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Application and Validation of Inter-Atomic Potentials for Modeling Helium-3 Bubble Growth in Aging Palladium Tritides

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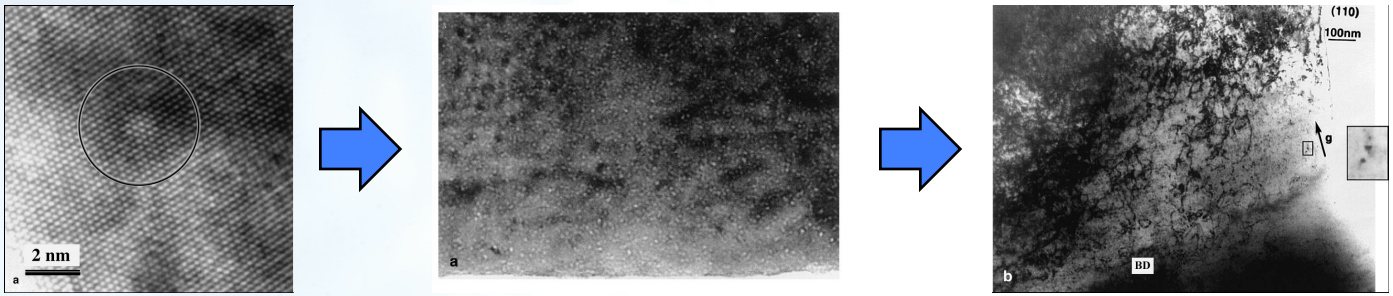
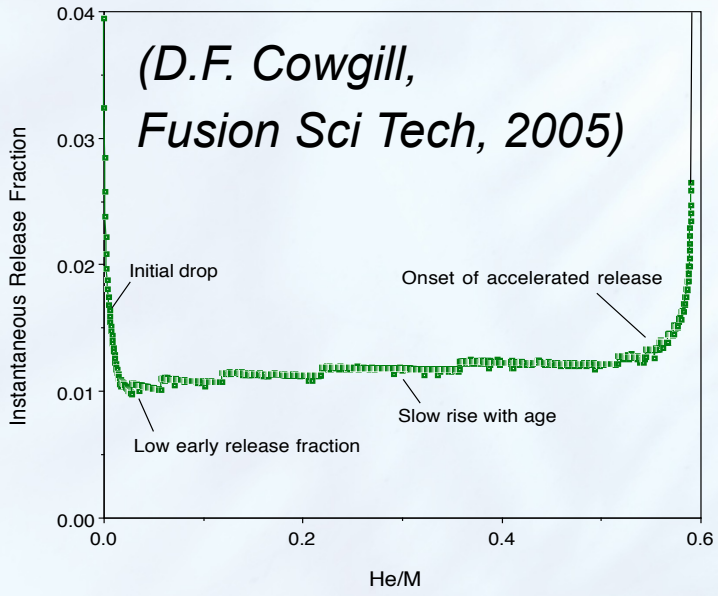
How do hydrogen-isotope storage materials fail?

- Hydrogen (H) and hydrogen-isotopes (D,T) in metals produce a variety of defect-mediated behaviors that can result in deformation, failure and fracture, e.g. H embrittlement (HE), H enhanced localized plasticity (HELP).
- Decay of tritium produces helium (He) atoms that cluster and form bubbles.
- For He in palladium (Pd), He gas is released from the metal at an accelerated rate at some critical concentration of He/Pd.
- Experiments reveal dislocation loops and other defects in these aged samples.

Determining the cause of accelerated release of helium gas



(S. Thiébaut et al, J Nucl Mater, 2000)



Our focus:

Identify physical mechanisms leading to accelerated release of He gas.

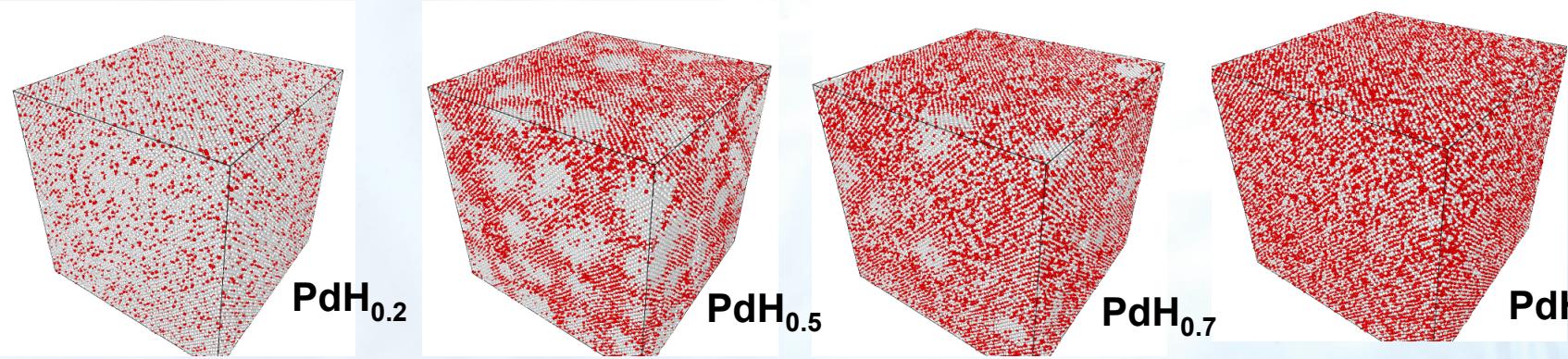
We simulate and examine the material defects that originate from having He bubbles in a metal lattice using atomistic modeling methods.

Research plan

- Use molecular dynamic simulations to investigate progression of yield mechanisms during bubble growth in PdT_y
  - Bubble volume and pressure
  - Dislocations and stacking faults
  - Signs of fracture
- Investigate the effect of alloying palladium with silver (Ag)
  - Perform bubble growth simulations for a variety of $Pd_{1-x}Ag_xT_y$ compositions
- We found that MD simulations did not agree with experimental observations and expectations from analytic models
  - Perform density functional theory calculations to calculate material properties key to analytic models

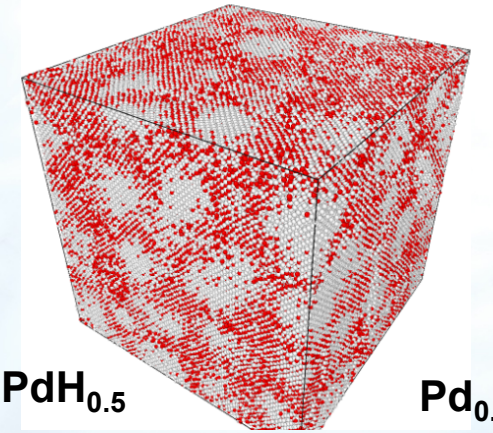
Pd-H(T) interatomic potential

- Embedded Atom Method (EAM) model
  - Pd-Pd interaction by Foiles and Hoyt *(SAND2001-0661)*
  - Pd-H and H-H interactions by Zhou, Zimmerman, Wong, and Hoyt *(J Mater Res, 23(3), 704-718, 2008)*
- Accurately models structural properties of palladium hydride
  - Displays miscibility gap and the formation of H-dilute (α) and H-rich (β) phases (expt: y_α = 0.03 and y_β = 0.6, pot: $y_\alpha \approx 0.0$ and $y_\beta \approx 0.85$); H in octahedral sites

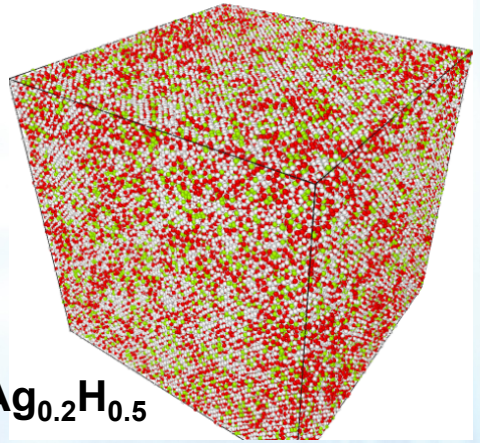


Pd-Ag-H(T) interatomic potential

- Start with EAM potential by Williams *et al* (*MSMSE*, 2006) for Ag
- Pd-Ag and Ag-H interaction fitted to Morse-style functions using DFT energy and structural data for ideal Pd3Ag systems with H added to both octahedral and tetrahedral sites (Hale *et al*, *MSMSE*, 21, 045005, 2013)
- Loss of miscibility gap noticed between 10% and 20% Ag, experiments show this occurs at 25% Ag.
- Lennard-Jones style potential by Westergren *et al (J Chem Phys, 1997)* for He-He, He-Pd, and He-Ag interactions.
- Developed He-H pair potential based on all-electron *ab initio* calculation.



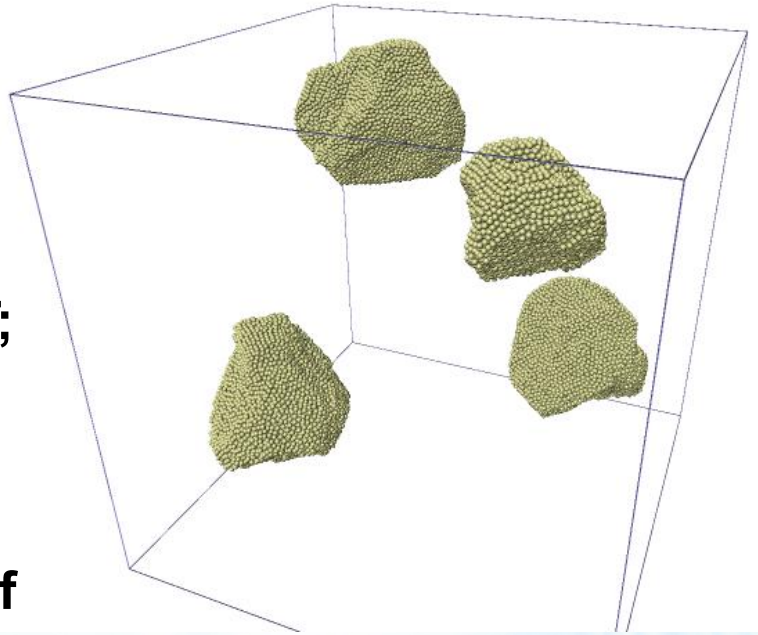
$PdH_{0.5}$



$Pd_{0.8}Ag_{0.2}H_{0.5}$

Bubble growth simulations

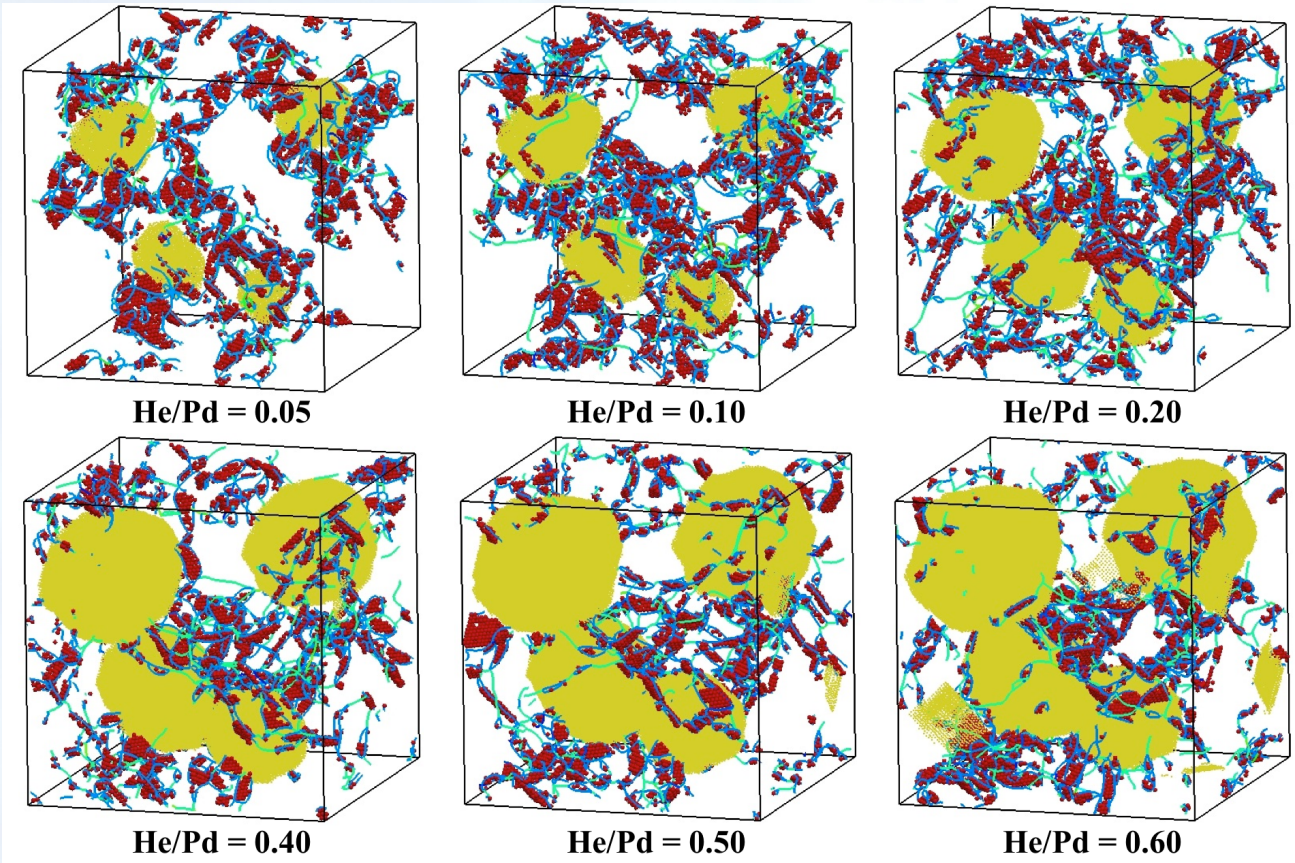
- Initial size ~740,000 atoms (cubes with sides of ~20 nm)
- Create 4 bubbles and add 20 atoms of He at a time into center of the bubbles – bubble density = 5 x 10^{23} m^{-3}
- Equilibrate the system for 11 ps before adding more He
- Isothermally held at 300 K
- Two types of (boundary) conditions:
  - Constrained volume
  - Constrained at zero pressure
- H(T) concentration at β phase for PdT; at y = 0.5 for $Pd_{1-x}Ag_xT_y$
- Calculations done on 1024 processors at a rate of ~18 million time steps per day, roughly 80 days of running to reach experimental He concentration for rapid release



Non-spherical bubbles

He bubble growth in $PdT_{0.85}$

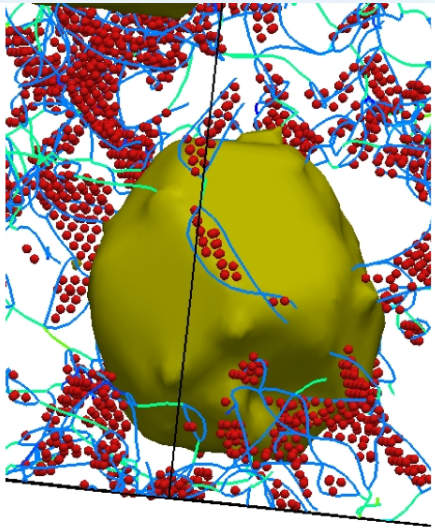
Constrained volume simulations

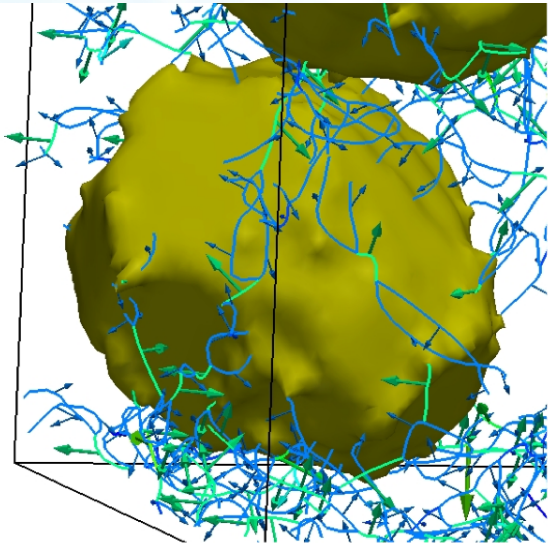


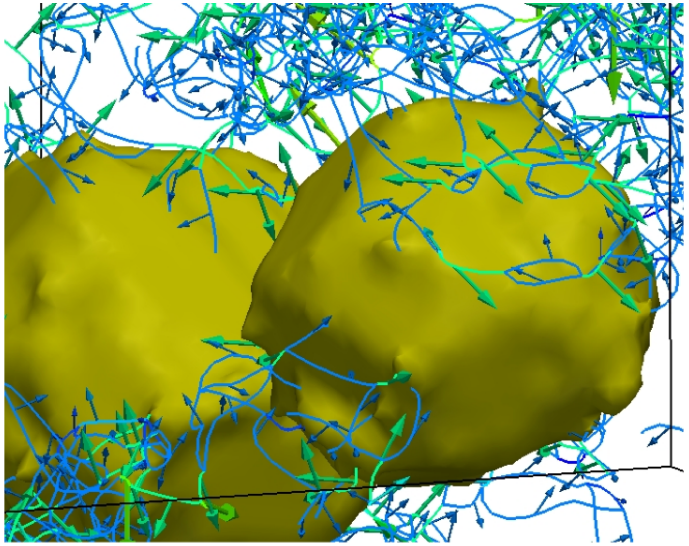
Dislocation eXtraction Algorithm (DXA, A. Stukowski and K. Albe, *MSMSE, 2010*) used for analysis

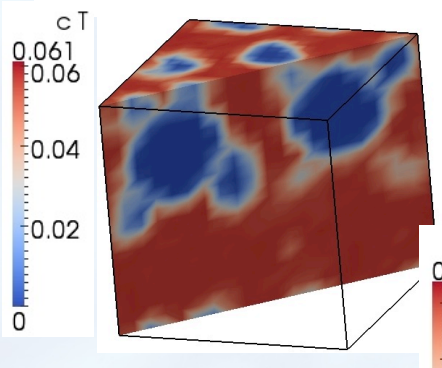
- **Dislocations (<112> and <110>) and stacking faults created; content appears to saturate above He/Pd = 0.2.**
- **At low amounts of ^{3}He, dislocation loops are isolated to single bubbles**
- **At moderate amounts of ^{3}He, loops form a network between bubbles**
- **No inter-bubble fracture.**

Prismatic and shear loops are present

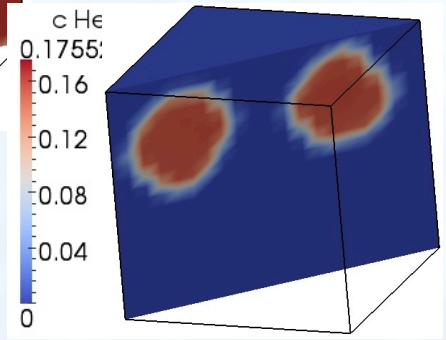


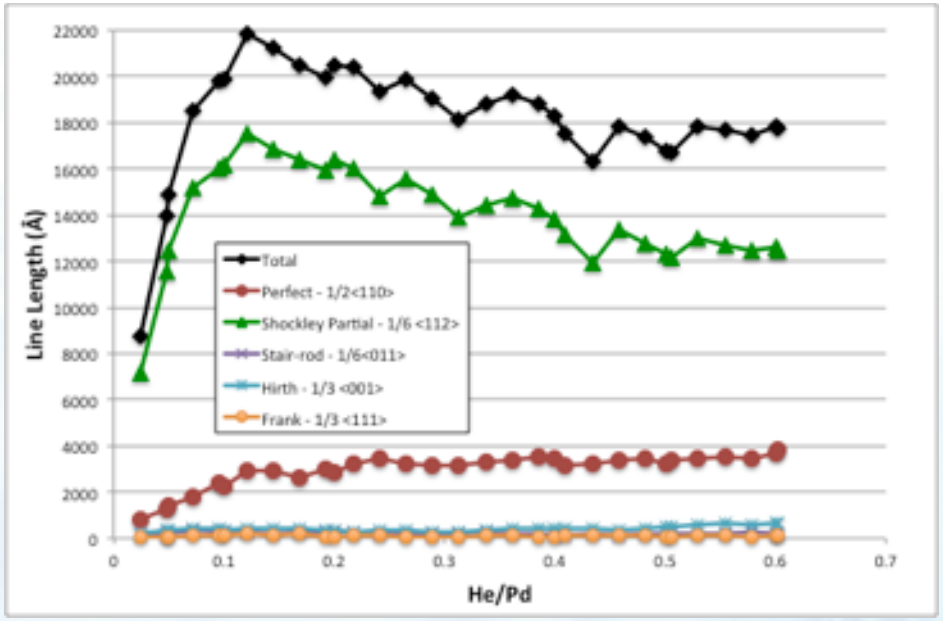






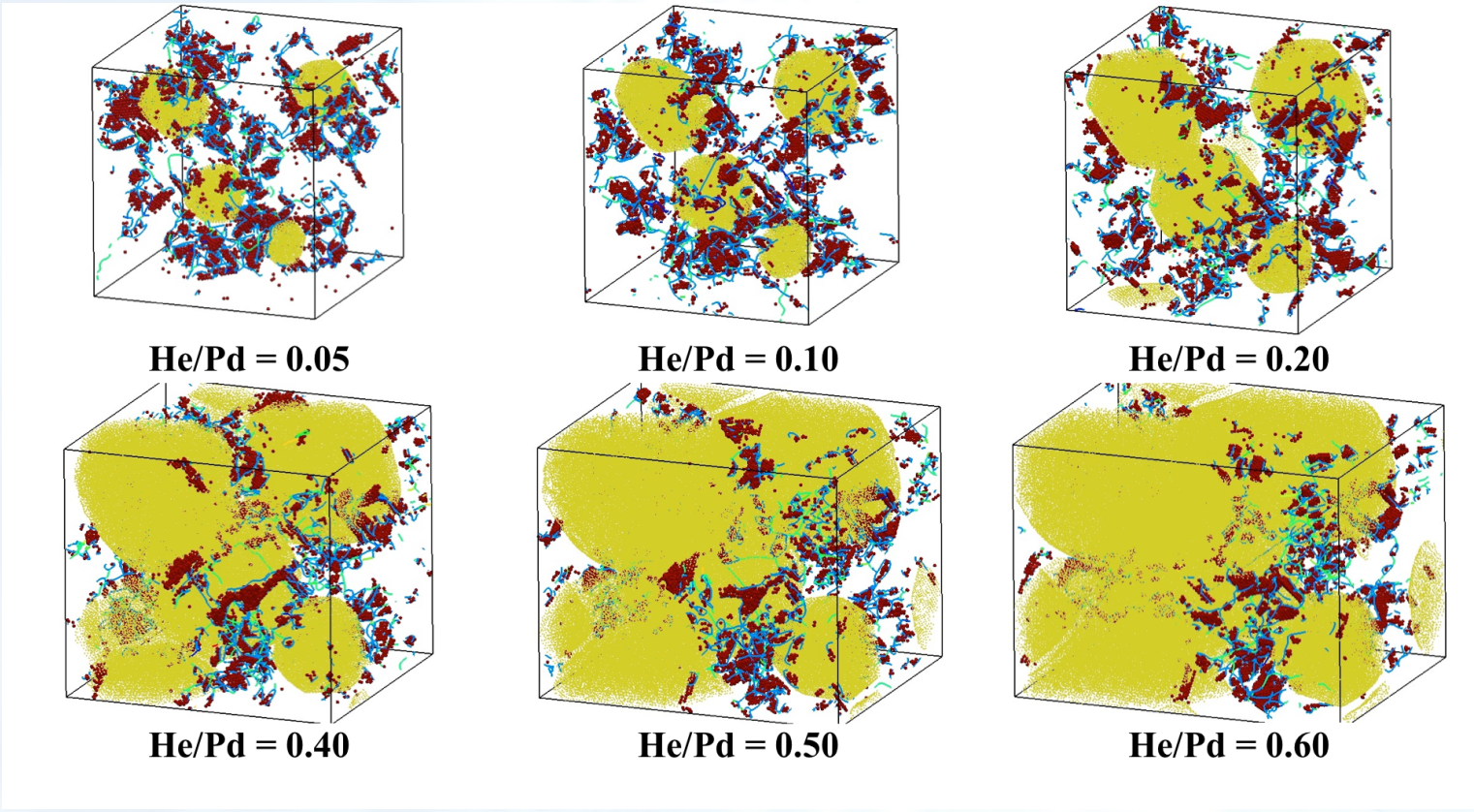
He/Pd = 0.40





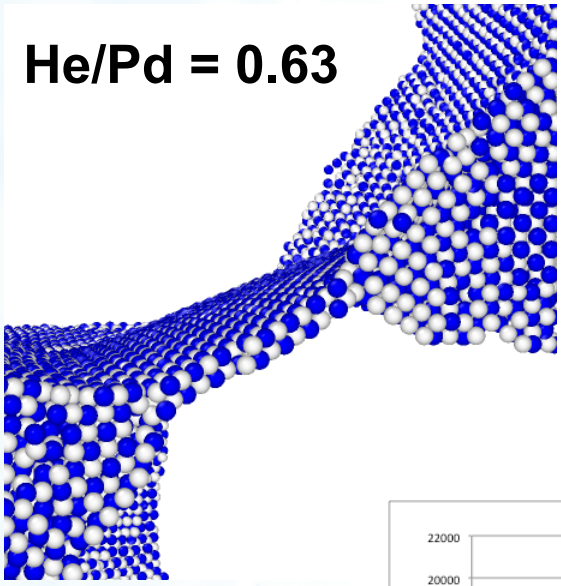
He bubble growth in $PdT_{0.85}$

Zero pressure simulations

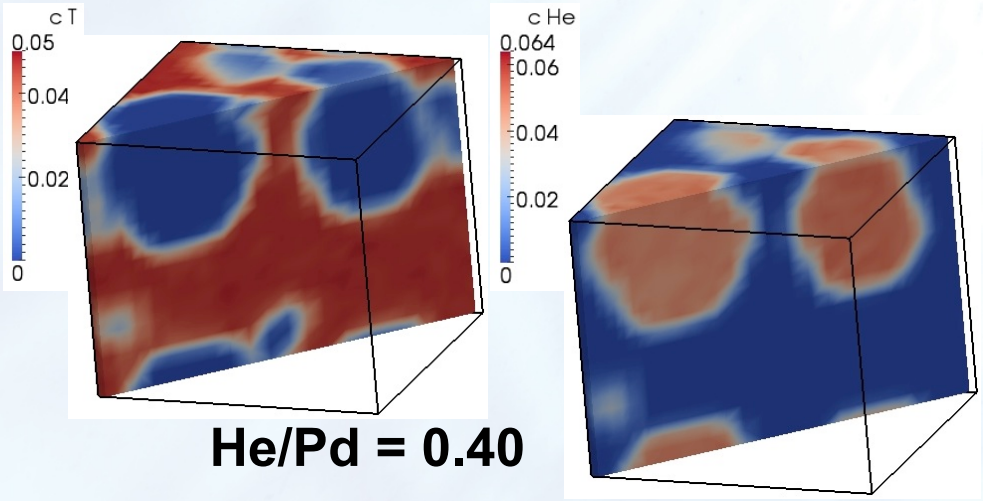


- Similar patterns of defects as for constrained volume case.
- Also evident is anisotropic swelling resulting in aspherical bubbles
- Again, no inter-bubble fracture or linkage occurs.

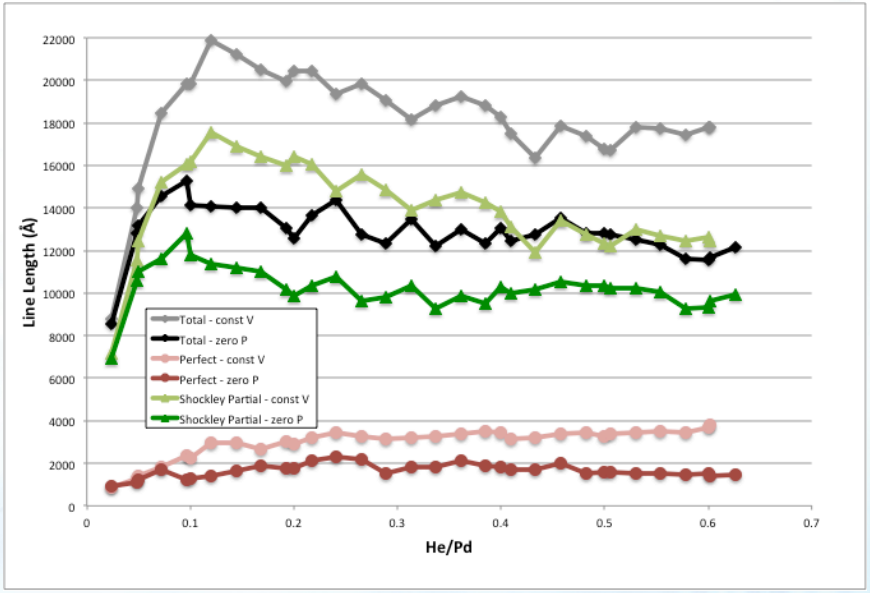
Why no inter-bubble fracture?



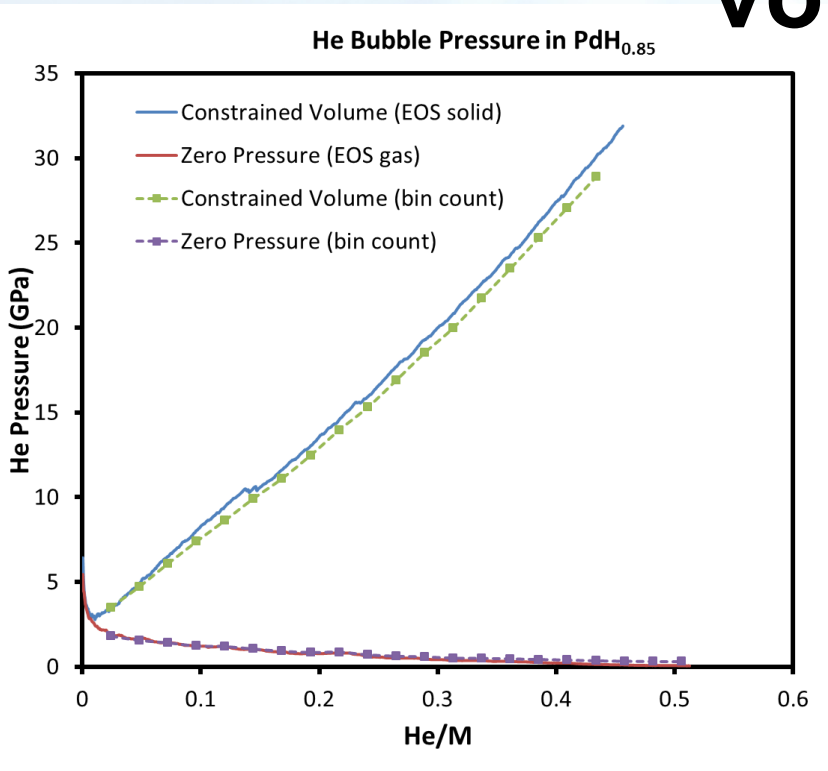
- As bubbles grow increasingly large, a thin (two atomic planes thick) metal-hydride membrane forms between bubbles.

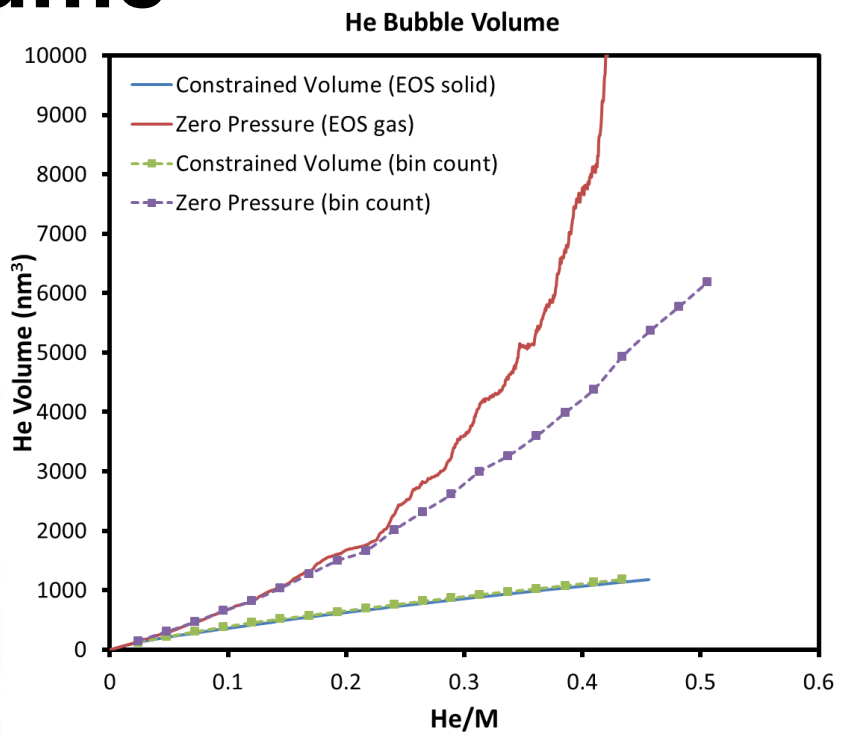


He/Pd = 0.40



Analysis of bubble pressure and volume



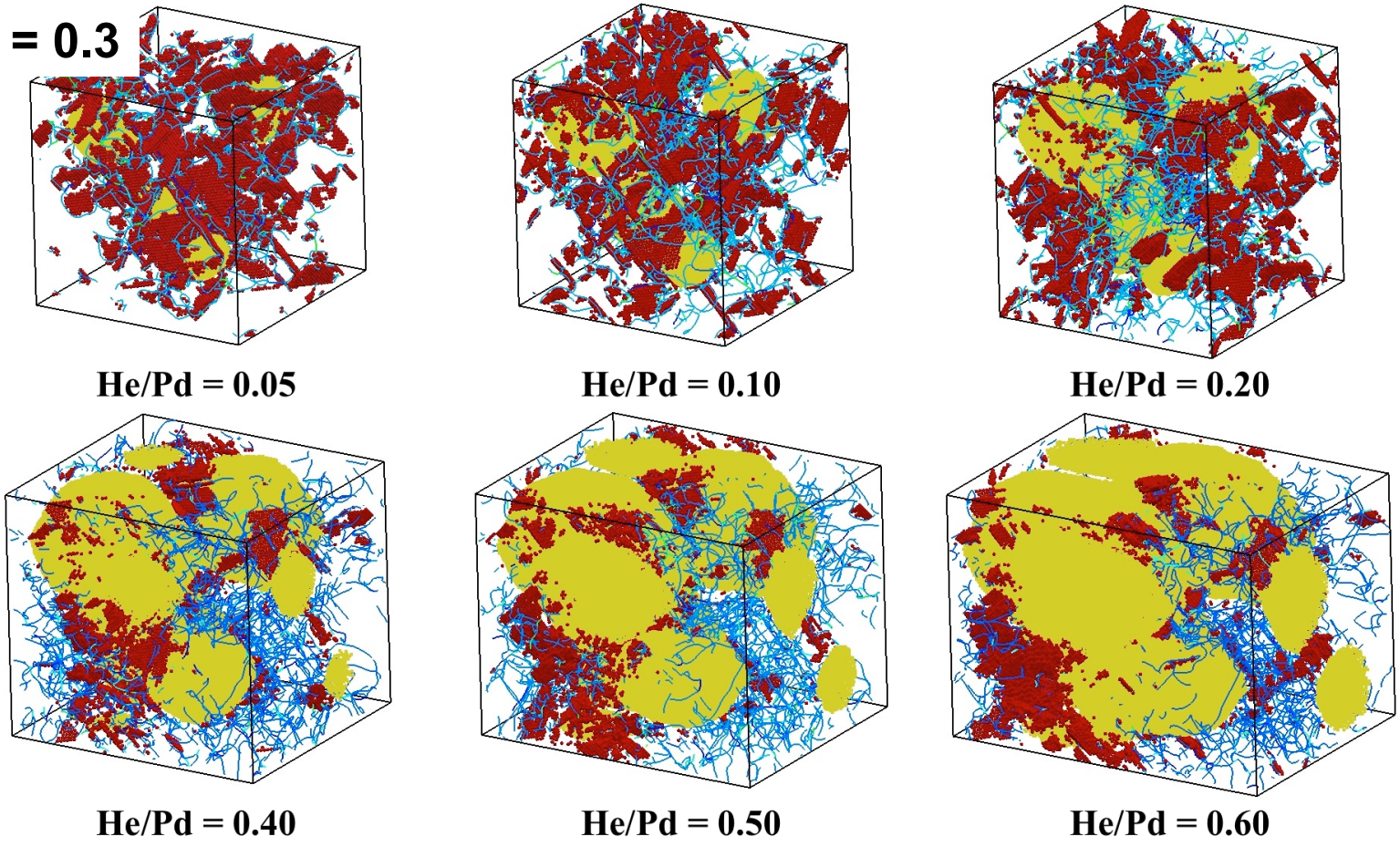


- **Expected trends in bubble pressure/volume with increasing He/Pd**
- **MD-based equation of state (EOS) to predict volume inaccurate for large amounts of He; use bin count method instead**
- **Bubble pressures considerably less than those predicted by Cowgill (*Fusion Sci Tech, 2005)***

He bubble growth in $Pd_{1-x}Ag_xT_{0.5}$

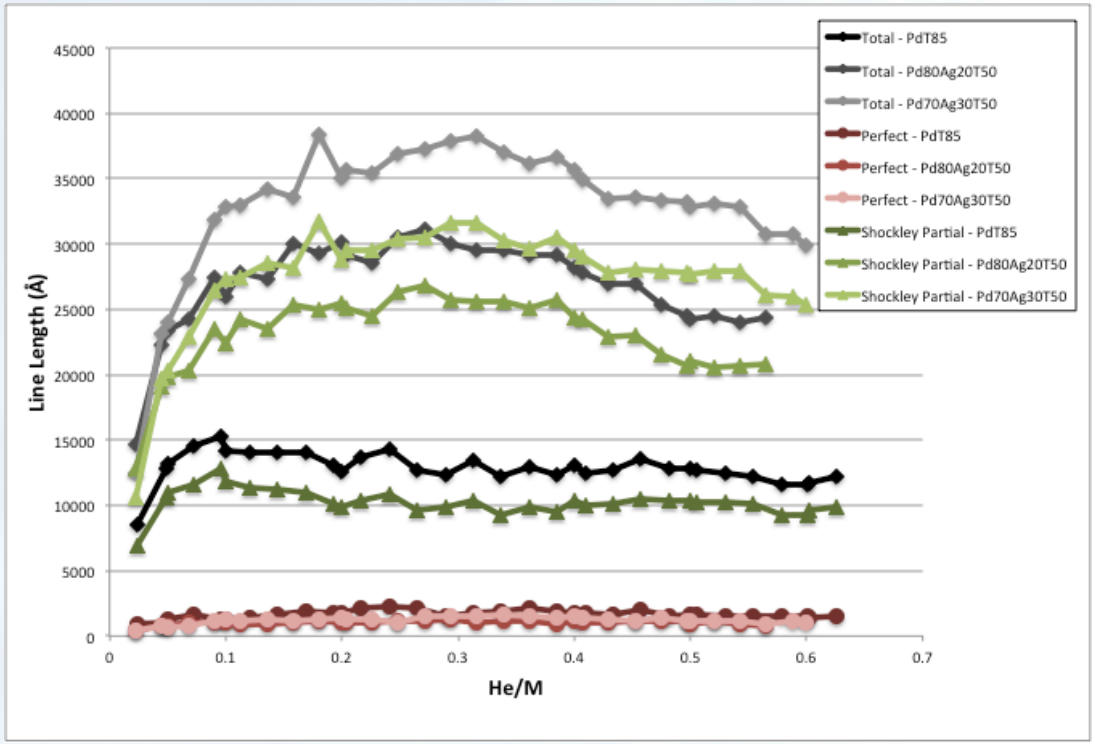
Zero pressure simulations

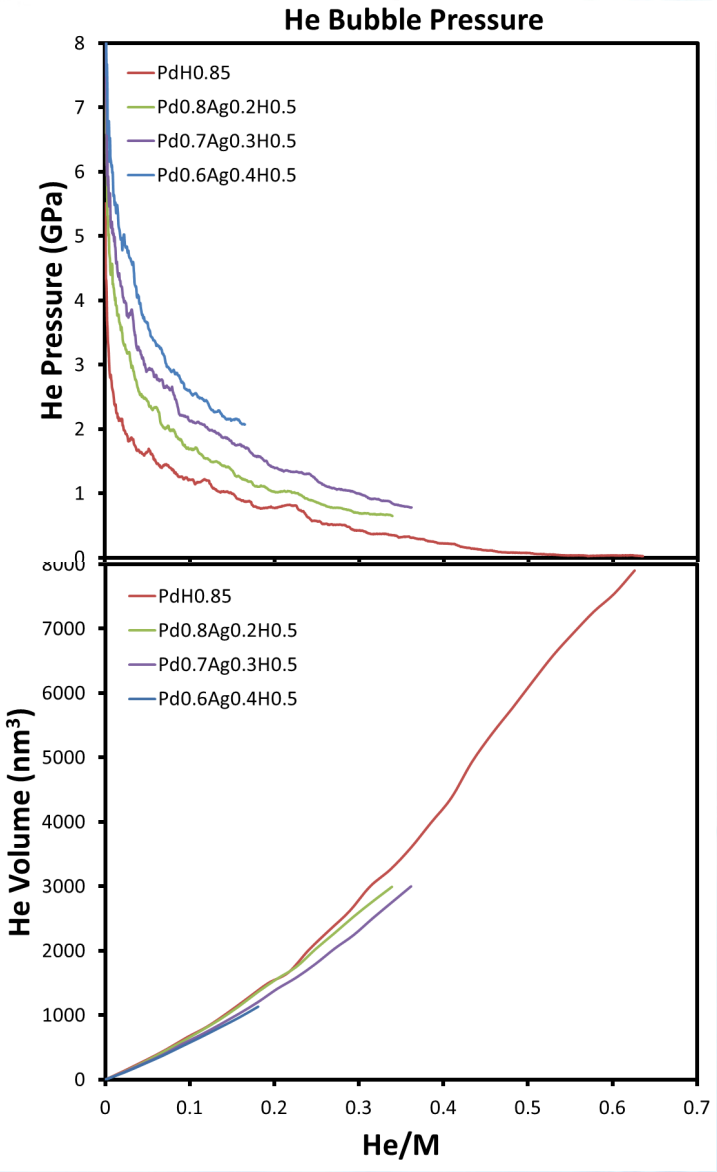
x = 0.3



- Far more stacking faults with addition of Ag
- Similar types and behavior for dislocations

Bubble growth characteristics

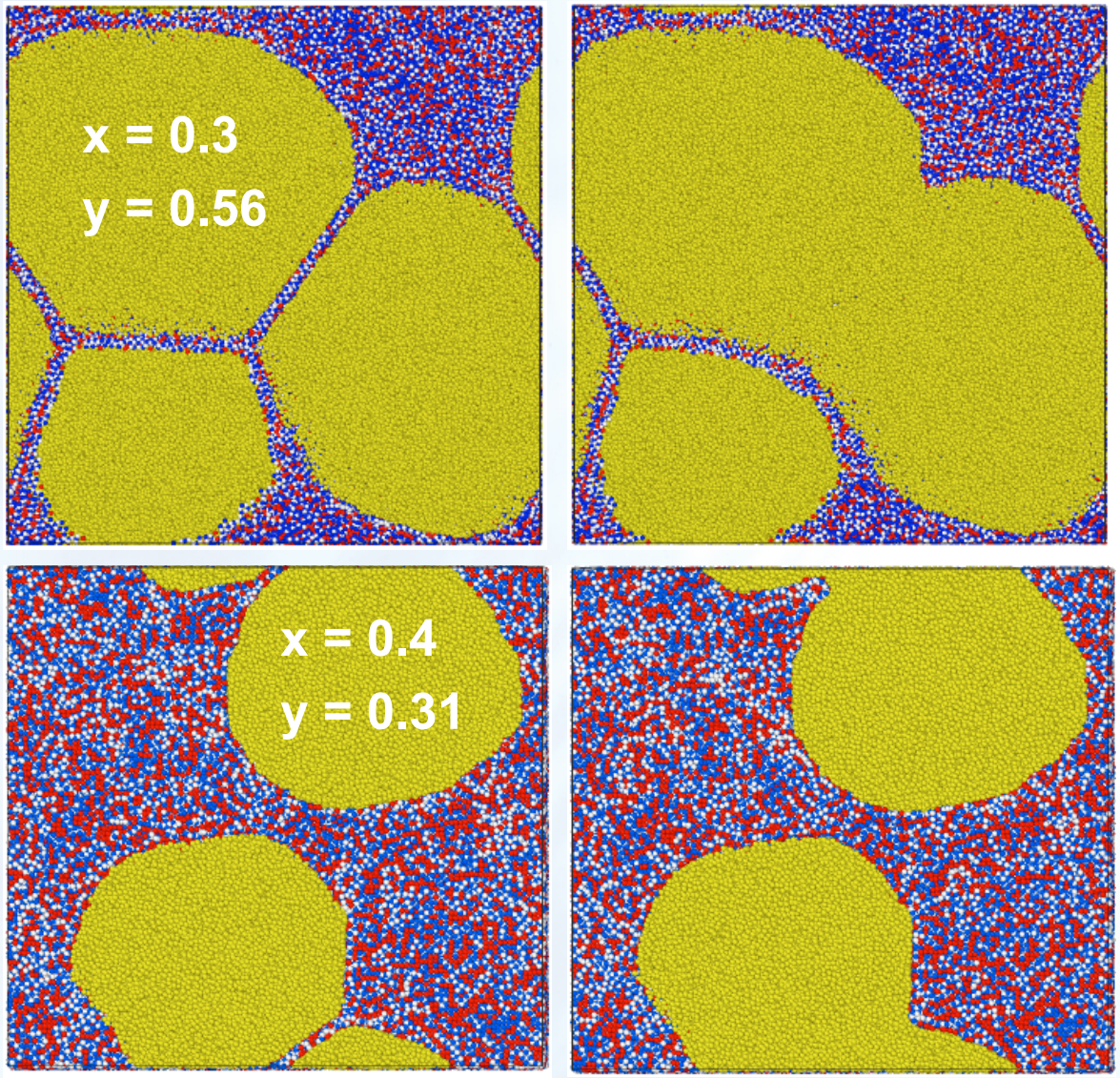




At a given He/M ratio:

- **More partial/total dislocation content with increasing Ag content**
- **Higher bubble pressure and lower volume with increasing Ag content**

Inter-bubble linkage occurs with Ag



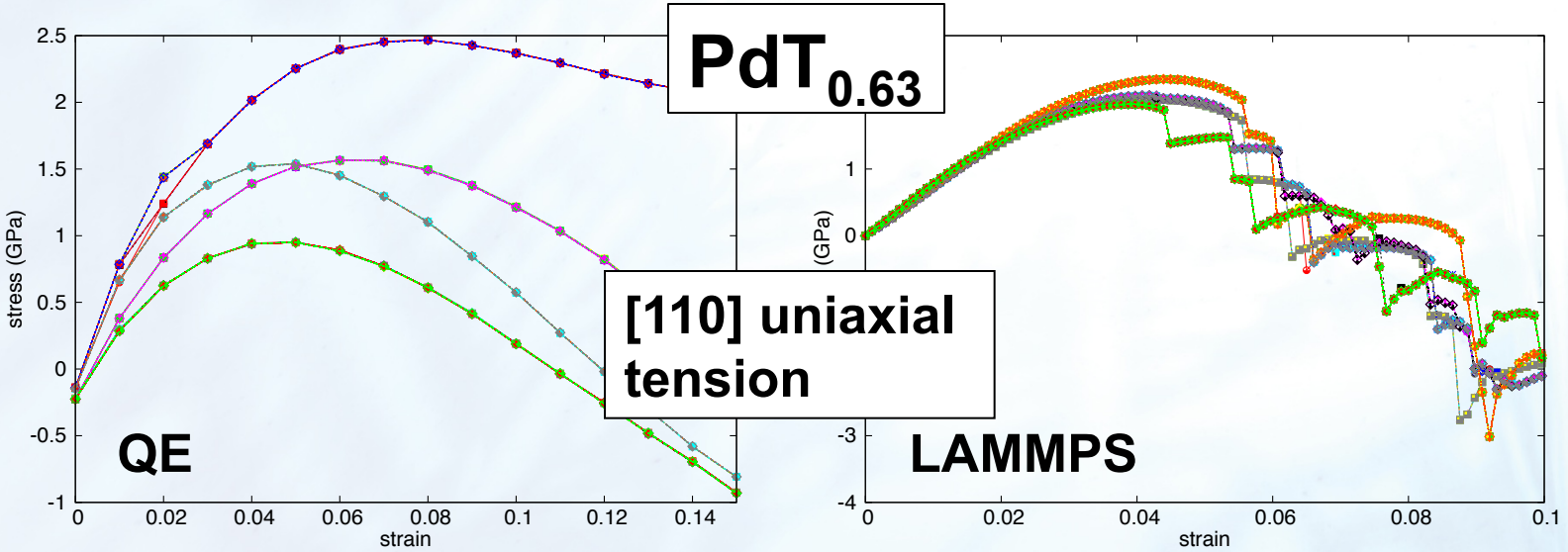
- As for the non-Ag cases, a thin membrane forms between impinging bubbles.
- Membrane collapses for 30% and 40% Ag, but not for 20%.

Wolfer's theory predicts that inter-bubble fracture occurs at a He content that depends on the ratio of ideal tensile strength to shear strength for the MH.

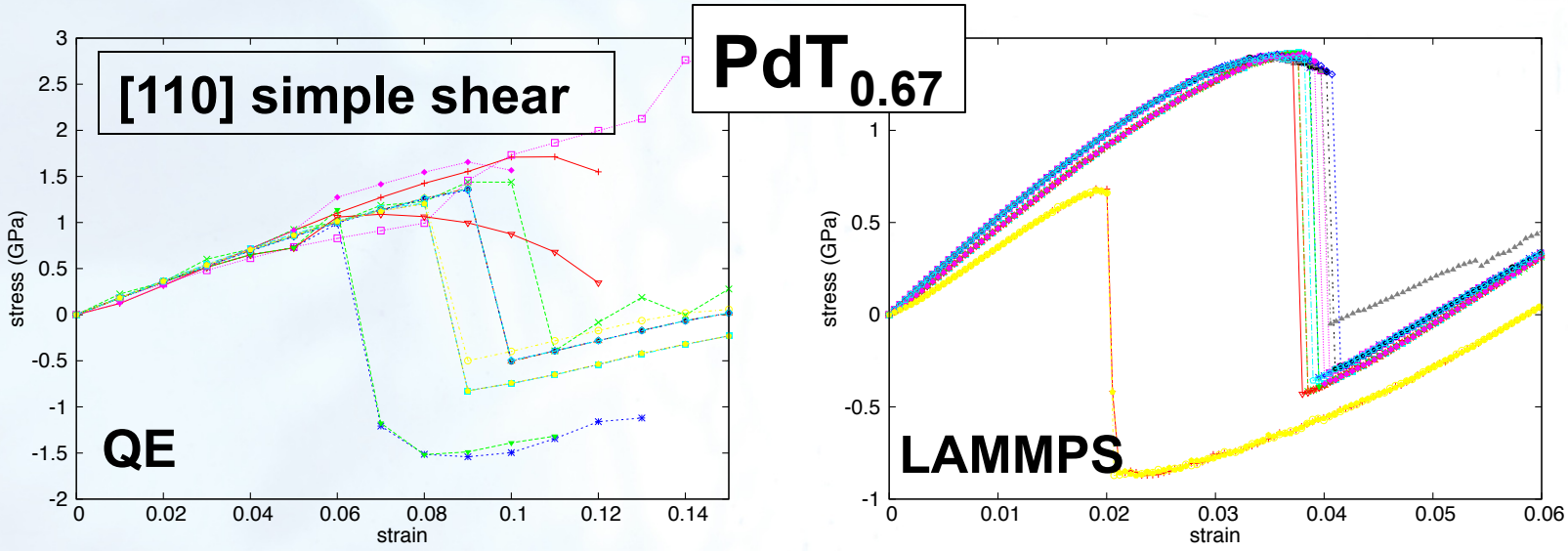
We can use DFT to assess the fidelity of our Pd-T potential.

DFT analysis of tensile and shear strengths

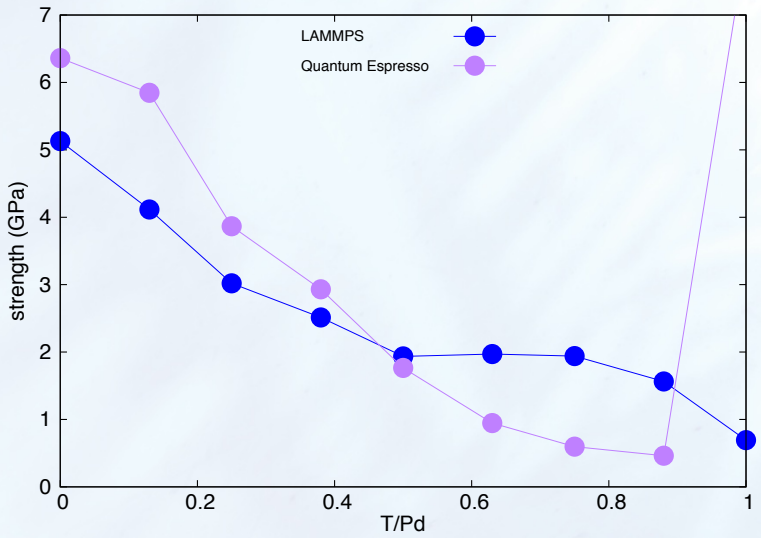
- DFT calculations to assess tensile & shear for Pd-T alloy system
- Used PWscf module within Quantum Espresso
- GGA, PAW pseudopotentials, dispersion-corrected PBE functional
- 4 to 12 atoms
- E_{cut} = 55 Ry (~750 eV), 12 x 12 x 12 k-point sampling
- Marzari-Vanderbilt fermi smearing (width = 0.06 Ry ~ 0.82 eV)
- Performed similar calculations with LAMMPS for comparison



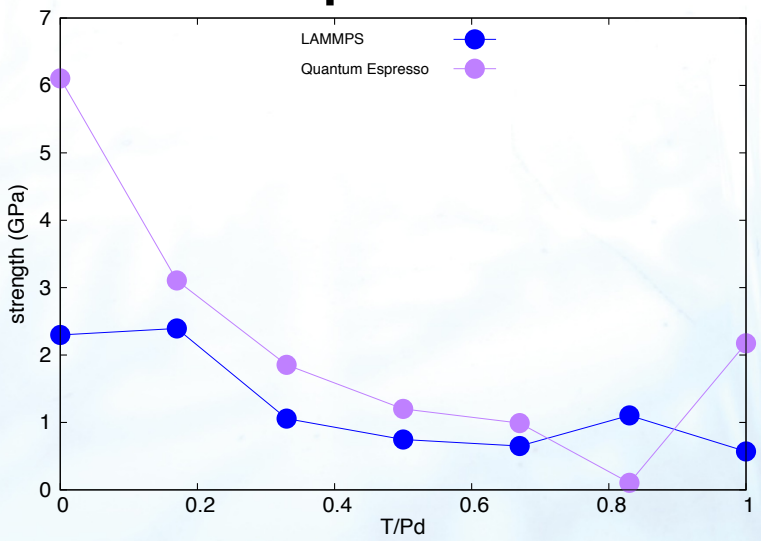
Compositional variation of strengths



Uniaxial tension



Simple shear



Comparison between QE and LAMMPS

- For [110] uniaxial tension:
  - at T/Pd = 0.65, σ_{QE} = 889 MPa, σ_{LAMMPS} = 1.966 GPa
  - at T/Pd = 0.85, σ_{QE} = 493 MPa, σ_{LAMMPS} = 1.650 GPa

- For [110] simple shear:
  - at T/Pd = 0.65, τ_{QE} = 1.016 GPa, τ_{LAMMPS} = 662 MPa
  - at T/Pd = 0.85, τ_{QE} = 348 MPa, τ_{LAMMPS} = 1.041 GPa

Wolfer's theory: $(He/M)_{cr} = 3/2*(\sigma/\tau) - 1$

For T/Pd = 0.65,

$(He/M)_{cr}$ = 0.3125 for QE → agrees with experiments by Thiébaut *et al* for continuously replenished systems

$(He/M)_{cr}$ = 3.45 for LAMMPS → unlimited loop punching

For T/Pd = 0.85,

$(He/M)_{cr}$ = 1.38 for LAMMPS → disagrees with experiments

Concluding remarks

- He bubble growth simulations show a complex evolution of defects, including perfect and partial dislocations, stacking faults, and even twins.
- This content is altered by the amount of Ag present, probably due to lower stacking fault energy of Ag to Pd.
- Inter-bubble linkage noticed only for high Ag content
- *Ab initio* calculations provide estimates of material strengths that, when used within Wolfer's theory, predict a transition from dislocation loop punching to inter-bubble rupture at a helium-to-metal ratio consistent with experimental observations.
- MD simulations performed with Sandia's LAMMPS code (http://lammps.sandia.gov).
- DFT calculations performed with Quantum Espresso (http://www.quantum-espresso.org)
- Questions? For further info: jzimmer@sandia.gov