SAND2017-9298C

Three-Dimensional Maps of Helium Nanobubbles in a Palladium Alloy

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2nd Asia-Pacific Symposium on Tritium Science
September 5, 2017

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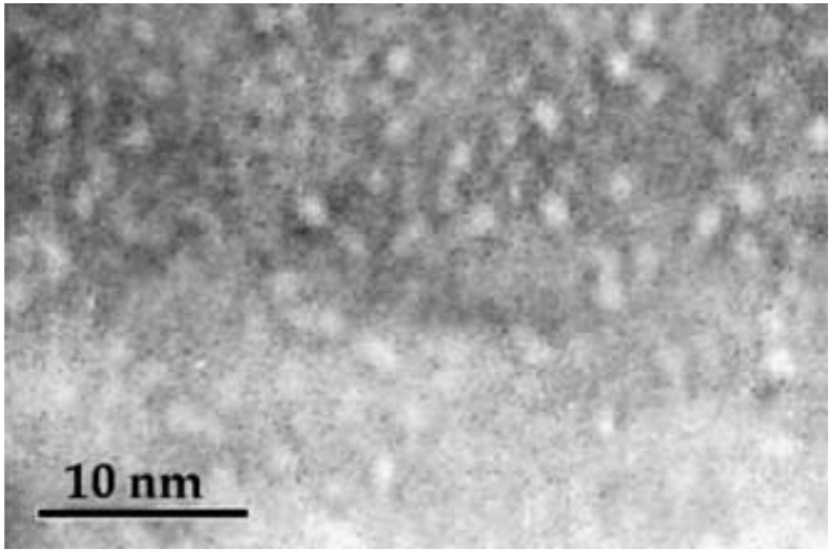
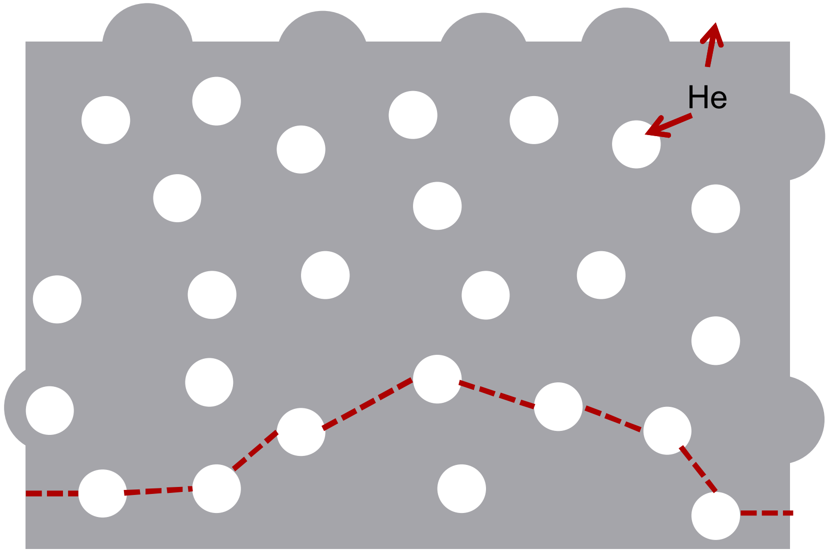
Bubbles of ^{3}He form in metal tritides



Fabre, et. al.



- ^{3}H decays to insoluble ^{3}He
- ^{3}He clusters displace metal atoms and form bubbles
- Bubbles create fracture paths, swelling, and deformation
- ^{3}He may escape at surfaces and through grain boundary paths

- An early nucleation process is thought to define bubble distributions and evolution of properties
- Material properties are believed to depend on size and spatial distribution of bubbles

(a) Cowgill, D. F. *Fusion Sci. Tech.* **2005**, *48,* 539. (b) Fabre, A.; Decamps. B.; Finot, E.; Penisson, J. M.; Demoment, J.; Thiébaut, S.; Contreras, S.; Percheron-Guegan, A. *J. Nuc. Mater.* **2005**, *342,* 101. (c) Montheillet, F.; Delaplanche, D.; Fabre, A.; Munier, E.; Thiébaut, S. *Mat. Sci. Eng. A* **2008**, *494*, 407.

Open questions about ^{3}He bubble nucleation and growth

Questions

- What determines helium bubble size distribution?
- What determines helium bubble spatial distribution?
- Do all helium bubbles nucleate within a narrow time range?

Goals

- To develop a model for how helium bubbles form and evolve
- To validate model with experimental observations

Approach

- Generate 3D images of helium bubble configurations by electron tomography and use them to deduce the history of bubble evolution
- Simulate helium bubble formation in a continuum model

Current theory of bubble growth based on capture volume

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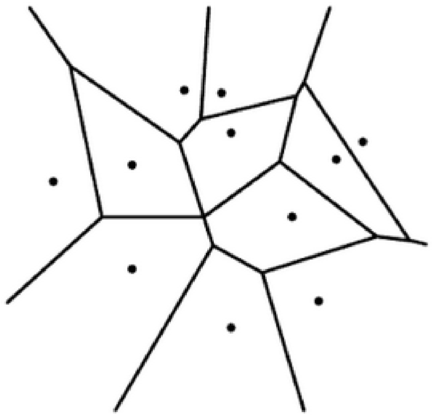
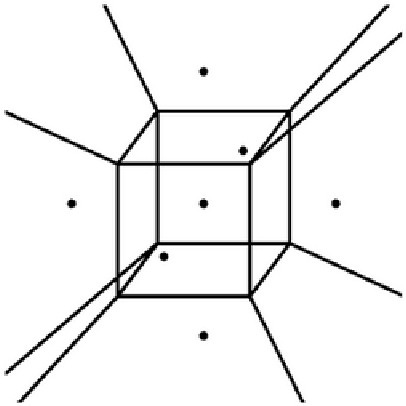


2D Voronoi tessellation



3D Voronoi tessellation

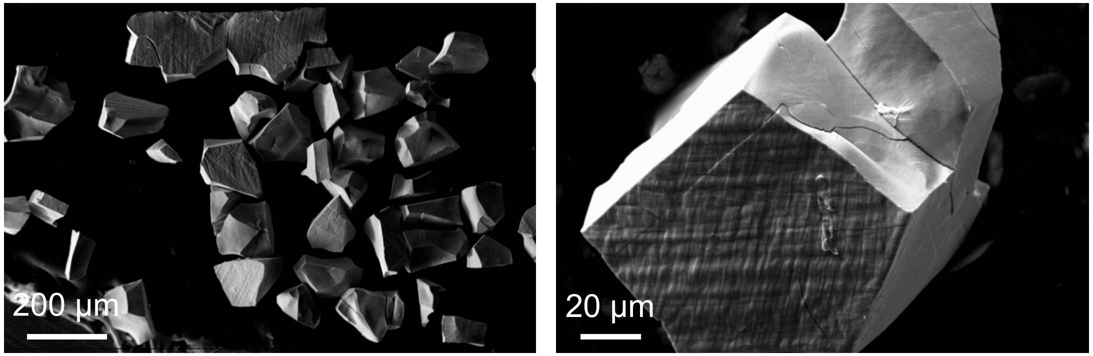
If all bubbles nucleate at same time and growth is diffusion limited, ^{3}He generated in a proximal capture region should comprise the bubble

Capture volume is described by Voronoi tessellation.

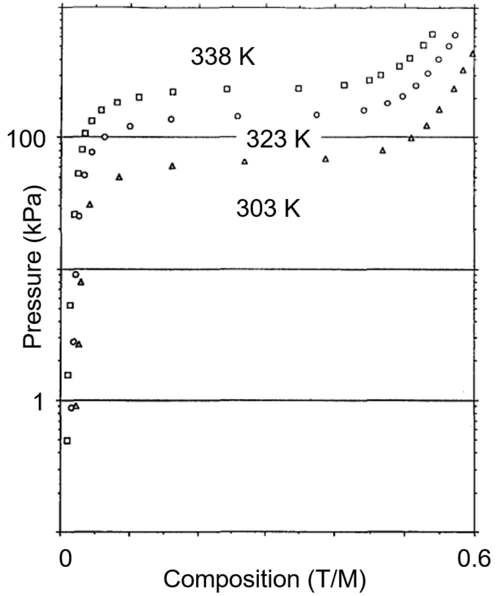
Small capture volume ➔ Small bubble?

Fortune, S. *Handbook of Discrete and Computational Geometry,* 2nd ed.; Goodman, J. E.; O'Rourke, J., Eds.; Chapman & Hall/CRC: Boca Raton, FL, 2004; pp 514.

Pd-Ni alloy tritide ribbon for study of aging effects



Tritium desorption isotherms



SEM images

5 atom % Ni

Aged 3.8 years

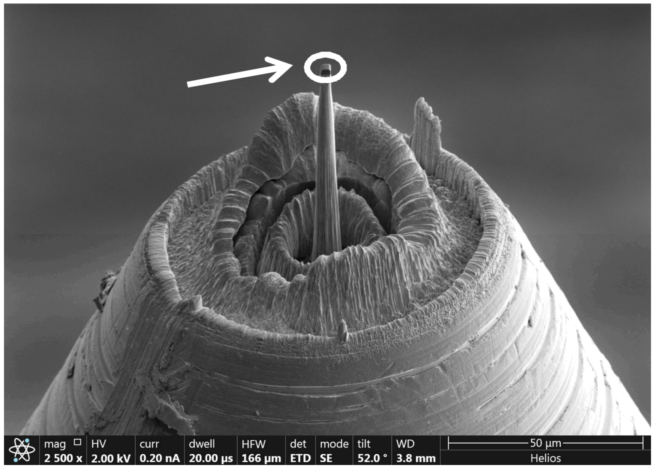
He/Pd ratio: 0.12

De-tritided by D_2-vacuum cycles

40 µCi / g by dissolution, liquid scintillation counting

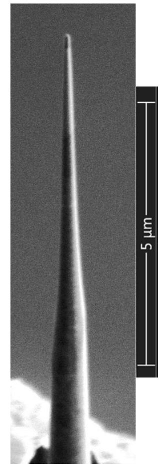
(a) Hölder, J. S.; Wermer, J. R. *J. Alloys Compounds* **1995**, *231*, 773. (b) Shanahan, K. L. *Fusion Sci. Tech.* **2017**, *71*, 555.

3D image of sample reconstructed by TEM tomography

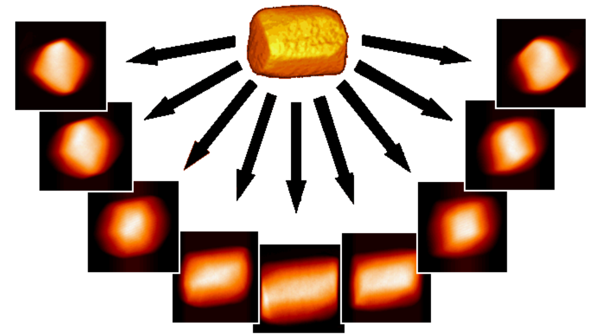


Sample prior to thinning

FIB

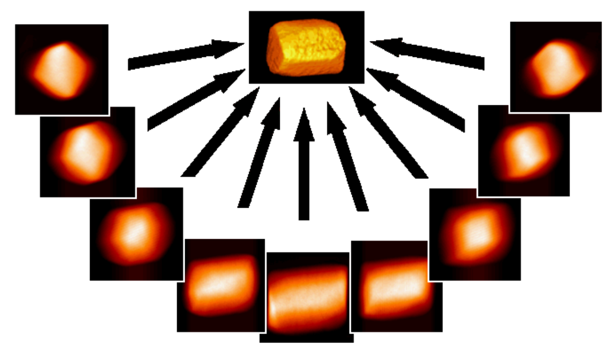


Sample for
TEM tilt series



Series of projection images

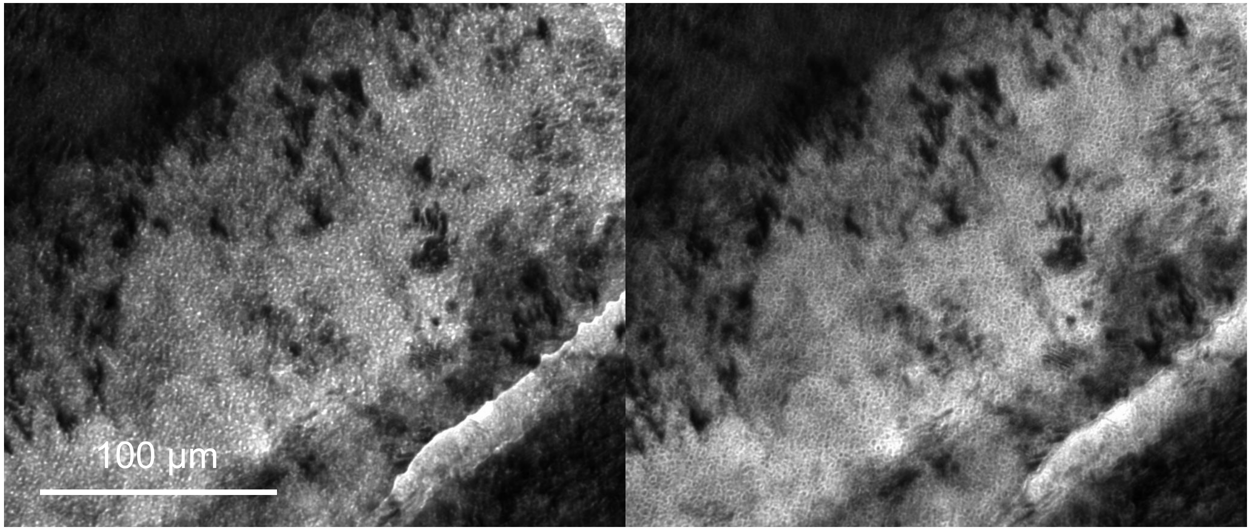
Reconstruction algorithm



Reconstructed 3D image

Sample is thinned with focused ion beam (FIB) to acquire series of images at various angles by tilting sample

Confirmation of bubble assignment by Fresnel contrast



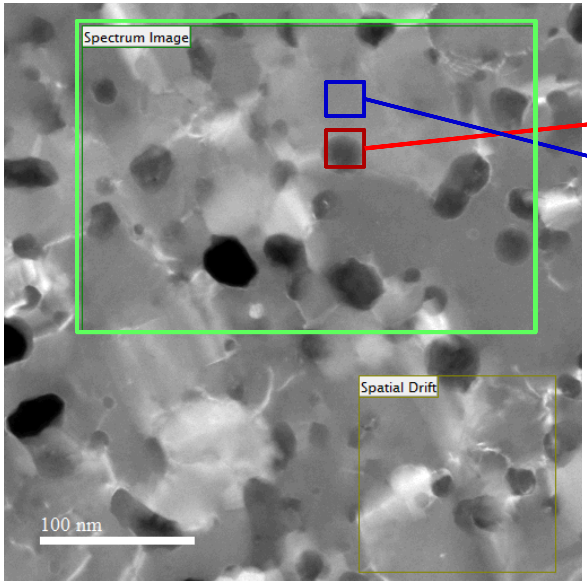
Underfocus TEM image　　　Overfocus TEM image

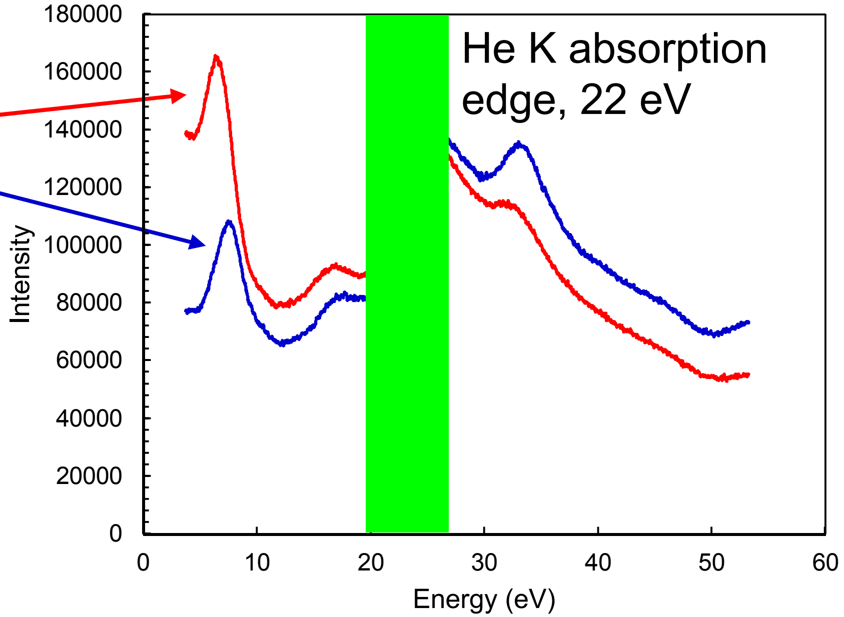
Lattice defects, such as voids, cause phase contrast by Fresnel diffraction

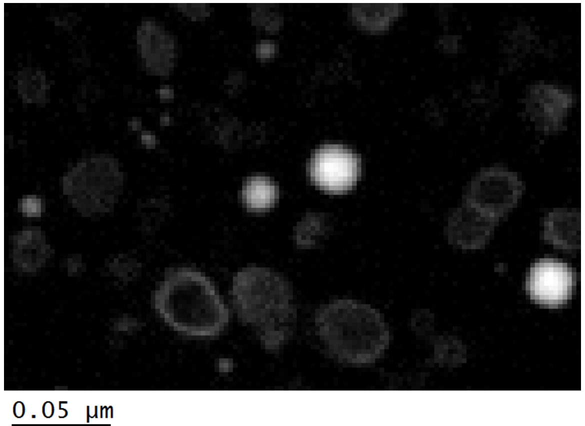
Voids appear bright in underfocus images and dark in overfocus images

Contrast reversal confirms TEM images depict void spaces, such as bubbles

Electron energy loss spectroscopy detects He in Pd







Linear background subtracted map of He K edge

Pd implanted with 1 x 10^{17} helium ions / cm^2

Annealed at 600°C for 2 hours

Upper left: STEM annular dark field image

High-pressure ^{3}He is shifted

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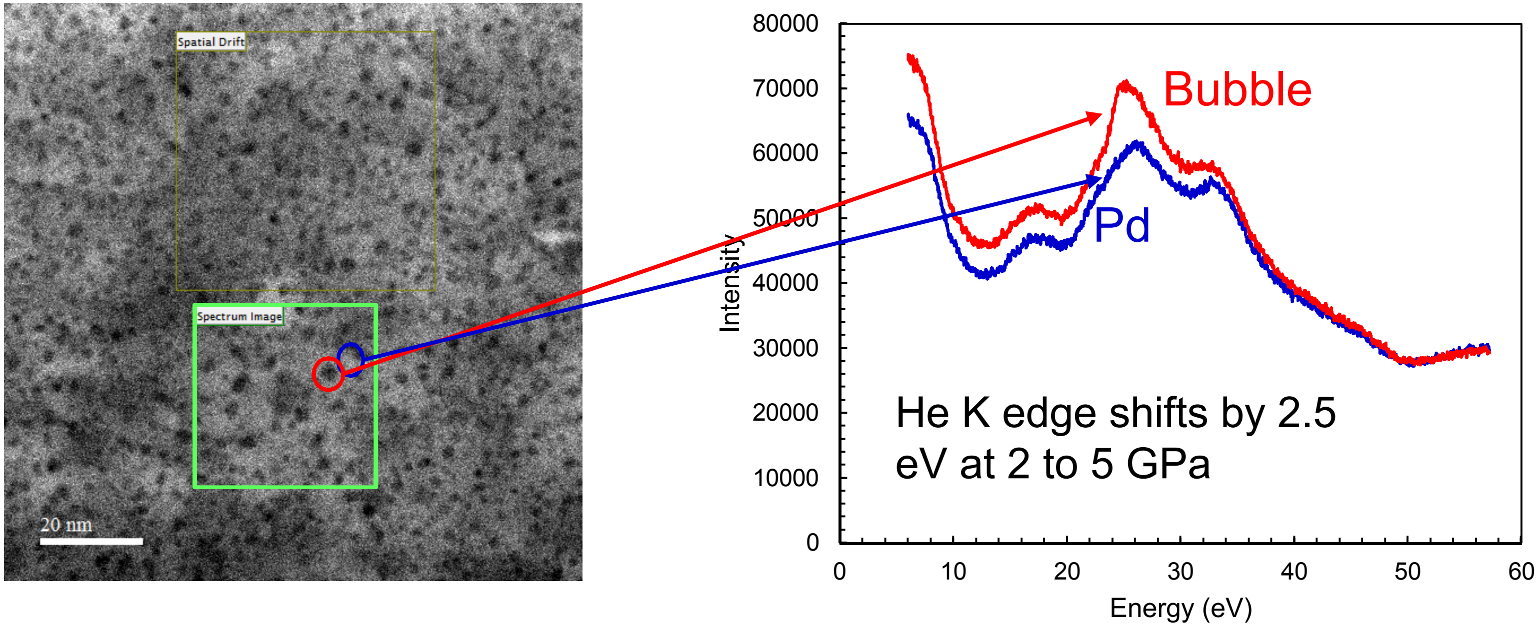
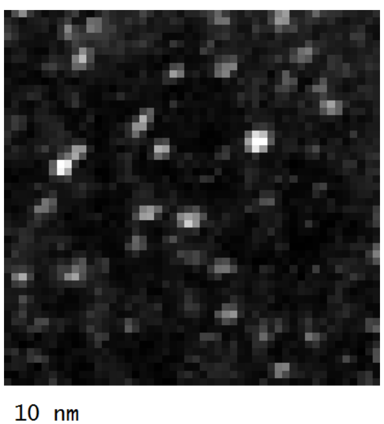
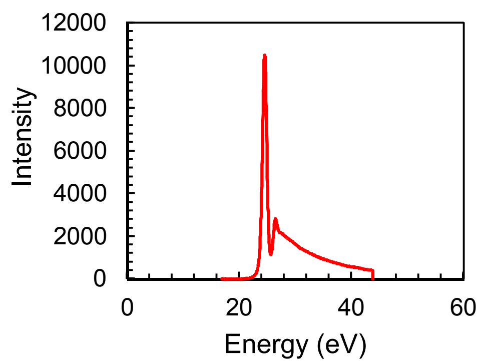
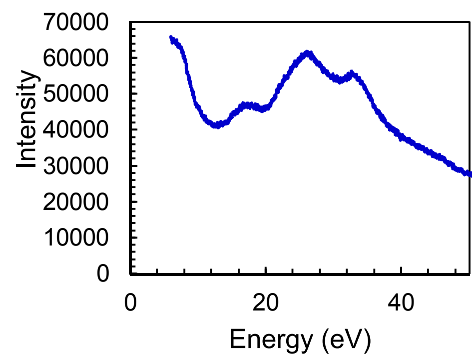
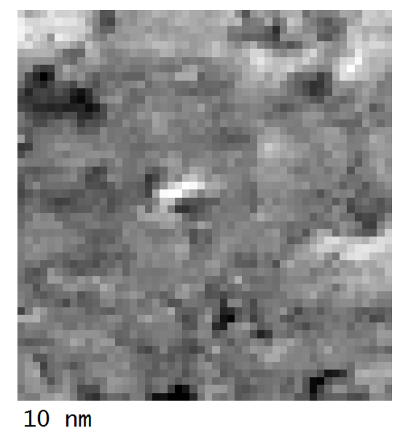






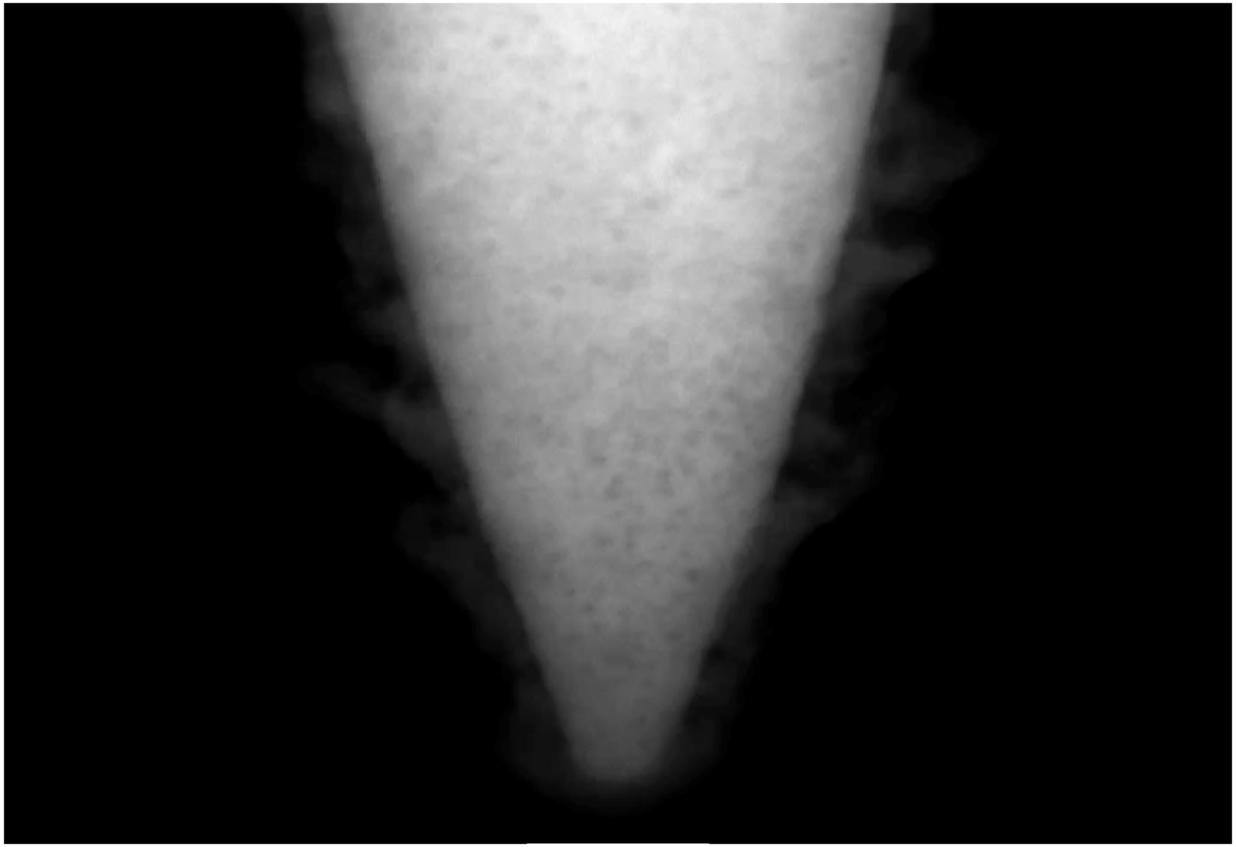




Mapping He based on shifted literature spectrum

Mapping Pd based on experimental spectrum

3D image by high-angle annular dark-field STEM



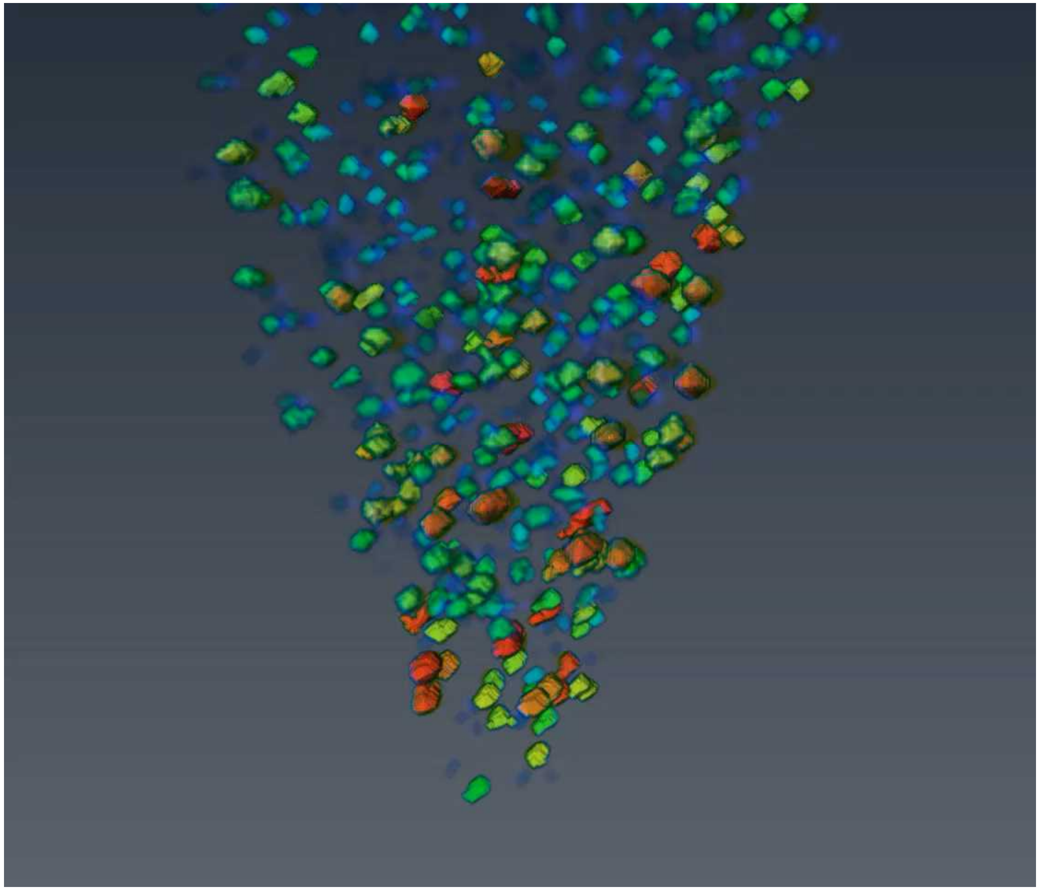
165 nm

Helium bubbles appear dark

3D image generated by simultaneous iterative reconstruction

Images taken from -70° to 70° in 1° increments

Helium bubbles identified with 3D visualization software

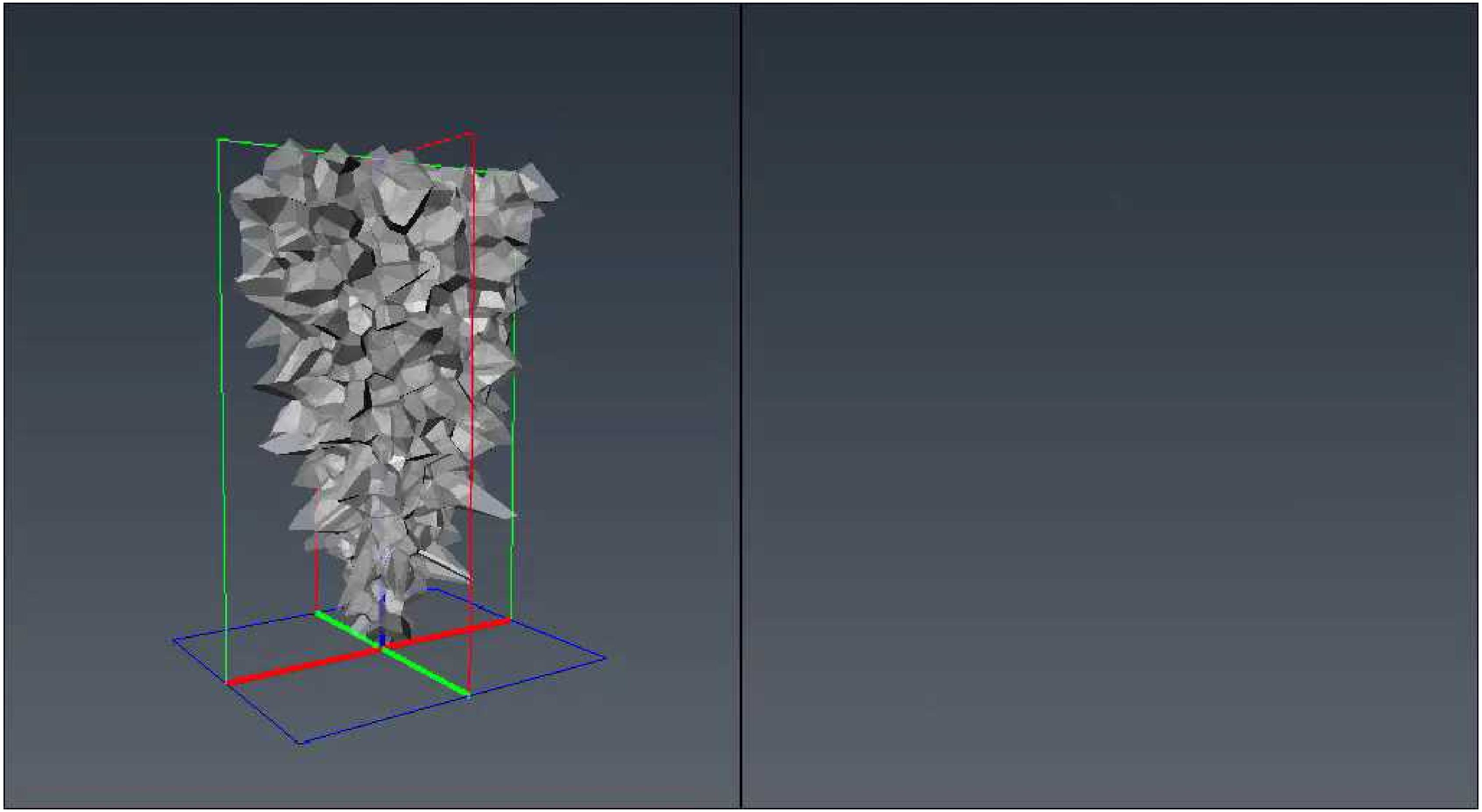


0.009 bubbles / nm^3

2 nm average bubble diameter

Size follows spectrum from large (red) to small (blue)

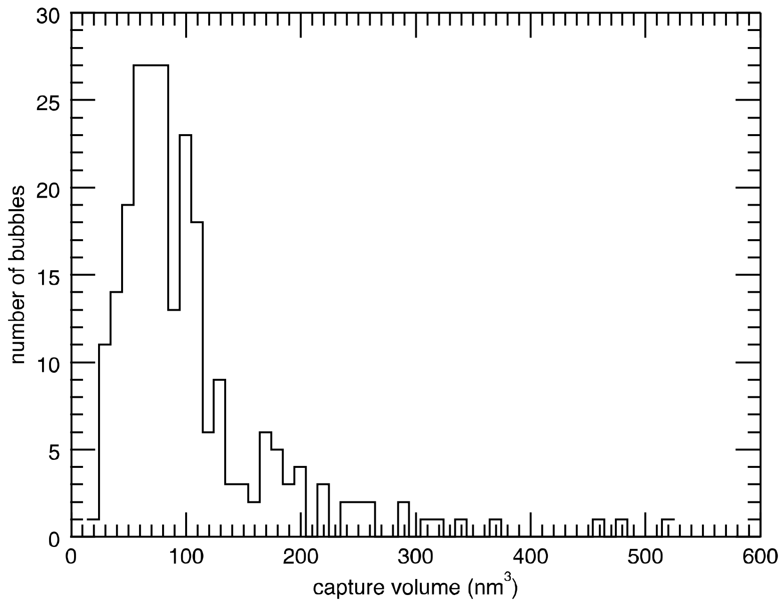
Capture volumes determined by Voronoi tessellation



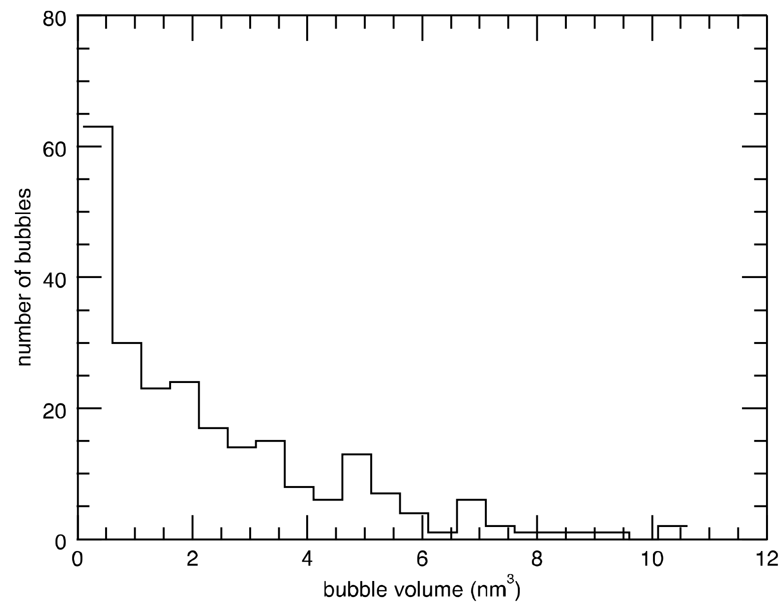
Outer layer of surface-crossing volumes is omitted from further analysis

Experimental distributions differ from expectation

Capture volume distribution: log-normal



Bubble volume distribution: not log-normal

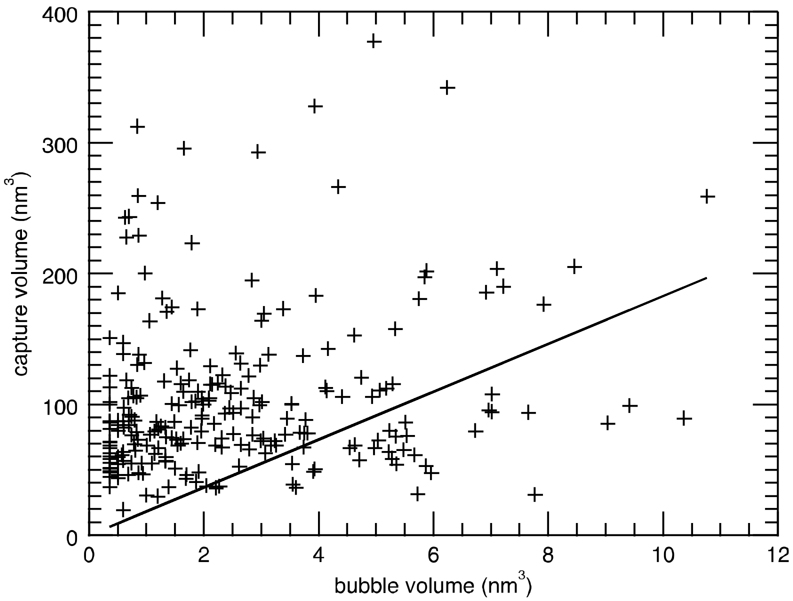


Theory suggests capture volume and bubble volume adhere to log-normal distributions

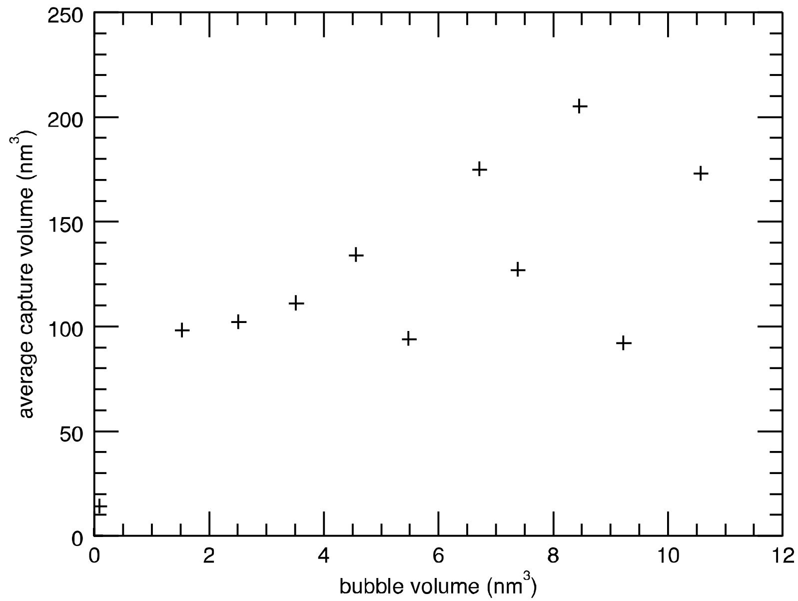
Large number of small bubbles: artifacts or indicative of late-stage nucleation

No correlation between bubble and capture volumes

Individual capture volumes



Average capture volumes



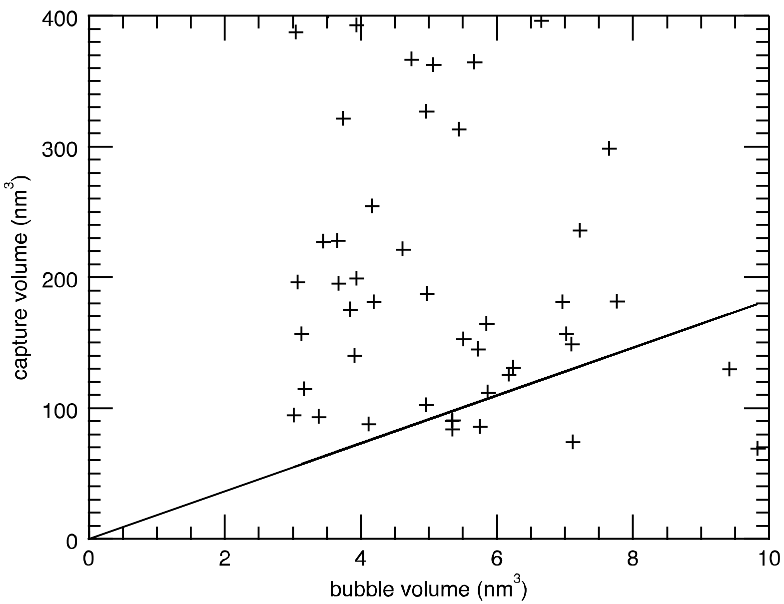
Solid line: prediction based on loop punching growth mechanism for 3.8 years of tritium decay, 1.2 He/Pd ratio, and 5 GPa bubble pressure

To first approximation, bubble volume is independent of capture volume

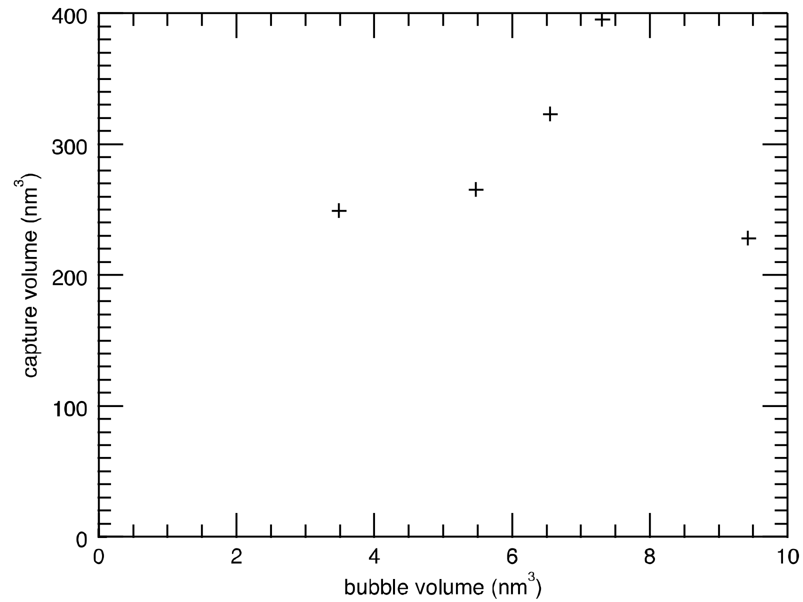
Cowgill, D. F. Sandia Report. 2004-1739.

No correlation when small bubbles are excluded

Individual capture volumes



Average capture volumes



All bubbles smaller than 3 nm^3 were discarded in case these resulted from late nucleation or errors in data reconstruction

Capture volume does not correspond with bubble volume even after removal of smallest bubbles

Continuum model for ^{3}He bubble nucleation and growth

Finite difference simulation solves the diffusion equation:

$$\frac{\partial \rho_{He}}{\partial t} = D\nabla^2 \rho_{He} + R\rho_T$$

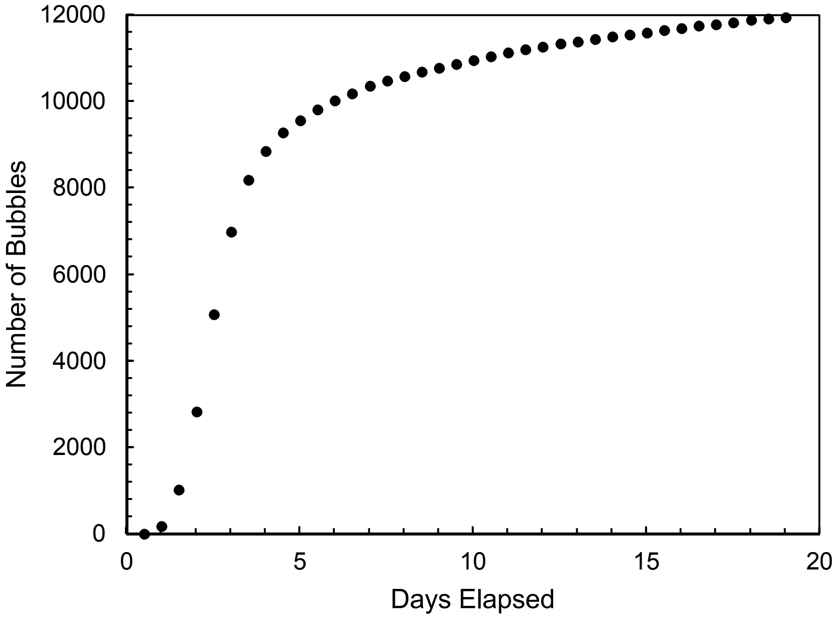
Assumptions:

- Tritium composition is constant
- Local bubble nucleation rate is proportional to square of local helium density
- Bubble size expansion occurs after a minimum internal pressure is reached
- Helium atoms cannot diffuse out of helium bubbles
- Small activation barrier to helium atom joining bubble
- Average bubble pressure of 2 GPa → 40 ^{3}He atoms / nm

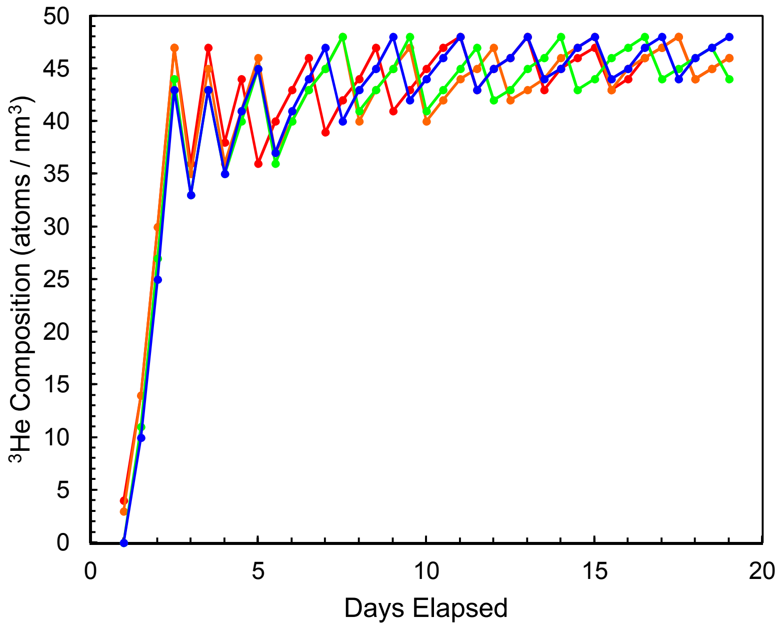
250 x 250 x 250 nm^3 grid, 1 nm spacing

Bubbles nucleate and grow as simulation adds ^3He

Bubble nucleation



Bubble growth



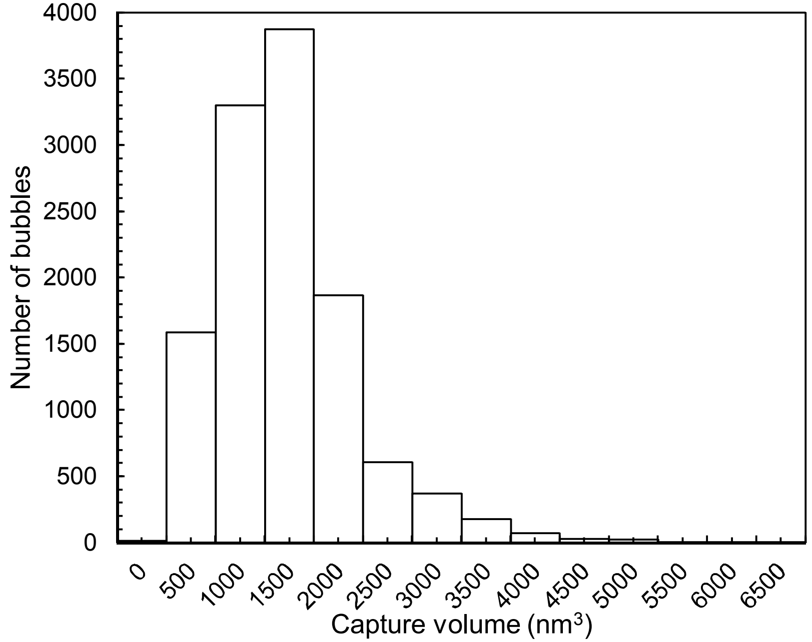
After initial burst of nucleation, rate of bubble formation decreases with increasing number of bubbles

Helium atom density increases until a maximum allowable pressure is reached, at which point bubble expands

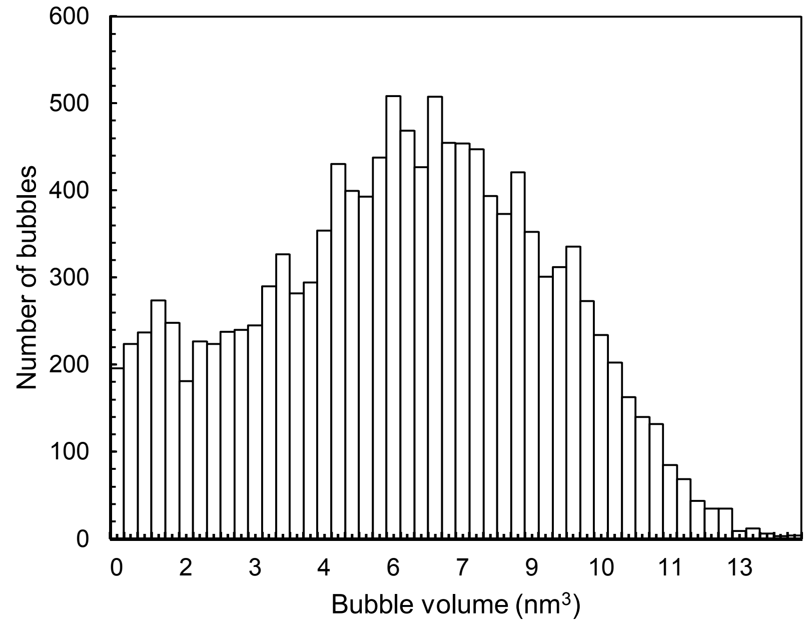
0.0007 bubbles / nm^3; order of magnitude lower than experiment

Simulation distributions reflect experimental data

Capture volume distribution: log-normal



Bubble volume distribution: not log-normal

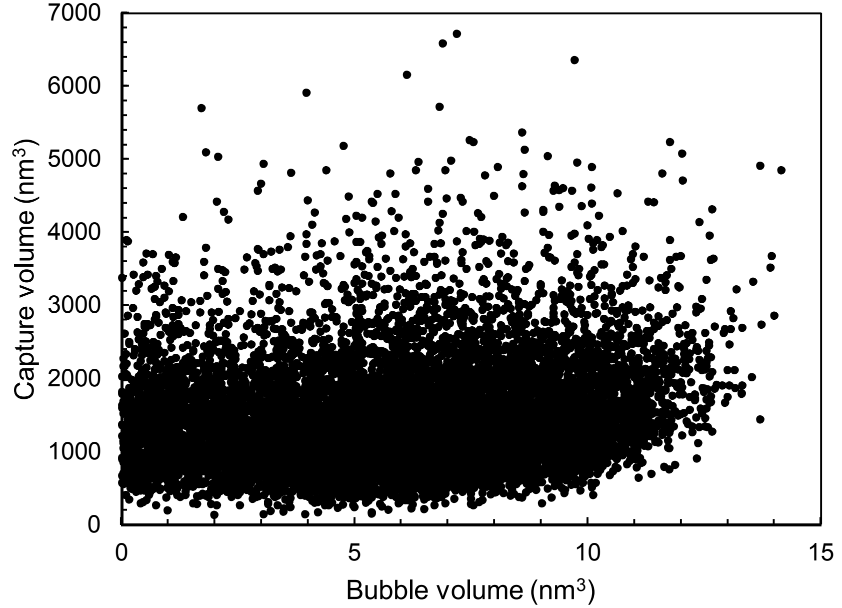


In correspondence with experimental data, capture volumes of simulated bubbles represent a log-normal distribution but bubble volumes do not

Distribution maxima are higher for simulation than experiment
More small bubbles in experiment

Simulation shows no bubble / capture volume correlation

Individual capture volumes



Similar to experiment, ^{3}He bubbles generated by the simulation showed no correlation between a bubble's size and its capture volume

Conclusions

- No correlation between capture volume and bubble size → a bubble's capture volume does not determine the bubble's size
- Bubble size distribution is not log-normal → late nucleation of bubbles may contribute to distribution; longer simulation times may help
- Better optimization of simulation parameters may achieve better matching of distribution positions to experiment
- Experiments to determine correlation between bubble size and helium content will help validate model

Acknowledgments

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Work at Savannah River National Laboratory was performed under contract number DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Simulation of ^{3}He bubble formation: parameters

- Tritium composition: $PdT_{0.7}$
- Temperature: $T = 300$ K
- Lattice constant: $a = 0.4$ nm
- Activation energy for ^{3}He diffusion: $Q = 0.2$ eV
- $D = 864$ nm^2/day → $D_0 = 1.98 \times 10^{-6}$ nm^2/day
- Activation energy for bubble growth by one atom, $dQ = 0.05$ eV
- Initial ratio of ^{3}He to Pd = 10^{-5} to 1
- Bubble nucleation rate = one bubble per 10^6 Pd atoms per two days
- Minimum internal pressure for bubble expansion to new cell = 2000 atm
- 19 day evolution period