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RECENT INTERATOMIC POTENTIAL DEVELOPMENT ACTIVITIES AT SANDIA

X. W. Zhou, N. Bartelt, R. B Sills, C. D. Spataru, and M. D. Allendorf

Sandia National Laboratories, CA, USA

S. Kang, T. W. Heo, and B. C. Wood

Lawrence Livermore National Laboratory, CA, USA

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Two Topics

- **Pd-H-He potential**
- **Mg-B-H potential**

Pd-H-He Potential - Motivation

- Pd is a solid-state tritium storage material
- Tritium decays to He, forming He bubbles
- Bubbles causes PCT shift, swelling, He release, all leading to failures
- MD can study bubble nucleation / growth

Criteria for Acceptable Pd-H-He Potential

- Octahedral interstitial sites in fcc
- Low He diffusion barrier (~0.1 eV)
- Large He swelling (~10 $Å^3$)
- Short He-He spacing in Pd (~1.7 Å)
- Non-bonding in pure He (equation of state)
- Strong He-He attraction in Pd (~-0.85 eV)
- Correct volume and energy for PdHe rock-salt
- Correct Pd vacancy and He insertion energies as a function of He number
- Stringent MD tests

Two Paradoxes

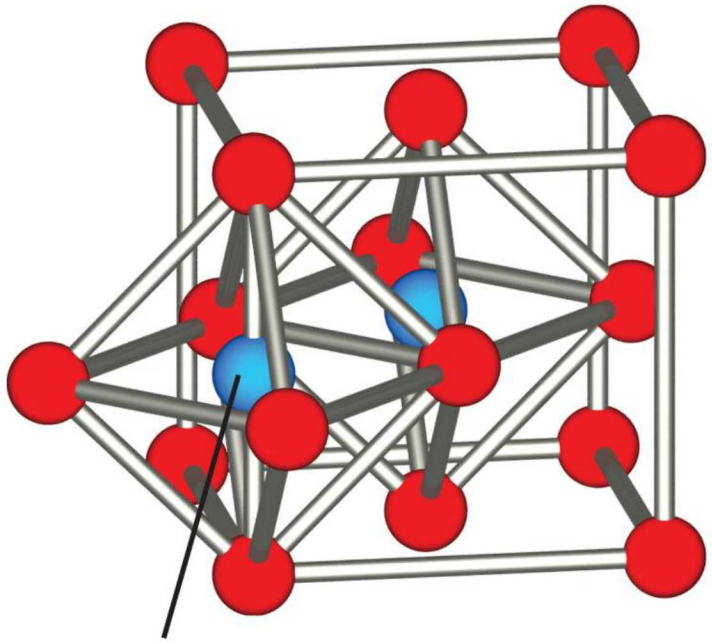
- Increasing swelling is against a low diffusion energy barrier
- Increasing He-He attraction in Pd is against He-He repulsion in pure He

Past MD Simulations of He Bubbles

- Two papers are published after 2016
- Nuc. Sci. Tech. 27, 106 (2016) prescribes incorrect tetrahedral H sites and manually creates He bubbles
- J. Chem. Phys. 144, 194705 (2016) prescribes a He diffusion energy barrier of > 3.0 eV
- He bubbles in W have been successfully studied, see, for example, Nucl. Fusion, 53, 073015 (2013), and J. Nucl. Mater., 432, 61 (2013)

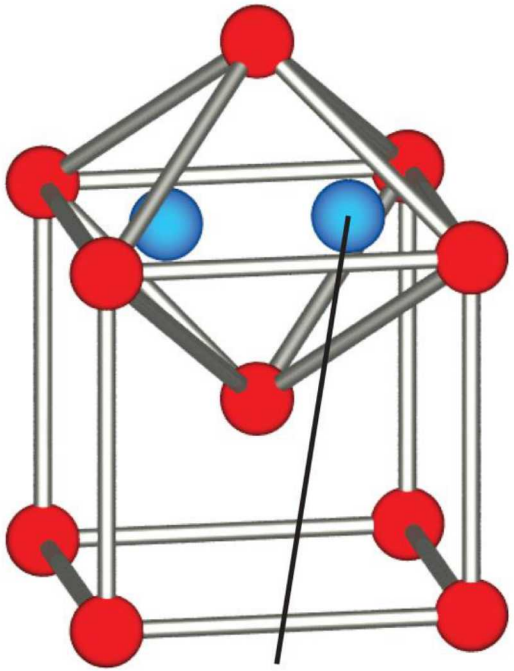
Difference between Pd and W

(a) He sites in fcc Pd



octahedral sites
(with spacing = 2.75 Å)

(b) He sites in bcc W



tetrahedral sites
(with spacing 1.58 Å)

DFT He-He spacing in Pd = 1.7 Å

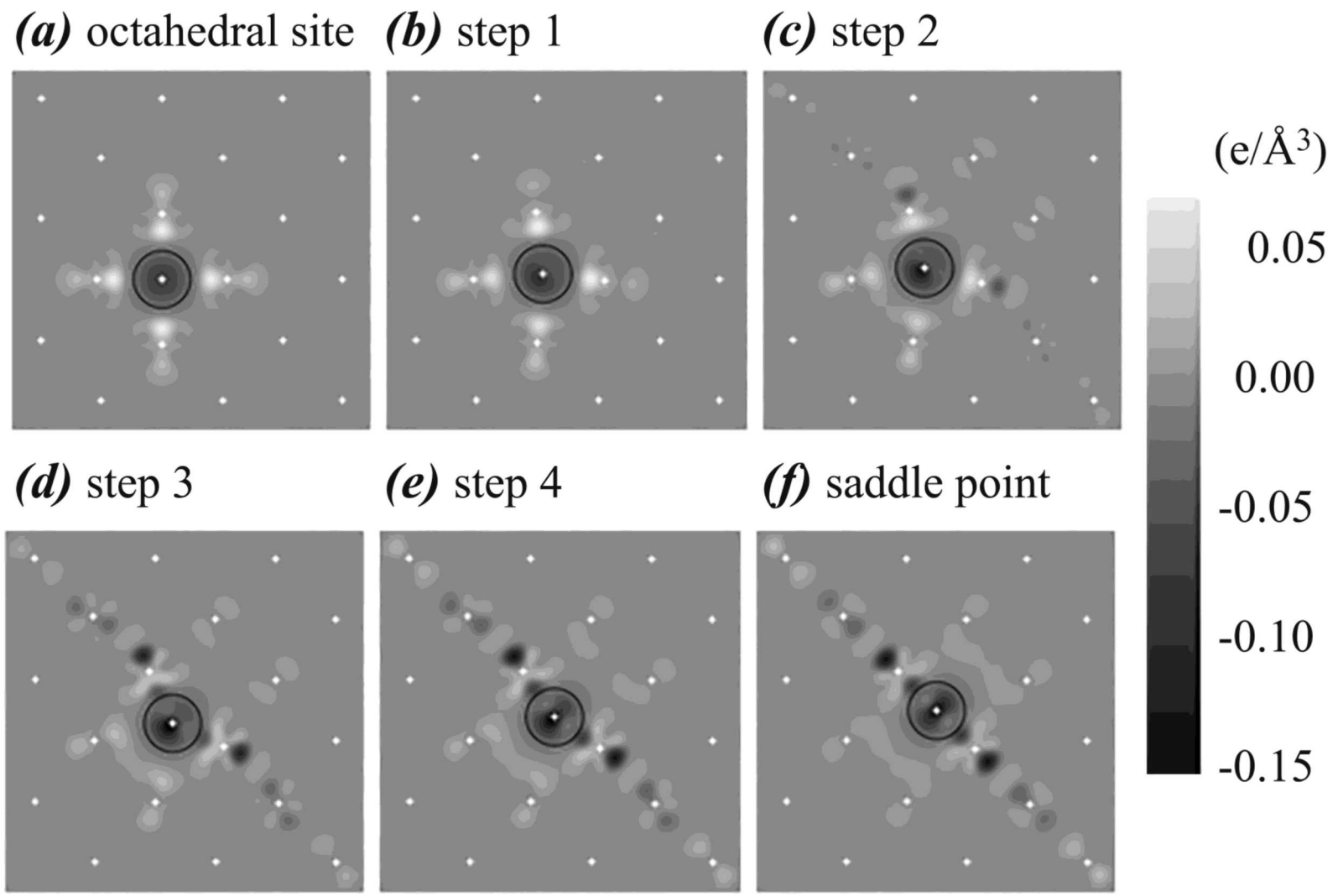
- **He at octa sites in fcc Pd but tetra sites in bcc W**
- **Diffusion barrier is smaller in bcc than in fcc**
- **Octa spacing in Pd is way longer than He-He spacing**
- **Tetra spacing in W is short than He-He spacing**

Solution

- **Use the EAM potential by Finnis-Sinclair*: $\rho_i = \rho_j^i(r_{ij})$, as opposed to the one by Daw-Baskes**: $\rho_i = \rho_j(r_{ij})$**
- **Electron density created by Pd at He sites is negative**
- **Electron density created by He at He sites is positive**
- **He embedding energy is minimum at zero electron density**
- **Use EAM's many-body effect to increase swelling**

*Phil. Mag. A 50, 45 (1984), **Phys. Rev B. 29, 6443 (1984).

DFT Justification

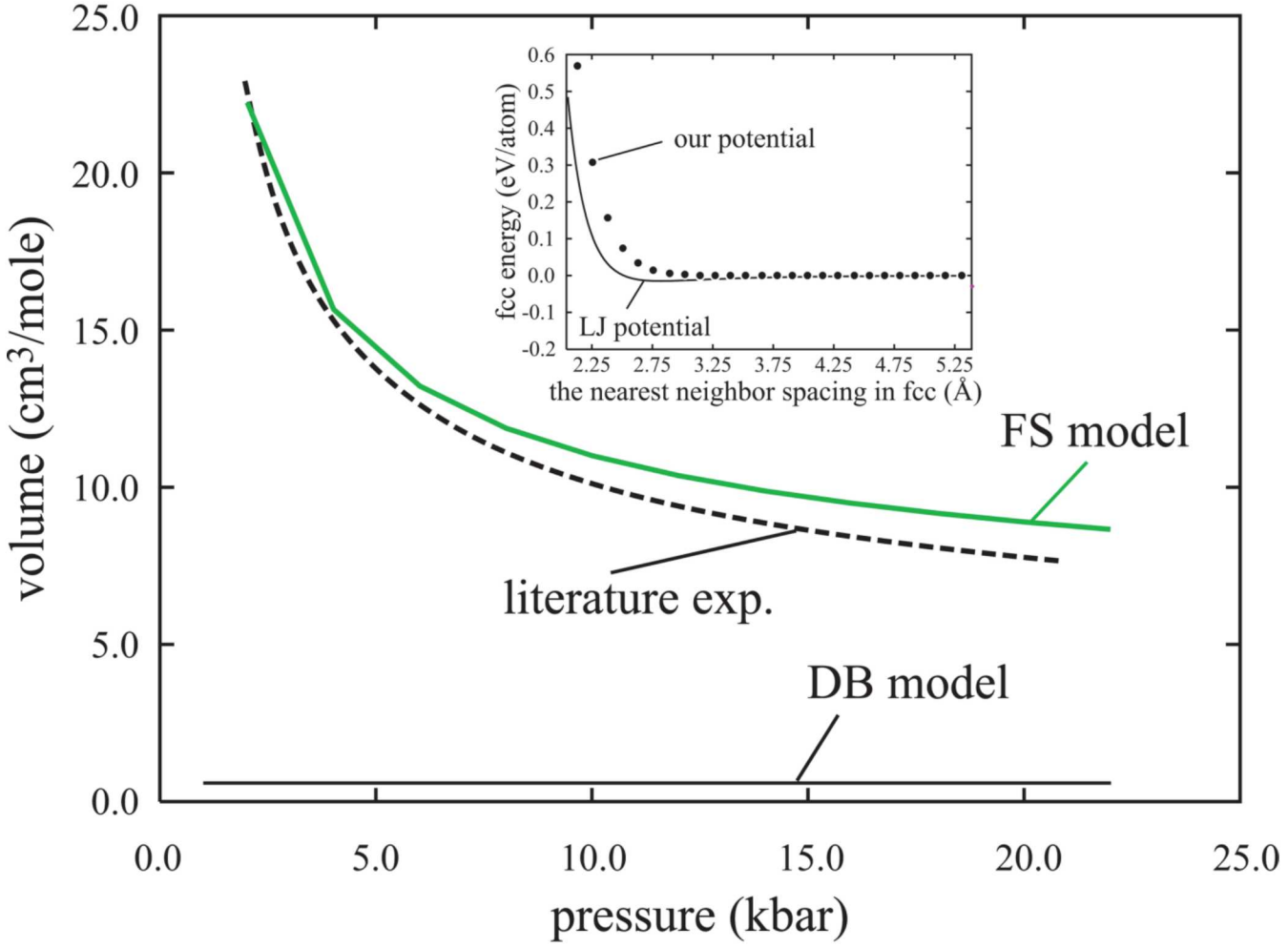


- He always repels electrons towards Pd
- The electron transfer processes are complex

Validation of Some Critical Properties

methods	Q_{He}	$\Omega_{0,He}$	$\Omega_{He,He}$	$\Omega_{H,He}$	E_{He}	r_{He-He}	E_{He-He}	$\Delta\Omega_{Pd\rightarrow PdHe}$	$\Delta E_{Pd\rightarrow PdHe}$
DB	0.19	10.1	10.0	9.7	3.63	1.75	-0.87	9.2	2.92
FS	0.14	8.7	18.8	8.4	4.04	1.72	-1.49	13.6	2.95
PBE	0.11	9.7	10.3	9.5	3.64	1.7	-0.87	6.7	2.99
LDA	0.07	7.3	8.0	10.1	3.63	1.7	-0.85	7.4	2.96

Validation of He Equation of State

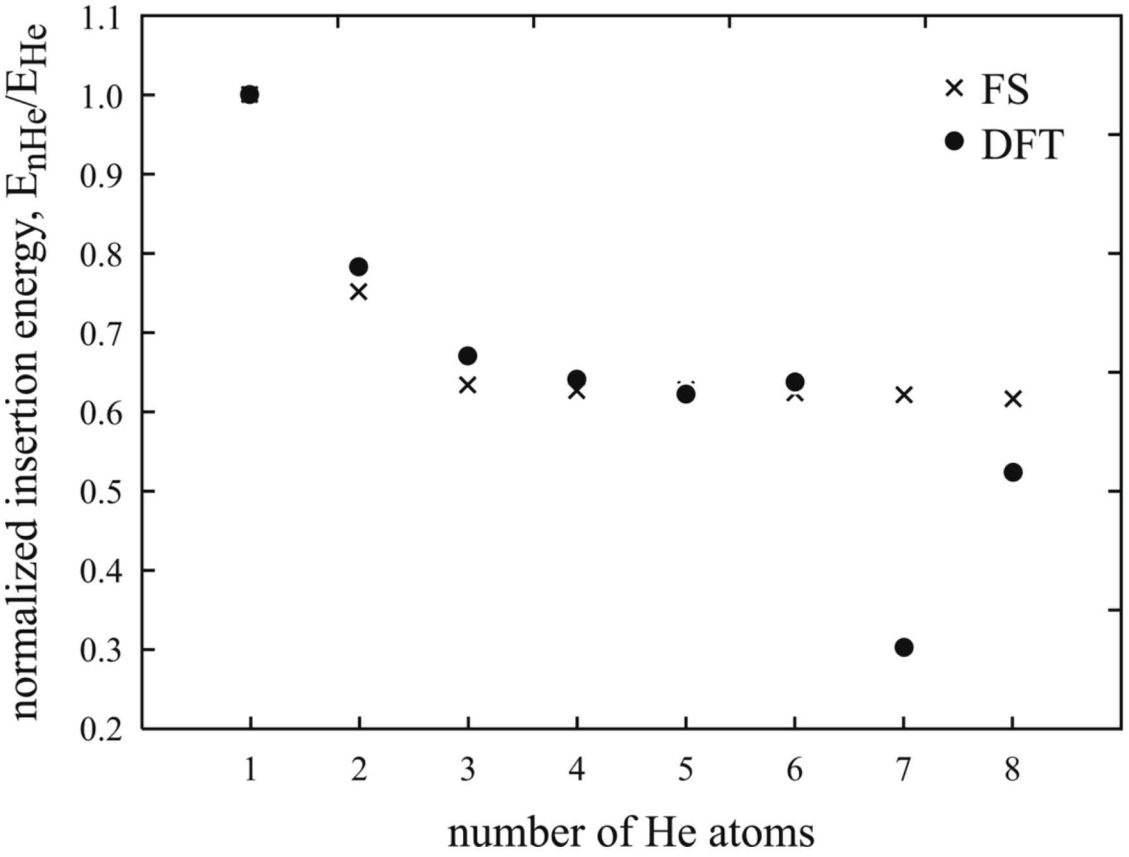


- **Our He-He interactions are purely repulsive and can capture well the He equation of state**
- **Our pure He potential is not that different from literature LJ potential****

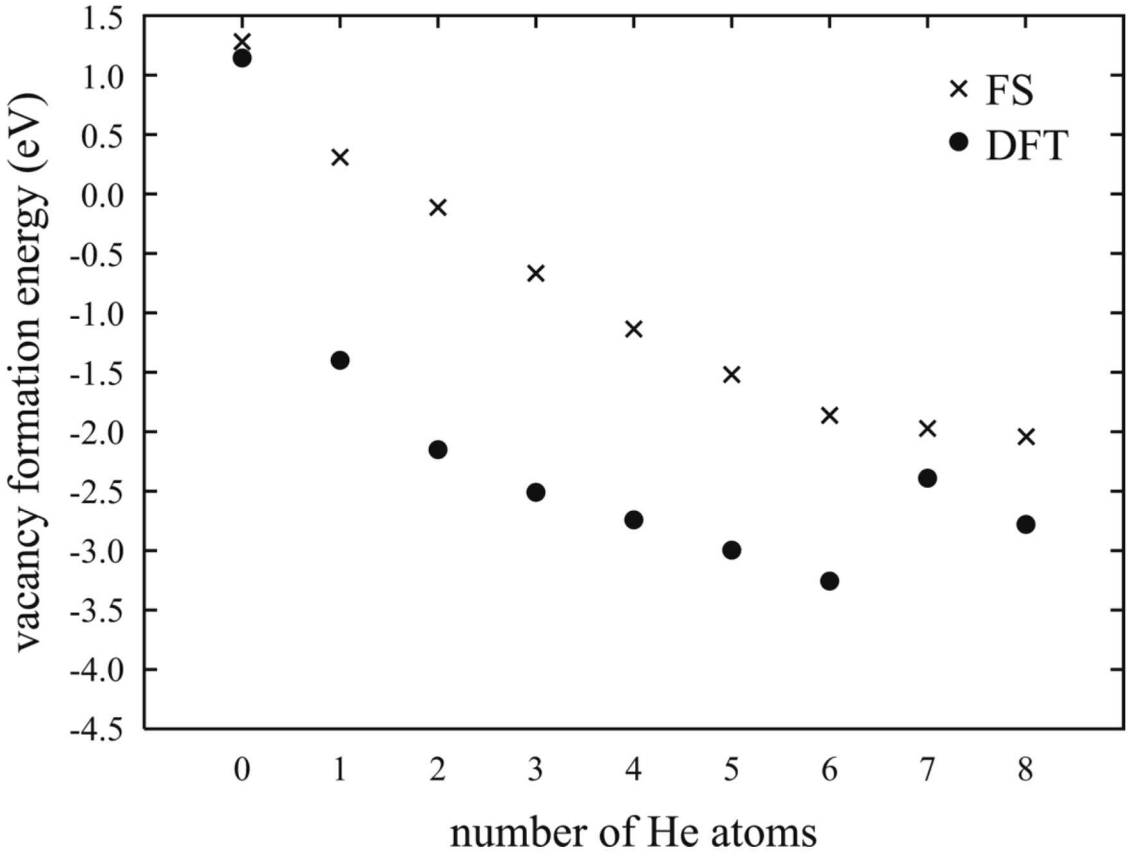
*literature equation of state: Phys. Rev. B, 21, 5137 (1980), **LJ: J. Chem. Phys. 144, 194705 (2016)

Validation of He Insertion and Pd Vacancy Energies

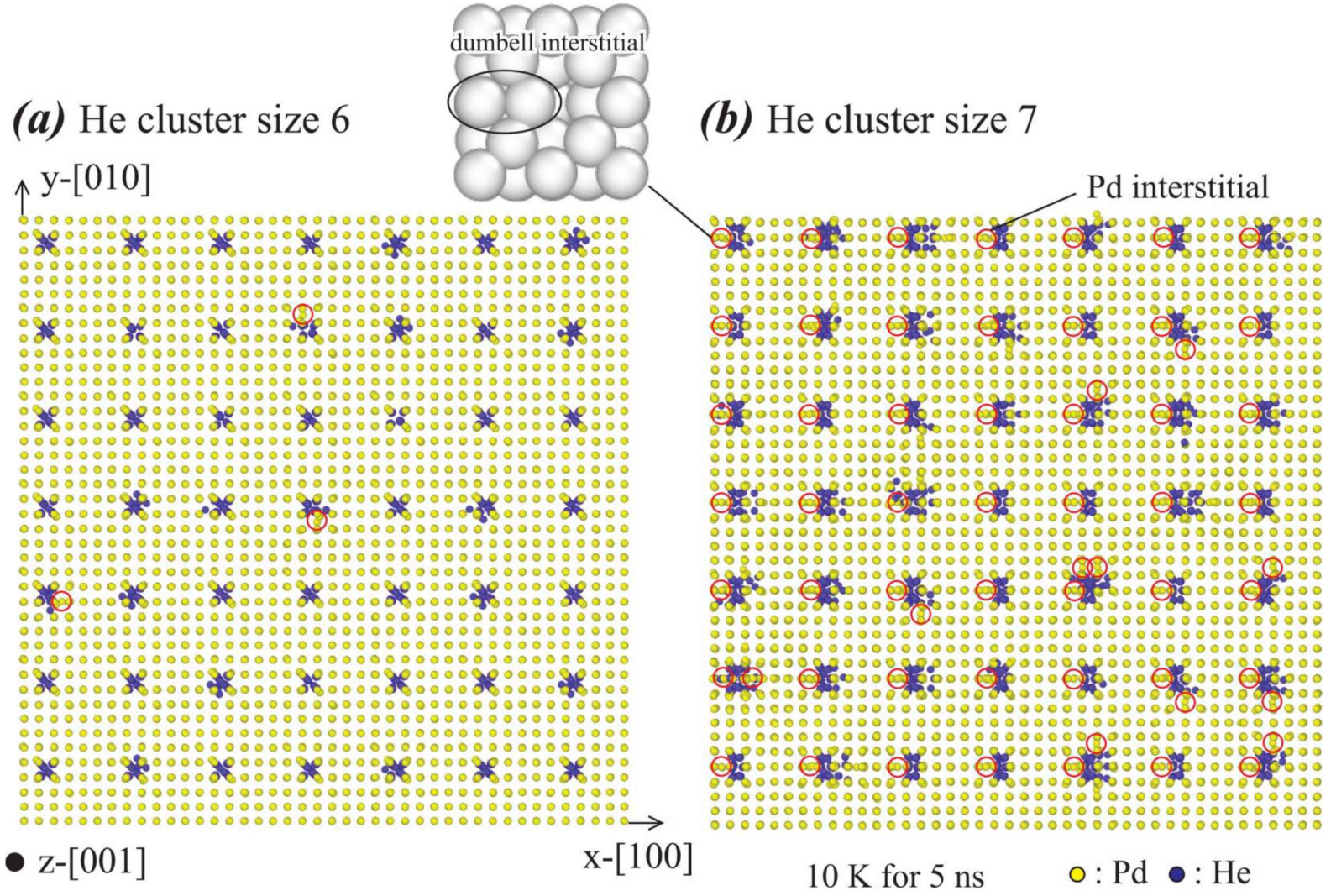
(a) normalized He insertion energy (at He # 1)



(b) Pd vacancy formation energy

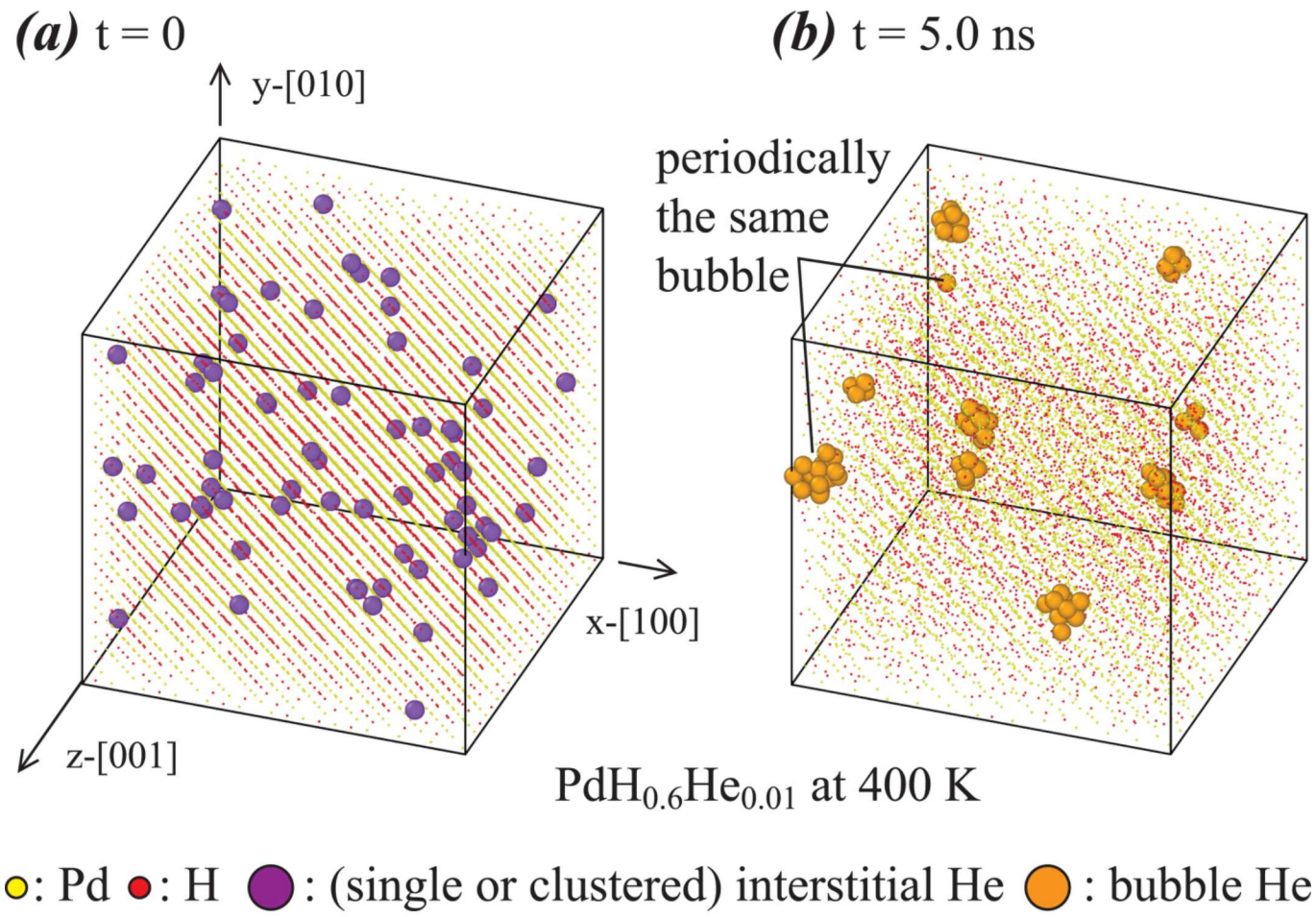


Validation of Critical He Size



- At He size 6, few Pd interstitials are seen
- At He size 7, all He clusters induce Pd interstitials, in good agreement with DFT results

Stringent MD Tests



- Initially, He atoms are randomly populated at octahedral sites in a $PdH_{0.6}$ lattice
- After MD simulations at 400 K for 5 ns, He bubbles are formed
- Enables simulations of bubble formation without assumptions

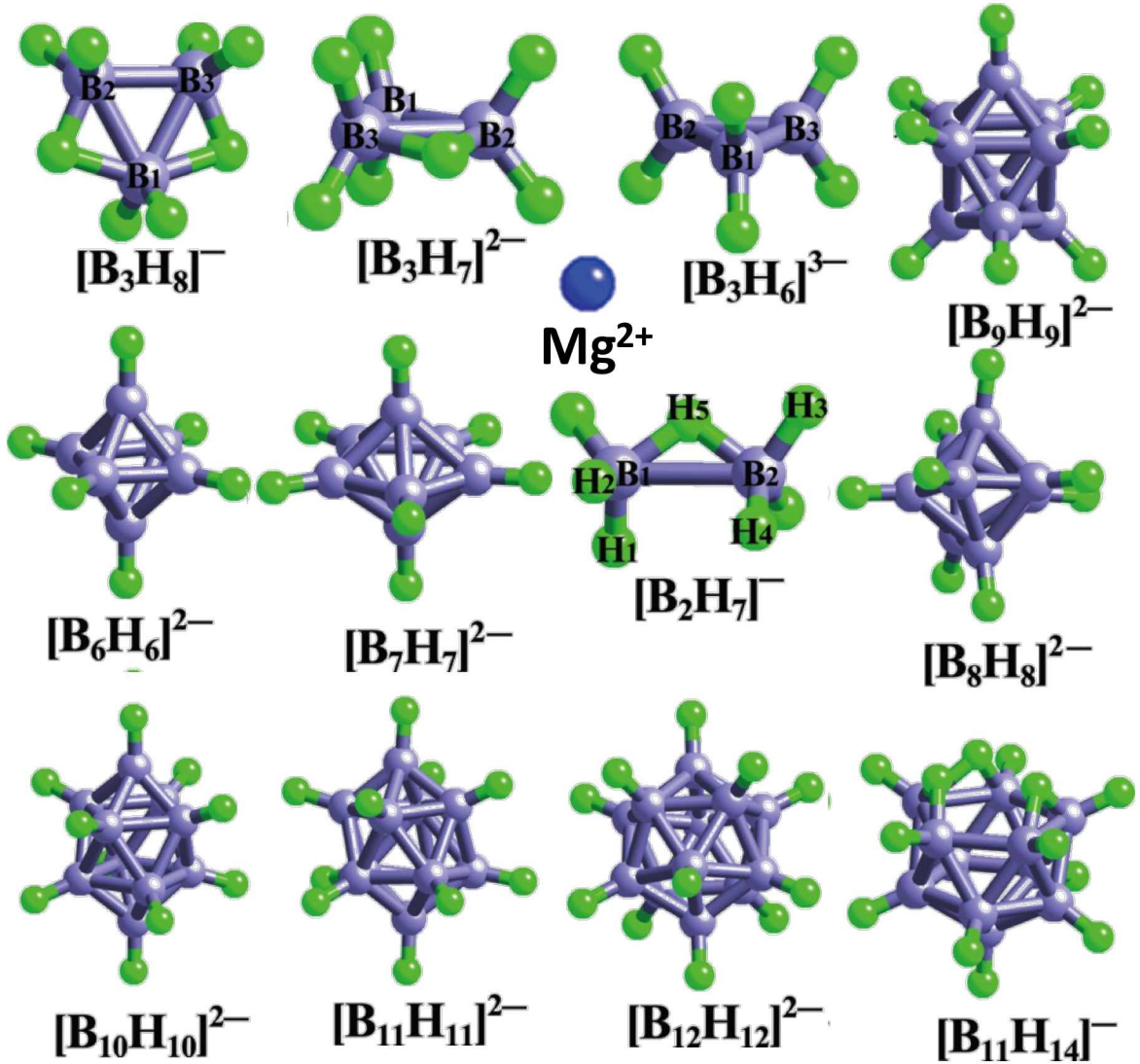
Mg-B-H Potential - Motivation

- 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 MgB_xH_y
- 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



MgB_xH_y: Two Goals

$Mg(BH_4)_2 \Leftrightarrow MgB_2 + 4H_2 \ldots$

$MgB_{12}H_{12}$

$Mg(B_3H_8)_2$

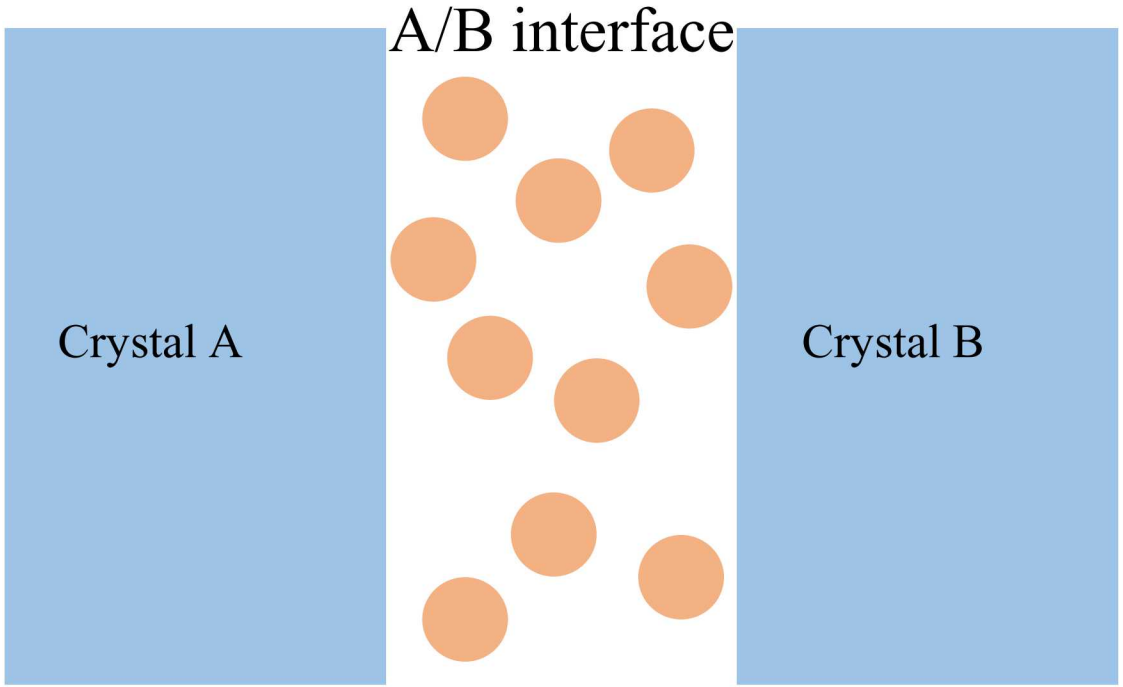
$MgB_{10}H_{10}$

MgB_xH_y

…

- Many molecules were observed in NMR, XES, XAS, but not XRD ⇒ amorphous
- DFT is not sufficient for amorphous complex hydrides

Goal 1: Use MD to evaluate stabilities of different intermediates



- Interfaces between crystalline solids are often exhibit amorphous "soup" containing different molecular species

Goal 2: Use MD to calculate interfacial energies

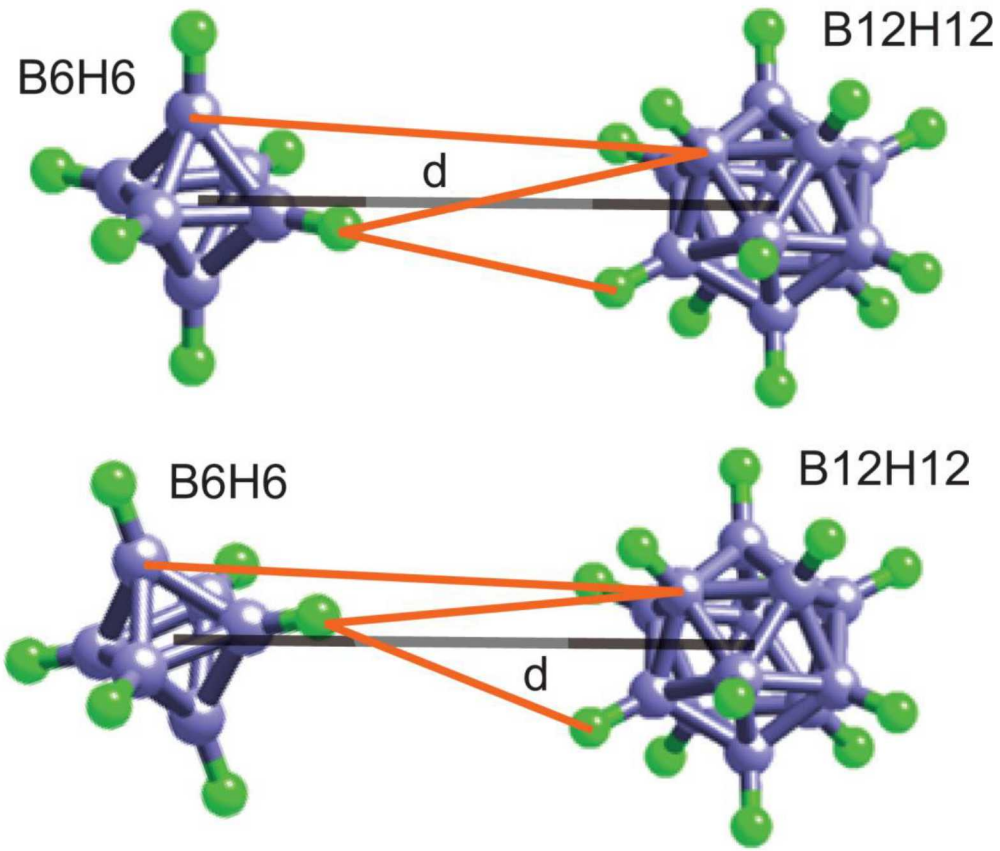
Molecular Dynamics Challenges

- 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

MgB_xH_y: Methods

- Energy comes from interactions between atoms from different (similar and dissimilar) molecules
- Perform DFT calculations of energies of all pairs of molecules at various distances and angles
- Fit pair potentials to DFT energies
- Implement the approach in LAMMPS

Interactions between different pairs of species are distinguished by rotation

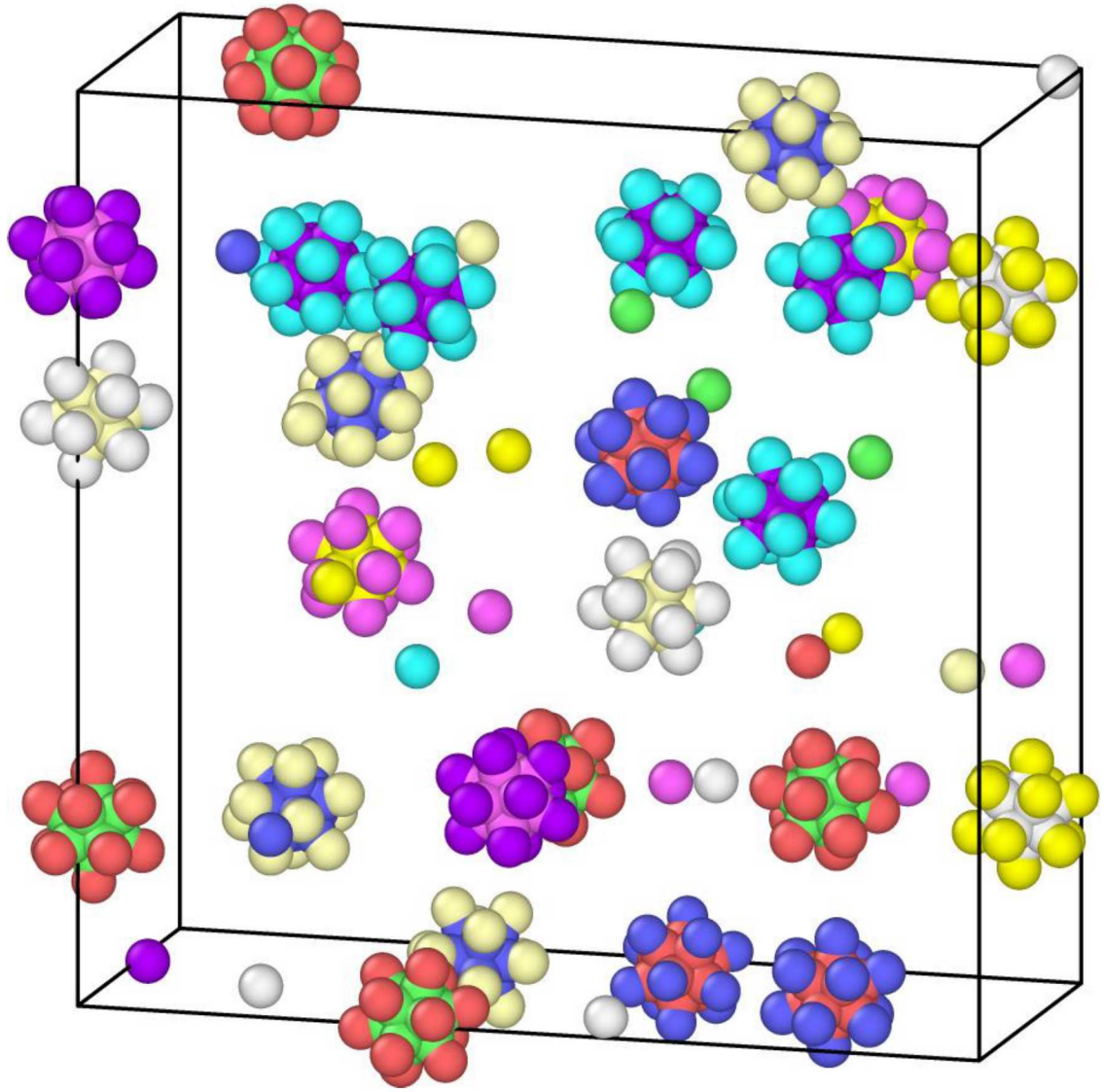


36 Inter-Molecule Interactions

- 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)

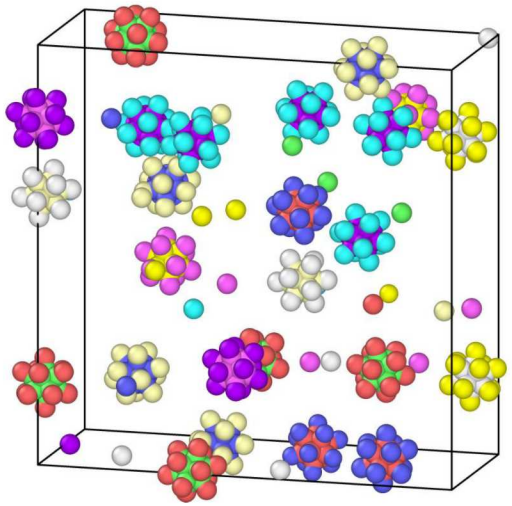
MD Implementation



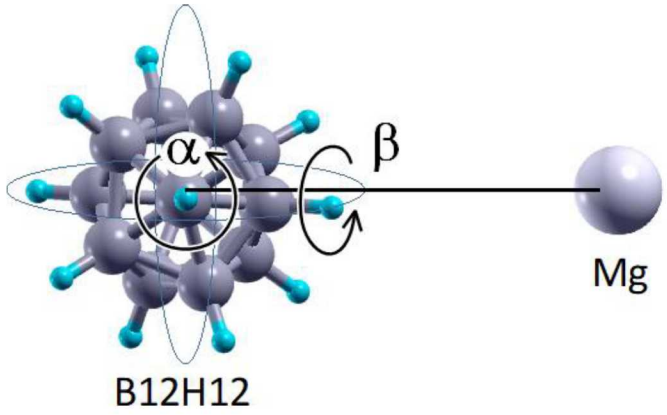
- Atom-based MD does not know molecules
- Assign different atom types for different molecules
- Create mapping tables between atom types and pair interactions

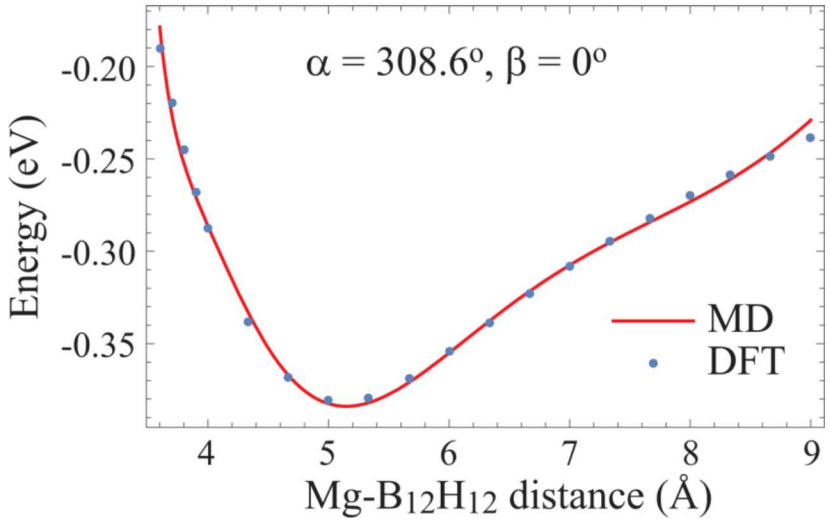
Progress

"Molecular" Dynamics Case



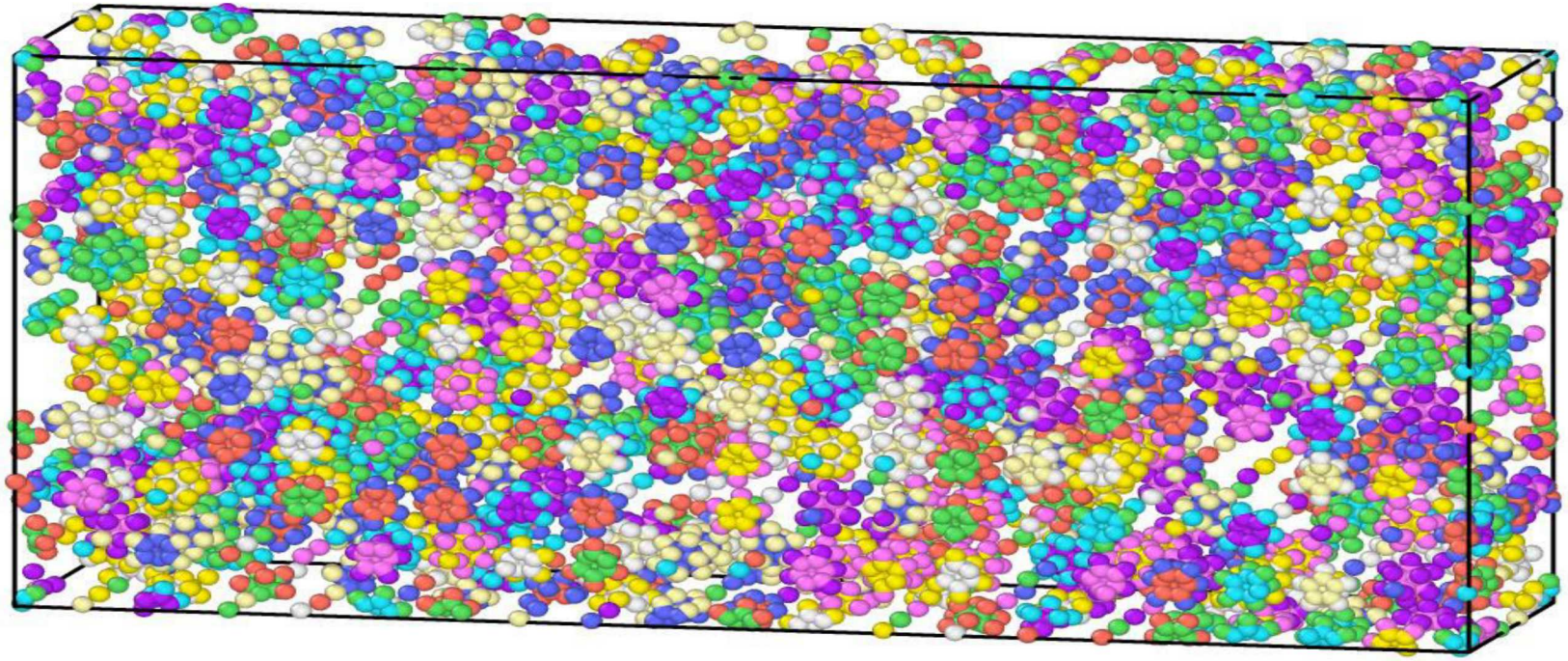
Example Mg-$B_{12}H_{12}$ Interaction



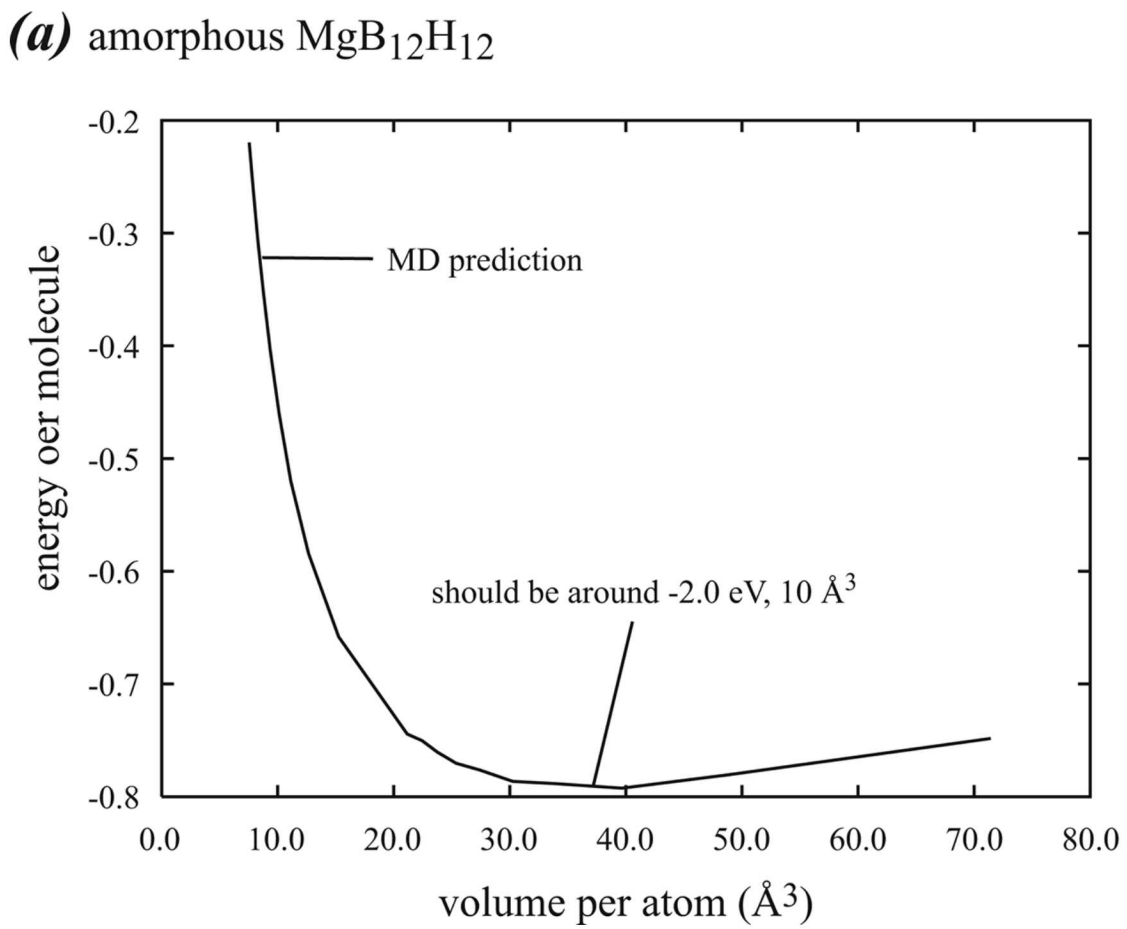


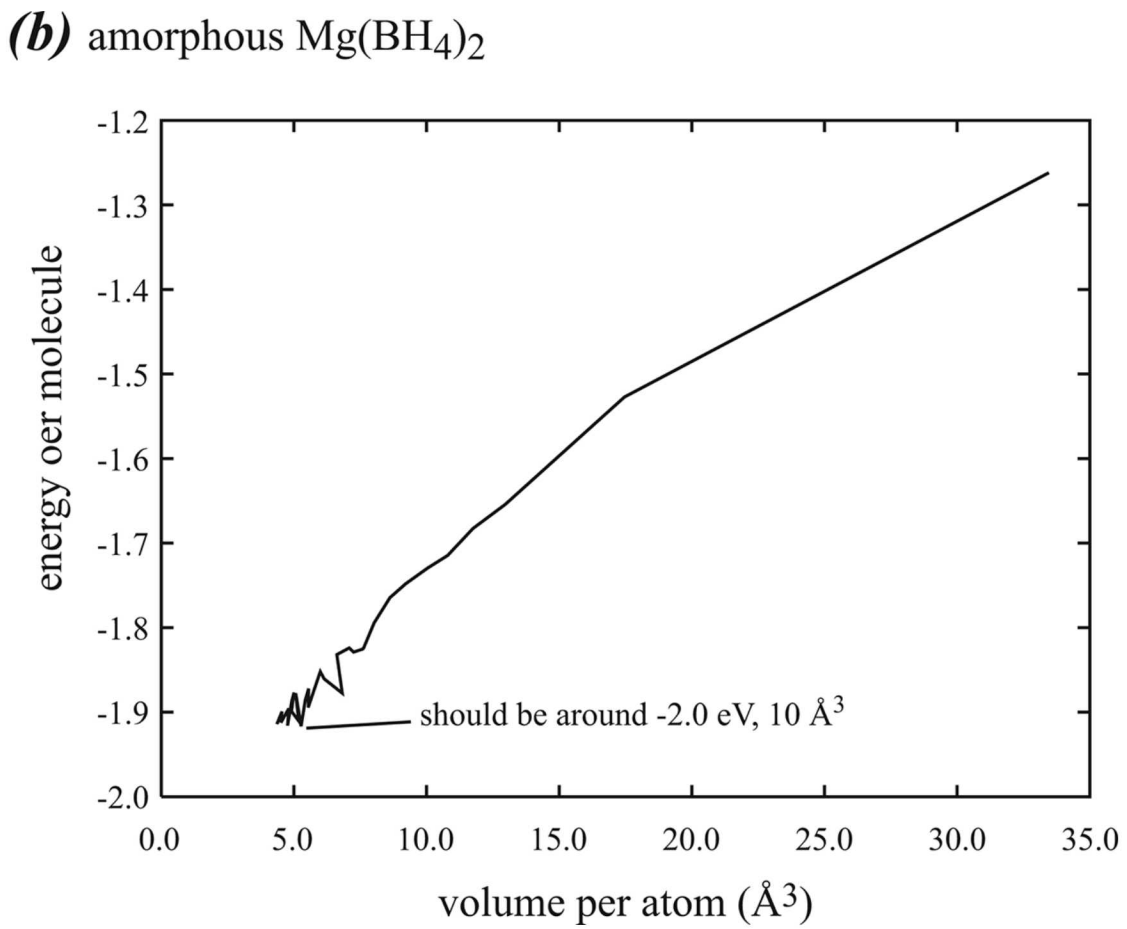
- Fitted all 36 molecular interactions needed for Mg, H_2, MgH_2, BH_4, $B_{12}H_{12}$
- Implemented the "molecular" dynamics method in LAMMPS
- Demonstrated successful "molecular" dynamics simulations
- Performed simulations for $MgB_{12}H_{12}$ and $Mg(BH_4)_2$

MgB_xH_y: "Molecular" Dynamics Simulation



Issues



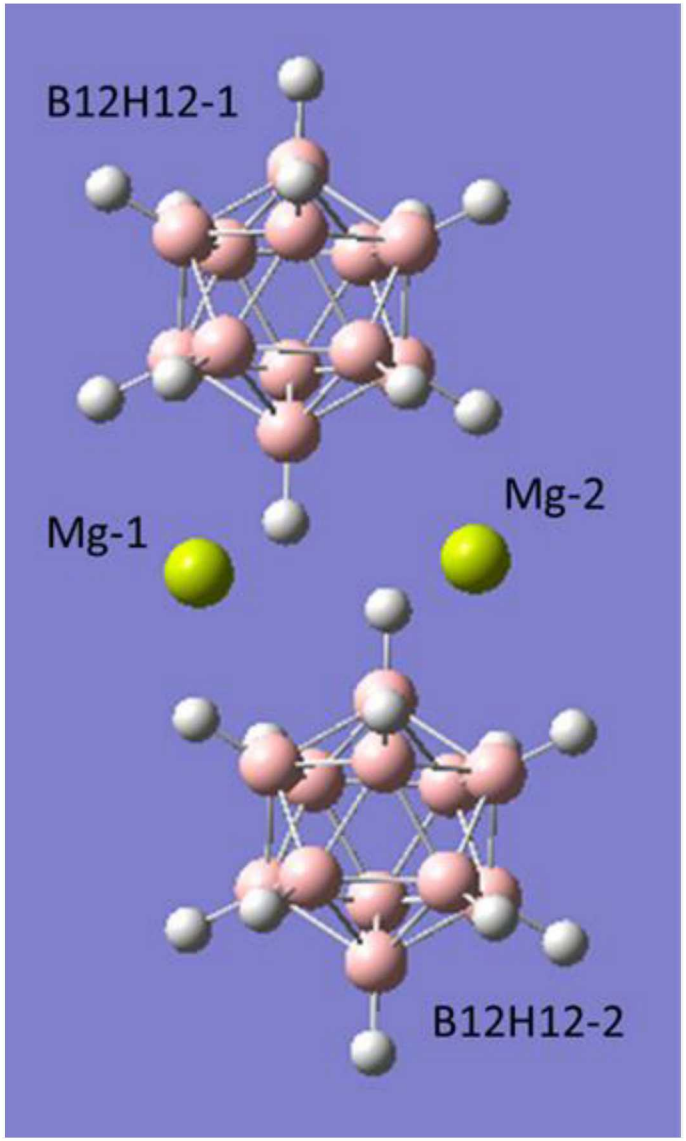


- ❑ MD matches DFT on isolated molecule-molecule cases, but not on condensed phases
- ❑ Solution: directly fit condensed phases

Origins of the Issues

DFT Energies do not sum up due to charge transfer

	ETOT (Hartree)	Interaction Energy (eV)
Mg (Charge = 2)	-199.2273	
B12H12-1 (Charge = -2)	-305.7702	
B12H12-2 (Charge = -2)	-305.7702	
Mg--Mg (Charge = 4)	-397.9869	12.7284
B12H12 -- B12H12 (Charge = -4)	-611.2426	8.1035
B12H12-1 -- Mg-1 (Charge = 0)	-505.7188	-19.6276
B12H12-1 -- Mg-2 (Charge = 0)	-505.7569	-20.6621
B12H12-2 -- Mg-1 (Charge = 0)	-505.7569	-20.6630
B12H12-2 -- Mg-2 (Charge = 0)	-505.7188	-19.6273
MgB12H12 (Charge = 0)	-505.7188	
MgB12H12 (Charge = 0)	-505.7188	
Mg2(B12H12)2 (Charge = 0)	-1011.6945	-6.9881



Highlights

- MD tools for PdH_x are mature, and have been applied to study various hydrogen storage problems including the diffusion example presented
- We have been working on a “molecular” dynamics tool to study complex hydrides such as MgB_xH_y