Multiscale modeling of interface kinetics within HyMARC

2019 DOE Hydrogen Annual Merit Review

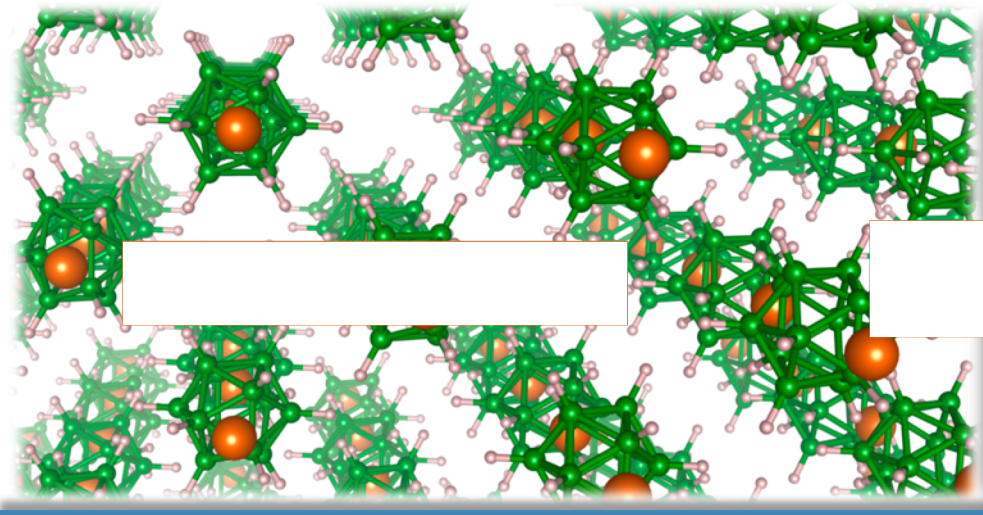
April 30, 2019

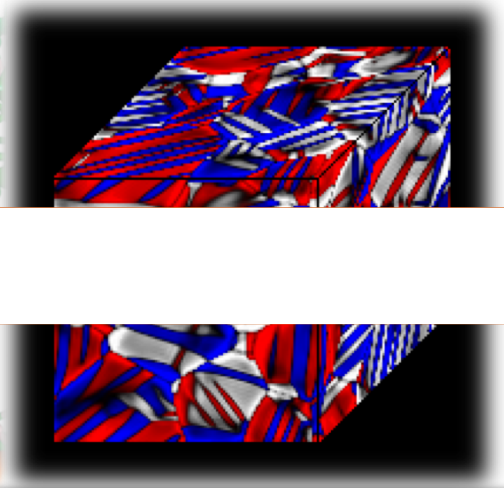
Presenter: Tae Wook Heo, LLNL

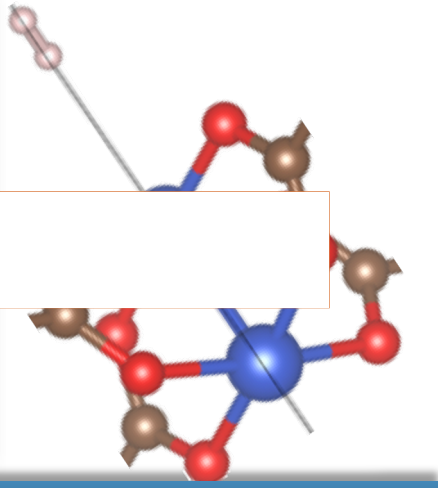
HyMARC
Hydrogen Materials Advanced Research Consortium

Enabling **twice the energy density** for onboard H_2 storage

Team: S. Kang, X.W. Zhou, S. Wan, K. Ray, R. Shi, T. Ogitsu, S. Bonev, P. Shea, B. Wood







Overview

Timeline

Project start date: 10/01/2018

Phase II end date: 09/30/2022

Barriers addressed

- **Lack of understanding of hydrogen physisorption and chemisorption (Barrier O)**
- System weight and volume (Barrier A)
- Charge/discharge rate (Barrier E)

Budget

Phase I DOE funding: $3040K

Phase II FY19 DOE funding (expected): $1250K

Funding determined annually by DOE

Partners

Sandia (lead)

NREL (lead)

PNNL

LBNL

NIST

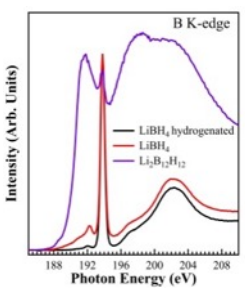
SLAC

ORNL

Relevance: Multiscale features of storage mechanisms

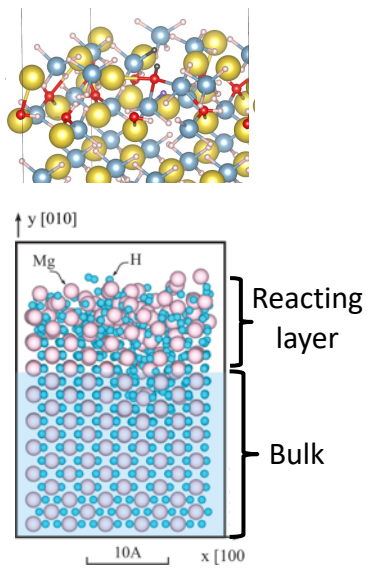
HyMARC provides i) community tools and ii) foundational understanding of multiscale phenomena for hydrogen storage mechanisms

Atomic/molecular (0 – 1 nm)	Molecular/micro (0.5 – 2 nm)	Mesoscale (2 - 100 nm)	Grains (≤ 10 µm)	Macroscale/Bulk

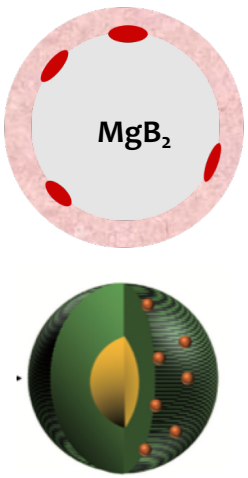


Computational Spectroscopy

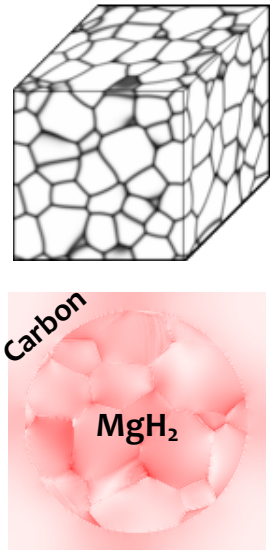
Hydrogen physi- or chemisorption



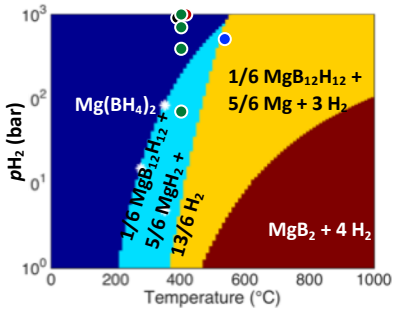
Surface/interface chemistry
Interatomic potentials



Nucleation kinetics
Phase microstructures



Grain boundaries
Particle size effects
Confinement
Stress/strain



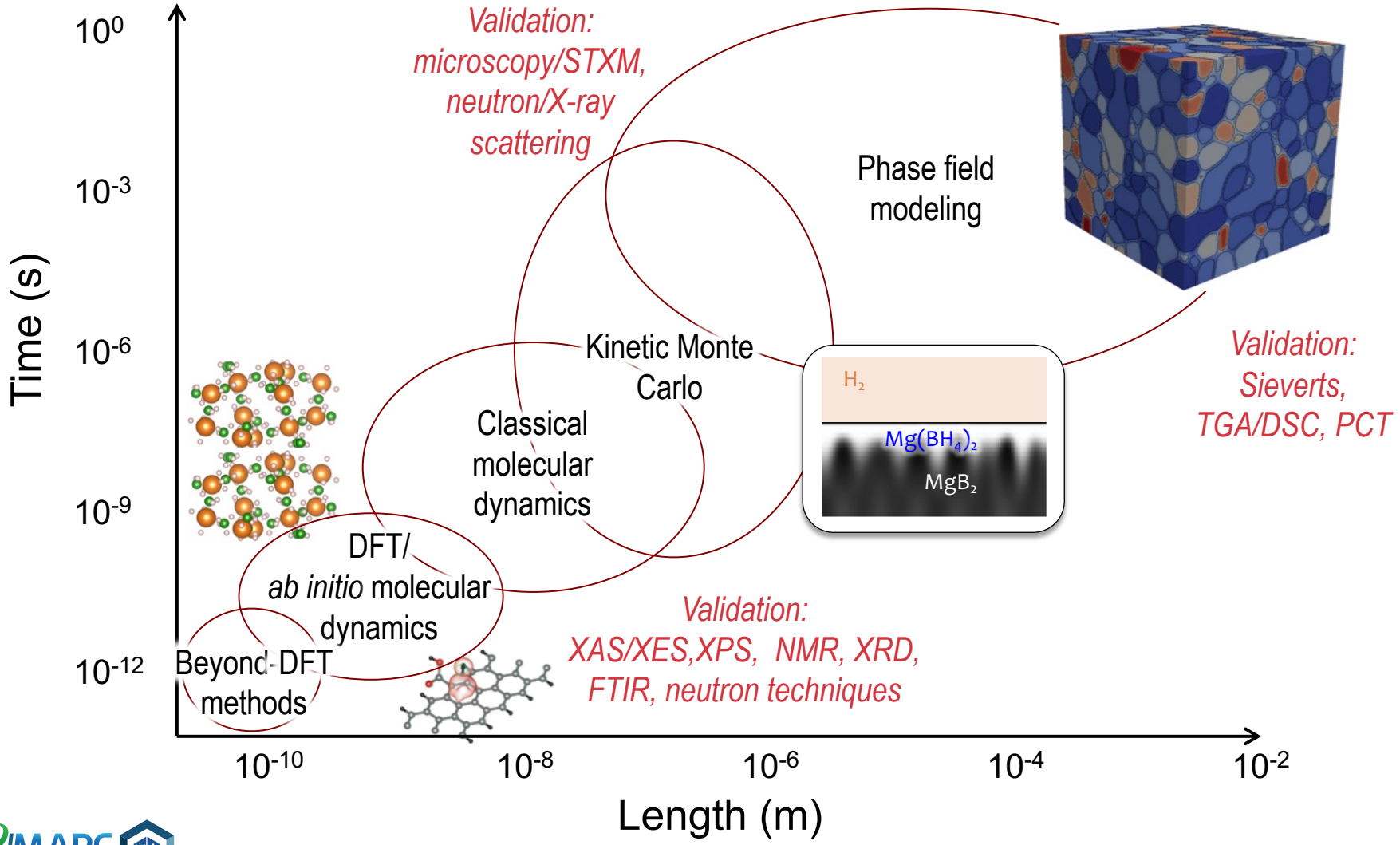
Thermodynamics

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

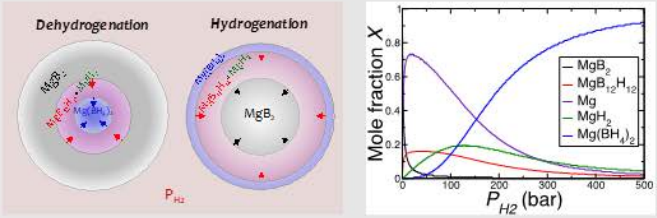
Approach: Validated multiscale modeling

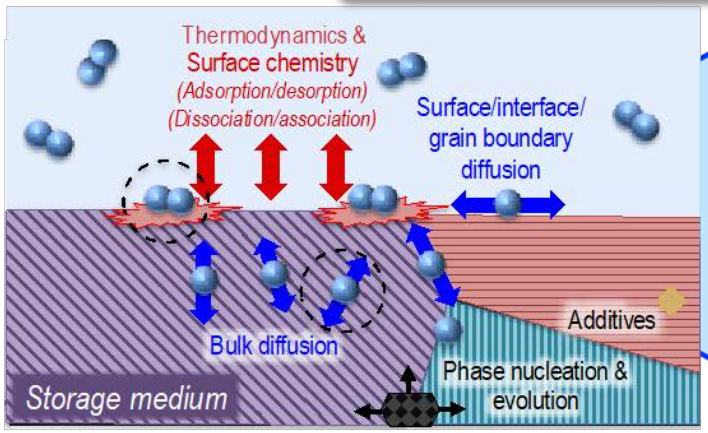
Modeling approach prioritizes (i) bridging scales via multiscale integration; (ii) improving descriptions of "real" materials; and (iii) leveraging experiment-theory feedback



Roles of multiscale modeling within *HyMARC*

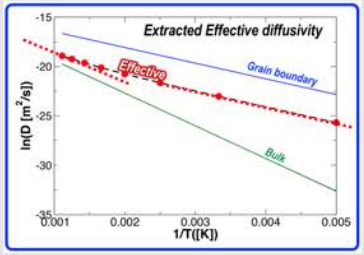
Beyond-ideal thermodynamics

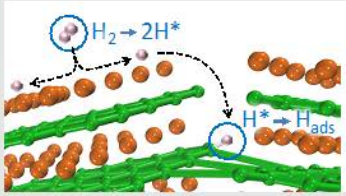




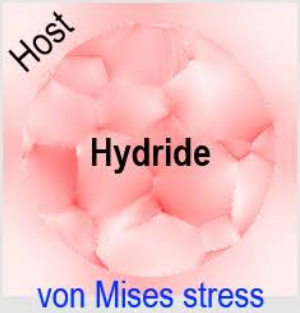
- Combine ***concurrent multiple*** materials & chemical processes
- Integrate ***multi-scale*** thermodynamic/kinetic parameters
- Include ***non-ideal*** and ***non-equilibrium*** physical/chemical/material factors

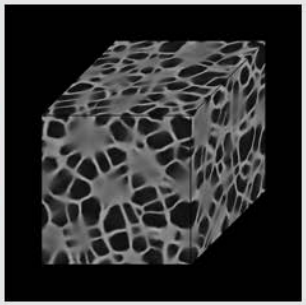
Mass transport kinetics





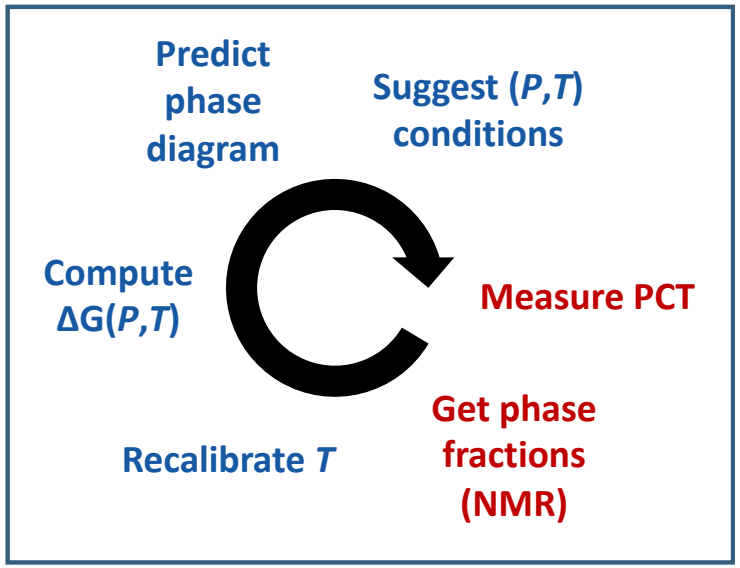
Interfaces/Phase transformations

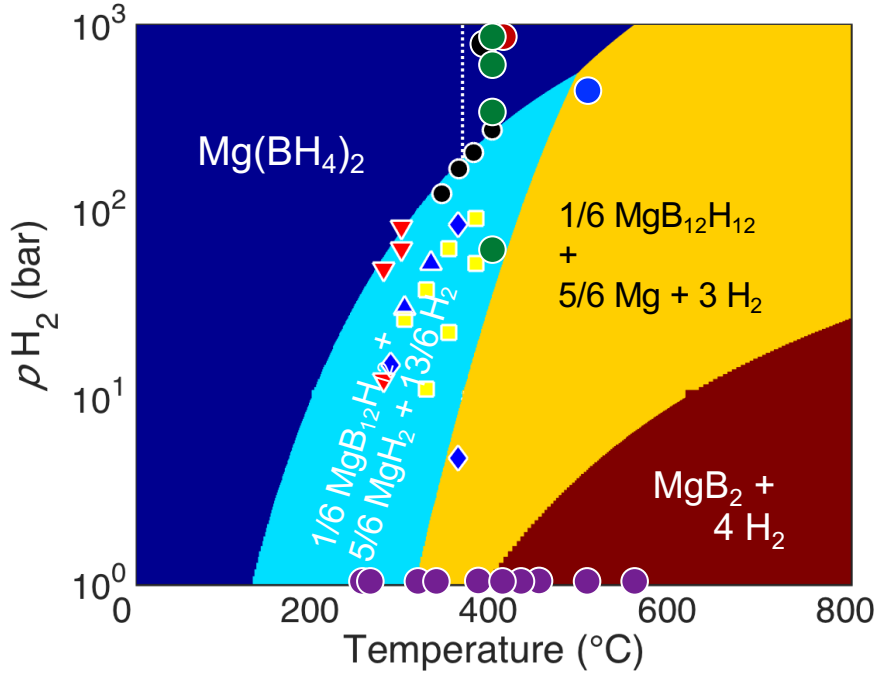




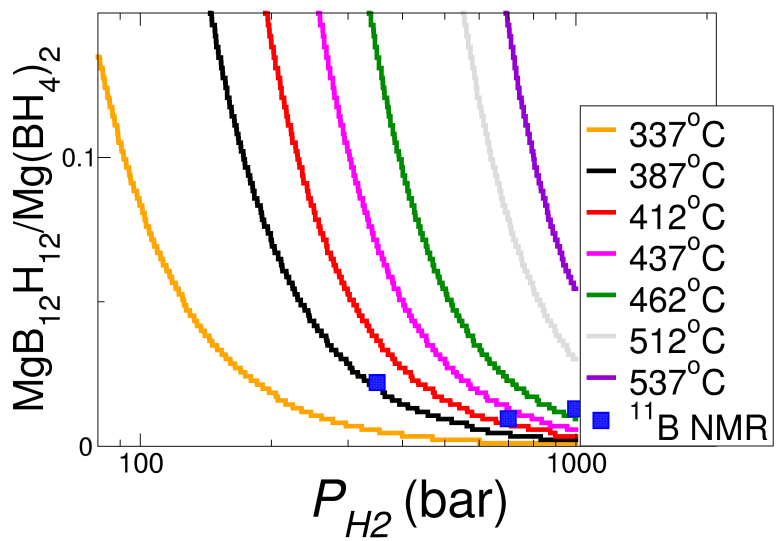
Accurate thermodynamic description of complex hydrides

Theory-Experiment Feedback Cycle





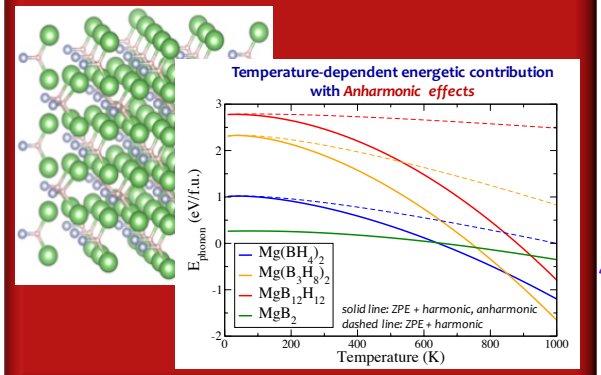
- **Compared to SNL PCT, our model predicts ΔS with 97% agreement and ΔH with 88% agreement.**
- **Phase equilibrium between $Mg(BH_4)_2$ and $MgB_{12}H_{12}$ is correctly predicted to within 10°C.**
- **Calibrated phase diagram can be used to:**
  - ✓ Identify thermodynamic conditions for avoiding intermediates
  - ✓ Understand high-P hydrogenation
  - ✓ Extrapolate to hard-to-access P/T conditions
  - ✓ Inform kinetic models

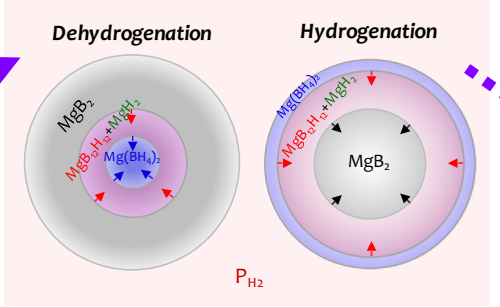


Beyond-ideal thermodynamics: Internal interfaces

Theoretical framework for predicting equilibrium phase fractions as function of temperature, pressure, and particle size

Thermodynamic database

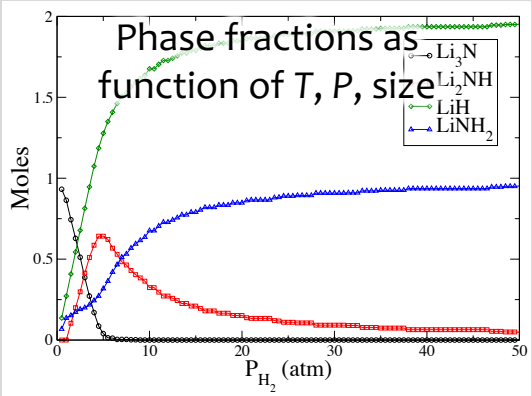




Bulk, surface, and interfacial free energies

Phase fraction code

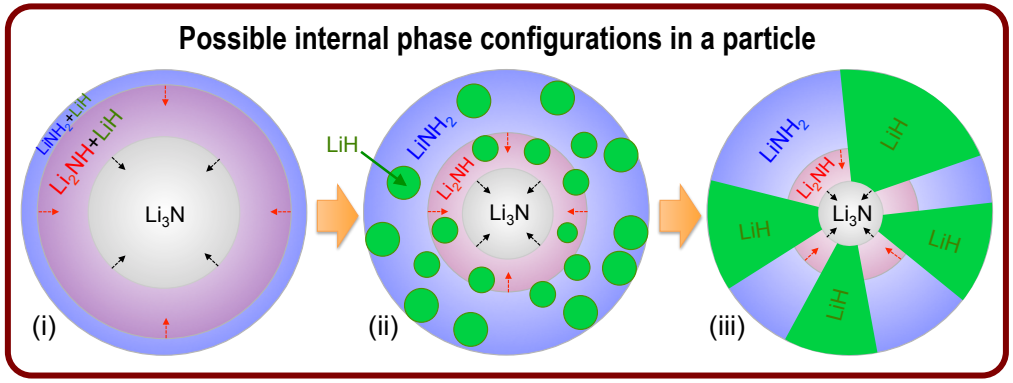
```
-----------------------------
H2 pressure(atm):   49.50000
Temperature(K):   1000.000
-----------------------------

#Phase contents (moles)#
Li3N(s): -5.9604645E-08
Li2NH(s):  5.0000001E-02
LiH(s):   1.950000
LiNH2(s):  0.9500000
H2(g):   11.56350


beta:  4.8000000E-02 gamma:  0.9520000
X1,X2,X3,X4:  0.0000000E+00  1.6260162E-02  0.6612466      0.3224932
n_H2:   11.69800


-----------------------------
H2 pressure(atm):   50.00000
Temperature(K):   1000.000
-----------------------------

#Phase contents (moles)#
Li3N(s):  0.0000000E+00
Li2NH(s):  4.8000000E-02
LiH(s):   1.952000
LiNH2(s):  0.9520000
H2(g):   11.69800
```



- Multiscale **beyond-ideal thermodynamic computational method** for phase fraction prediction integrating <u>advanced bulk, surface, and interfacial DFT thermodynamics</u>, plus <u>thermodynamics of mixing</u>
- Generally applicable to several types of metal hydrides

Beyond-ideal thermodynamics: Internal interfaces

Demonstrated thermodynamic phase fraction prediction for Li-N-H



Large particles

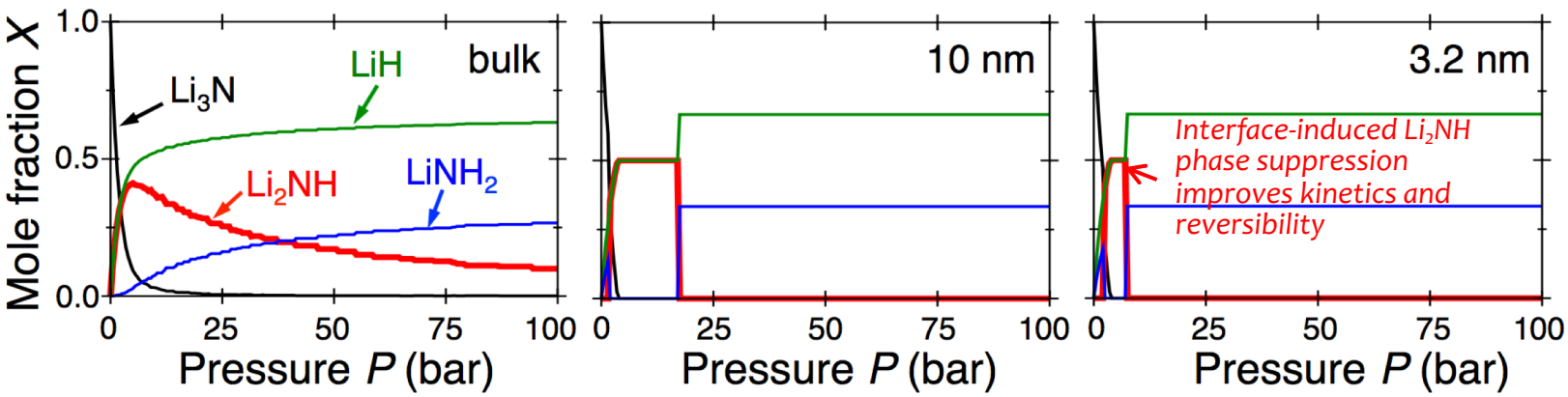
$Li_3N + H_2 \leftrightarrow Li_2NH + LiH$

$Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH$

Small particles

$Li_3N + 2H_2 \leftrightarrow LiNH_2 + 2LiH$

Predicted size-dependent phase fractions for hydrogenation of $Li_3N/[LiNH_2+2LiH]$ system in core-shell microstructure



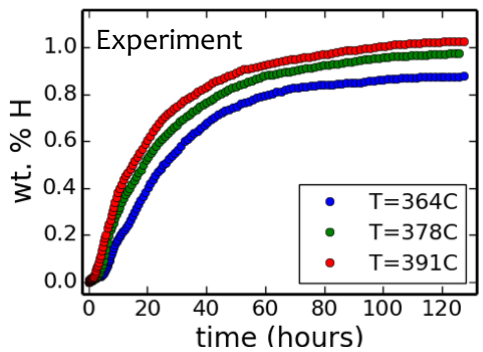
Successfully predicted experimentally characterized reaction pathway in nanoconfined Li-N-H and confirmed relevance of interfaces in determining phase stability

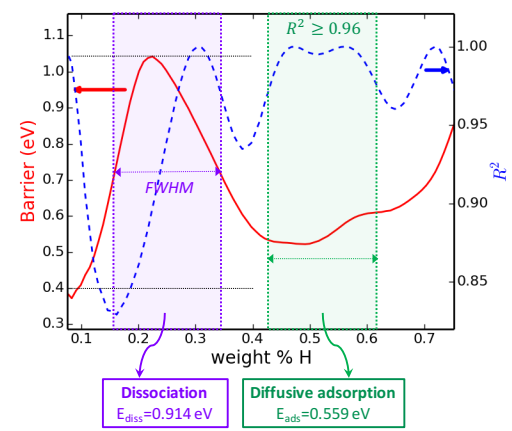
Wood *et al.*, *Adv. Mater. Interfaces*, **4**, 1600803 (2017)

Mass transport kinetics: concurrent chemical & materials processes

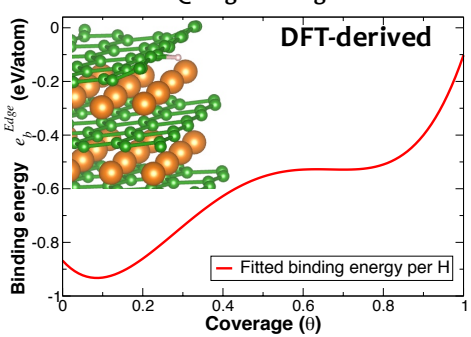
Information from Exp. & Theory

MgB_2 hydrogenation@145bar



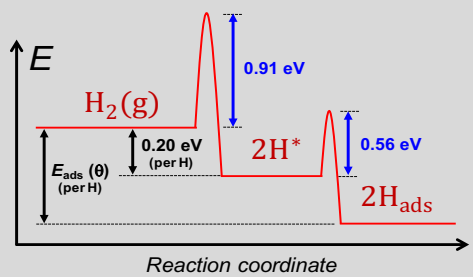


H @ edge binding sites



Modeling capability development

Kinetic modeling

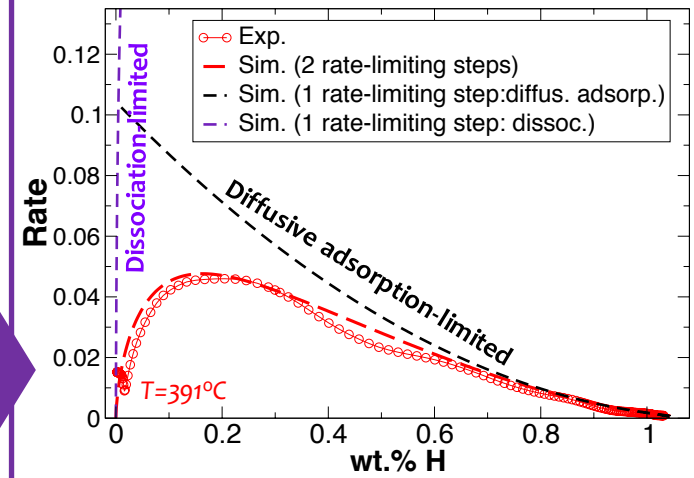


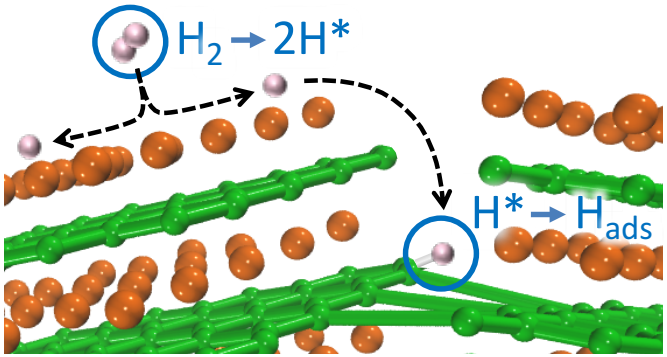
$$H_2\,(g) \leftrightarrow 2H^* \leftrightarrow 2H_{ads}$$

$$\frac{\partial c_{H^*}}{\partial t} = k_1 \cdot P_{H_2} - \tilde{k}_1 \cdot c_{H^*}^2 - \frac{\partial c_H^{ads}}{\partial t}$$

$$\frac{\partial c_H^{ads}}{\partial t} = k_2 \cdot c_{H^*}^2 \cdot c_s^3 \cdot (1-\theta)^2 - \tilde{k}_2 \cdot c_s^3 \cdot \theta^2$$

Mechanistic understanding





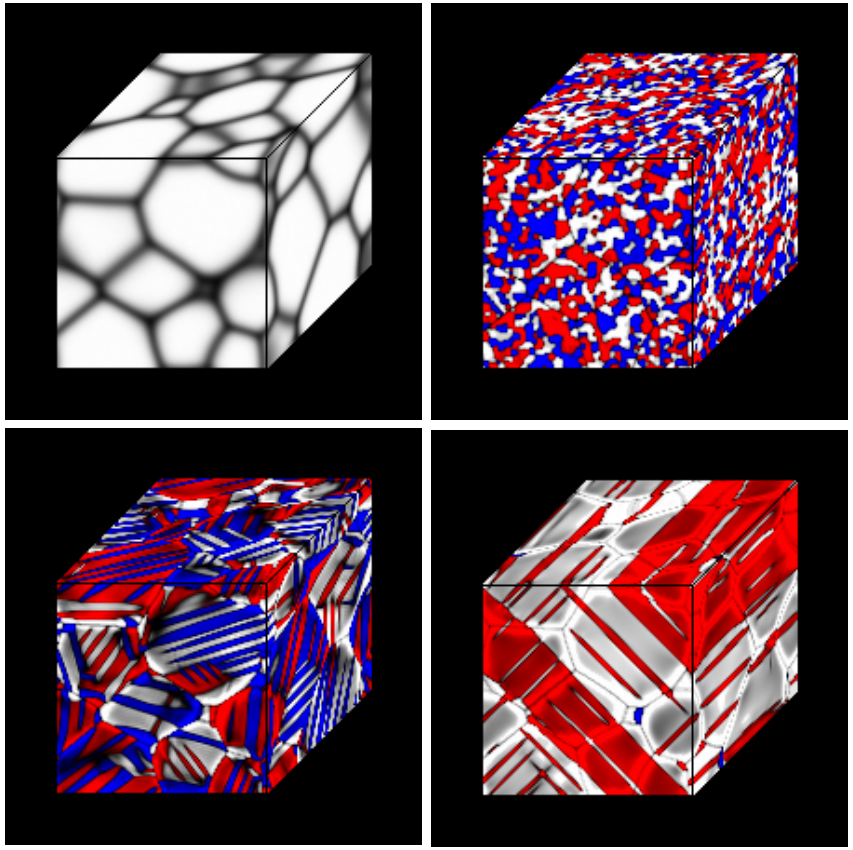
Multiscale kinetic model for analyzing surface hydrogen reaction and transport mechanisms for initial hydrogenation of the Mg-B-H system

Ray *et al.*, *PCCP*, **19**, 22646 (2017)

Multiscale approach for computing effective diffusion property

Developed efficient modeling approach for extracting effective transport properties of realistic hydride microstructures

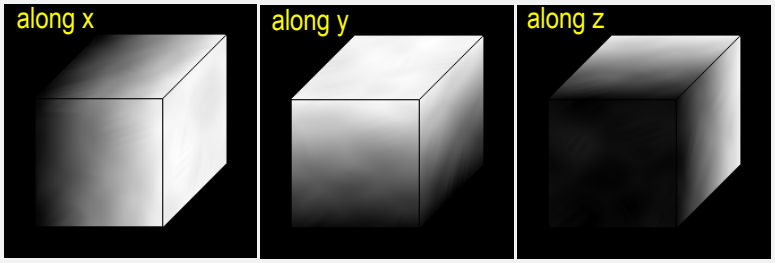
More realistic grain/phase microstructures



by phase-field simulations

Computational procedure

- Reconstruct a digital hydride microstructure using a ***phase-field (PF) simulation*** or using ***experimental information***
- Assign individual diffusivities derived from atomistic simulations to corresponding grains/phases of the PF simulated microstructure
- Compute steady state profiles under macroscopic concentration gradients using the ***Fourier-spectral iterative perturbation method***

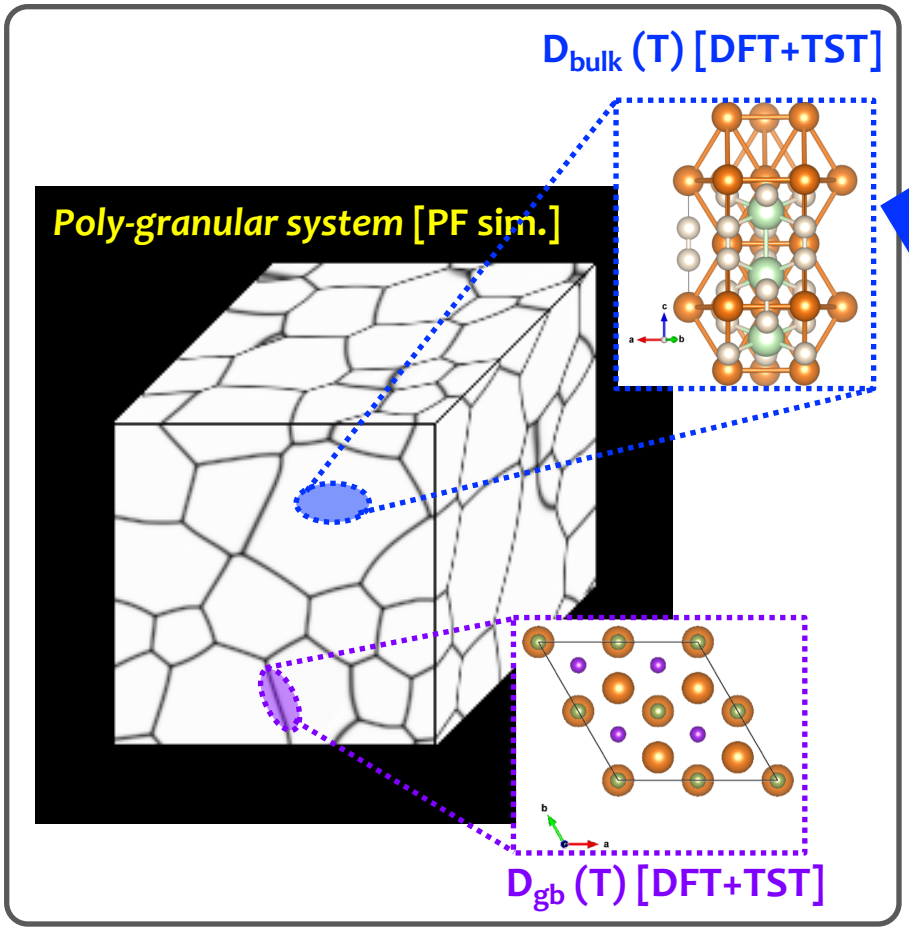


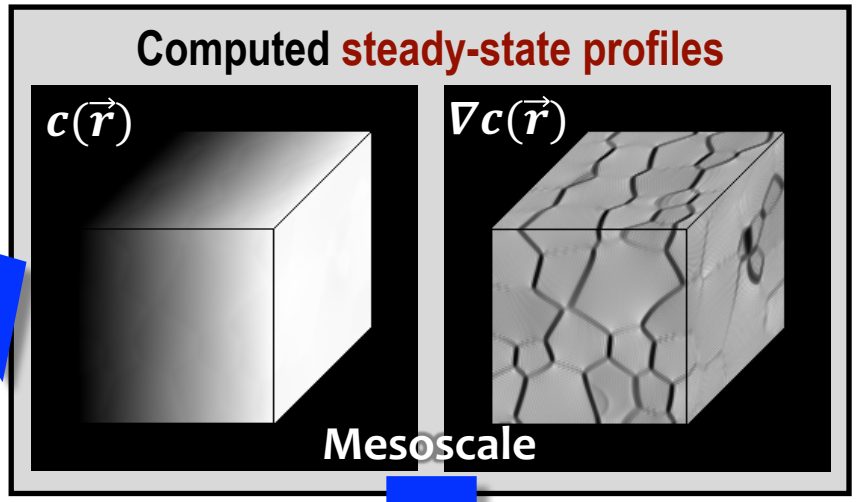
- Extract effective diffusivity tensor

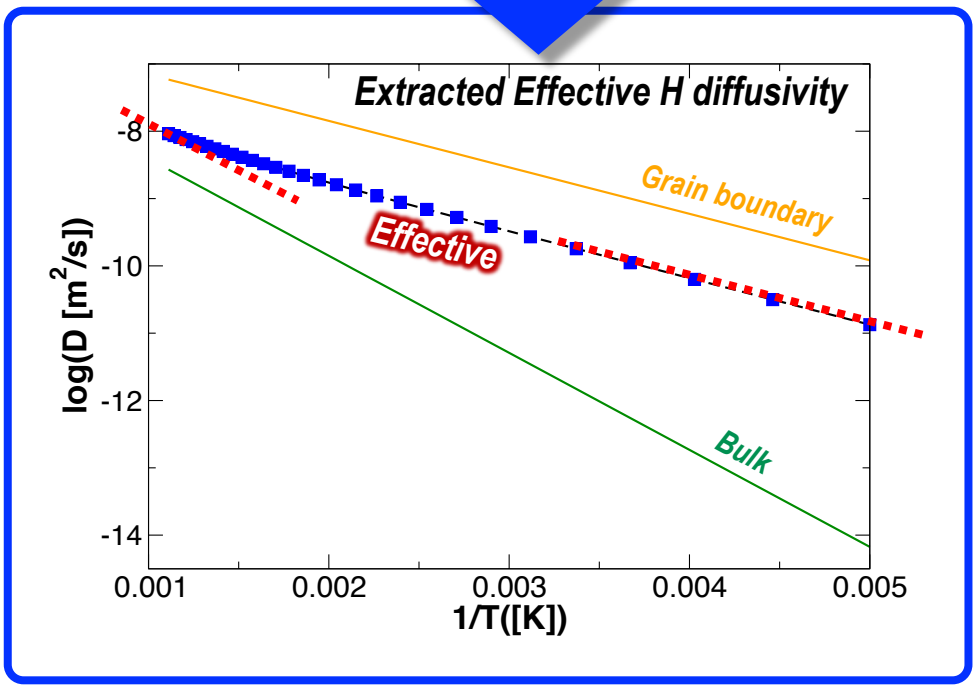
$$D_{ij}^{eff} = - < j_i(r) > / \overline{q}_j$$

Multiscale approach for computing effective diffusion property

Developed method was applied to the Mg-H system







***Refs. for DFT calculations of diffusivities:**

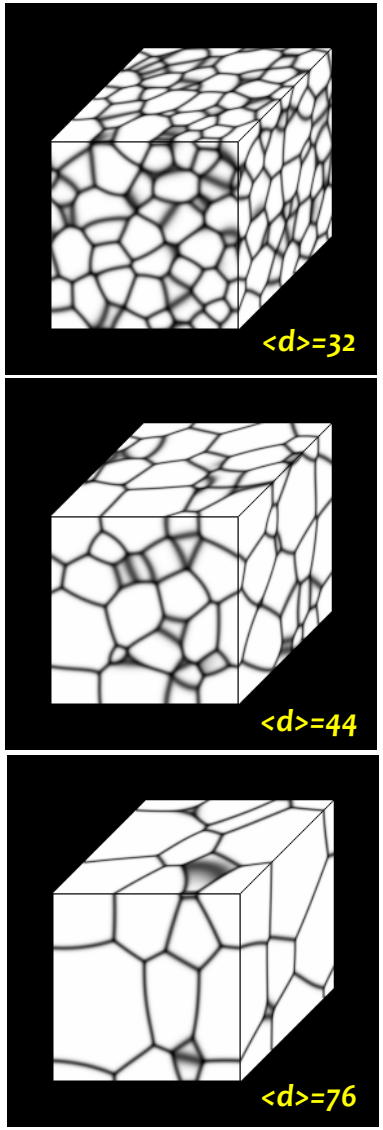
Bulk: L. Ismer *et al.*, *Phys. Rev. B*, **80**, 184110 (2009)

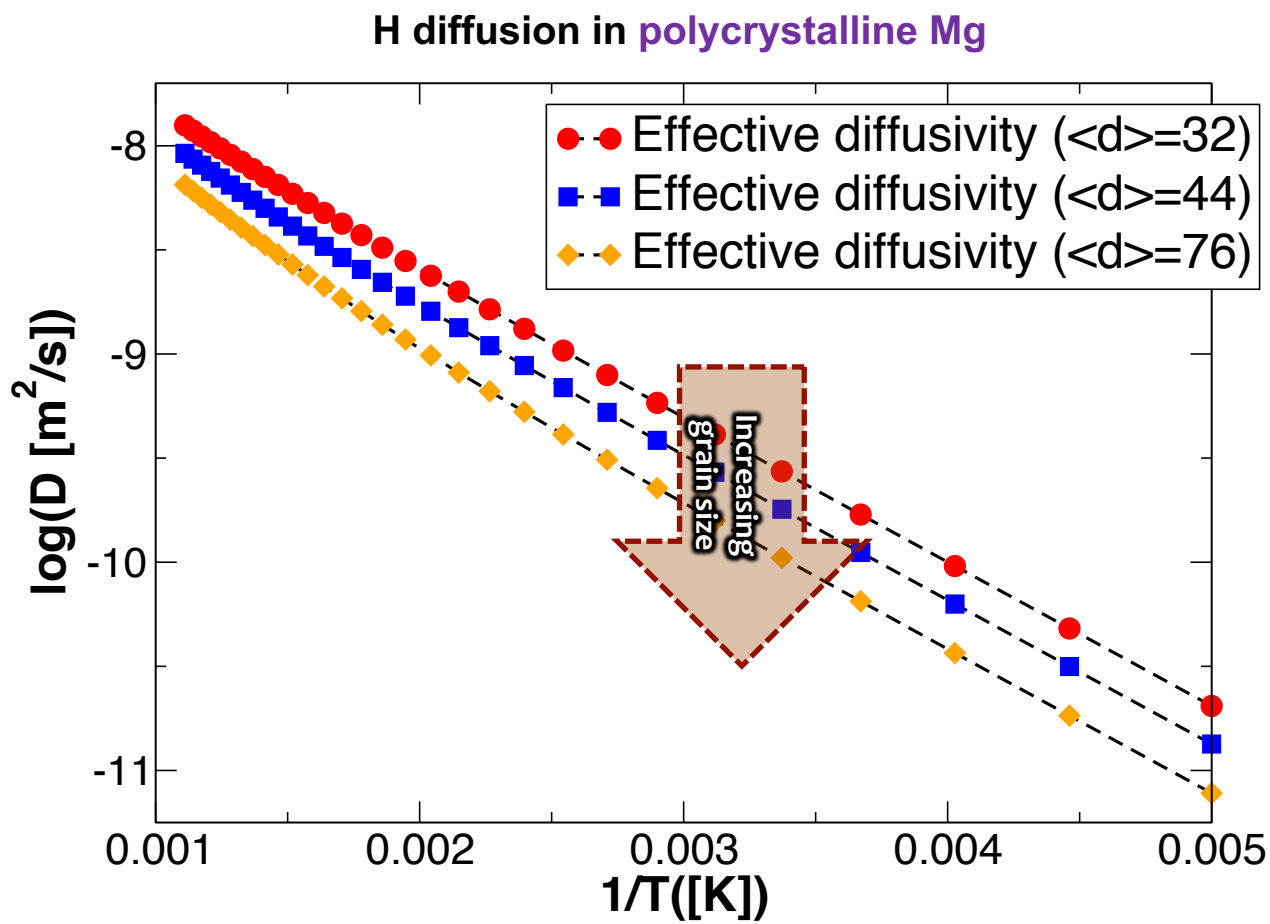
Grain boundary: T. Vegge, *Phys. Rev. B*, **70**, 035412 (2004)

HyMARC

Multiscale approach for computing effective diffusion property

Demonstrated flexibility of microstructural morphology in computation

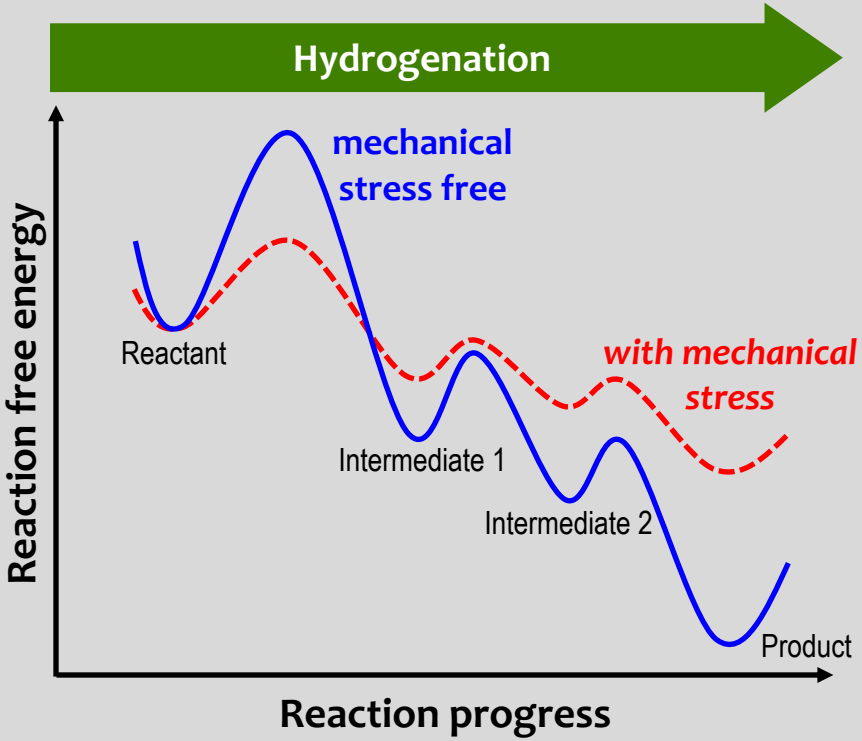




Our developed method can flexibly handle hydride microstructural features (*e.g.*, particle shape, size, *etc.*) for extracting effective mass transport properties.

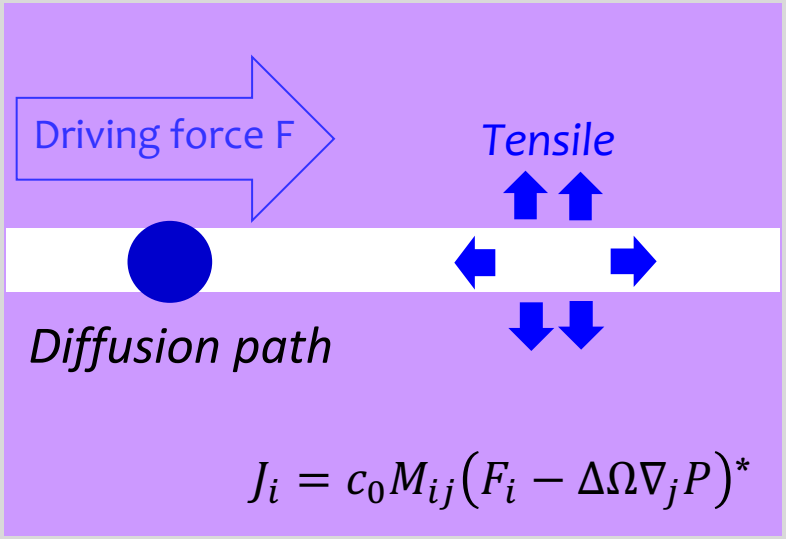
Possible impacts of mechanical stress/strain

Thermodynamics



- Destabilizing intermediates and product hydride
- Flattening the energy landscape
- Engineering thermodynamics ($P \cdot V$ term) for better reversibility & reaction kinetics

Diffusion kinetics



$$J_i = c_0 M_{ij}\left(F_i - \Delta\Omega \nabla_j P\right)^*$$

(J_i: flux, c_0: total concentration, M_{ij}: mobility, F_i: Driving force, $\Delta\Omega$: atomic dilation, P: local pressure)

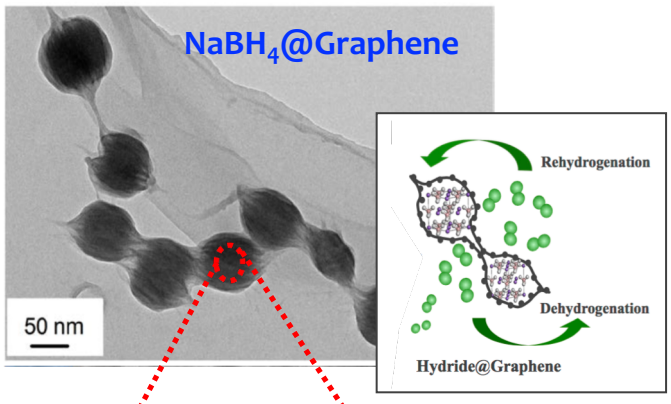
Local pressure

$$P = -\frac{\sigma_{ii} + \sigma_{jj} + \sigma_{kk}}{3}$$

* R. W. Balluffi, S. M. Allen and W. C. Carter, Kinetics of Materials, John-Wiley and Sons (2005)

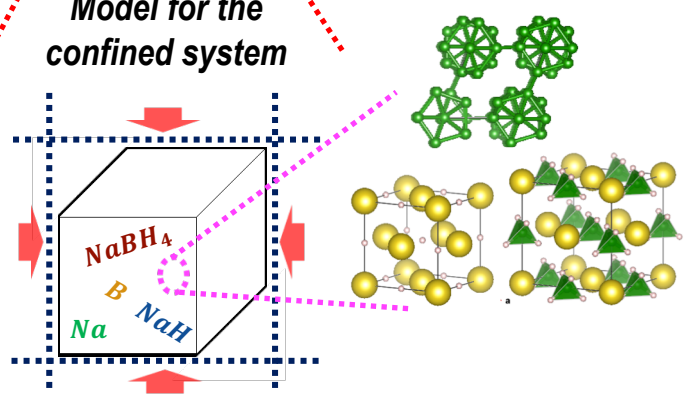
Multiscale modeling approach for computing strain energy

Hydrogenation induces significant volume expansion/structural transformation, leading to mechanical stress within hydrides in a confining medium



D.J. Liu et al., 2017 Annual Merit Review

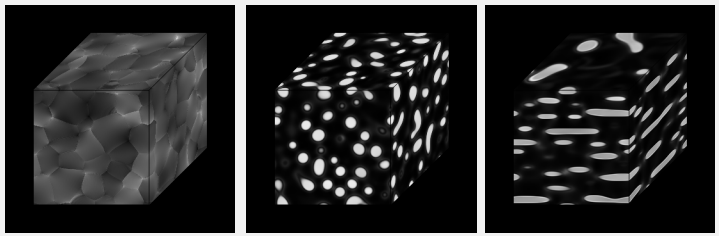
Model for the confined system



Computational procedure

- Generate a metal hydride microstructure using a ***phase-field simulation***
- Assign ***DFT-derived phase-dependent ideal elastic moduli & lattice parameters*** to corresponding grains/phases of the simulated microstructure
- Compute ***mesoscopic*** stress/strain fields for mechanical equilibrium under loads using the ***Microelasticity theory/computation method***

$$\nabla_j \sigma_{ij} = \nabla_j \left[C_{ijkl}(\vec{r}) \cdot \left\{ \bar{\epsilon}_{kl} + \delta\epsilon_{kl}(\vec{r}) - \epsilon^0_{kl}(\vec{r}) \right\} \right] = 0$$

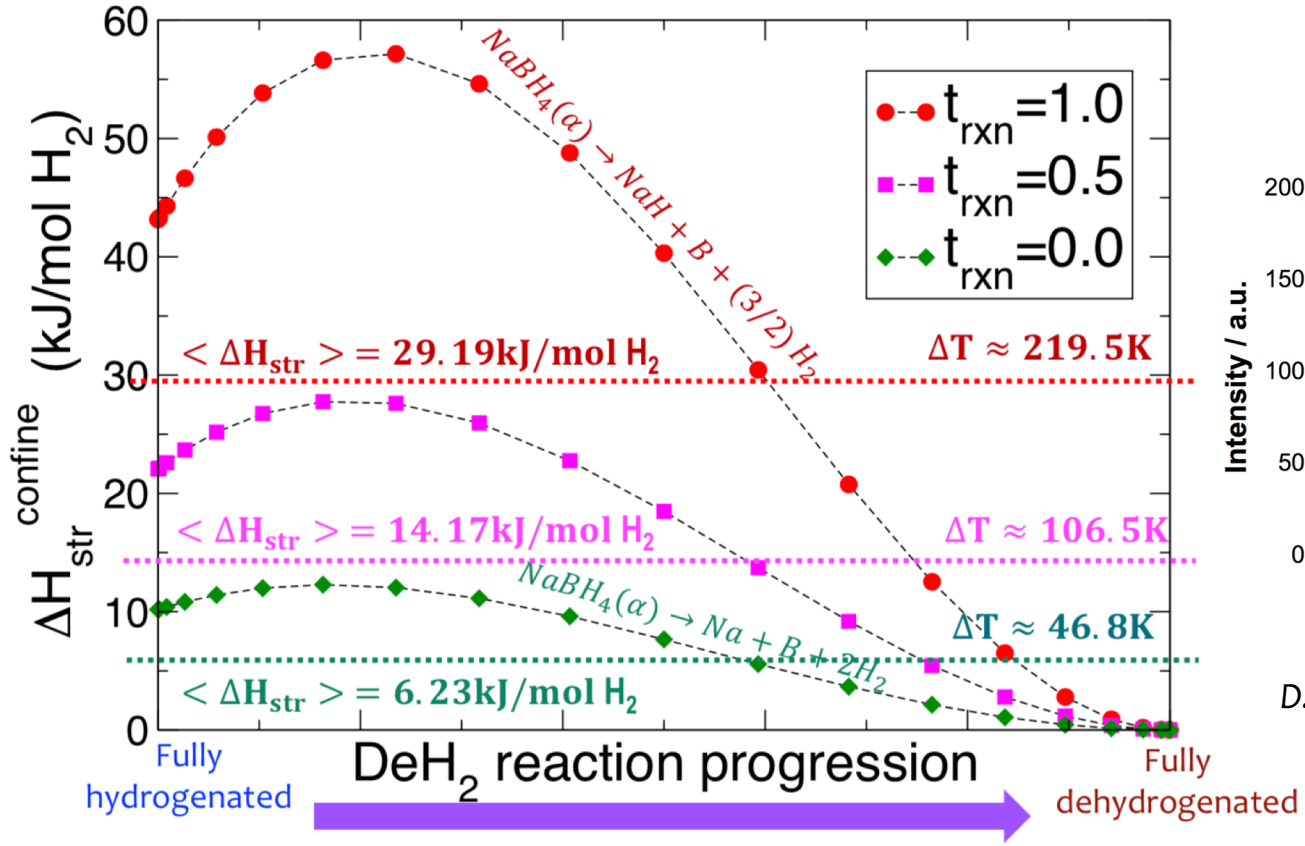


- Compute strain energy

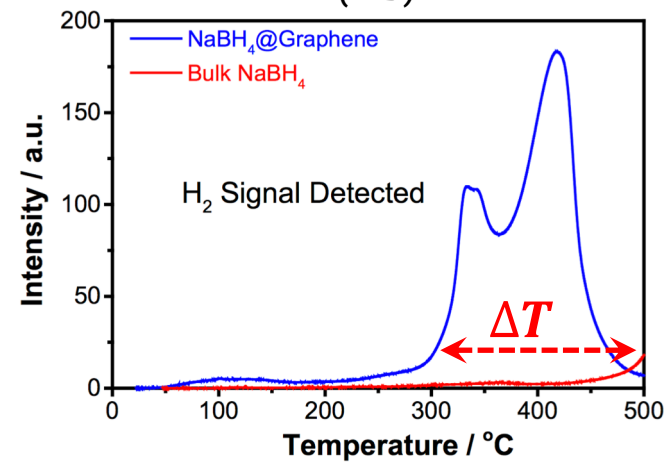
$$E_{str}(\vec{r}) = \frac{1}{2} C_{ijkl}(\vec{r}) \cdot \left\{ \bar{\epsilon}_{ij} + \delta\epsilon_{ij}(\vec{r}) - \epsilon^0_{ij}(\vec{r}) \right\} \cdot \left\{ \bar{\epsilon}_{kl} + \delta\epsilon_{kl}(\vec{r}) - \epsilon^0_{kl}(\vec{r}) \right\}$$

Impact of confinement strain energy on thermodynamics

HyMARC's multiscale modeling approach quantifies the destabilizing effect of confinement stress on reaction enthalpy due to volume expansion upon hydrogenation



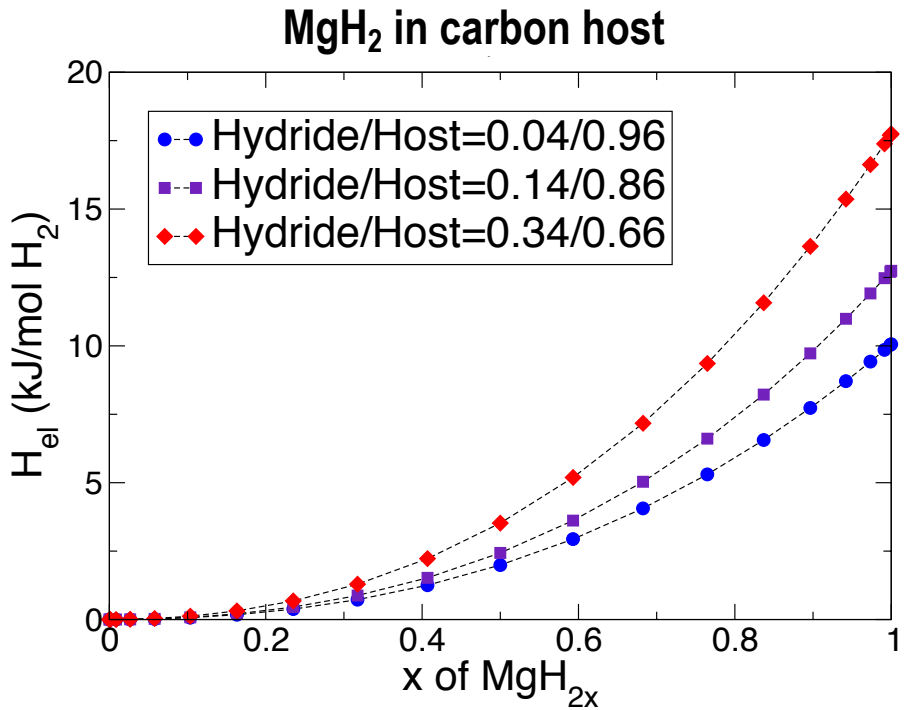
Temperature Programmable Desorption (TPD)

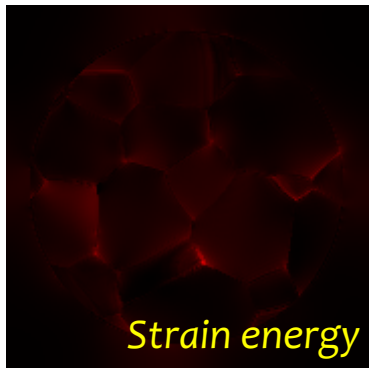


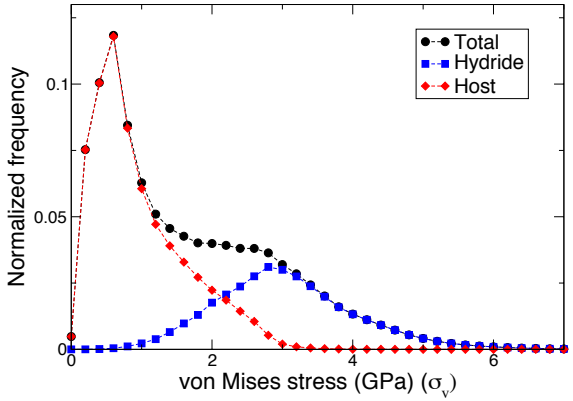
D.J. Liu et al., 2017 Annual Merit Review

Computed strain energy is relevant to the experimentally measured confinement effect on ΔT exhibited in TPD measurement of $NaBH_4$ (Interaction with ANL (D.J. Liu) seedling project).

Impact of confinement: Effect of loading





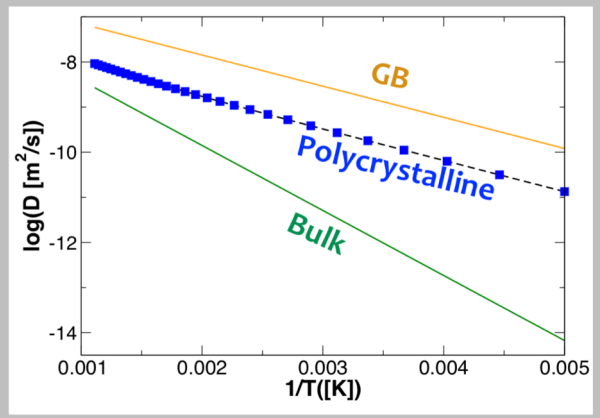


Loading can have a large effect on confinement stress

Impact of internal stress on diffusion property

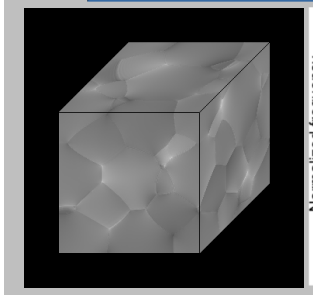
Diffusion property differently responds to internal stress depending on grain/particle size

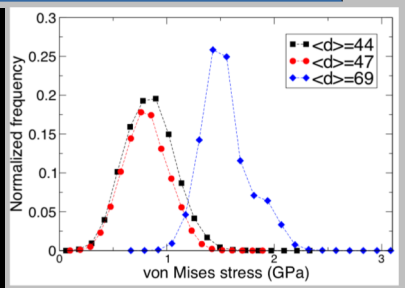
Effective diffusivity modeling



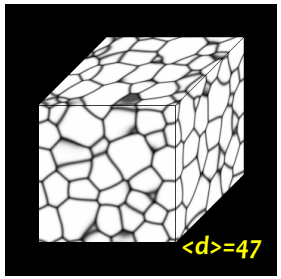
+

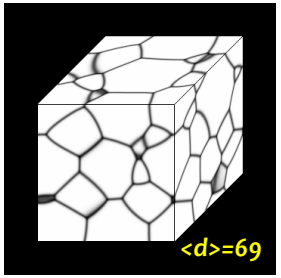
Internal stress/strain modeling

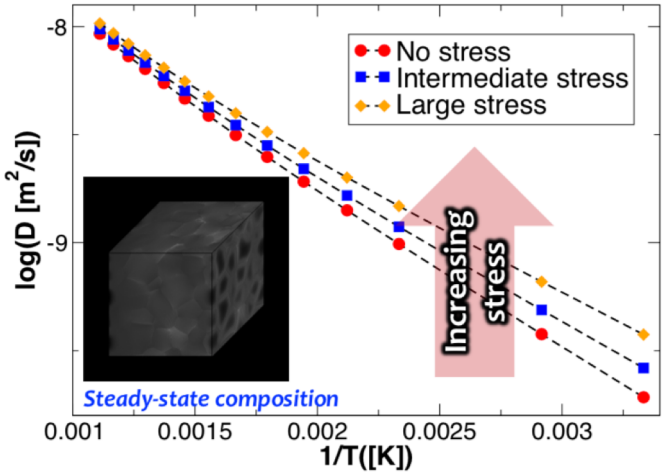


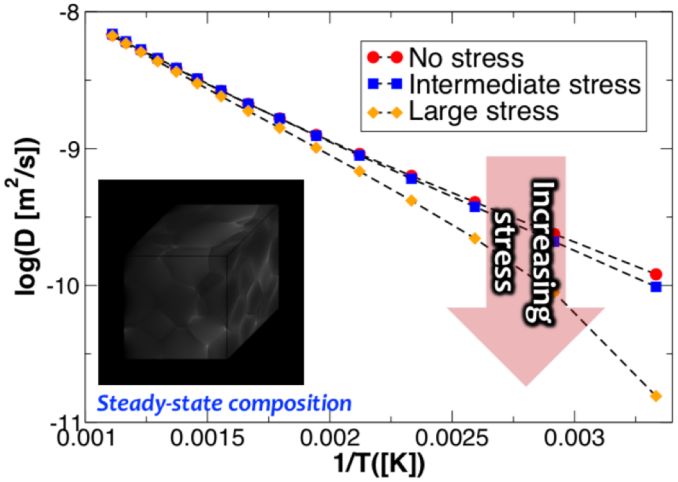


$$\nabla_i \cdot \left(D_{ij} \nabla_j X + (D_{ij} X / RT) \Delta\Omega \nabla_j P \right) = 0$$





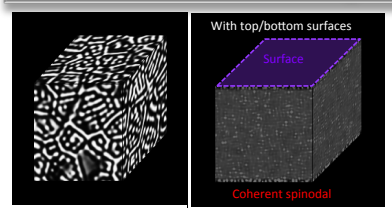




Grain/particle size affects not only diffusion length, but also internal stress distribution, resulting in diffusion property variation.

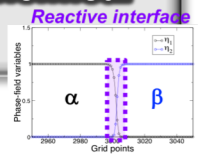
Modeling phase transformation mechanisms of metal hydrides

Model for Diffusional processes with surfaces and grain boundaries

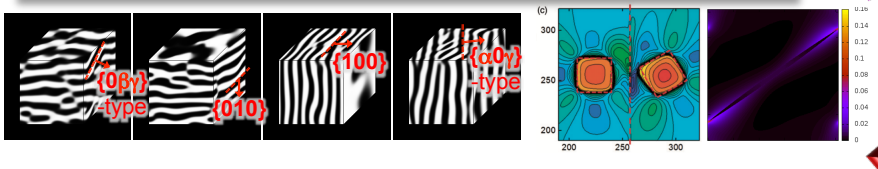


*e.g., **H diffusion** for Pd to PdH iso-structural transformation*

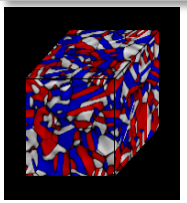
Model for Interfacial chemical reactions



Model for Mechanical stress effects due to lattice & volumetric strain

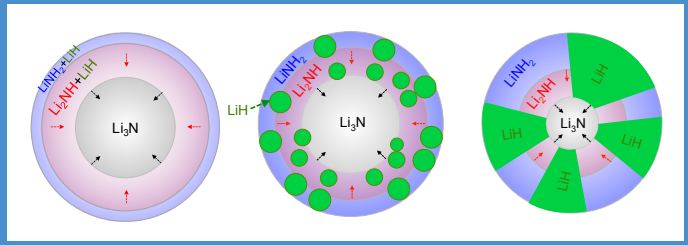


Model for Structural transformation with with surfaces and grain boundaries



*e.g., **hcp to tetragonal structural change** for Mg to MgH_2 hydriding*

Hydrogen storage materials with concurrent/complex phase transformations



e.g., $Mg(BH_4)_2$, $LiNH_2$/LiH, $NaAlH_4$, MgH_2, etc.

Diffusion

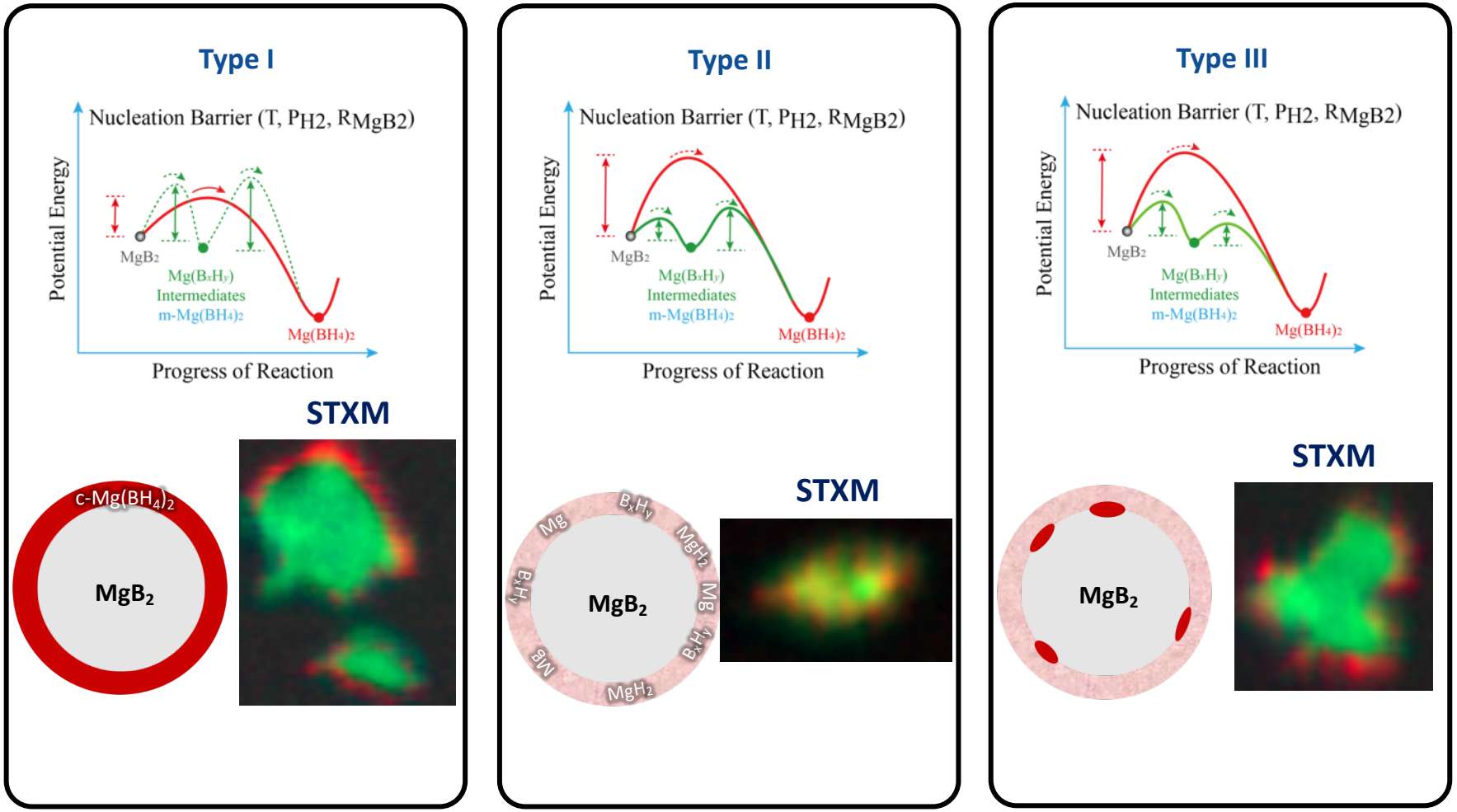
- Conventional atomic-jump mechanism
- Structural diffusion mechanism

Structural modification

- Crystallographic structural change mechanism
- Order-disorder transition mechanism

Phase nucleation kinetics modeling

Advanced nucleation model identifies three possible pathways of phase formation

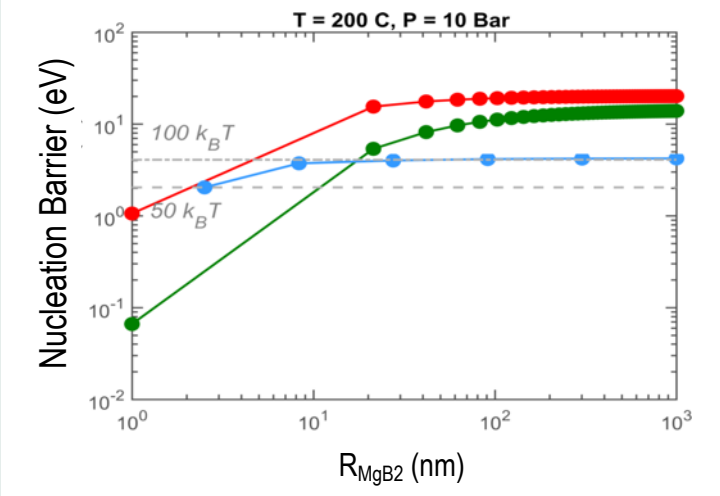


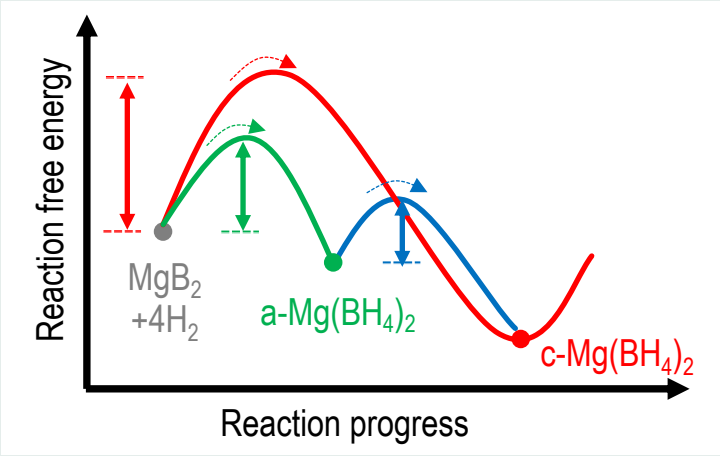
Predicted phase morphologies are being compared with STXM to identify pathways

Phase nucleation kinetics modeling

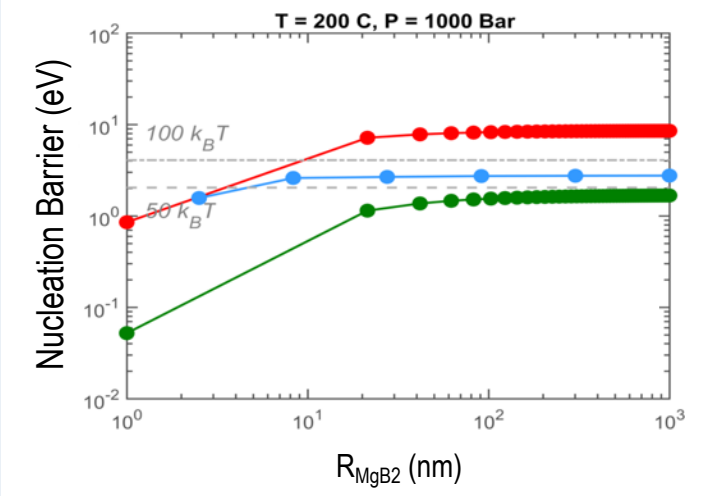
Nucleation kinetics favor two-step condensation-crystallization mechanism with pressure-dependent rate limitations

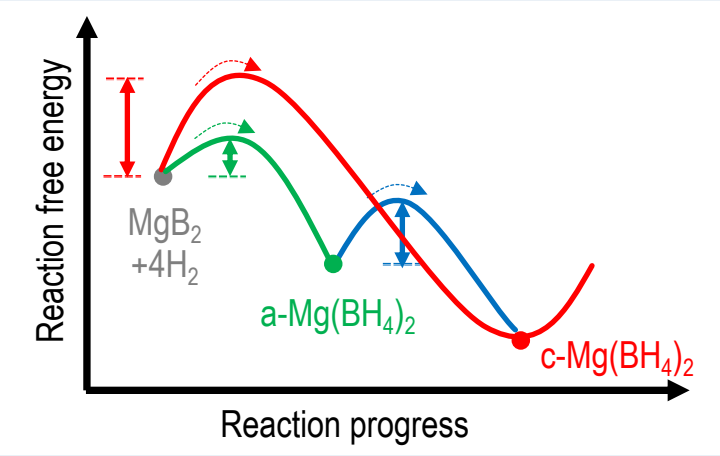
Low H_2 pressure





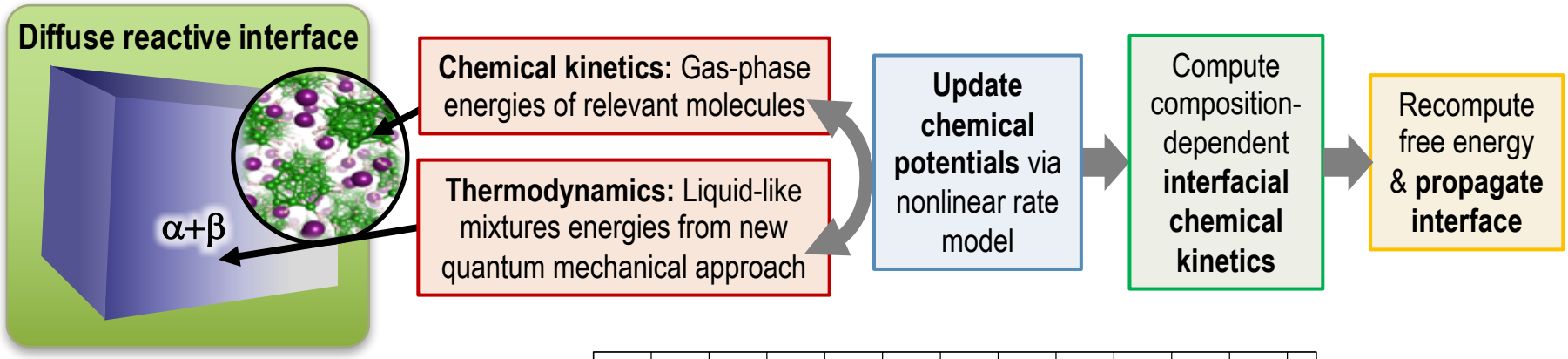
High H_2 pressure



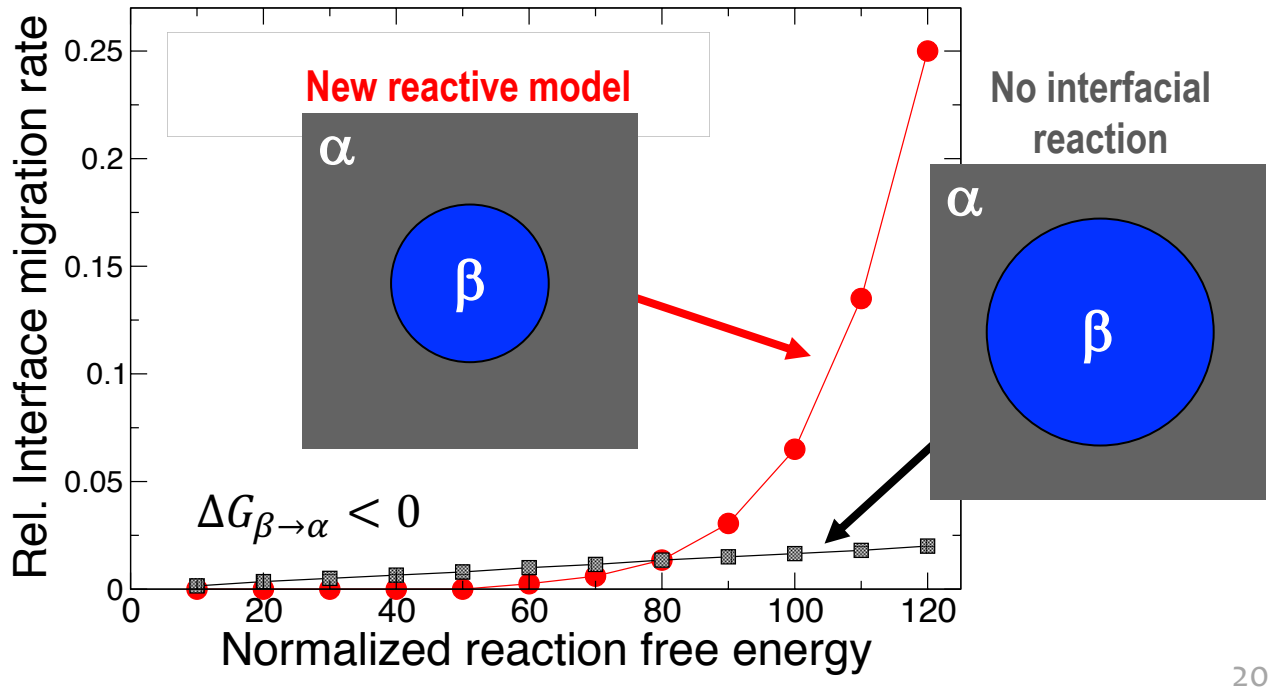


Modeling coupled processes of (re/de)hydrogenation

Diffuse Reactive Interface Nonlinear Kinetics (DRINK) model for (de)hydrogenation fronts controlled by materials & chemical kinetic processes



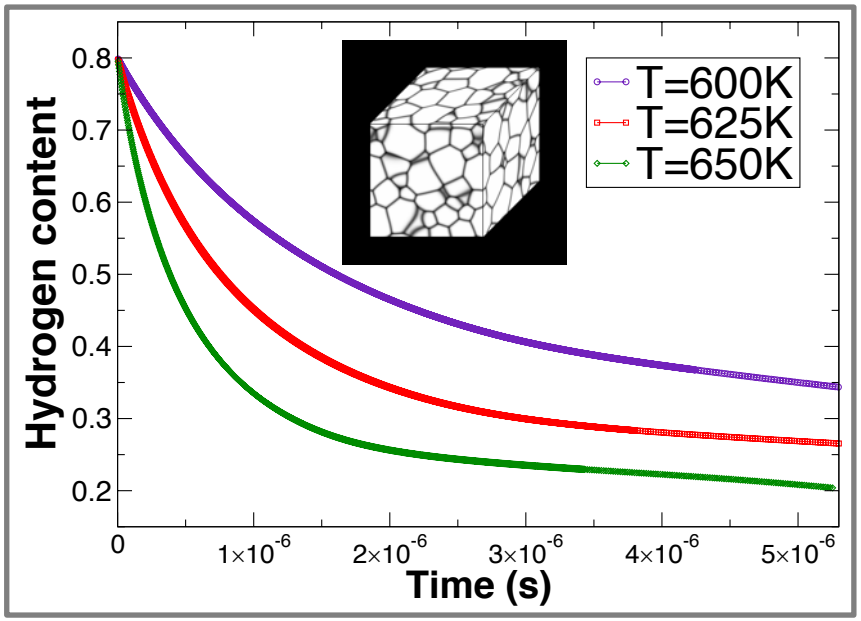
- **Integrate interfacial "chemical" and "materials" processes**
- **Generic approach for interfacial processes of metal hydrides (*e.g.*, Mg-B-H, Li-N-H, etc.)**

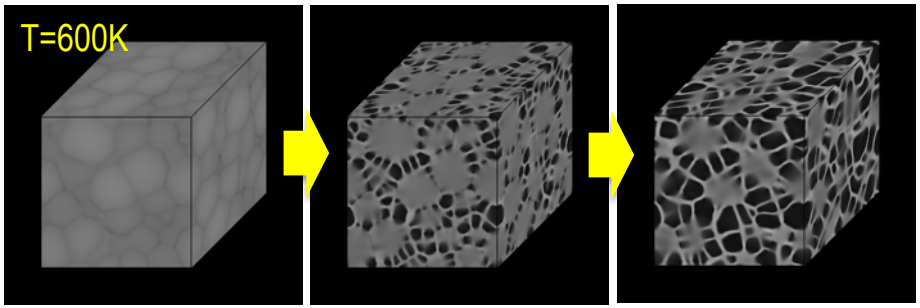


DRINK model progress: PdH_x dehydrogenation kinetics

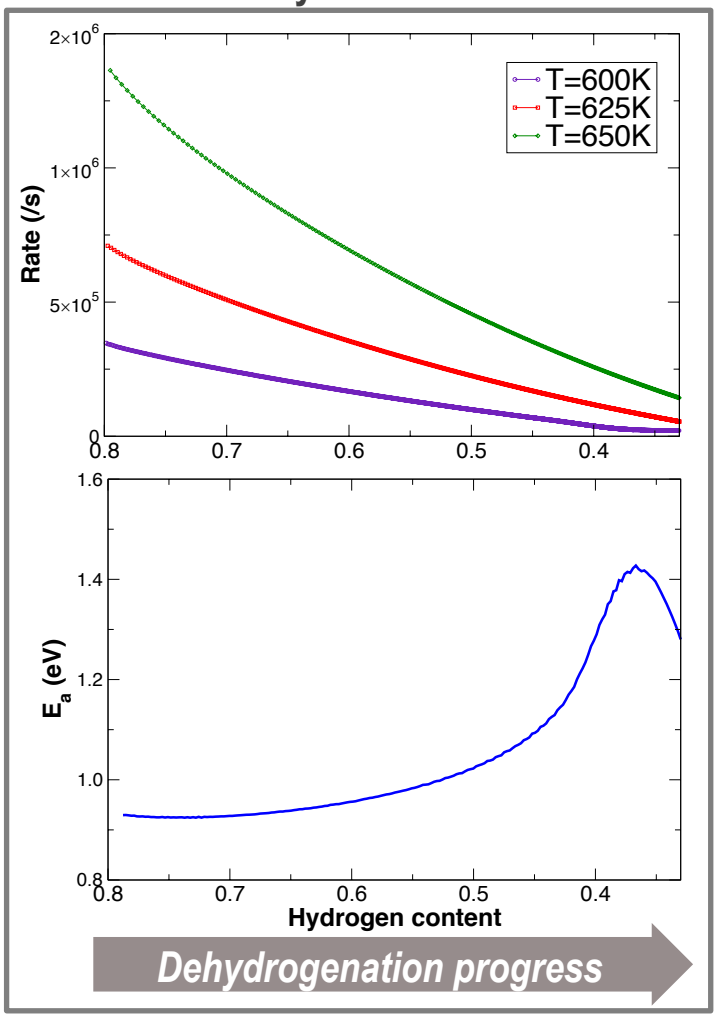
Diffuse Reactive Interface Nonlinear Kinetics model incorporates diffusion, phase transformation, stress, and chemistry to simulate (de)hydrogenation

Simulated dehydrogenation





Kinetic analysis of simulations



T.W. Heo, X. Zhou, S. Kang, B.C. Wood, *in preparation*

Summary

- EMN multi-national labs consortium ***HyMARC*** currently include and is actively developing validated modeling capabilities for investigating multiscale chemical and materials processes for hydrogen storage.
- Multiscale modeling plays significant roles in combining and integrating ***multiple chemical/materials processes*** taking place at ***various length and time scales*** as well as ***non-ideal*** materials factors.
- Integrated multiscale approaches are applied to investigate simple and complex hydrides focusing on
  - ***Beyond-ideal thermodynamics***
  - ***Mass transport kinetics***
  - ***Solid-solid interfaces/phase transformations***

Technical backup slides

Multi-scale modeling framework for simulating solid-solid phase transformation

Thermodynamics / kinetics parameters (Atomistic simulation)

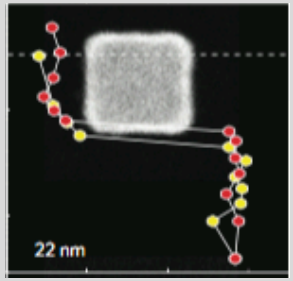
- Bulk, interface, surface energies
- Diffusivities
- Crystal structure and elastic moduli

Interfacial processes (Mechanistic understanding)

- Intercalation (*e.g.*, Pd-H)
- Diffusion with structure change (*e.g.*, Mg-H)
- Chemical reactions of ions (*e.g.*, Mg-B-H)

Particle geometry & reaction conditions

Experiment



Baldi *et al.*, *Nature Mater.* (2014)

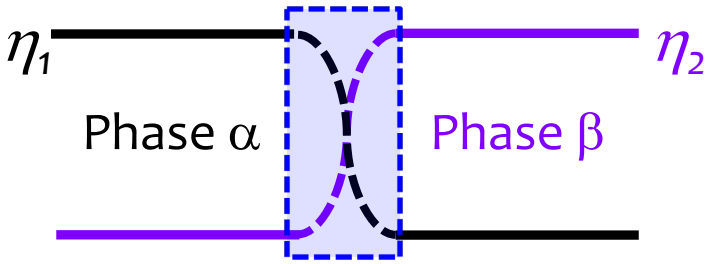
Simulation setup

Cuboidal crystal

Reaction condition (T, p_{H_2})

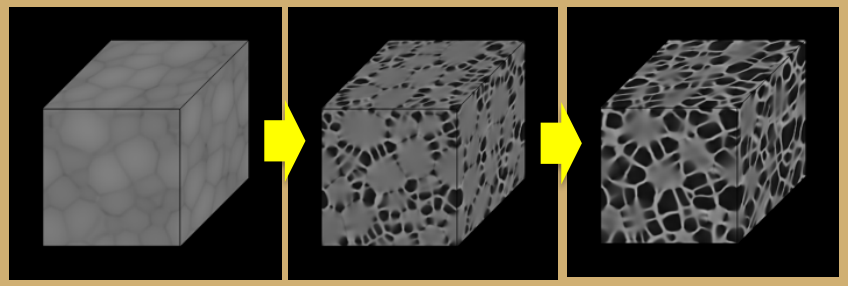
Phase-field modeling

Models for interfacial processes



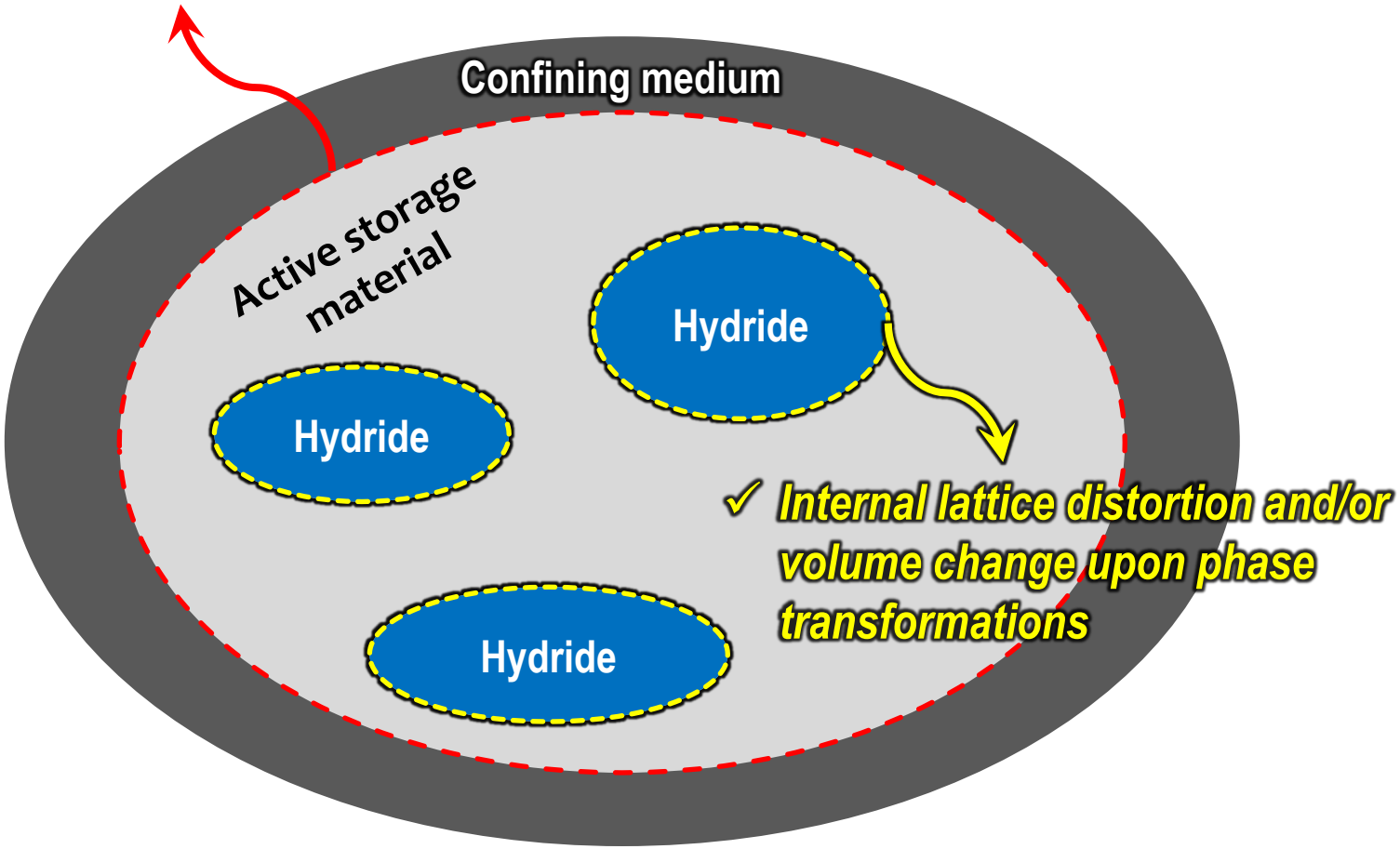
η_p: phase-field variable for phase p

Phase transformation during (de)hydrogenation



Sources of mechanical stresses during hydride formation

✓ *External constraint by the confining medium*



✓ *Internal lattice distortion and/or volume change upon phase transformations*