# Towards Accurate Molecular Dynamics Simulations of Helium Bubble Nucleation in Palladium Tritide

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## ABSTRACT

**Due to tritium-to-helium decay, helium bubbles develop in palladium tritide. Understanding the helium bubble nucleation mechanisms is critical to predicting material properties with age. To enable molecular-dynamics simulations of helium bubble formation with quantified uncertainty, we have developed numerous versions of Pd-H-He embedded-atom-method potentials based on extensive density-functional-theory (DFT) calculations. Our potentials are accurate because they capture the DFT values of energy and lattice constant of the rock-salt PdHe phase, the bond length and interaction energy of two nearest helium interstitials in the lattice, the swelling volume and energy change when inserting a helium atom into the lattice, the swelling volume of two nearest helium interstitials, and the diffusion energy barrier of a single helium atom. Our molecular-dynamics models enable studies of helium bubble formation because we find that the nucleation of helium bubbles from helium interstitials occurs within time scale of < 5 ns..**

## Embedded-Atom Method (EAM) Formalism

$$\phi_{PdHe}(r) = E_{0,PdHe} exp\left(-\alpha_{PdHe}\frac{r-r_{0,PdHe}}{r_{0,PdHe}}\right) f_c(r, r_{s,PdHe}, r_{c,PdHe}),$$

$$f_c(r, r_s, r_c) = \begin{cases} \frac{1}{2} erfc\left[\frac{\mu(r-r_s)+\nu(r_c-r)}{r_c-r_s}\right], & r < r_c \\ 0, & r \geq r_c \end{cases}.$$

$$\phi_{IJ}(r) = \frac{E_{0,IJ} \cdot f_c(r, r_{s,IJ}, r_{c,IJ})}{\beta_{IJ}-\alpha_{IJ}} \left\{\beta_{IJ} exp\left[-\alpha_{IJ}\frac{(r-r_{0,IJ})}{r_{0,IJ}}\right] - \alpha_{IJ} exp\left[-\beta_{IJ}\frac{(r-r_{0,IJ})}{r_{0,IJ}}\right]\right\},$$

$$F_{He}(\rho) = \begin{cases} F_{0,He}\left\{\frac{1}{2} + \frac{1}{2} sin\left(-\frac{\pi}{2} + \pi\frac{\rho}{\rho_{0,He}}\right)\right\}, & \rho < \rho_{0,He} \\ F_{0,He}, & \rho_{0,He} \leq \rho \leq \rho_{1,He}, \\ F_{0,He} + F_{2,He}\frac{(\rho-\rho_{1,He})^2}{2} + F_{3,He}\frac{(\rho-\rho_{1,He})^3}{6}, & \rho_{1,He} < \rho \end{cases}$$

$$\rho^I_{He}(r) = f^I_{He} exp(-\gamma^I_{He} r) f_c(r, r^I_{s,He}, r^I_{c,He}),$$

Here μ and ν are constants defined by ½ erfc(μ) = $10^{-5}$ and ½ erfc(ν) = 0.9

- Add He to an existing Pd-H EAM (X. W. Zhou, J. A. Zimmerman, B. M. Wong, and J. J. Hoyt, J. Mater. Res. 23, 704, 2008)
- Fit both Daw-Baskes (DB) and Finnis-Sinclair (SF) models
- DB model is the same as SF model except that the parameters are constrained at $f^{Pd}_{He} = f^{H}_{He} = f^{He}_{He}$, $\gamma^{Pd}_{He} = \gamma^{H}_{He} = \gamma^{He}_{He}$, $r^{Pd}_{s,He} = r^{H}_{s,He} = r^{He}_{s,He}$, $r^{Pd}_{c,He} = r^{H}_{c,He} = r^{He}_{c,He}$.

## Parameters of Potentials

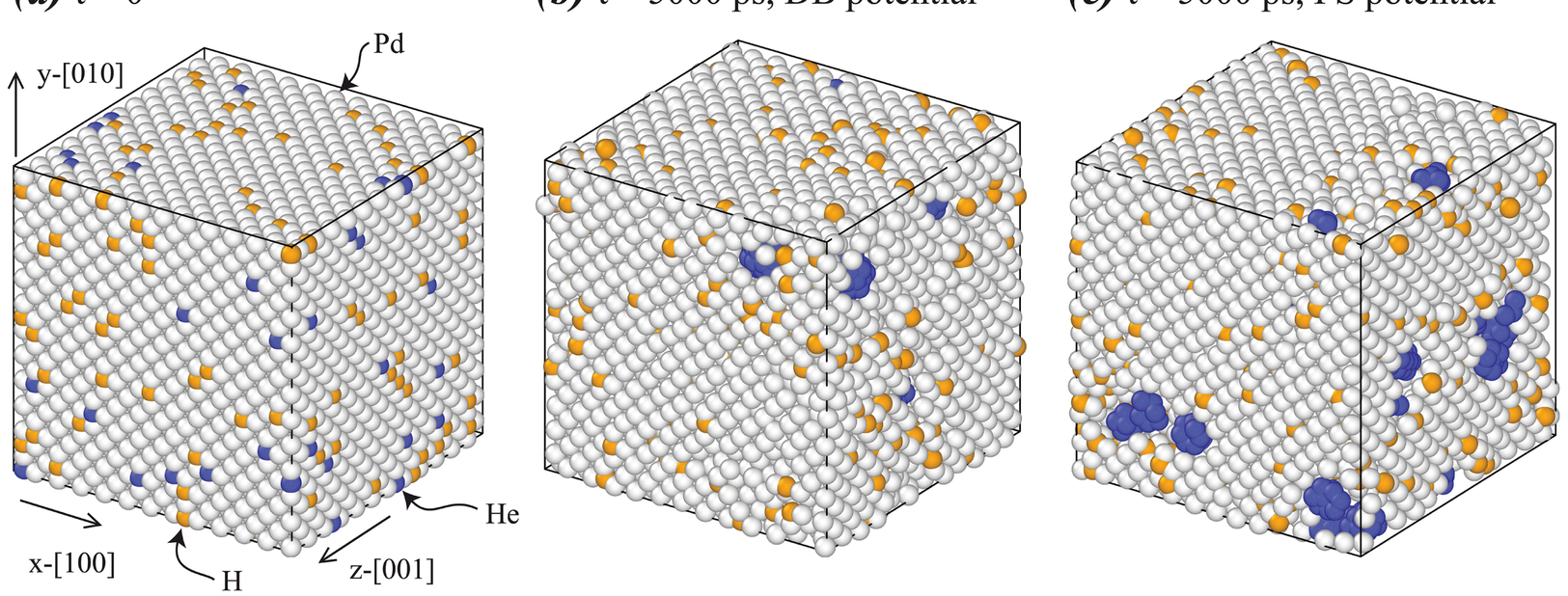
Daw-Baskes EAM model

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $E_{0,PdHe}$ | 0.002000 | $r_{0,HHe}$ | 3.120972 | $F_{0,He}$ | 3.288065 | $f^H_{He}$ | 1.592508 |
| $a_{PdHe}$ | 11.274271 | $r_{s,HHe}$ | 4.295500 | $F_{2,He}$ | 0 | $\gamma^H_{He}$ | 0.221689 |
| $b_{PdHe}$ | ----- | $r_{c,HHe}$ | 5.655147 | $F_{3,He}$ | 0 | $r^H_{s,He}$ | 2.575412 |
| $r_{0,PdHe}$ | 2.488746 | $E_{0,HeHe}$ | -1.219337 | $r_{0,He}$ | 13.742806 | $r^H_{c,He}$ | 7.975412 |
| $r_{s,PdHe}$ | 1.924805 | $\alpha_{HeHe}$ | 6.401310 | $r_{1,He}$ | 200.000000 | $f^{He}_{He}$ | 1.592508 |
| $r_{c,PdHe}$ | 2.319795 | $\beta_{HeHe}$ | 2.680178 | $f^{Pd}_{He}$ | 1.592508 | $\gamma^{He}_{He}$ | 0.221689 |
| $E_{0,HHe}$ | -0.181660 | $r_{0,HeHe}$ | 1.680000 | $\gamma^{Pd}_{He}$ | 0.221689 | $r^{He}_{s,He}$ | 2.575412 |
| $\alpha_{HHe}$ | 21.168969 | $r_{s,HeHe}$ | 3.289651 | $r^{Pd}_{s,He}$ | 2.575412 | $r^{He}_{c,He}$ | 7.975412 |
| $\beta_{HHe}$ | 12.057009 | $r_{c,HeHe}$ | 4.440681 | $r^{Pd}_{c,He}$ | 7.975412 | | |

Finnis-Sinclair EAM model

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $E_{0,PdHe}$ | 0.002000 | $r_{0,HHe}$ | 3.223129 | $F_{0,He}$ | 3.288065 | $f^H_{He}$ | 1.592508 |
| $a_{PdHe}$ | 11.274271 | $r_{s,HHe}$ | 3.570637 | $F_{2,He}$ | 0.775470 | $\gamma^H_{He}$ | 0.221689 |
| $b_{PdHe}$ | ----- | $r_{c,HHe}$ | 5.151069 | $F_{3,He}$ | 0 | $r^H_{s,He}$ | 2.575412 |
| $r_{0,PdHe}$ | 2.488746 | $E_{0,HeHe}$ | -1.180238 | $r_{0,He}$ | 13.742806 | $r^H_{c,He}$ | 7.975412 |
| $r_{s,PdHe}$ | 1.924805 | $\alpha_{HeHe}$ | 5.027132 | $r_{1,He}$ | 20.000000 | $f^{He}_{He}$ | 1.808367 |
| $r_{c,PdHe}$ | 2.319795 | $\beta_{HeHe}$ | 2.741660 | $f^{Pd}_{He}$ | 1.592508 | $\gamma^{He}_{He}$ | 0.321006 |
| $E_{0,HHe}$ | -0.005000 | $r_{0,HeHe}$ | 1.680000 | $\gamma^{Pd}_{He}$ | 0.221689 | $r^{He}_{s,He}$ | 4.787534 |
| $\alpha_{HHe}$ | 13.048548 | $r_{s,HeHe}$ | 3.042884 | $r^{Pd}_{s,He}$ | 2.575412 | $r^{He}_{c,He}$ | 5.487536 |
| $\beta_{HHe}$ | 6.467075 | $r_{c,HeHe}$ | 6.658132 | $r^{Pd}_{c,He}$ | 7.975412 | | |

## Stringent Molecular Dynamics Simulation Tests




MD annealing of a $PdH_{0.1}He_{0.05}$ structure at 600 K for 5000 ps using the two potentials: (a) initial configuration; (b) final configuration from the DB potential; and (c) final configuration from the FS potential.

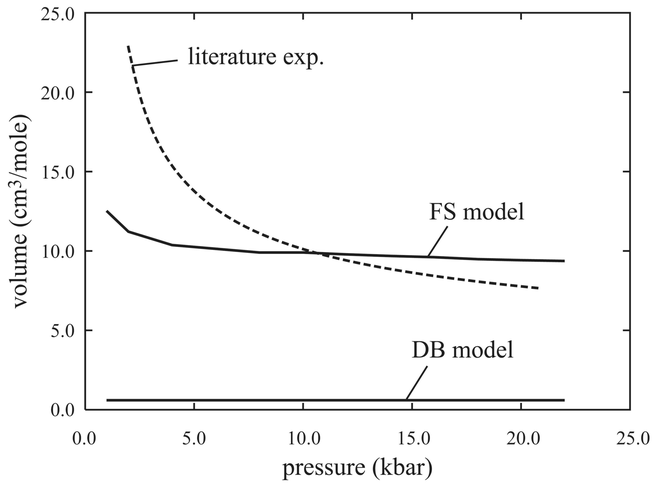
**MD simulations reveal formation of He bubbles from He atoms without assumptions!**

## Static Properties

Potentials capture well DFT values of diffusion barrier $Q_{He}$ (eV), swelling volumes $\Omega_{0,He}$, $\Omega_{He,He}$, and $\Omega_{H,He}$ (Å$^3$), insertion energy $E_{He}$(eV), bond length $r_{He\text{-}He}$ (Å), bond energy $E_{He\text{-}He}$ (eV) of He neighbors, lattice constant $a_{PdHe}$ (Å) and cohesive energy $E_{c,PdHe}$ (eV/atom) of rock-salt PdHe crystal.

| methods | $Q_{He}$ | $\Omega_{0,He}$ | $\Omega_{He,He}$ | $\Omega_{H,He}$ | $E_{He}$ | $r_{He\text{-}He}$ | $E_{He\text{-}He}$ | $a_{PdHe}$ | $E_{c,PdHe}$ |
|---|---|---|---|---|---|---|---|---|---|
| DB | 0.19 | 10.1 | 10.0 | 9.7 | 3.6 | 1.7 | -0.87 | 4.57 | -0.50 |
| FS | 0.19 | 10.1 | 9.6 | 10.0 | 3.6 | 1.7 | -0.83 | 4.59 | -0.50 |
| DFT | 0.10 | 10.0 | 10.3 | 9.5 | | 1.7 | -0.84 | 4.59 | -0.50 |

## Helium Equation of State




**The FS model captures an experimental equation of state (R. L. Mills, D. H. Liebenberg, and J. C. Bronson, Phys. Rev. B, 21, 5137, 1980)**

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## Conclusions

**We have developed two Pd-H-He embedded-atom method potentials based respectively on Daw-Baskes and Finnis-Sinclair formalisms. Both potentials accurately capture He diffusion energy barrier, He swelling volume, He insertion energy, He-He bond length and bond energy, and lattice constant and cohesive energy rock-salt PdHe crystal. The Finnis-Sinclair formalism further captures the He equation of state. Direct molecular dynamics simulations using both potentials indicate nucleation of helium bubbles from helium atoms, opening opportunities to study helium bubble nucleation without any prior assumptions on the bubbles.**