ATOMISTIC SIMULATIONS OF HYDROGEN STORAGE MATERIALS

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Three Topics

1. H Diffusion in PdH_x
2. Molecular Dynamics for MgH_x
3. “Molecular” Dynamics for Mg-B-H

The First Topics

H Diffusion in PdH_x

Statistically Averaged Diffusivities

- Coordinates of N hydrogen atoms (i = 1, 2, …, N) at t = jΔt, j = 1, 2, …, m (m = $t_{MD}/\Delta t$) are $\alpha_i(t)$.
- m+1-k displacement measurements for hydrogen atom i over a kΔt period: $\Delta\alpha_{i,j}(k\Delta t) = \alpha_i(j\Delta t - \Delta t + k\Delta t) - \alpha_i(j\Delta t - \Delta t)$ where j = 1, 2, …, m+1-k.
- This allows calculations of hydrogen mean square displacement
- Mean square displacement is fitted to diffusivities D

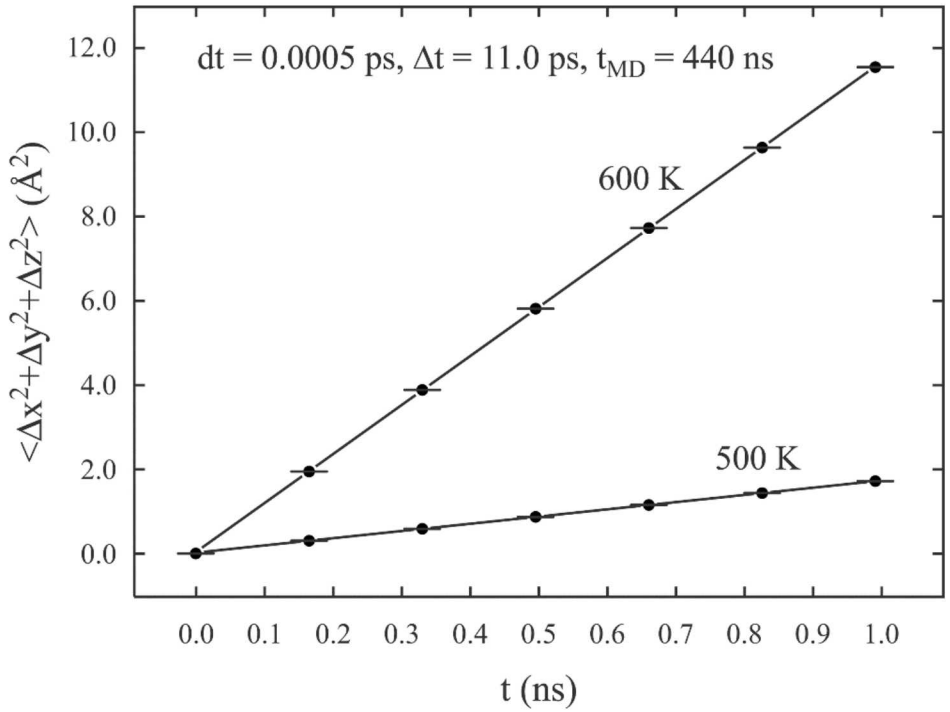
$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = \frac{\sum_{i=1}^{N}\sum_{j=1}^{m+1-k}\left[\Delta\alpha_{i,j}(k\Delta t)\right]^2}{N(m+1-k)}$$

$$\left\langle \left[\Delta\alpha(k\Delta t)\right]^2 \right\rangle = 2D_\alpha t$$

$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 4D_{xz} t$$

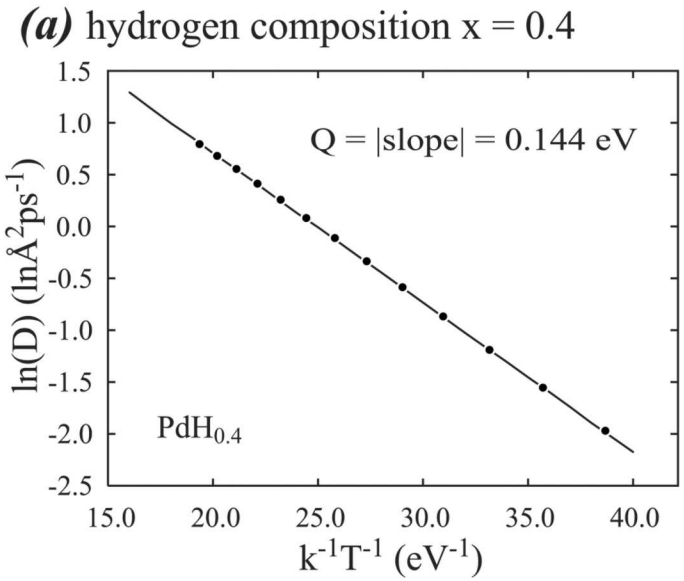
$$\left\langle \left[\Delta x(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta y(k\Delta t)\right]^2 \right\rangle + \left\langle \left[\Delta z(k\Delta t)\right]^2 \right\rangle = 6D_{xyz} t$$

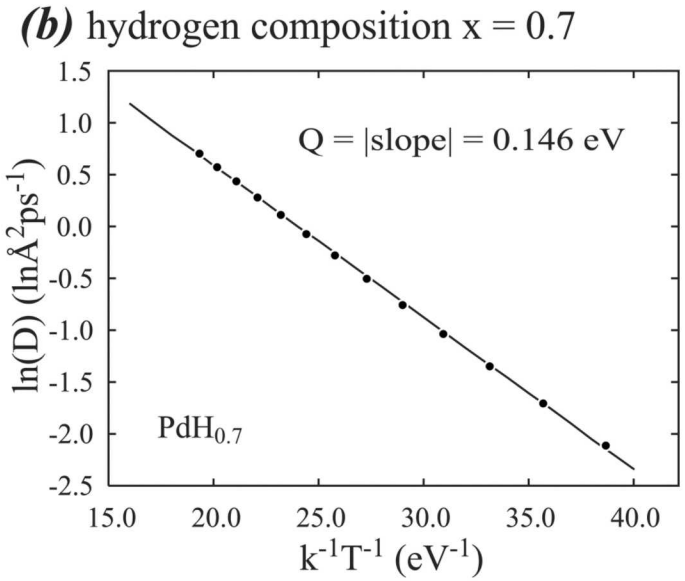
MSD

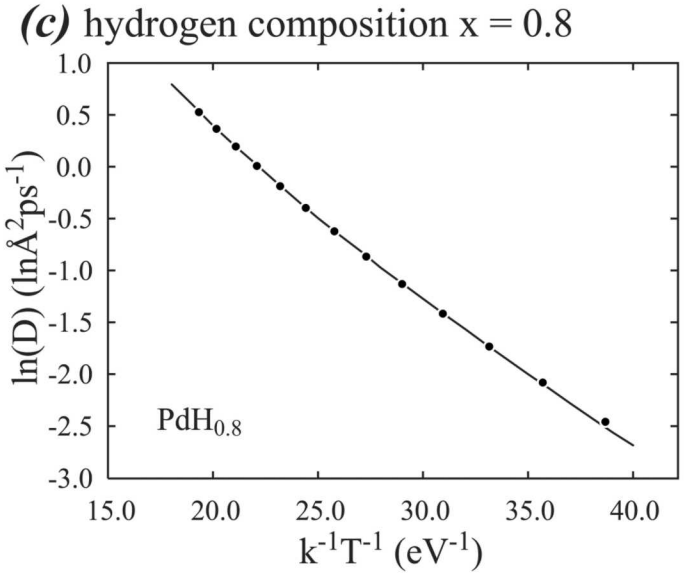


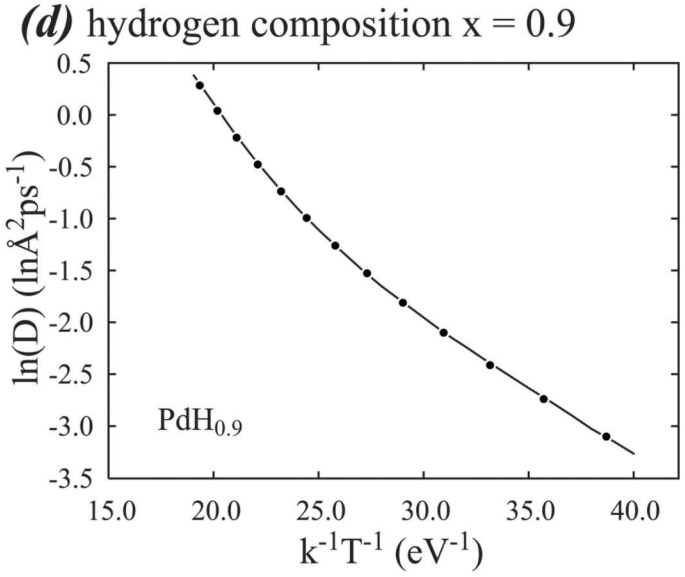
PdH_x: Bulk Diffusion

t_{MD} = 2.2 ns









- Arrhenius plots account for all diffusion pathways
- MD results fall exactly on lines (~ 0 errors)
- The MD does not have time and length scale issues
- Hydrogenation leads to non-linear Arrhenius behavior

PdH_x: Experimental Validation

Table I. Measured and predicted activation energy Q and pre-exponential factor D_0 as a function of phase and temperature.

Authors	Phase	T (K)	Q (eV)	D_0 (Å^2/ps)
Arons et al [2,3]	β	110-300	0.210	---
		50-100	0.150	---
Cornell et al [4]	β	195-300	0.228	---
		100-195	0.100	---
Mazzolai et al [5]	β	250-270	0.210	---
		130-200	0.130	---
Burger et al [6]	β	230-320	0.210	---
		180-230	0.060	---
Torrey et al [7]	β	>220	0.240	---
		<220	0.080	---
Beg et al [15]	β	293-473	0.146	1.10×10^{1}
Seymour et al [16]	β	296-413	0.229	9.30×10^{0}
Davis et al [17]	β	300-400	0.228	3.00×10^{1}
Majorowski et al [18]	β	208-338	0.287	1.13×10^{2}
Bucur [19]	α	278-323	0.054	2.48×10^{1}
Holleck [20]	α	533-913	0.055	2.94×10^{1}
Simmons et al [21]	α	273-650	0.062	6.10×10^{1}
Maeda et al [22]	α	773-1373	0.215	2.80×10^{1}
Hara et al [23]	α	523-773	0.219	2.40×10^{1}
Pietrzak et al [24,25]	α	273-473	0.230	2.20×10^{1}
Yoshihara et al [26]	α	273-350	0.231	2.91×10^{1}
Zuchner [27]	α	200-700	0.250	5.25×10^{1}
MD fitted Eqs. (1) - (5)	α	300-600	~0.15	$\sim3.5\times10^{1}$
	β (x=0.8)	600	~0.20	$\sim7.8\times10^{1}$
	β (x=0.8)	300	~0.14	$\sim1.7\times10^{1}$

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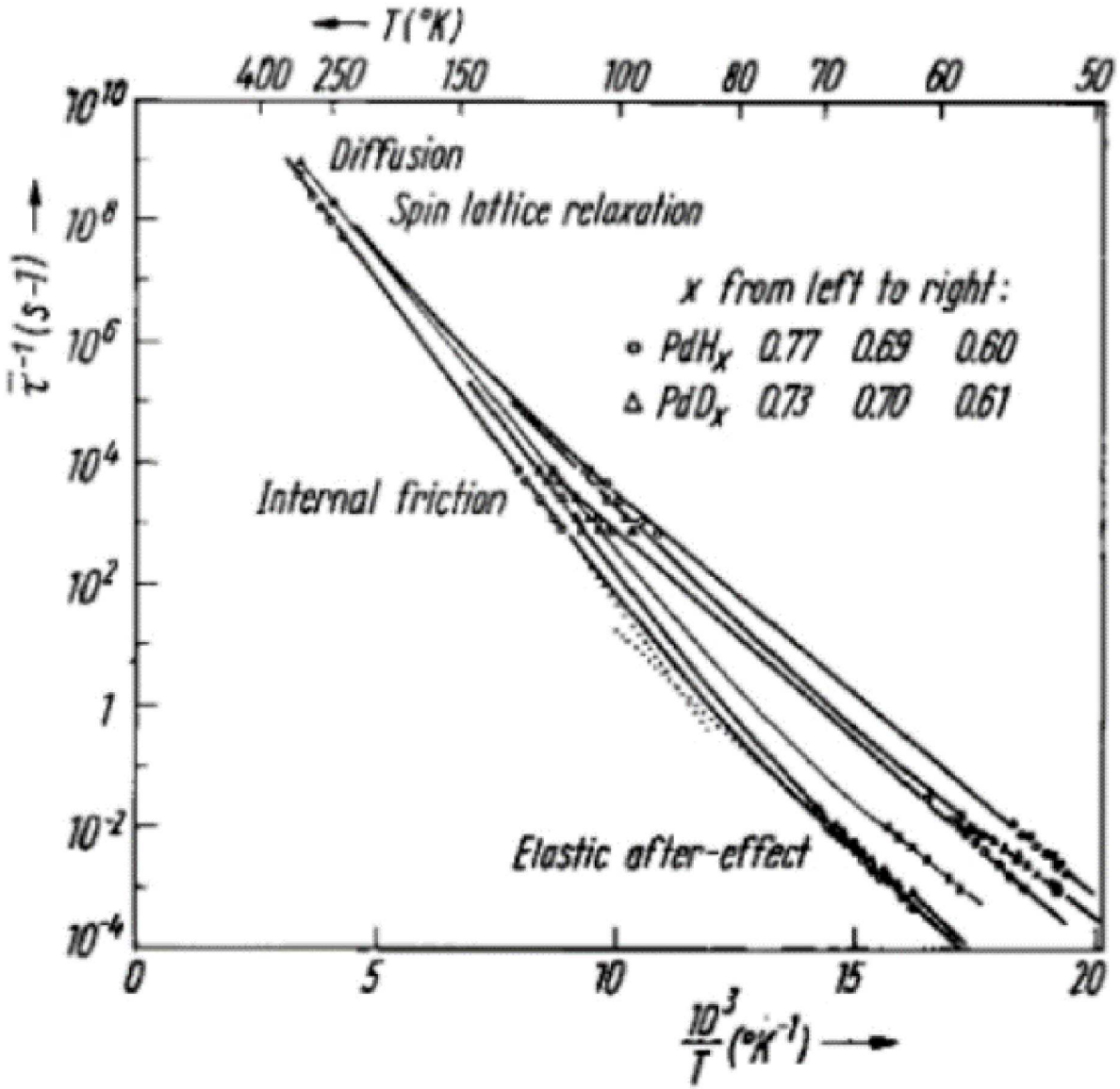


Arons et al, Phys. Stat. Sol. 1970, 40, 107

The Second Topic

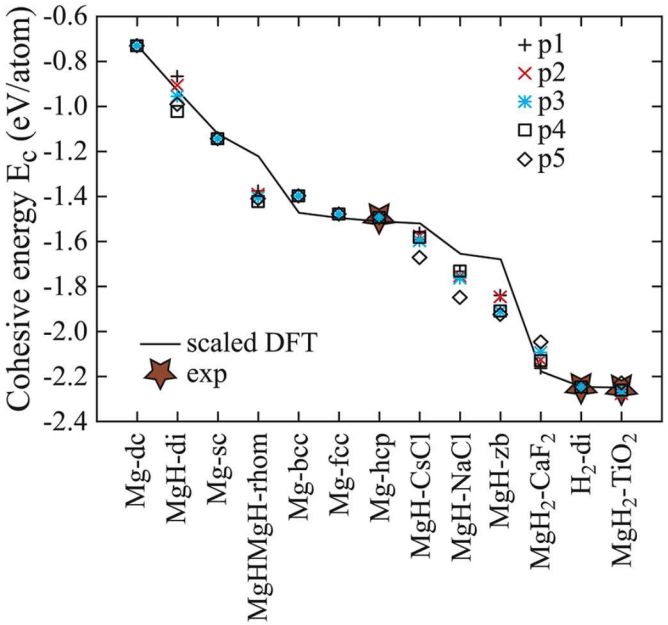
Molecular Dynamics for MgH_x

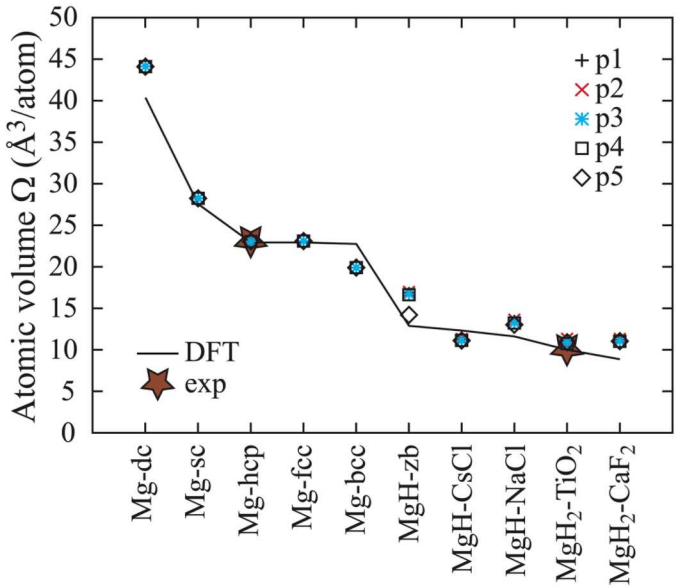
One Criterion to Emphasize for Potential

1. Must ensure stable simulations of the phase being studied
2. This phase therefore has a lower energy than any other configurations
3. Any other configurations include infinite number of amorphous structures
4. Very difficult to achieve because cannot possibly include infinite number of amorphous phases in the fitting
5. Crystalline growth simulation is sufficient to validate that a potential satisfies this criterion

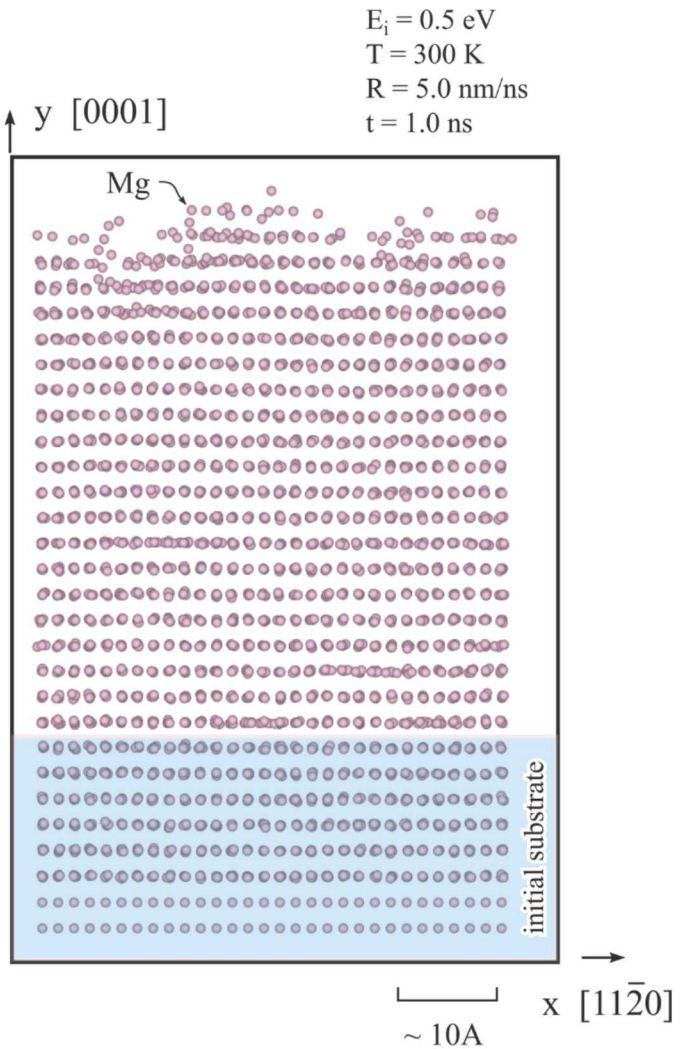
MgH_x: Transferability

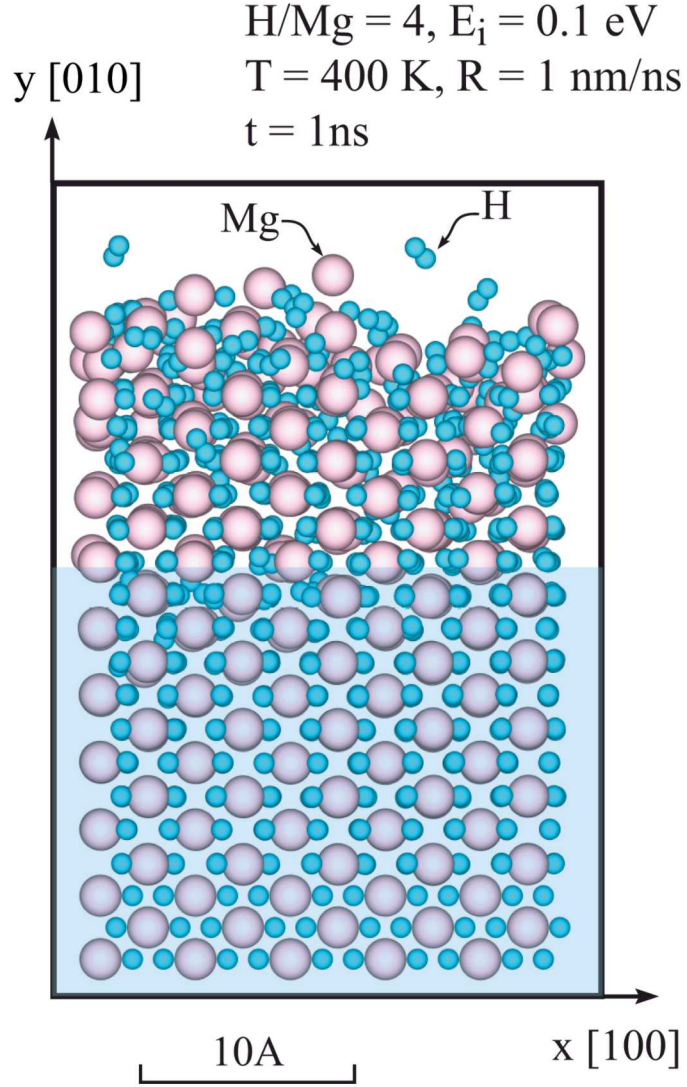
Energy / volume trends of phases





Mg-hcp and MgH_2-rutile growth simulations





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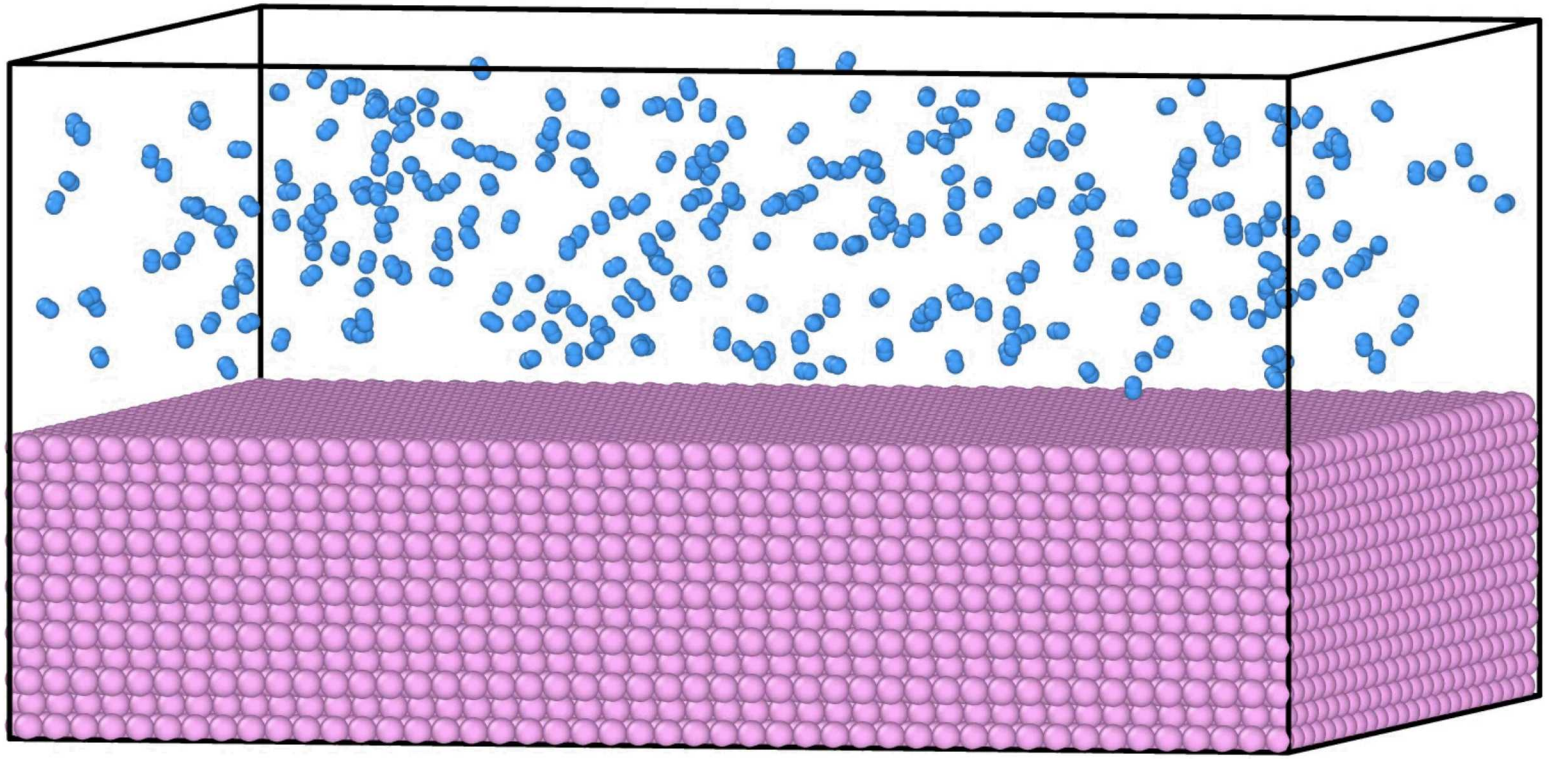
MgH_x: H Component



The Third Topic

“Molecular” Dynamics for Mg-B-H

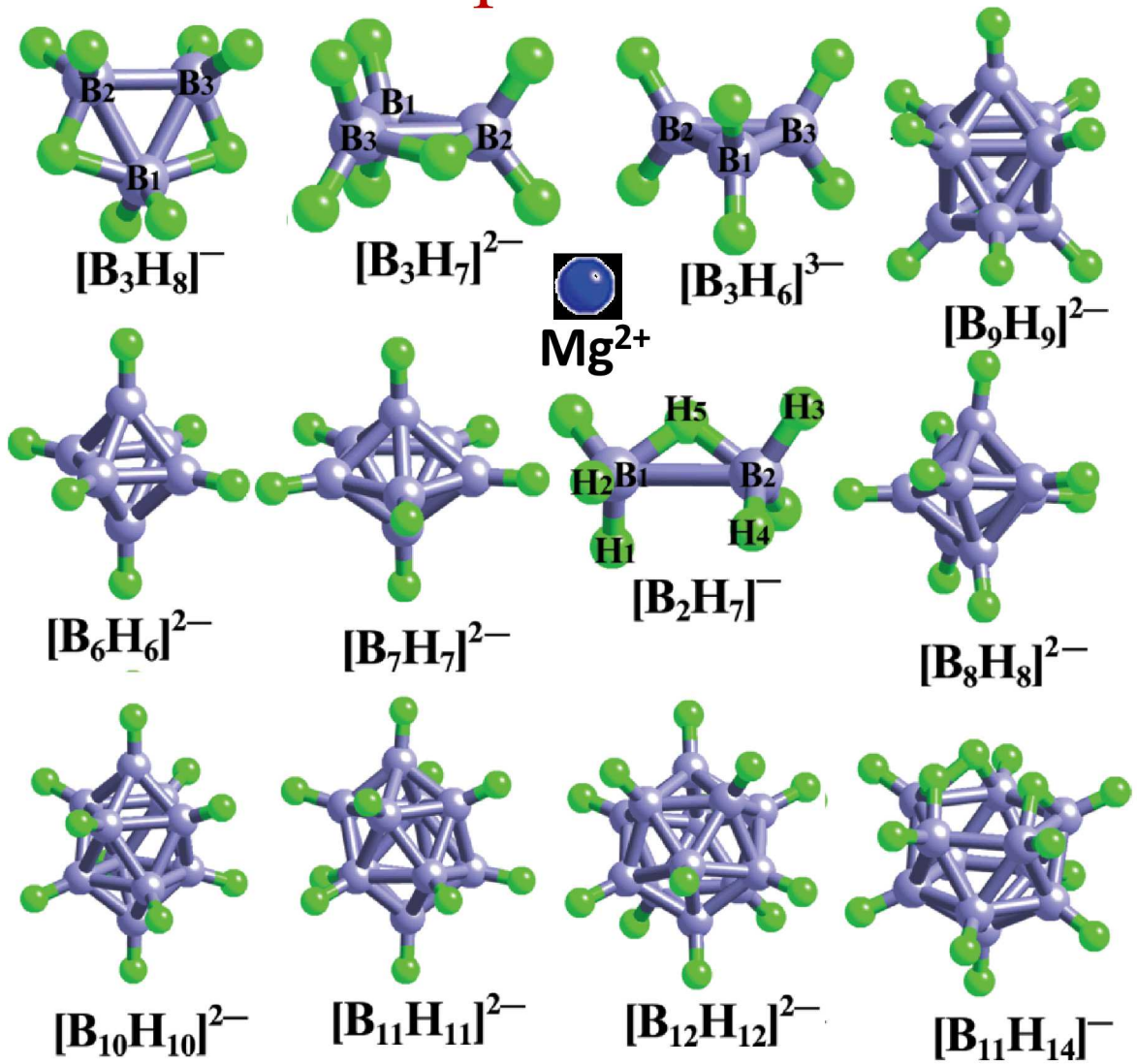
Mg-B-H Potential - Motivation

- Hydrogen is an efficient and clean energy carrier
- Solid state hydrogen storage materials draw interests due to an ideal combination of volumetric and gravimetric densities
- HyMARC (Hydrogen Materials Advanced Research Consortium) aims to develop an understanding on how to improve (de)hydrogenation kinetics
- Magnesium boron hydrides are one type of materials being explored within HyMARC

Perspective

- LLNL is developing a phase field model for (de)hydrogenation kinetics of MgBxHy
- The phase field model requires thermodynamic and kinetic properties as inputs
- Many molecules may occur, and many exhibit amorphous structures ⇒ challenging for DFT studies
- We will use MD to fill the gaps

Example Molecules



Molecular Dynamics Challenges

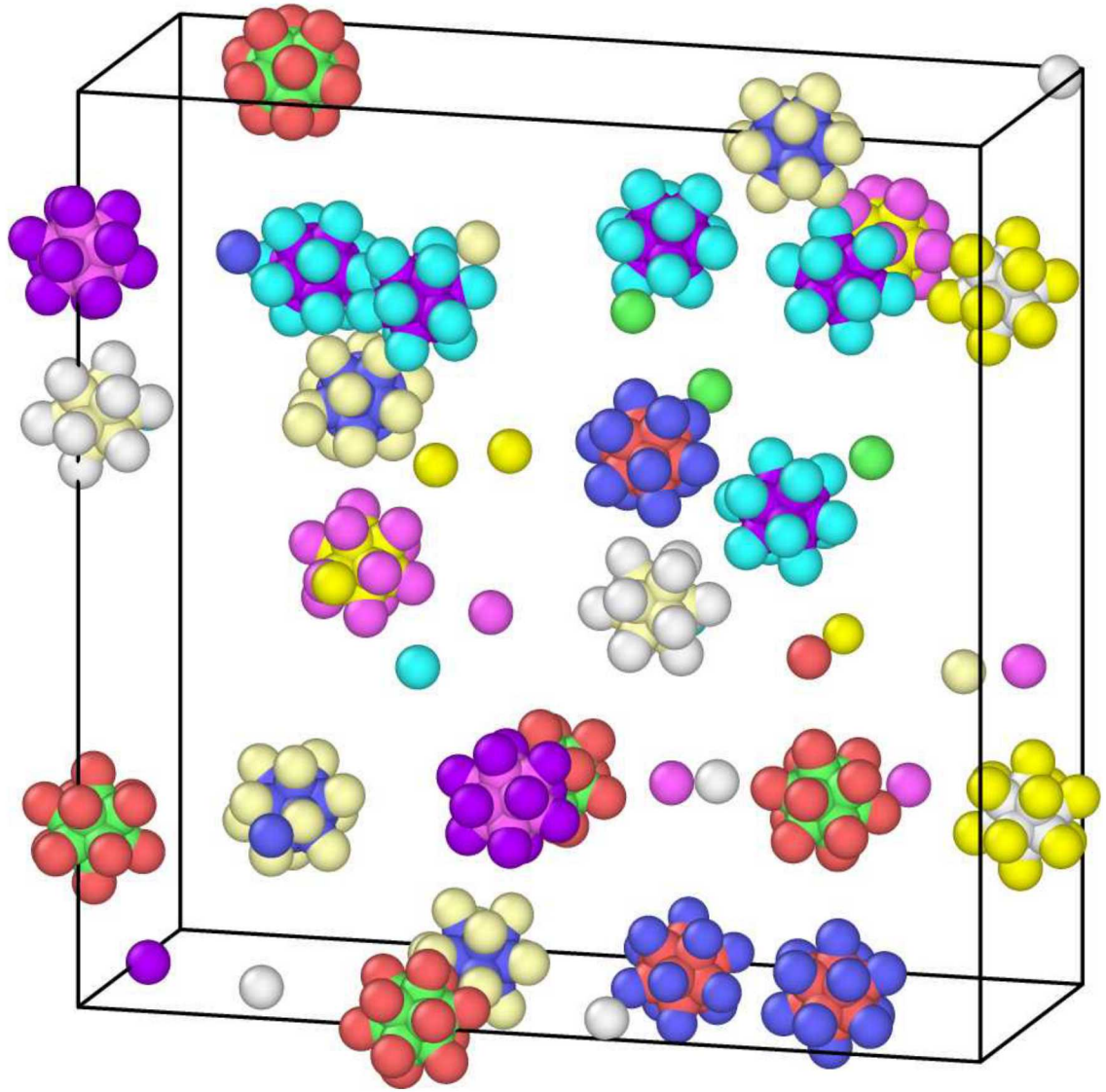
- Traditional MD can only simulate atoms, but we have molecules
- We will develop an innovative "molecular" dynamics method
  - An intra-molecule force field to stabilize molecules
  - An inter-molecule force field to capture energetics
  - MD must track which atom is in which molecule
- As a first trial, we parameterize force fields DFT energies between two isolated molecules
- Five molecules (Mg, H_2, MgH_2, BH_4, $B_{12}H_{12}$) are considered

36 Inter-Molecule Interactions

- For a Mg + H_2 + BH_4 + MgH_2 + $B_{12}H_{12}$ model, there are 36 inter-molecule interactions:

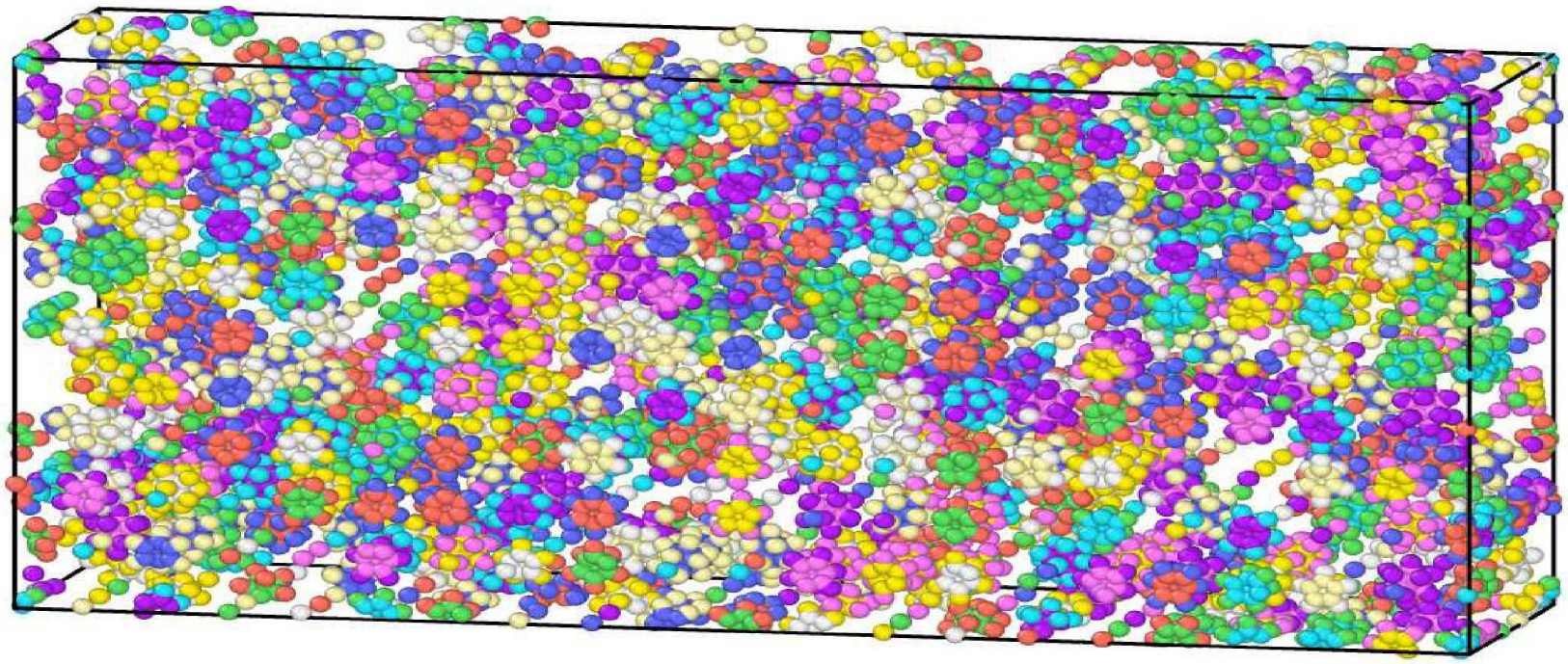
Mg-Mg(Mg-Mg), Mg-H_2(Mg-H), Mg-BH_4(Mg-B,Mg-H), Mg-MgH_2(Mg-Mg,Mg-H), Mg-$B_{12}H_{12}$(Mg-B,Mg-H), H_2-H_2(H-H), H_2-BH_4(H-B,H-H), H_2-MgH_2(H-Mg,H-H), H_2-$B_{12}H_{12}$ (H-B,H-H), BH_4-BH_4(B-B,B-H,H-H), BH_4-MgH_2(B-Mg,B-H,H-Mg,H-H), BH_4-$B_{12}H_{12}$(B-B,B-H,H-B,H-H), MgH_2-MgH_2(Mg-Mg,Mg-H,H-H), MgH_2-$B_{12}H_{12}$(Mg-B,Mg-H,H-B,H-H),$B_{12}H_{12}$-$B_{12}H_{12}$(B-B,B-H,H-H)

MD Implementation



- Atom-based MD does not know molecules
- Assign different atom types for different molecules
- Create mapping tables between atom types and pair interactions

MgB_xH_y: "Molecular" Dynamics Simulation



SUMMARIES

- MD effectively determine H diffusivities in PdH_x
- Our Mg-H bond order potential can simulate MgH_2 growth
- "Molecular" dynamics simulations of Mg-B-H systems are possible