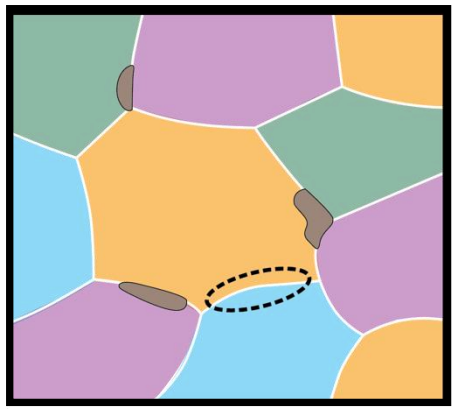

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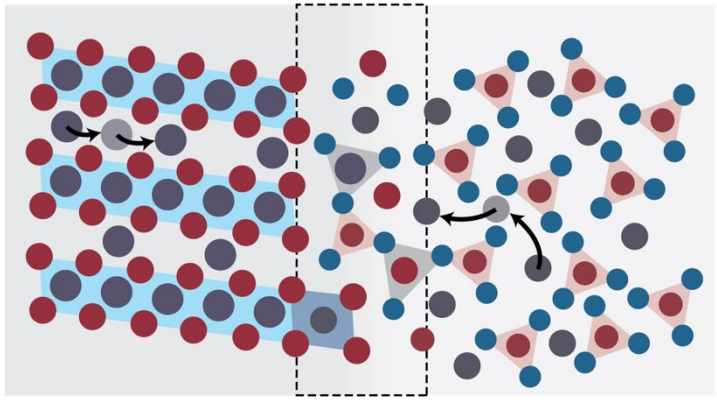
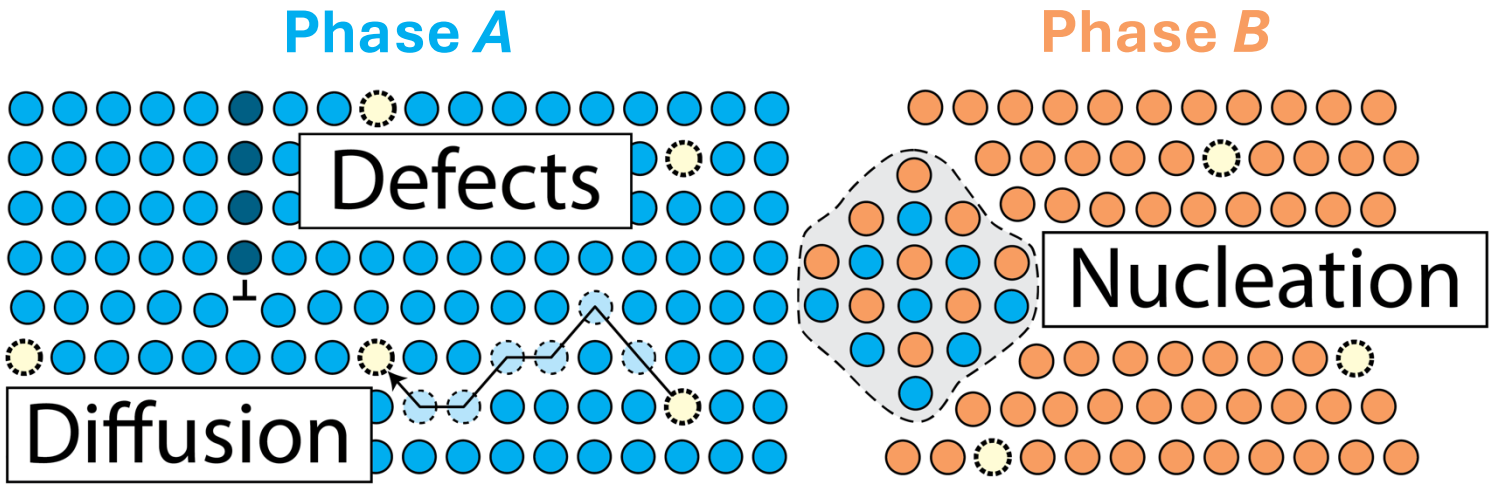


Do they react? If so, what forms?

What happens at the interface?



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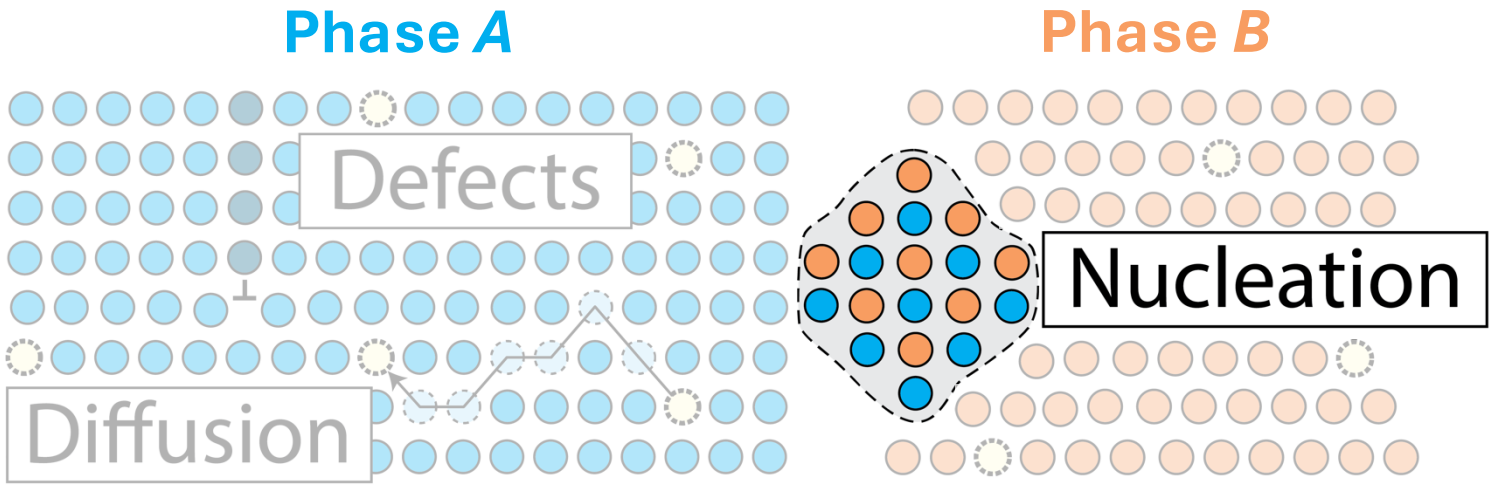
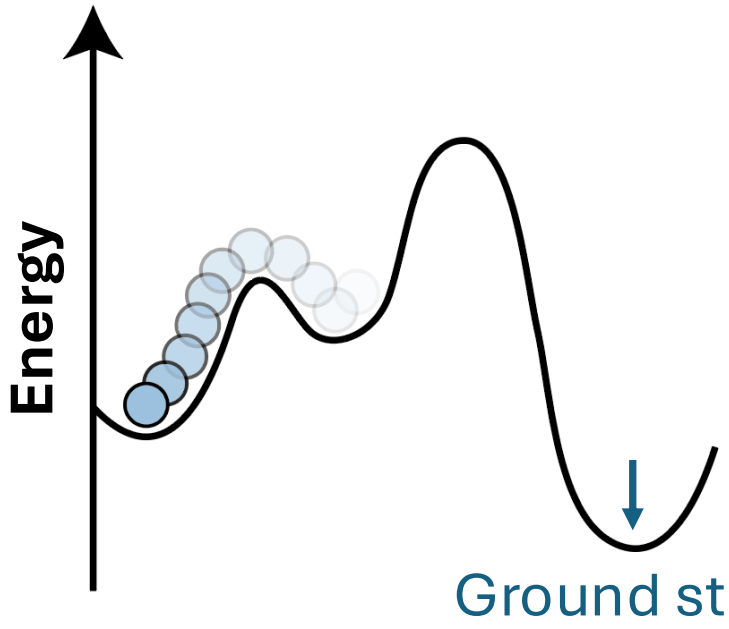


How can we predict what forms at the interface?

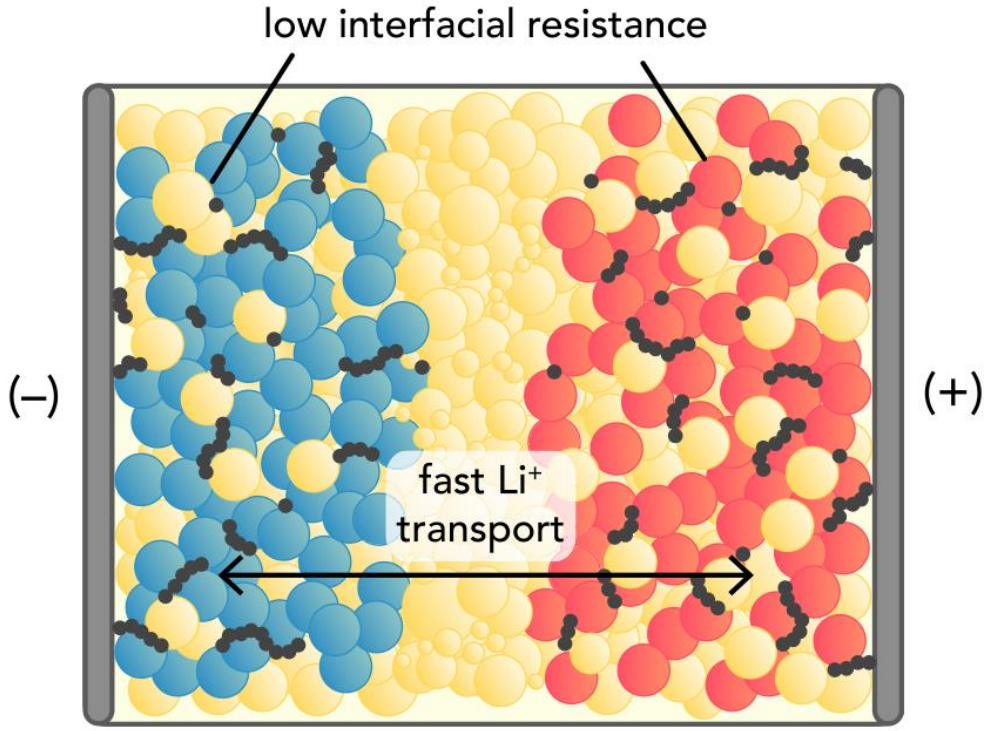


Which product is *easiest* to form

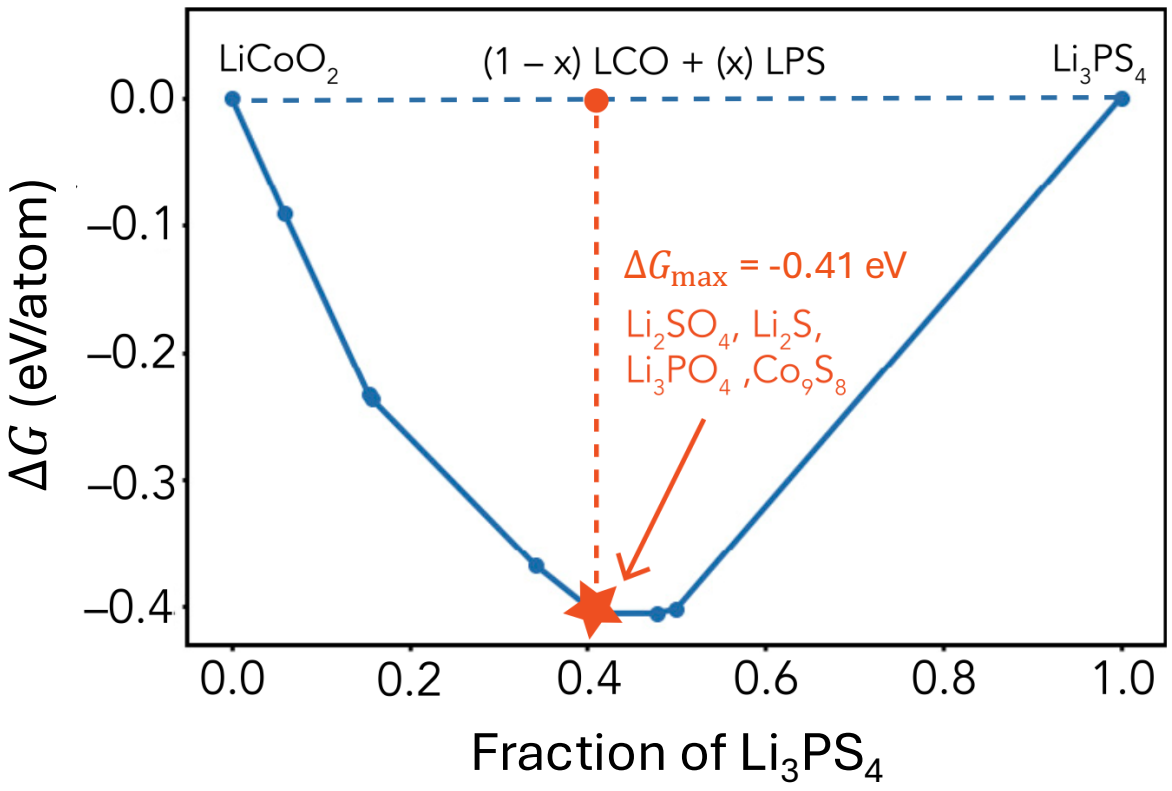
This problem is inherently **kinetic**, but can we use **thermodynamics** as a first step?

Which product the system *wants* to form

We can describe interfaces using *convex hulls*



Nolan *et al.*, Joule (2016).



Li_3PS_4 electrolyte

$LiCoO_2$ cathode

Li metal anode

Conducting additive

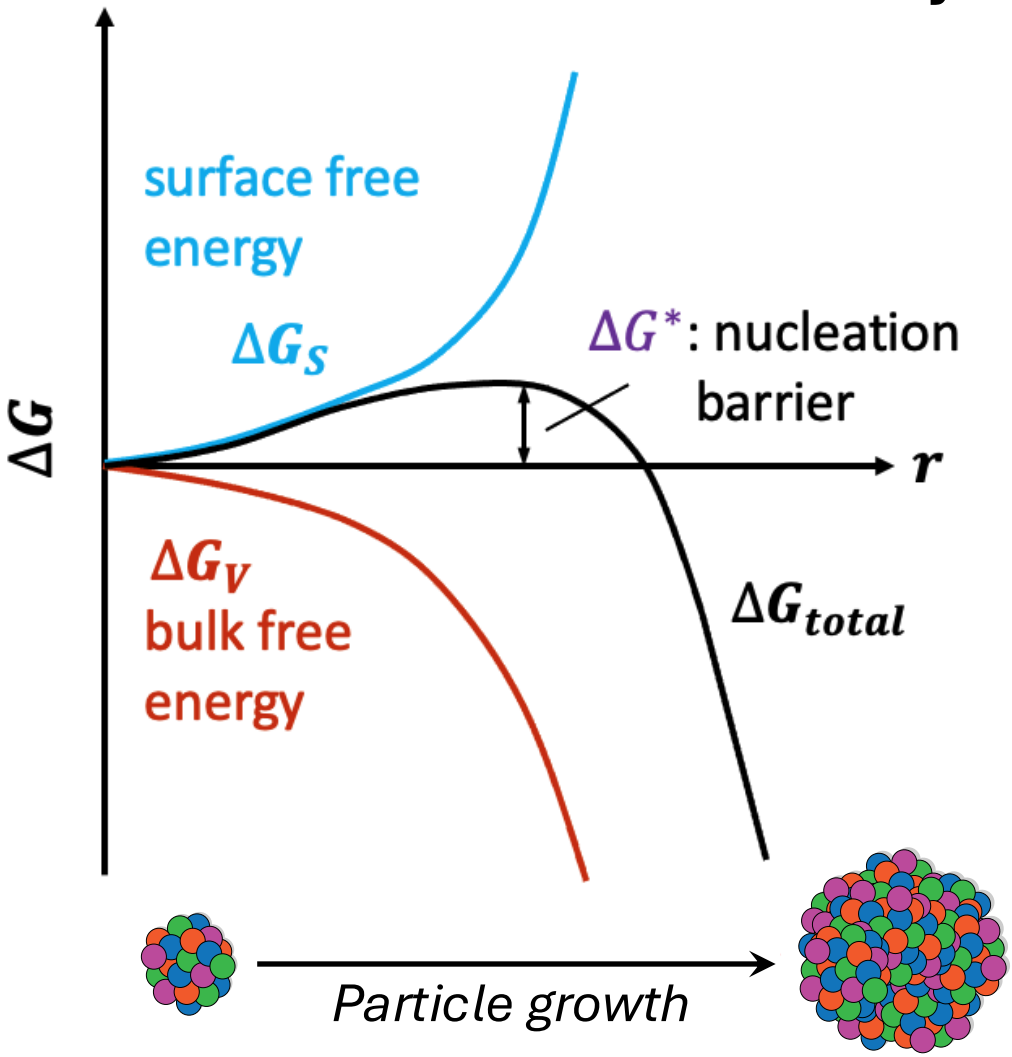
ΔG = the change in Gibbs energy

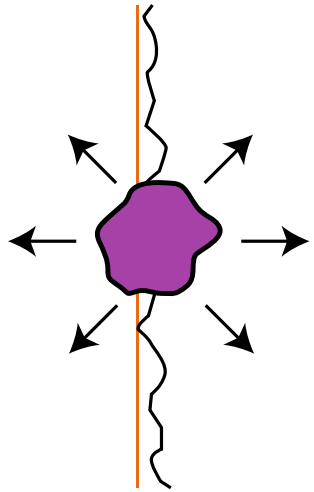
$(G_{products} - G_{reactants})$

Can we predict what forms based on *thermodynamics* alone?

Some justification using nucleation theory

Classical nucleation theory

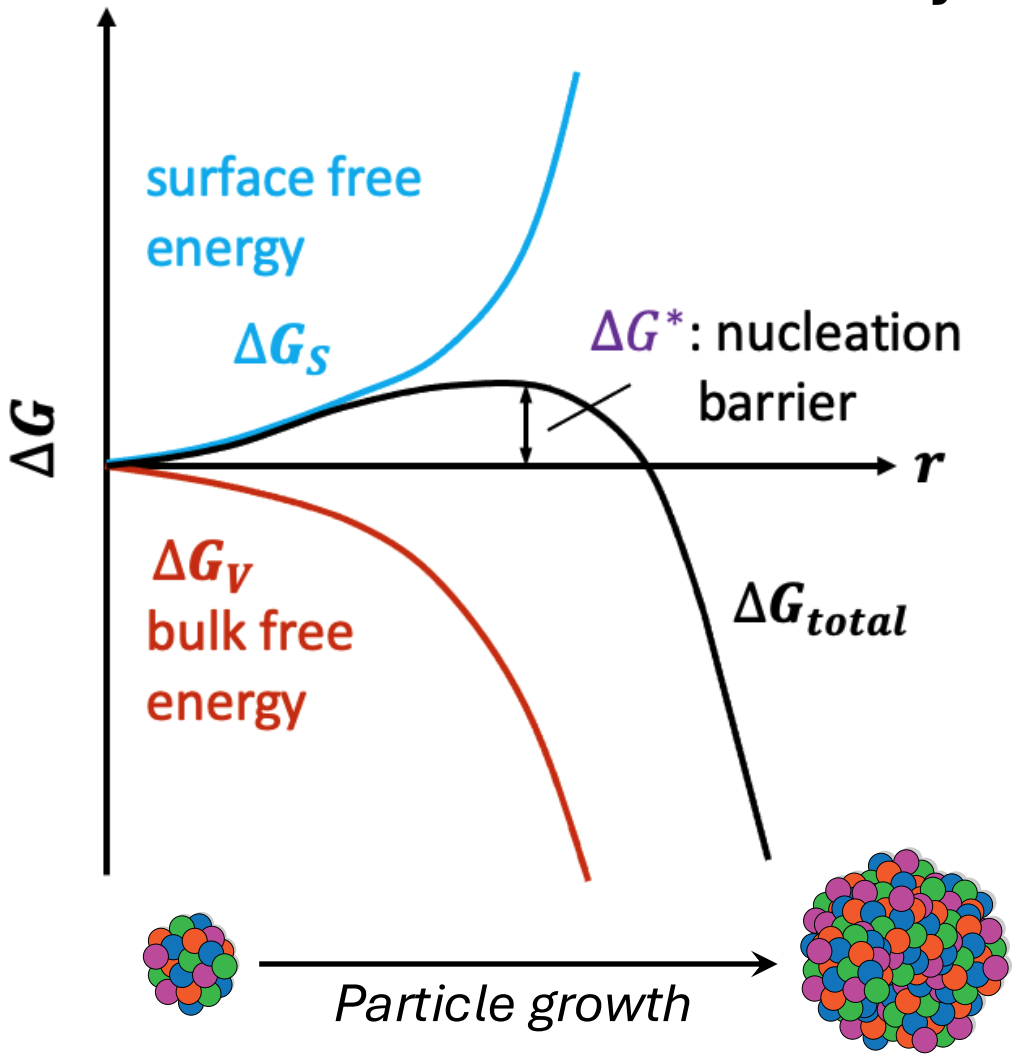




What is the rate at which this nucleus forms?

Some justification using nucleation theory

Classical nucleation theory



Nucleation rate:

$$Q = \mathrm{A}\exp\left(-\frac{\Delta G^*}{k_\mathrm{B}T}\right)$$

Nucleation barrier:

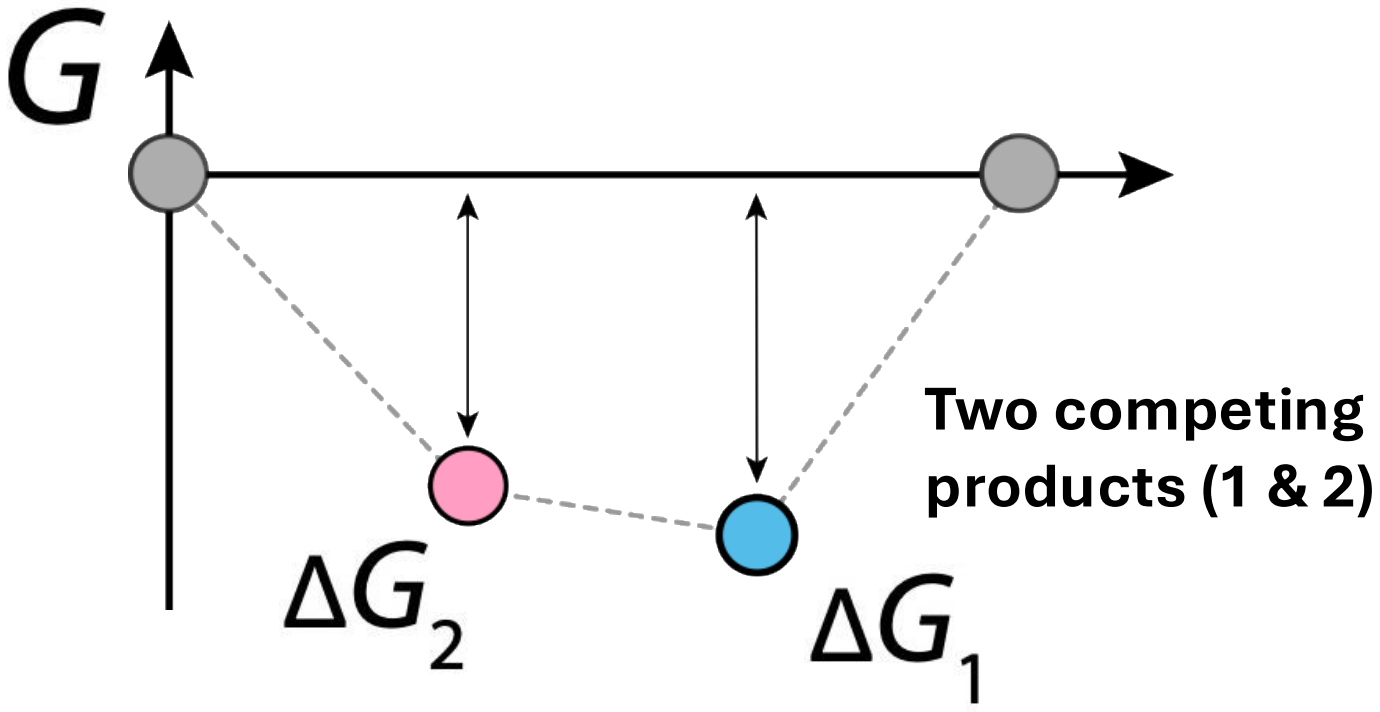
$$\Delta G^* = \frac{16\pi\sigma^3}{3(n\Delta G)^2}$$

Surface energy

Atomic density

Bulk reaction energy

Can we use ΔG to predict what forms first?

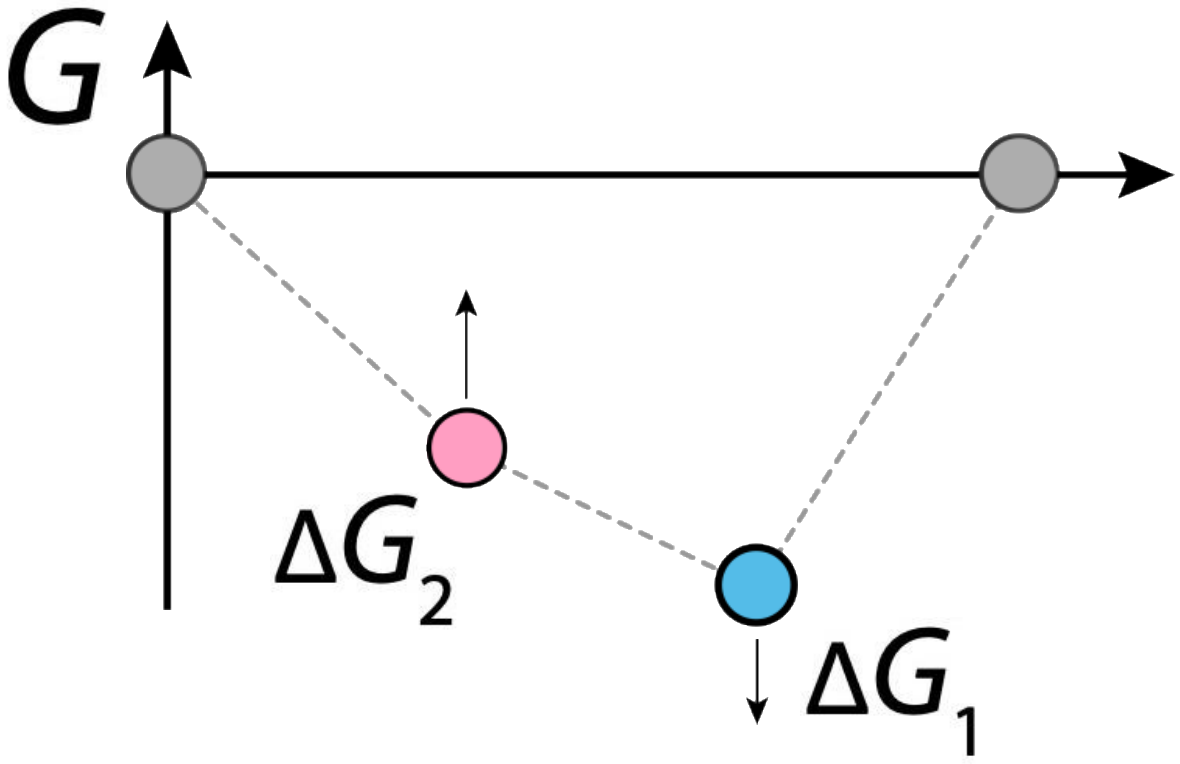


$$\ln(\boldsymbol{Q_1}/\boldsymbol{Q_2}) = \frac{16\pi}{3n^2 k_B T}\left(\frac{(\sigma_1)^3}{(\Delta G_1)^2} - \frac{(\sigma_2)^3}{(\Delta G_2)^2}\right)$$

Surface energy

Bulk reaction energy

Can we use ΔG to predict what forms first?



How large is "sufficiently large"

Hypothesis:

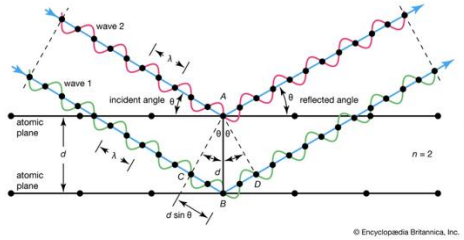
If the difference between ΔG_1 and ΔG_2 is **sufficiently large**, it outweighs any difference between σ_1 and σ_2

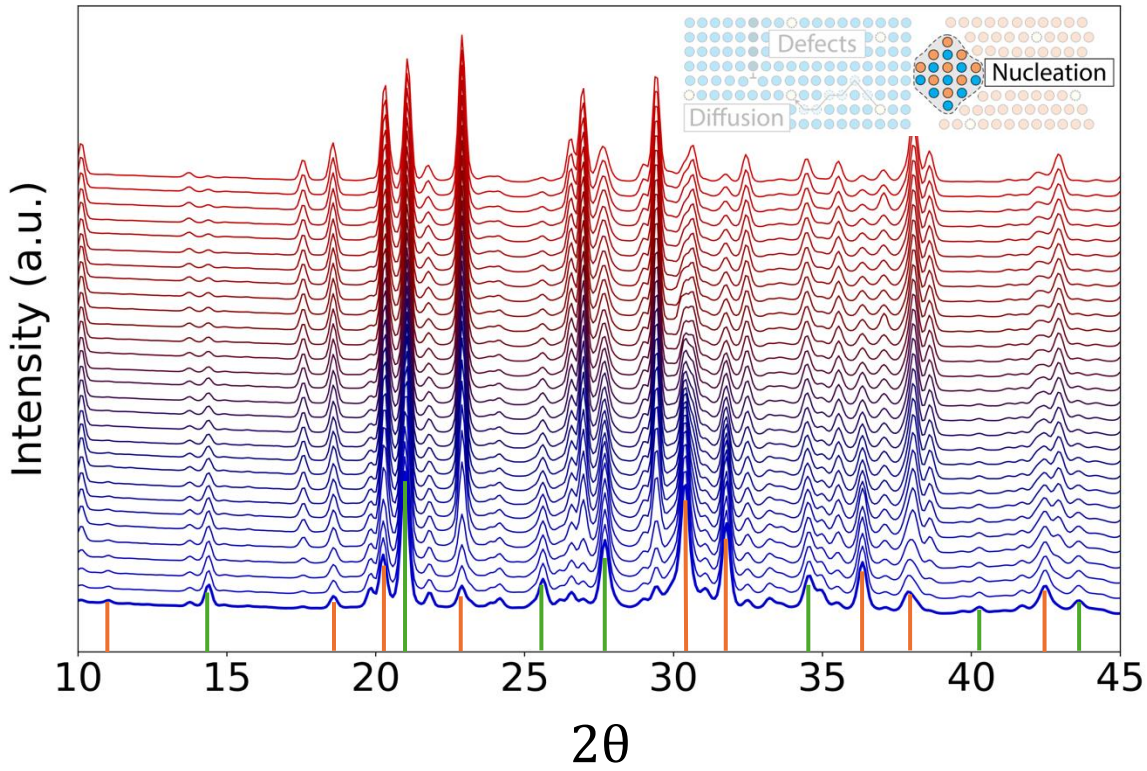
$$\ln(\boldsymbol{Q_1}/\boldsymbol{Q_2}) = \frac{16\pi}{3n^2 k_B T}\left(\frac{(\sigma_1)^3}{(\boldsymbol{\Delta G_1})^2} - \frac{(\sigma_2)^3}{(\boldsymbol{\Delta G_2})^2}\right)$$

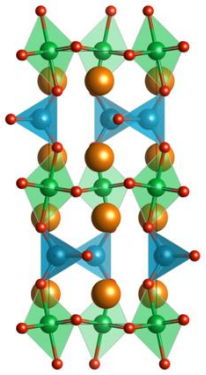
Surface energy

Bulk reaction energy

Quantify the limit using *in-situ* XRD







These XRD patterns act as structural “fingerprints” to identify which phases have formed

Szymanski *et al.*, Science Advances (2024).

We used 37 oxides as a test case

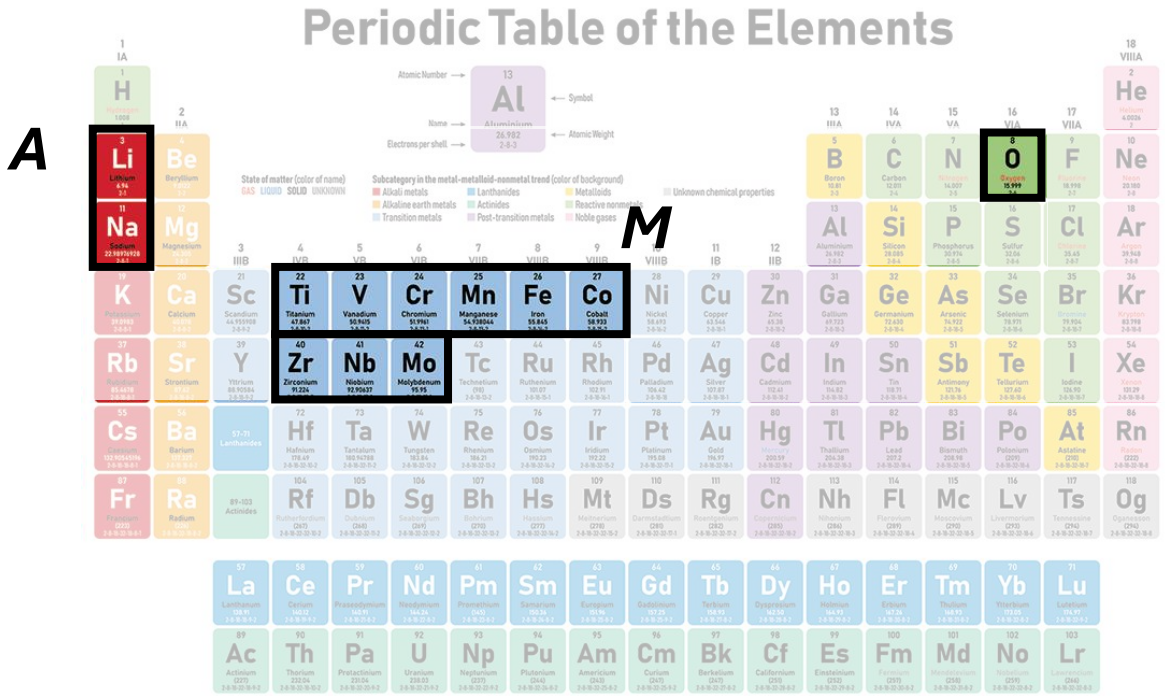
We took **alkali (*A*) precursors**:

Li_2CO_3, LiOH, Li_2O, $NaNO_3$, …

Mixed them with **metal (*M*) precursors**:

MnO, Mn_3O_4, MnO_2, Cr_2O_3, …

In a **1:1 ratio of *A*:*M*** for each sample, which was then **heated to 600 °C** while XRD scans were performed.

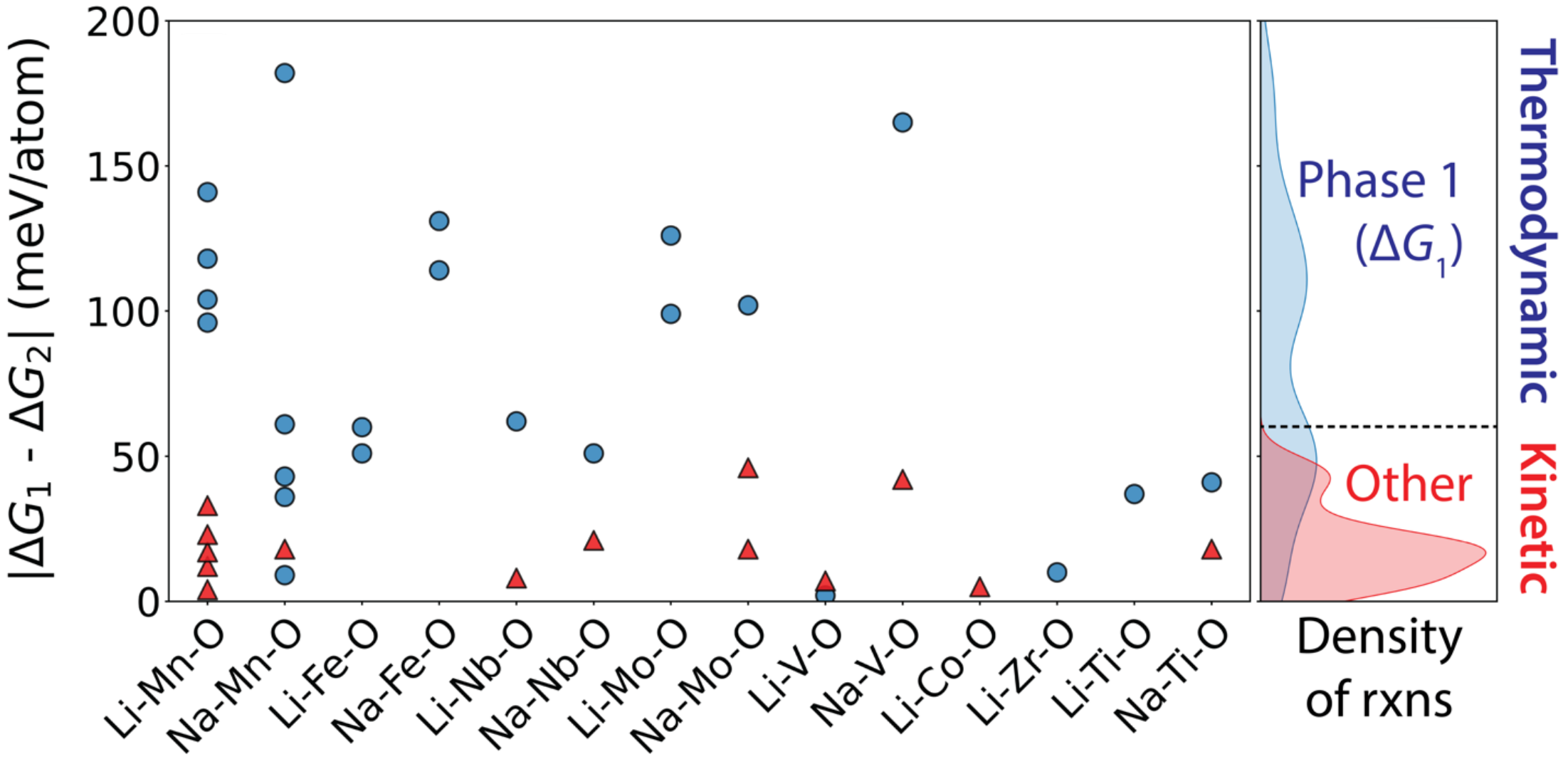


Exp. Observation ⟷ **Comp. Prediction**

?

Szymanski *et al.*, Science Advances (2024).

Outcomes show a regime of ΔG control



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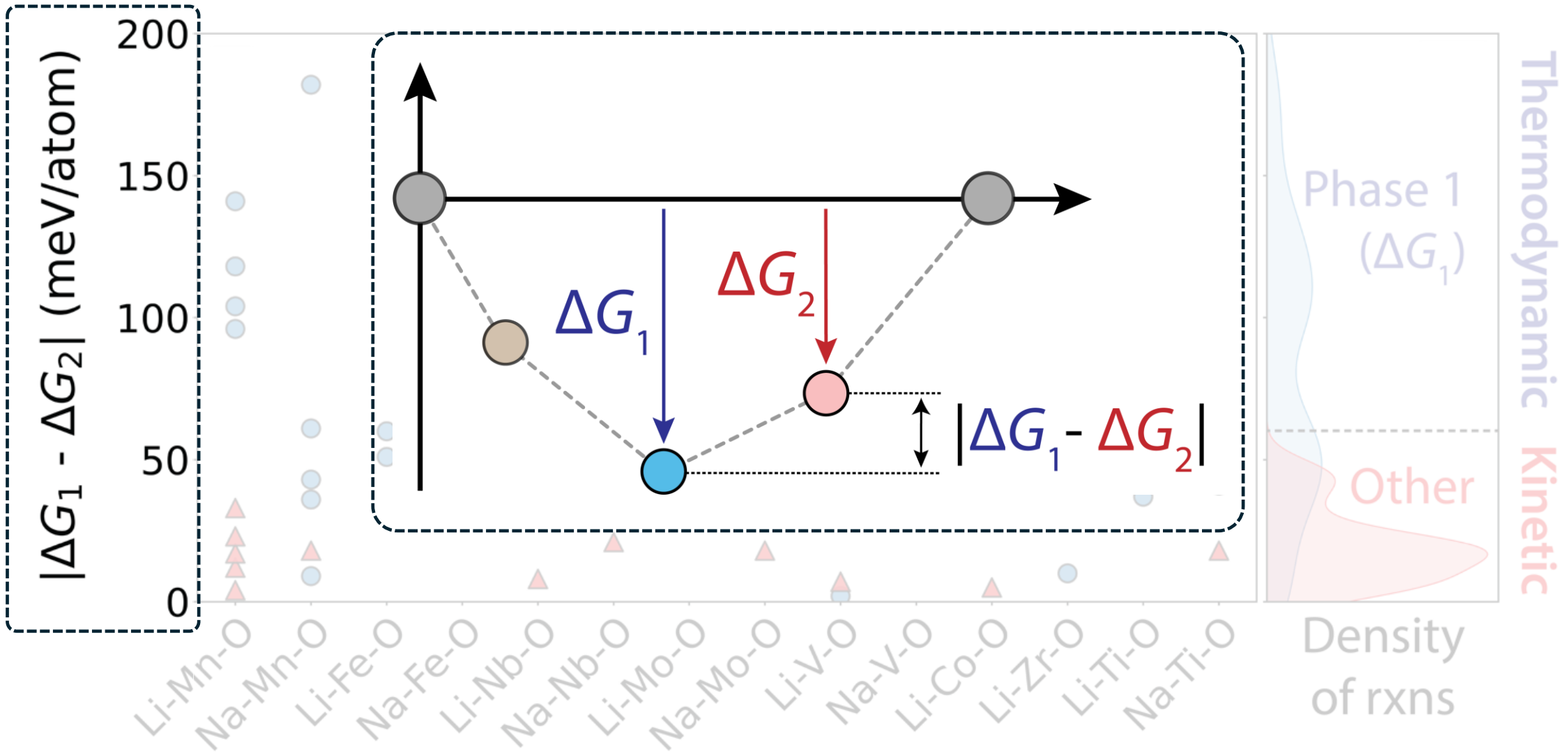

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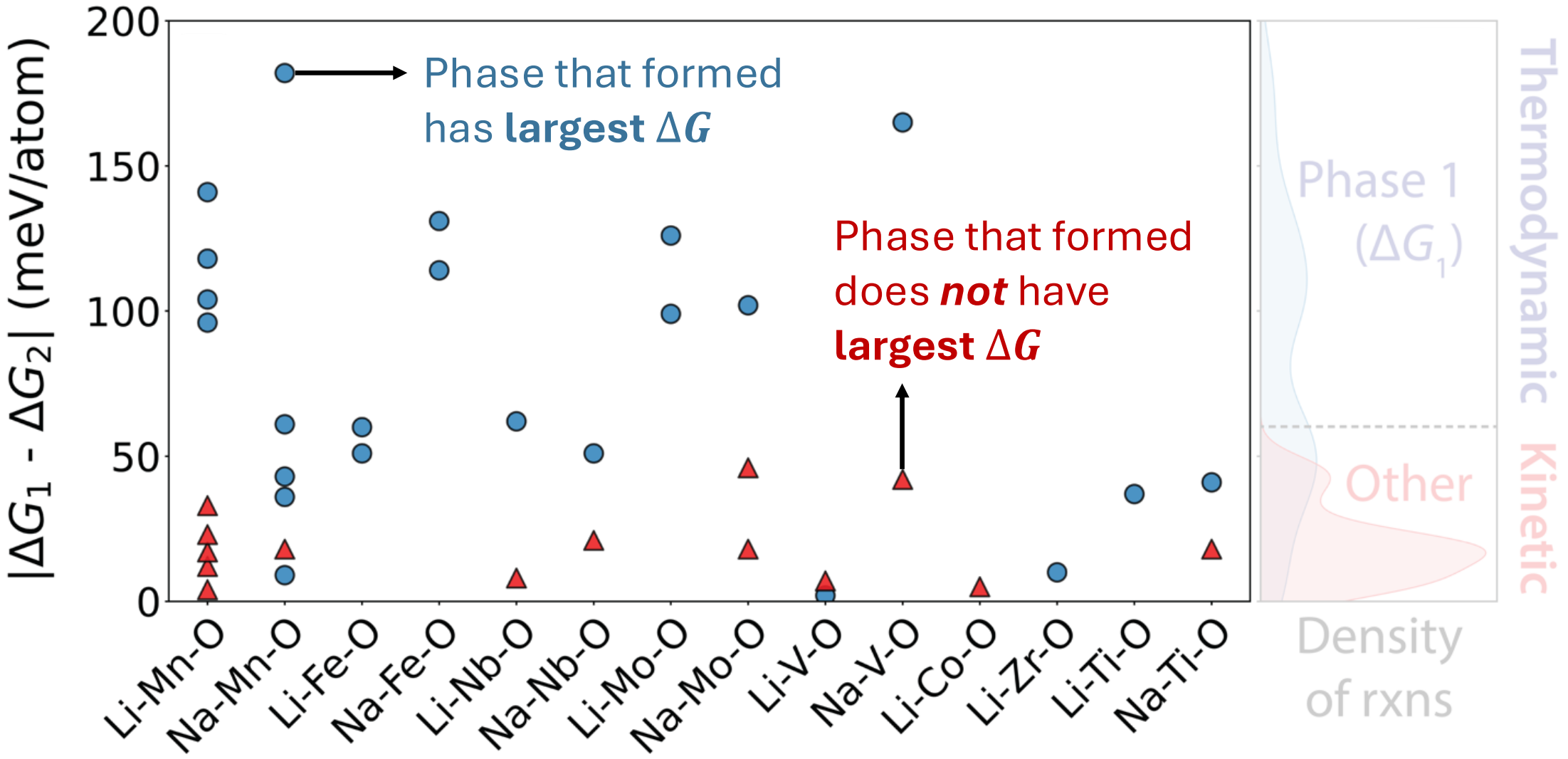

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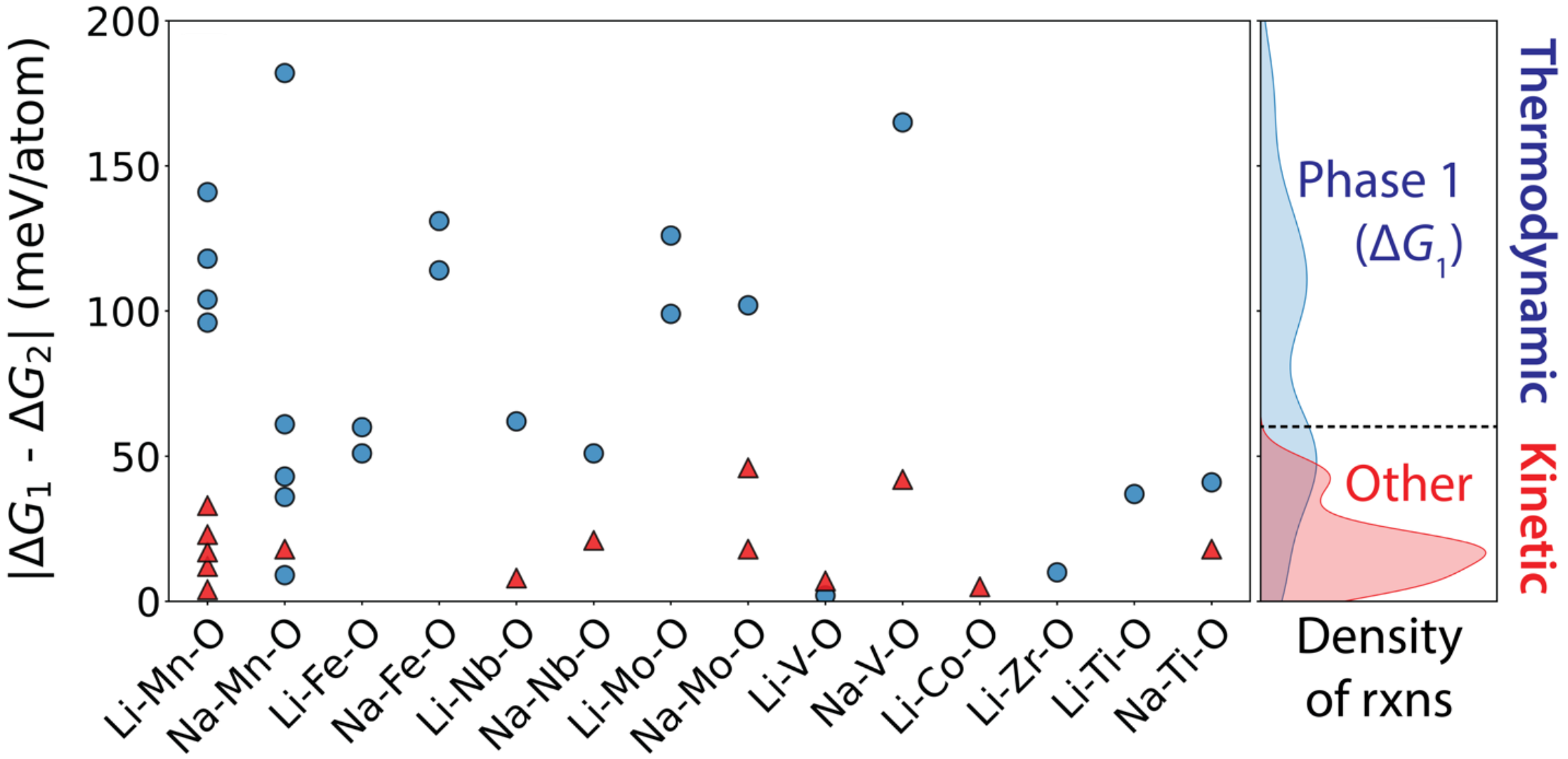

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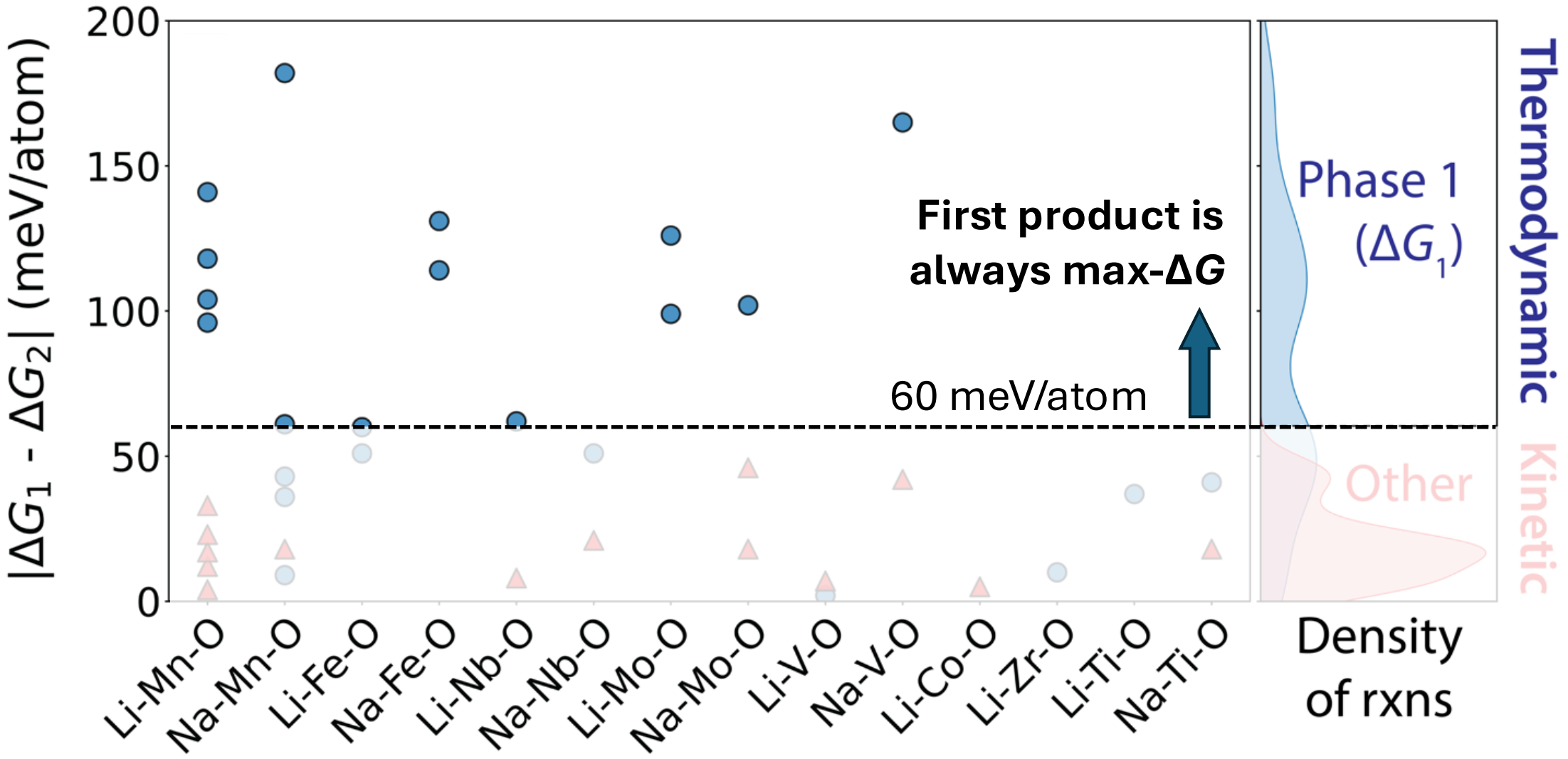
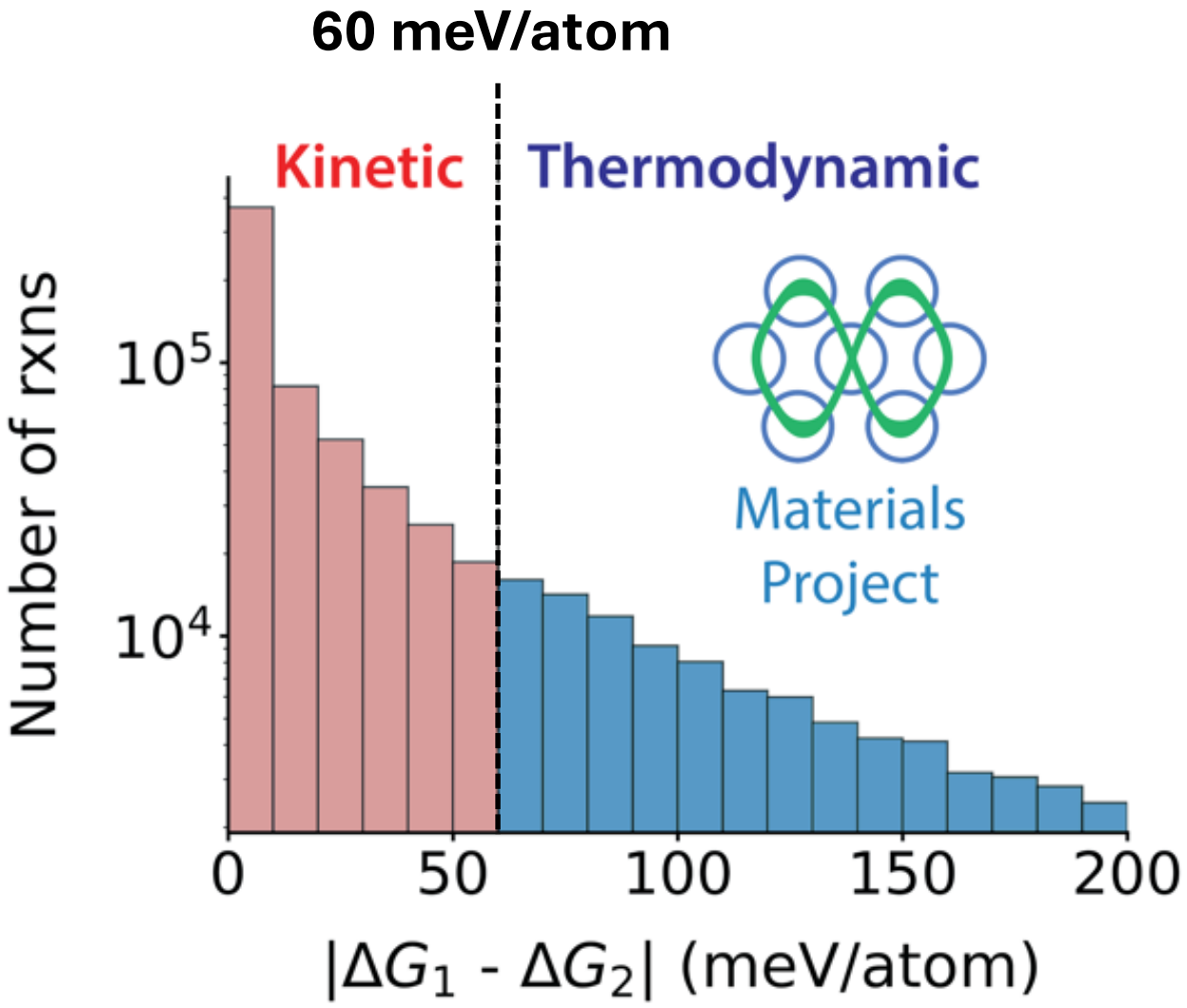
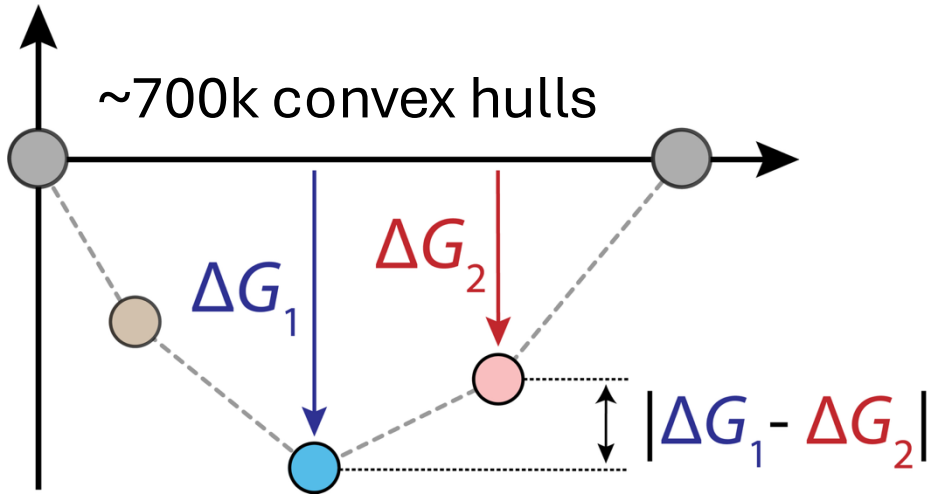


Szymanski *et al.*, Science Advances (2024).

But most reactions are *not* in this regime



Only **15% of reactions** fall above the proposed threshold of 60 meV/atom

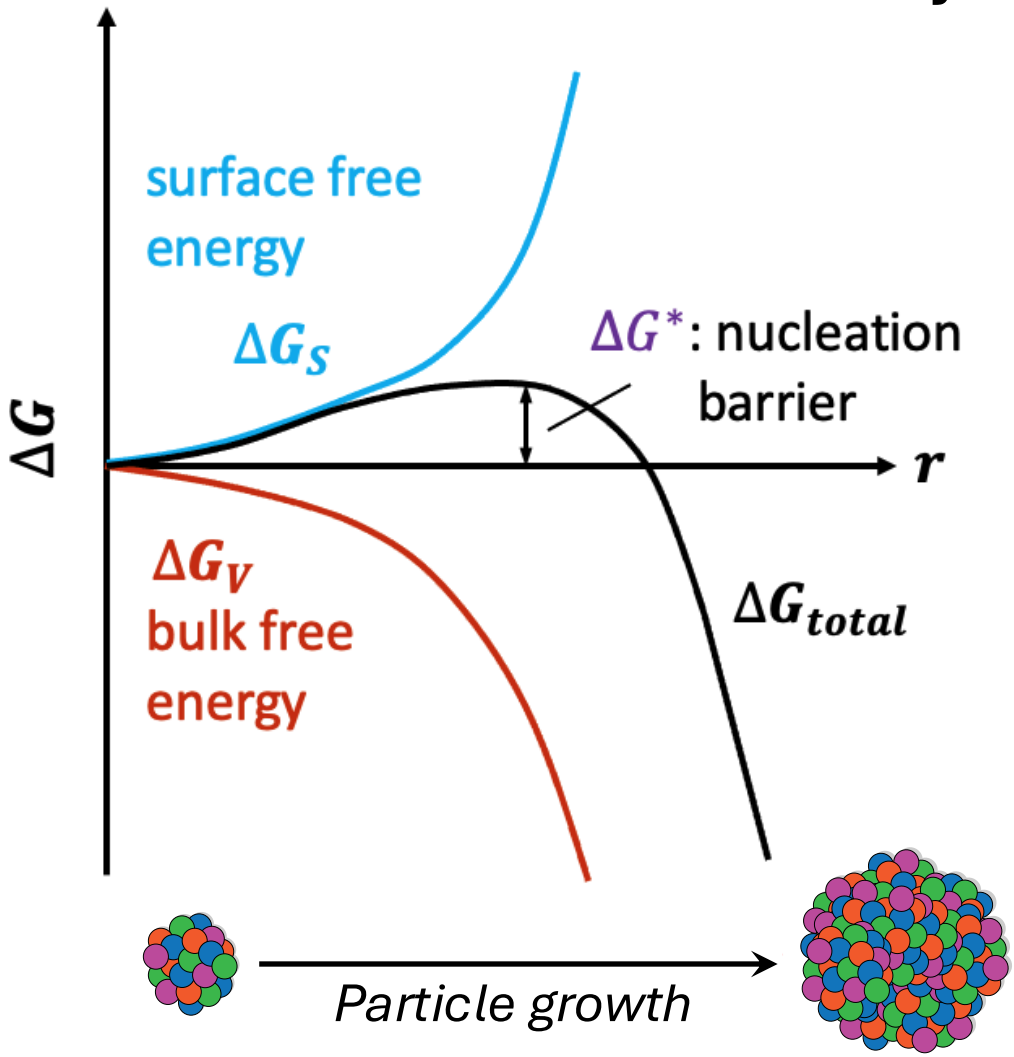


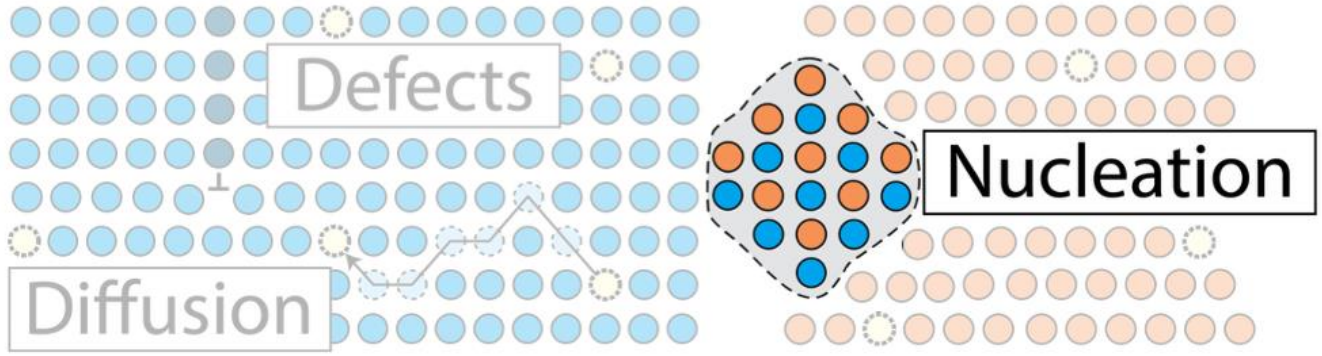
85% of reactions *cannot* be predicted using ΔG alone!

Szymanski *et al.*, Science Advances (2024).

How to deal with the remaining 85% of reactions?

Classical nucleation theory





Nucleation barrier:

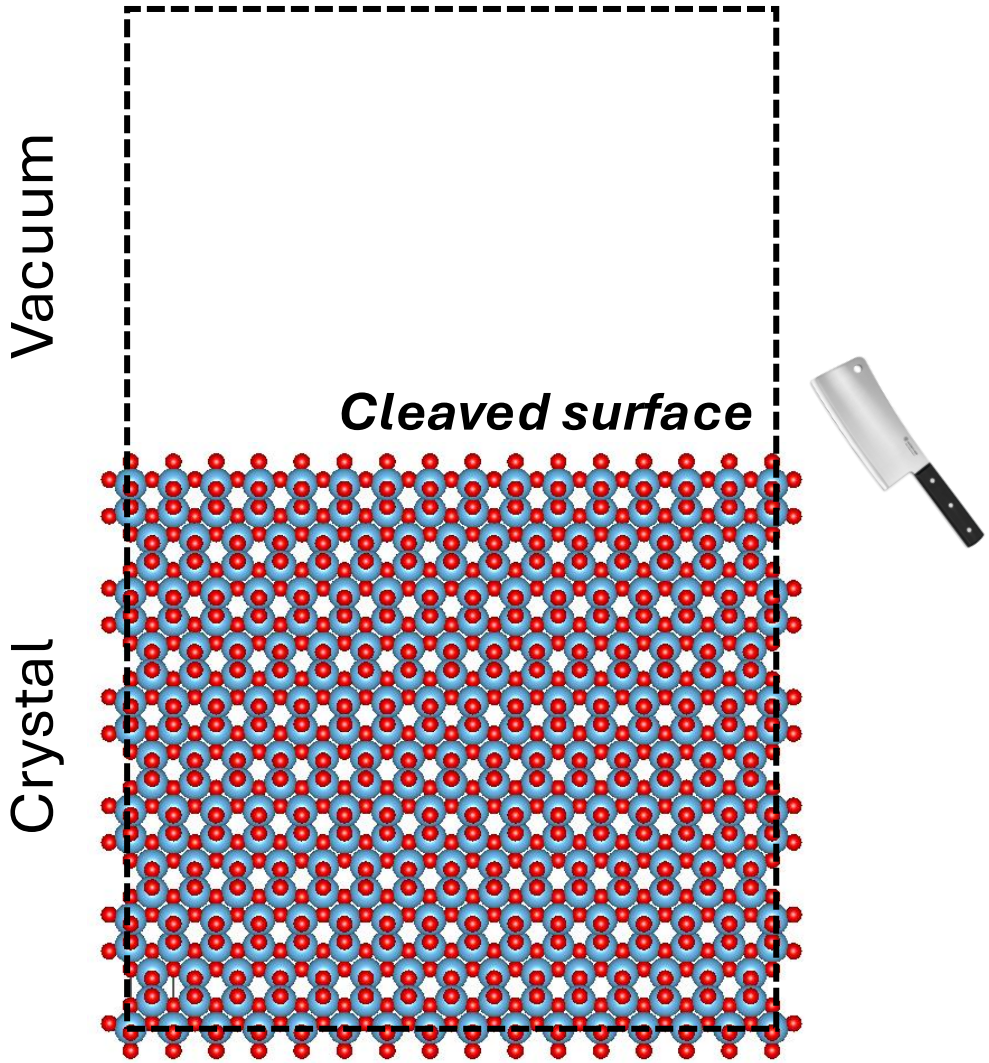
$$\Delta G^* = \frac{16\pi\sigma^3}{3(n\Delta G)^2}$$

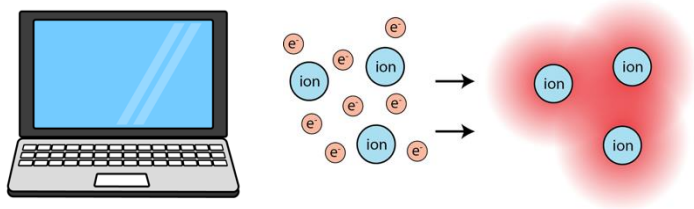
Surface energy

Atomic density

Bulk reaction energy

Computing the surface energy





DFT can be used to compute the surface energy

$$\sigma = (E_{\text{slab}} - nE_{\text{bulk}})/2A$$

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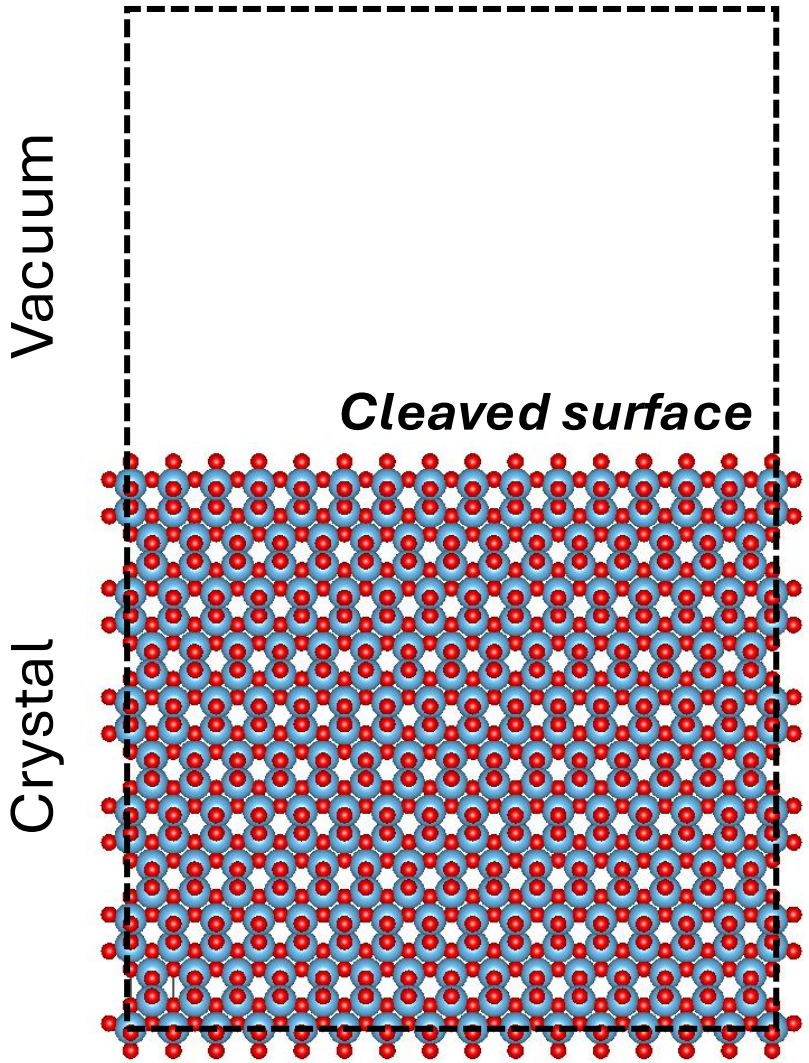
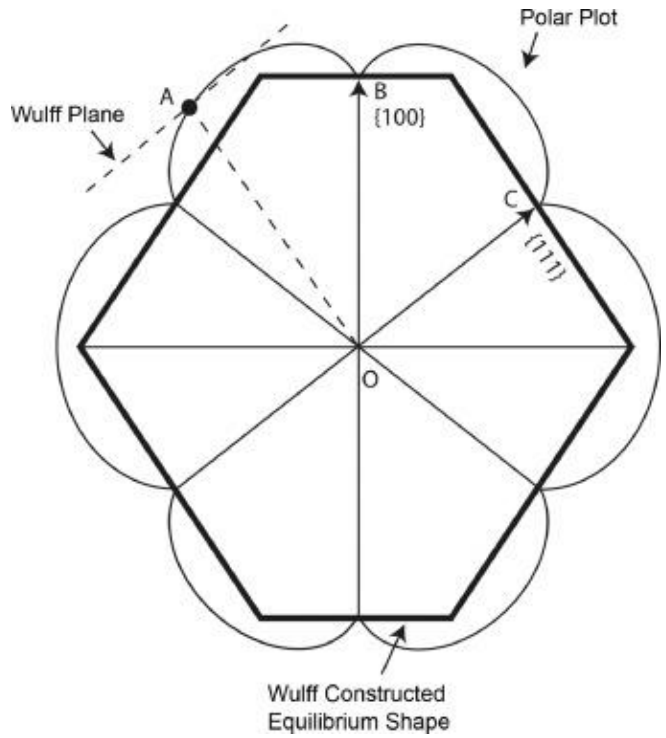
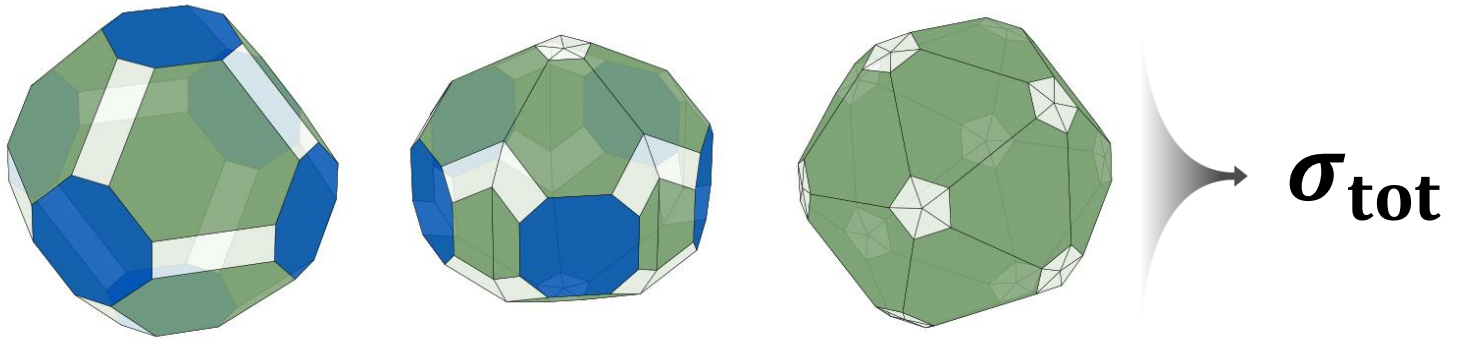


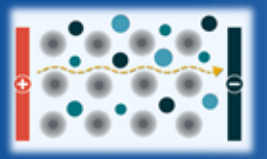


We compute the energy of many possible surfaces at different orientations to predict **equilibrium particle shape**

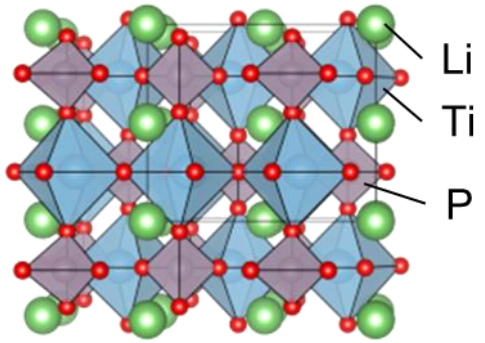


σ_{tot}

A real example: $LiTiOPO_4$ (LTOPO)



Ground state

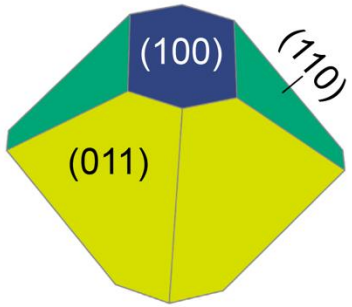


Orthorhombic polymorph
***o*-LTOPO**

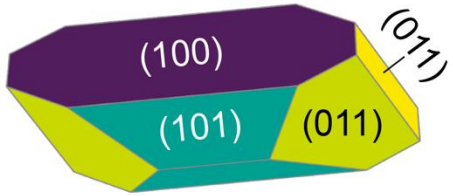
Lower bulk energy

$\leftarrow \Delta G_{\text{bulk}} \approx 13$ meV/atom

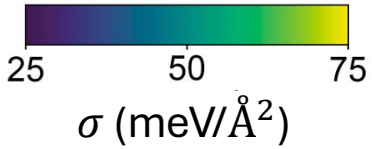
$\Delta\sigma \approx 16$ meV/Å^2 $\longrightarrow$



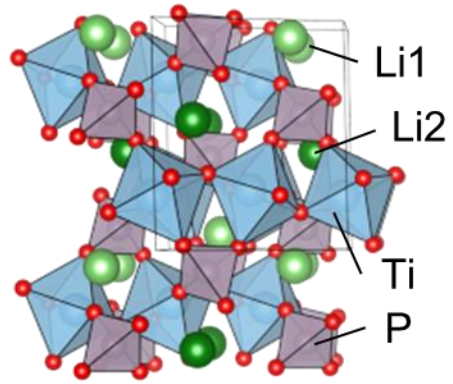
o-LTOPO



t-LTOPO



Metastable



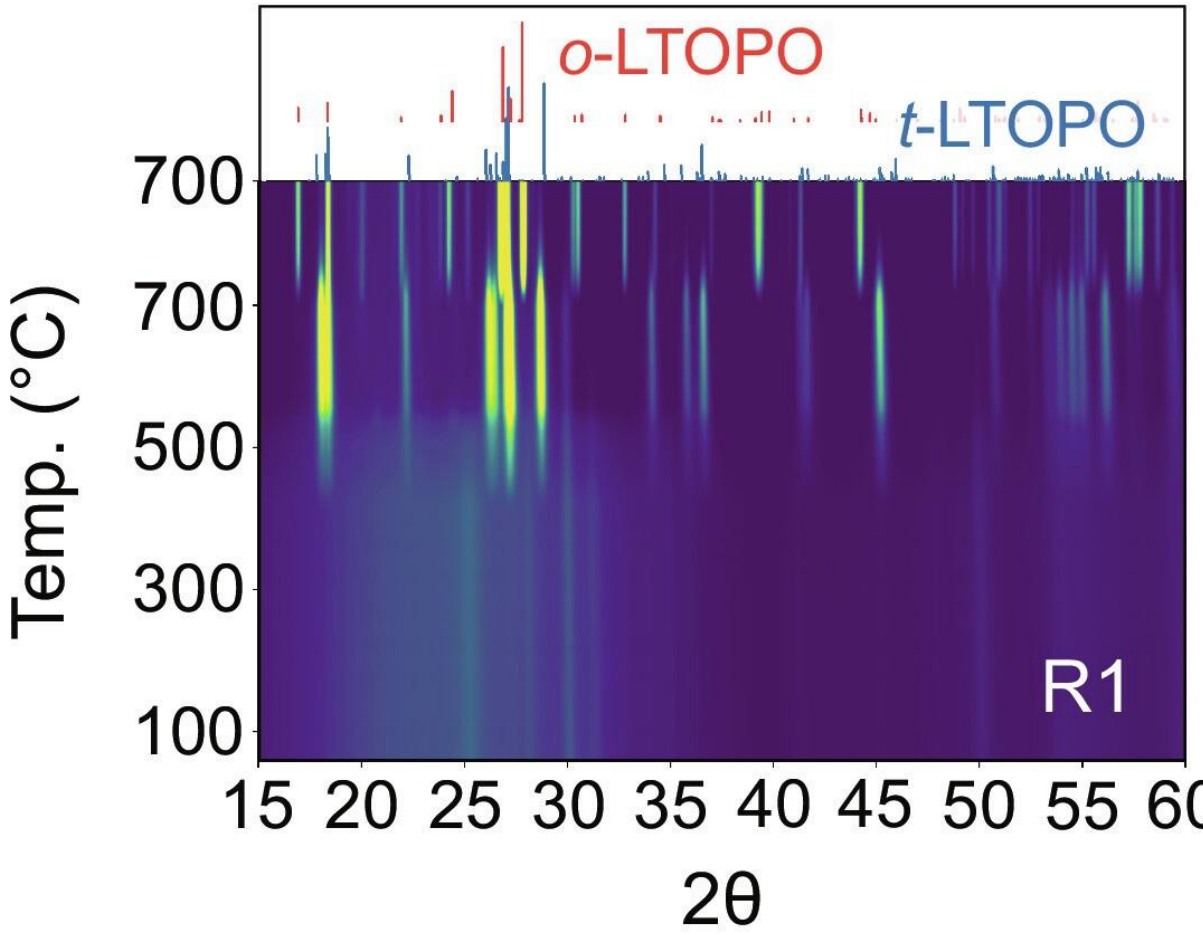
Triclinic polymorph
***t*-LTOPO**

Lower surface energy

Zeng & **Szymanski**, *Sci. Adv.* (2023).

Experiment #1: the metastable phase forms

Reactants: $Li_2O + 2\ TiO_2 + P_2O_5$

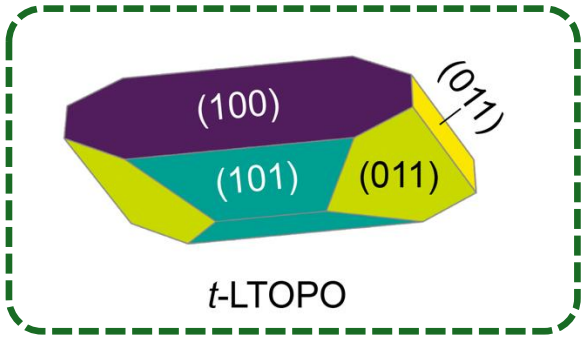


← Transition to ground state

Pure *t*-LTOPO initially forms
(surface energy wins)

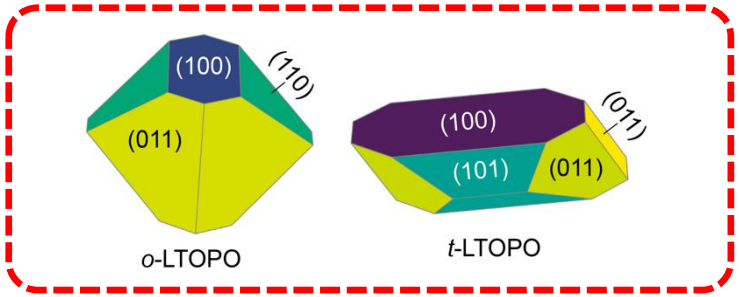
Starting reactants

Metastable polymorph



Zeng & **Szymanski**, *Sci. Adv.* (2023).

Experiment #2: the ground state forms



Both polymorphs are observed →

We've only changed the reactants:

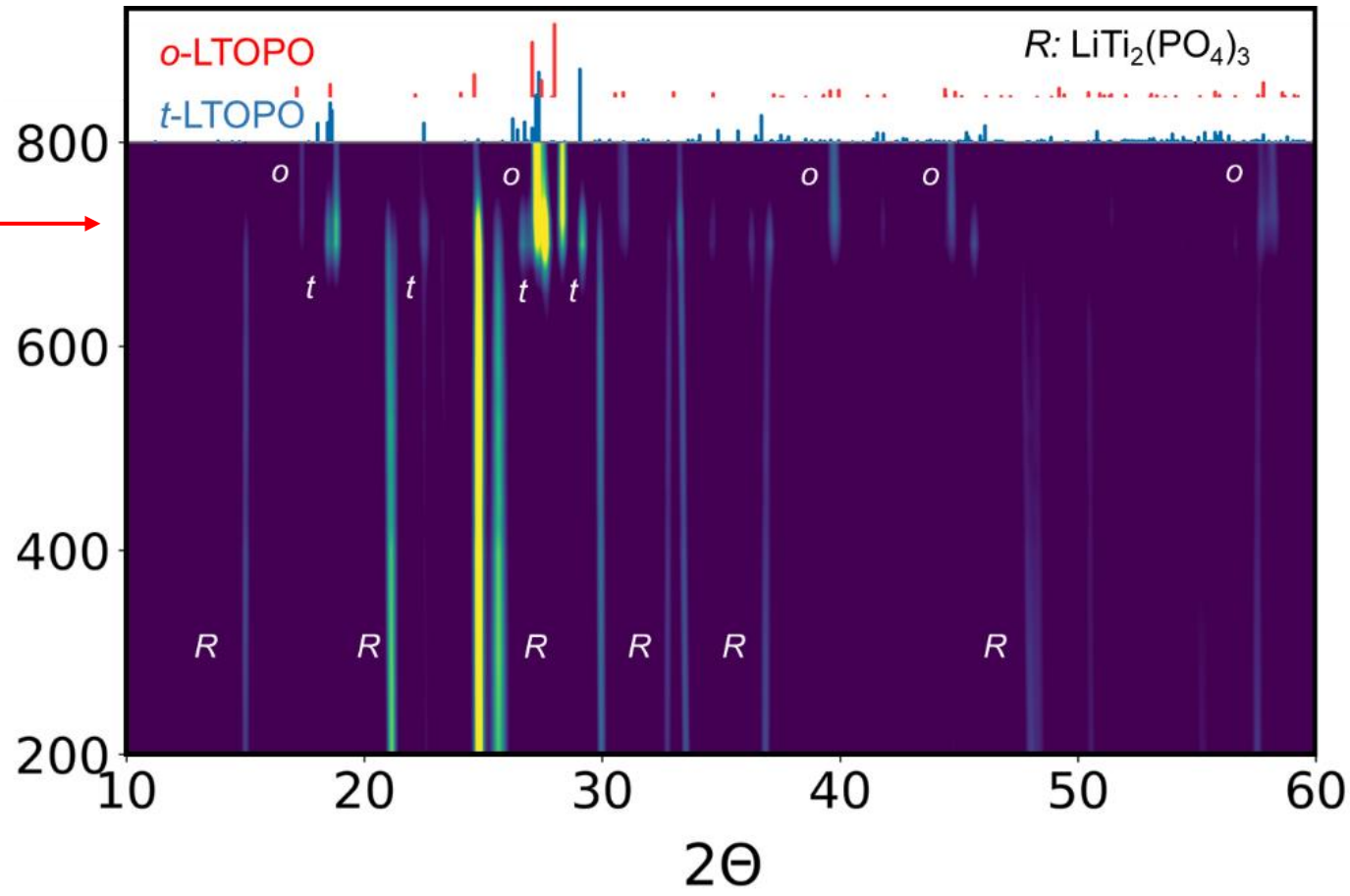
$Li_2O + 2\ TiO_2 + P_2O_5$

$(\Delta G_{rxn} = -279$ **meV/atom**$)$

$LiTi_2(PO_4)_3 + Li_3PO_4 + 2\ TiO_2$

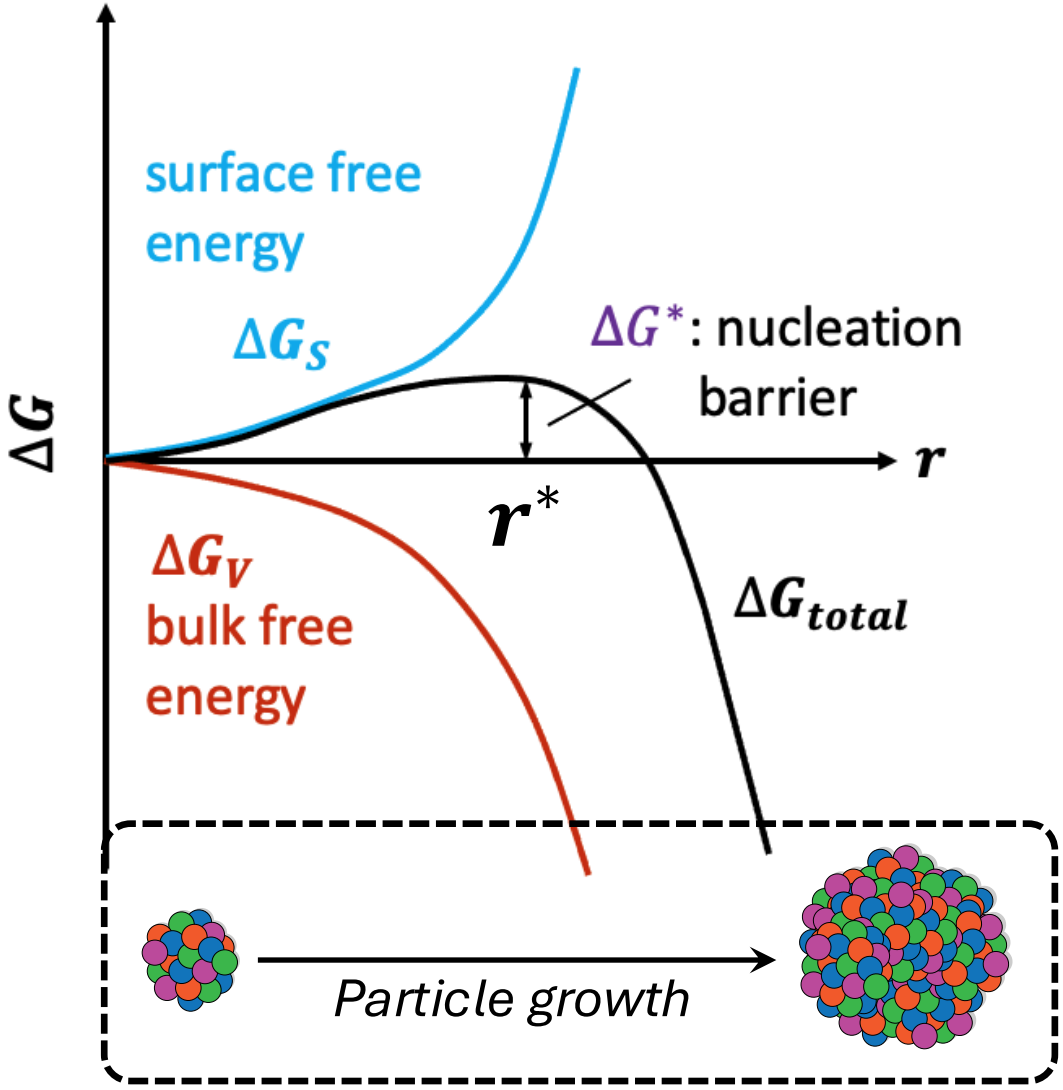
$(\Delta G_{rxn} = -40$ **meV/atom**$)$

Reactants: $LiTi_2(PO_4)_3 + Li_3PO_4 + 2\ TiO_2$



Zeng & **Szymanski**, *Sci. Adv.* (2023).

ΔG sets the ratio of surface area to volume



Large driving force (ΔG_{rxn}) leads to the formation of **small critical nuclei** where the **surface energy is dominant**

Surface stabilized

Large ΔG_{rxn}

Small ΔG_{rxn}

Bulk stabilized

$\frac{\text{Surface Area}}{\text{Volume}}$ is large

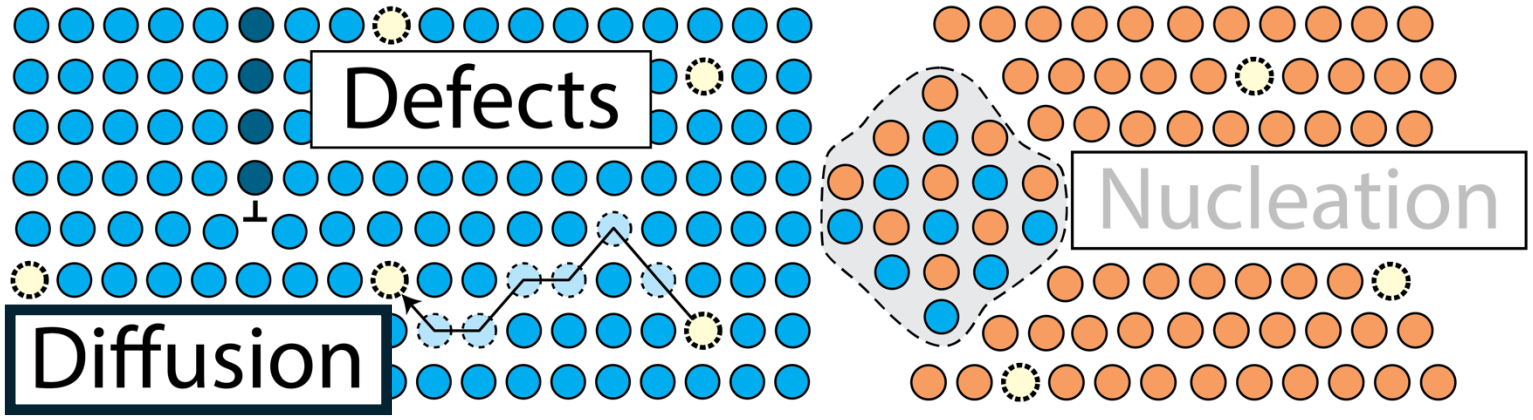
σ matters more

$\frac{\text{Surface Area}}{\text{Volume}}$ is small

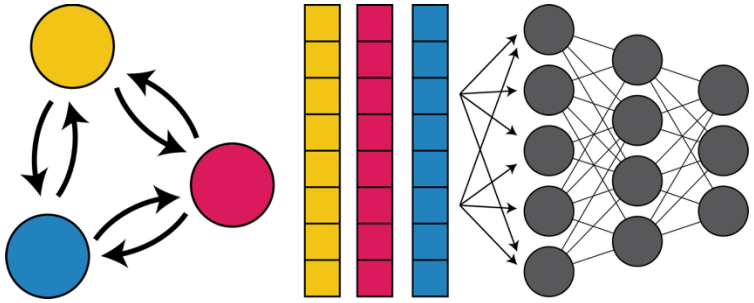
ΔG_{rxn} matters more

We've so far been ignoring diffusion…

Atoms need to diffuse and reach the interface to facilitate growth



Validation and fine-tuning are often needed!



MLIPs are increasingly used to simulate diffusion and interfacial reactions

UMA

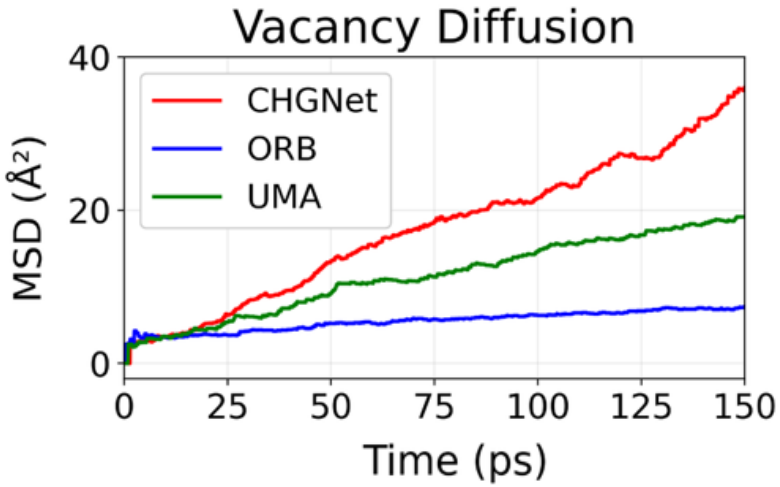
UPET
UNIVERSAL ATOMISTIC MODELS

Orbital Materials

ICAMS
GRACE

CHGNet

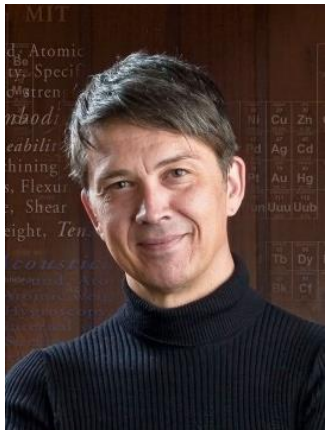
SevenNet











Happy to answer any questions!

MD² LAB
MATERIALS DESIGN THROUGH DYNAMICS

Samueli
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