Lawrence Livermore National Laboratory

Kinetics of Helium Accumulation in Solids (U)

Hydrogen and Helium Isotopes in Materials, Feb. 6-7, 2008

W. G. Wolfer, A. Kubota
Physical Sciences, LLNL

K. Morishita
Kyoto University, Japan

Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551
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Mechanisms and Issues

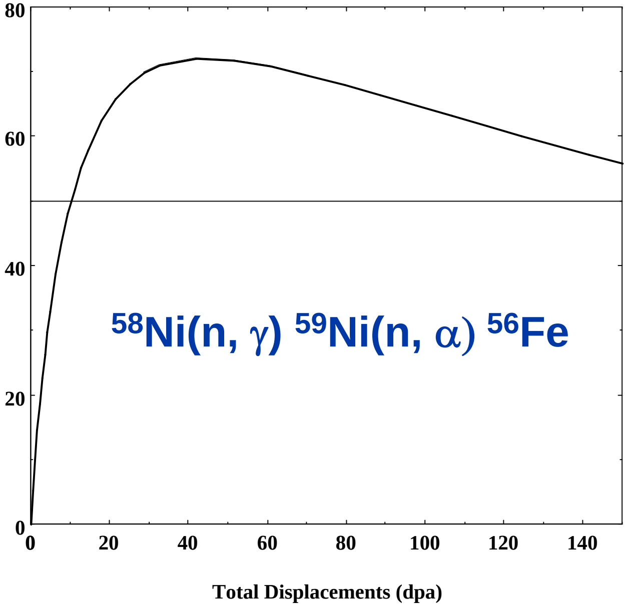
- Helium from Nuclear Transmutation: *Production Rates & Recoil Energies*
- Helium Migration and Trapping
- Helium Aggregation Kinetics: *Bubble Densities & Size Distributions*
- Helium Densities in Bubbles or Precipitates
- Equation of State for Helium
- Helium-Induced Changes in Lattice Parameter & Sample Dimensions
- Radiation-Induced Resolution of Helium in Bubbles

Helium from Nuclear Transmutations

(n, α) Energies, MeV

Isotope	Q	He Recoil
Ni-59	5.096	4.751
Zn-65	6.481	6.082
Fe-55	3.584	3.323
Co-58	3.511	3.269
Co-57	1.618	1.504

He generation rate in SS 316 irradiated in HFIR

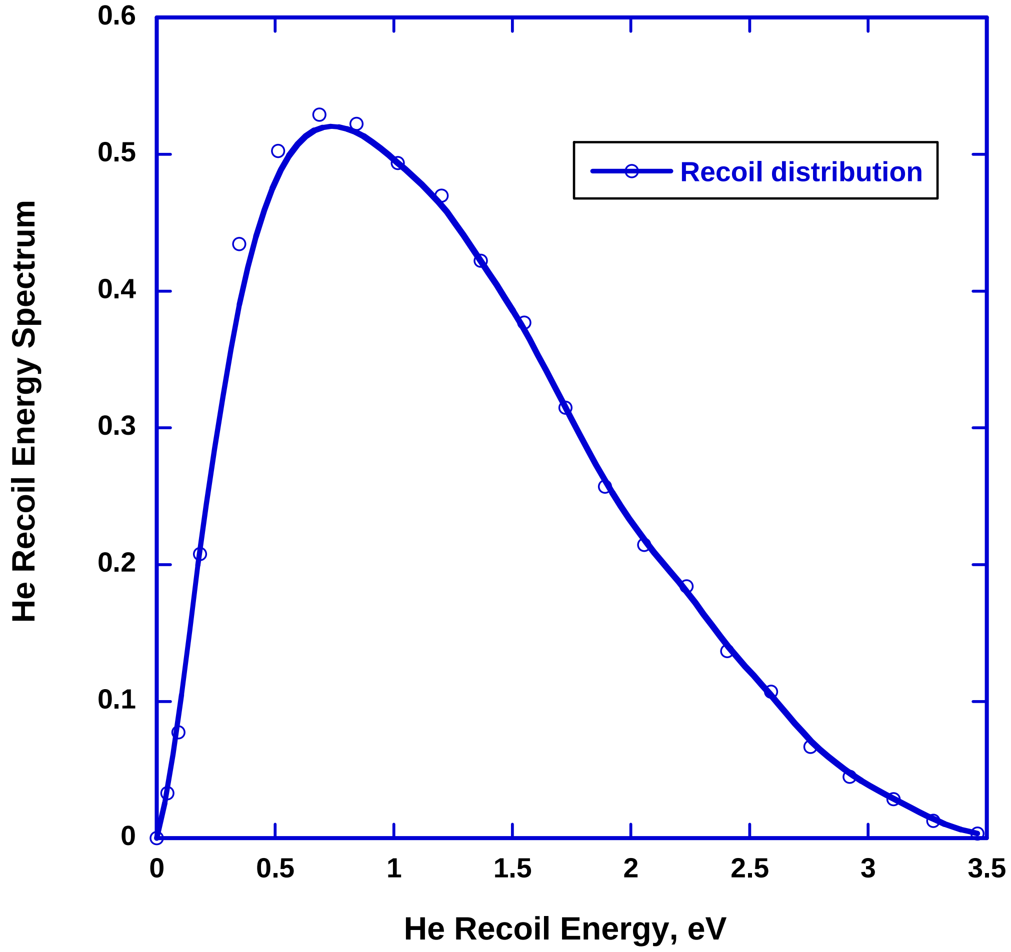


appm He / dpa Ratios

FFTF	EBR-II	HFIR	HFIR	Fusion	PWR	BWR	Pu	$PdT_{0.65}$
SS304	SS304	SS304	Nickel	1st Wall	Baffle	Grid plate	WG	
0.1-1	0.2-0.3	60	600	15	14-25	72	400	infinite

At the end of its range (5-15 μm), Helium generates a displacement cascade with 100-300 Frenkel pairs. Helium will come to rest in a vacancy or vacancy cluster.

Helium from Tritium Decay starts as an Interstitial



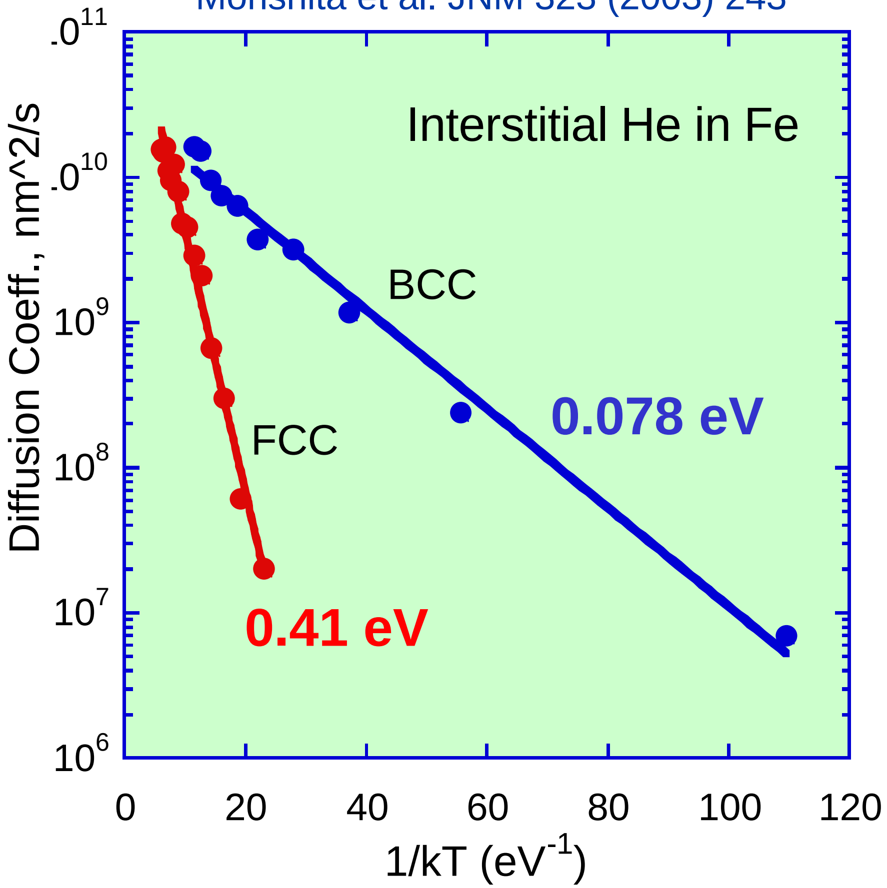
Tritium resides mostly in interstitial positions.

Helium recoil energy is too low to create a Frenkel Pair.

$T \rightarrow {}^{3}He + \beta^{-} + \underline{\nu} + 18.6\ keV$

Helium as an interstitial is highly mobile ...

Morishita et al. JNM 323 (2003) 243



Enthalpy of Helium as Interstitial

$$E^{F}_{\text{Int.He}} = \begin{cases} 4.25eV & \textbf{BCC Fe} \\ 5.25eV & \textbf{FCC Fe} \end{cases}$$

Diffusion of Helium as Interstitial

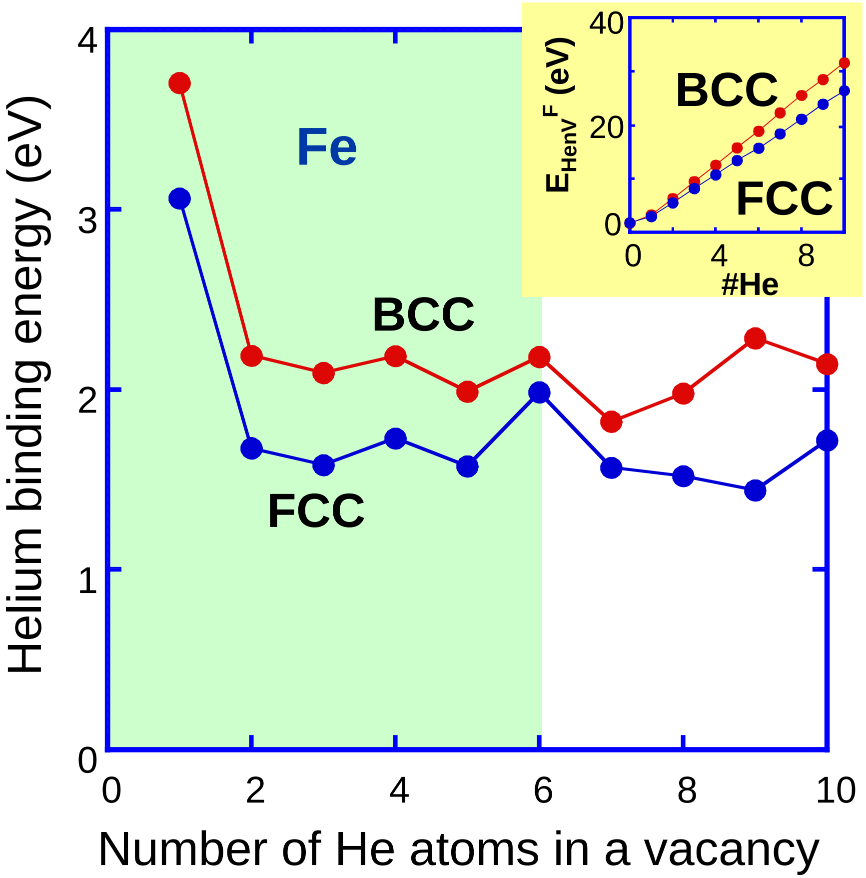
$$D_{\text{int.He}} = \begin{cases} 2.80\times10^{10}\exp\left(-\dfrac{0.078eV}{k_BT}\right) & \textbf{BCC Fe} \\ 2.62\times10^{11}\exp\left(-\dfrac{0.41eV}{k_BT}\right) & \textbf{FCC Fe} \end{cases}$$

nm^2/s

... but is is also very unstable and strongly trapped by vacancies.

A vacancy can trap any number of Helium atoms…

Courtesy of Prof. Morishita, Kyoto Univ.



$He_nV \rightarrow He_{n-1}V + He_{Int.}$

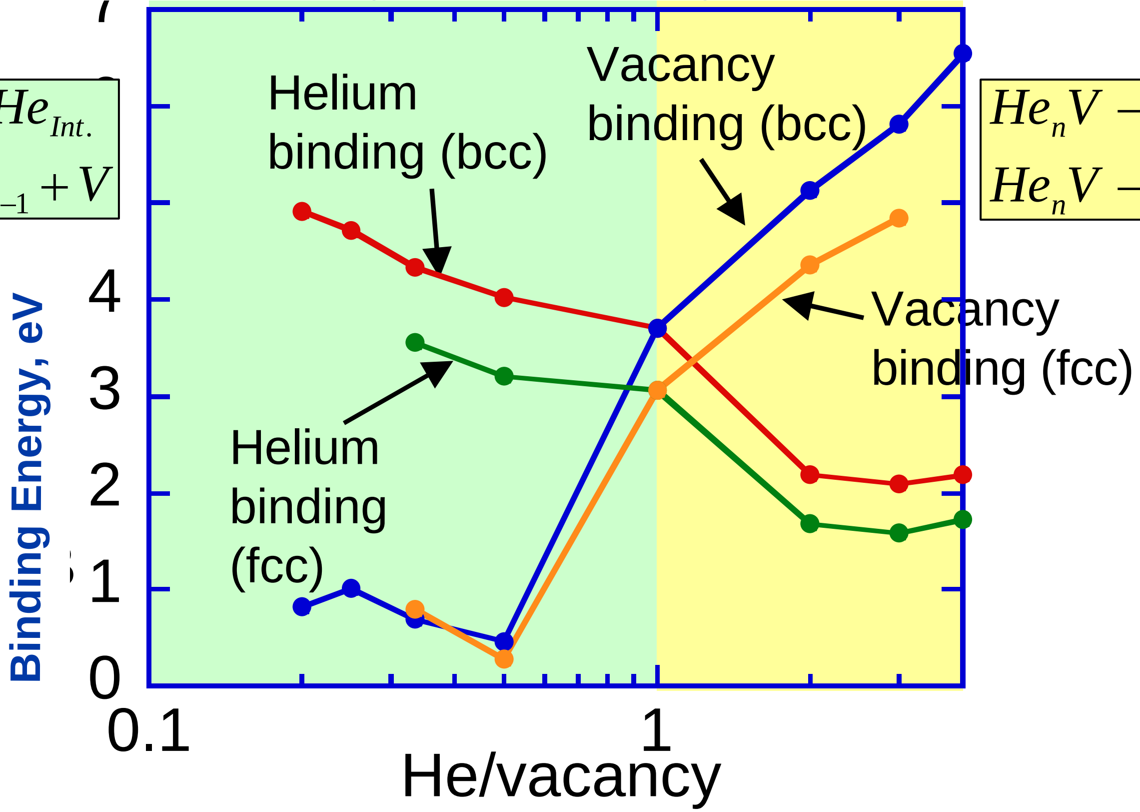
… and when the number exceeds more than 5, a metal atom is expelled as a self-interstitial rather than a helium atom.

(First discovered in computer simulations by Bill Wilson and later confirmed by many.)

Clusters with a Helium/Vacancy ratio ≥ 1 are very stable

Courtesy of Prof. Morishita, Kyoto Univ.

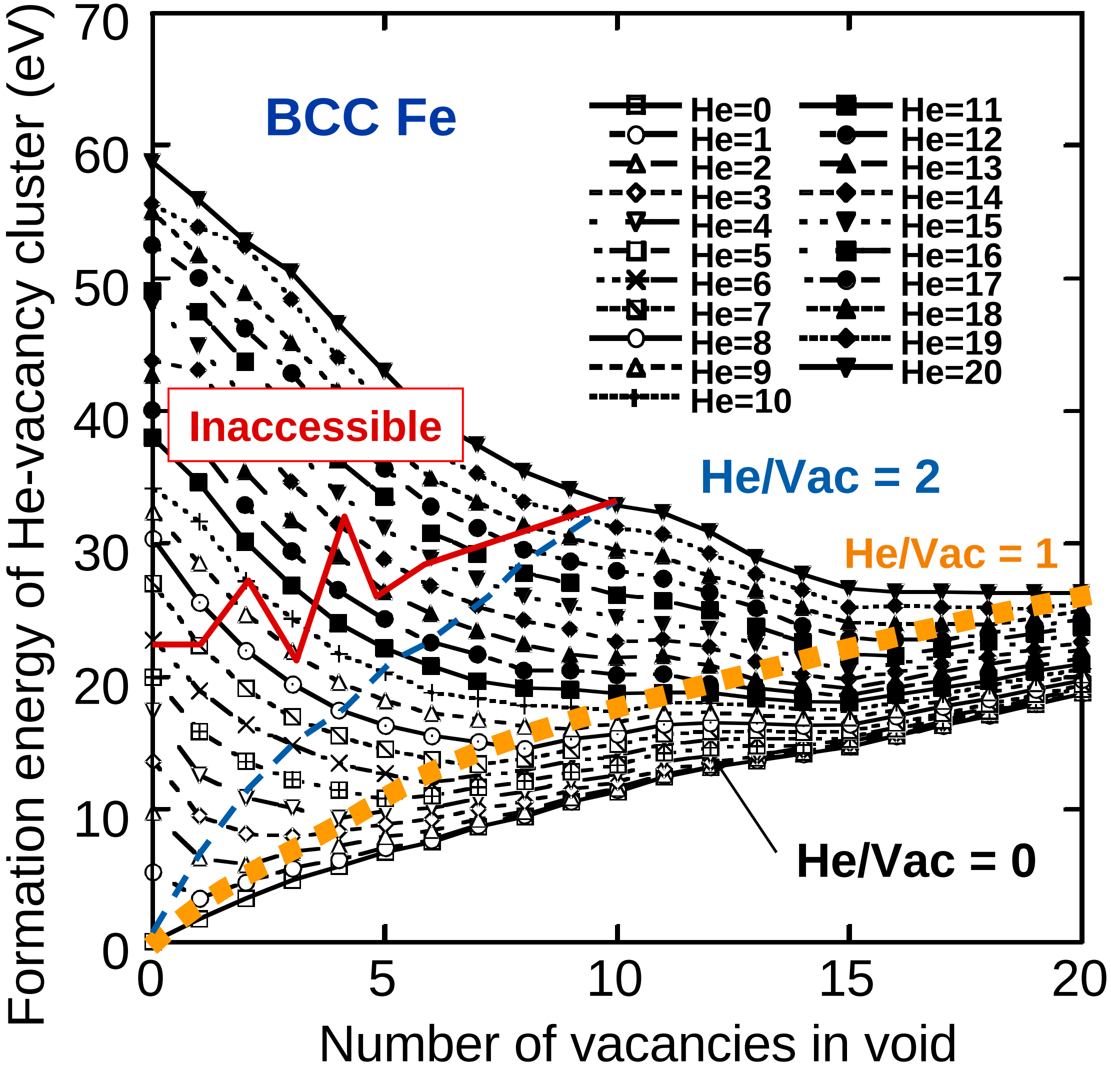
$$HeV_m \rightarrow V_m + He_{Int.}$$
$$HeV_m \rightarrow HeV_{m-1} + V$$



$$He_nV \rightarrow He_{n-\text{int.}} + V$$
$$He_nV \rightarrow He_{n-1}V + He_{Int.}$$

Density of Helium in small bubbles is more conveniently expresses in terms of numbers of He atoms per vacant site, or simply as He/vacancy ratio.

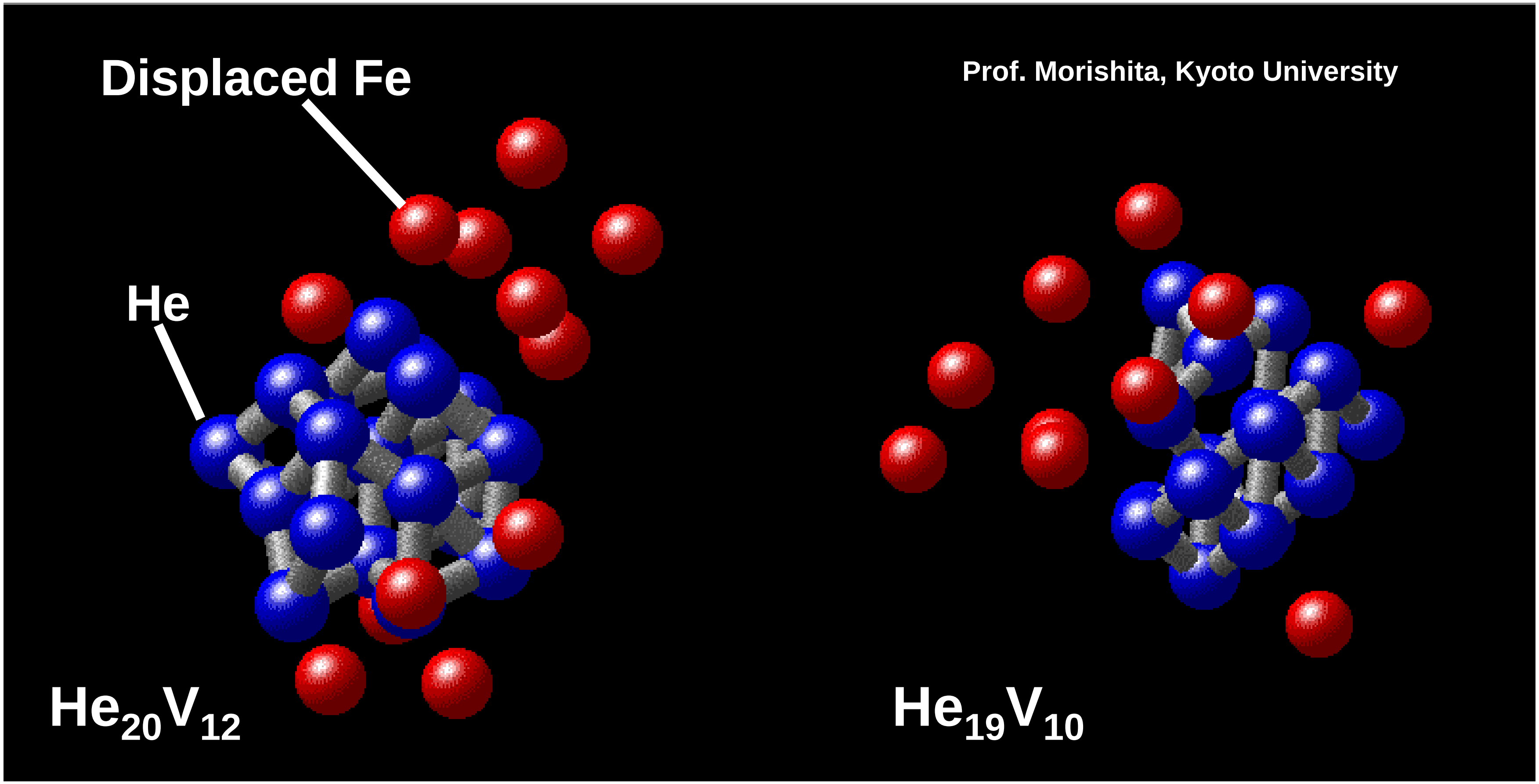
Energy Landscape of Helium-Vacancy Clusters



Clusters above red curve are unstable and convert by self-interstitial emission or by dislocation loop punching to clusters with lower He/Vac. Ratios.

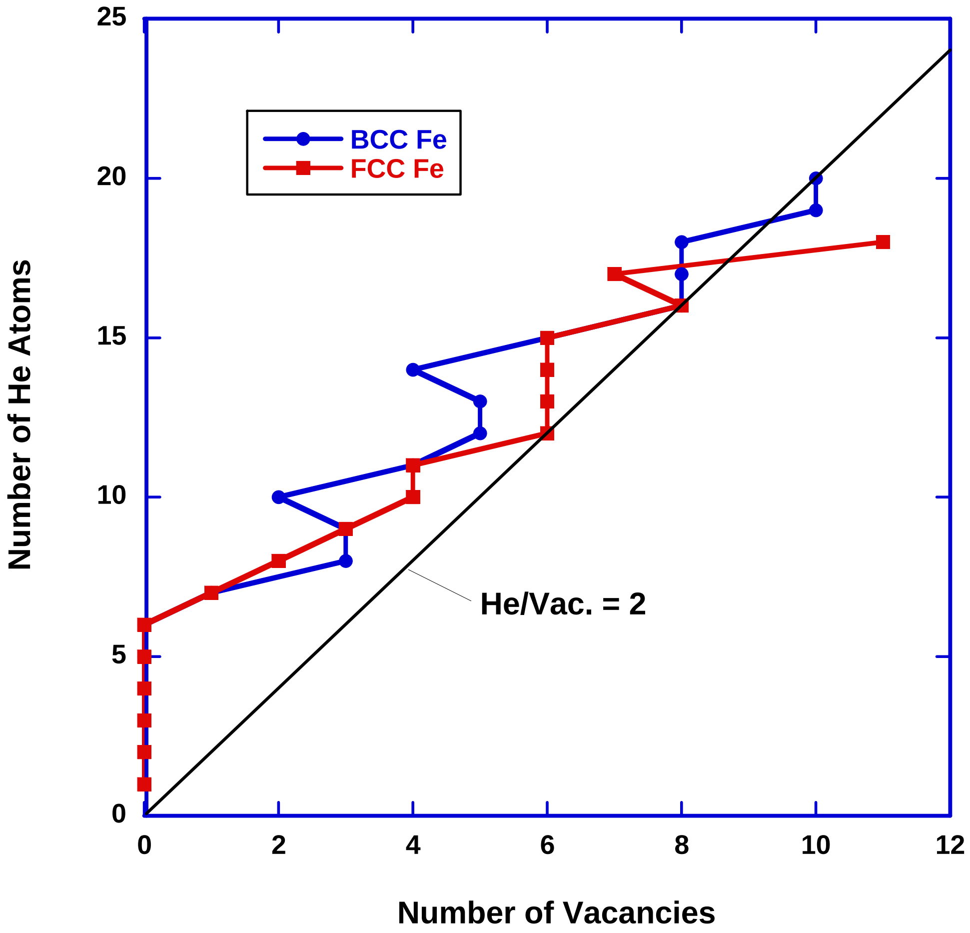
Courtesy of Prof. Morishita & Phil. Mag. 87 (2007) 1139

Expelled self-interstitials remain attached to helium-vacancy cluster as a loose aggregate



For larger bubbles, these aggregates become prismatic interstitial-type loops

Mechanically stable He-V clusters in Fe

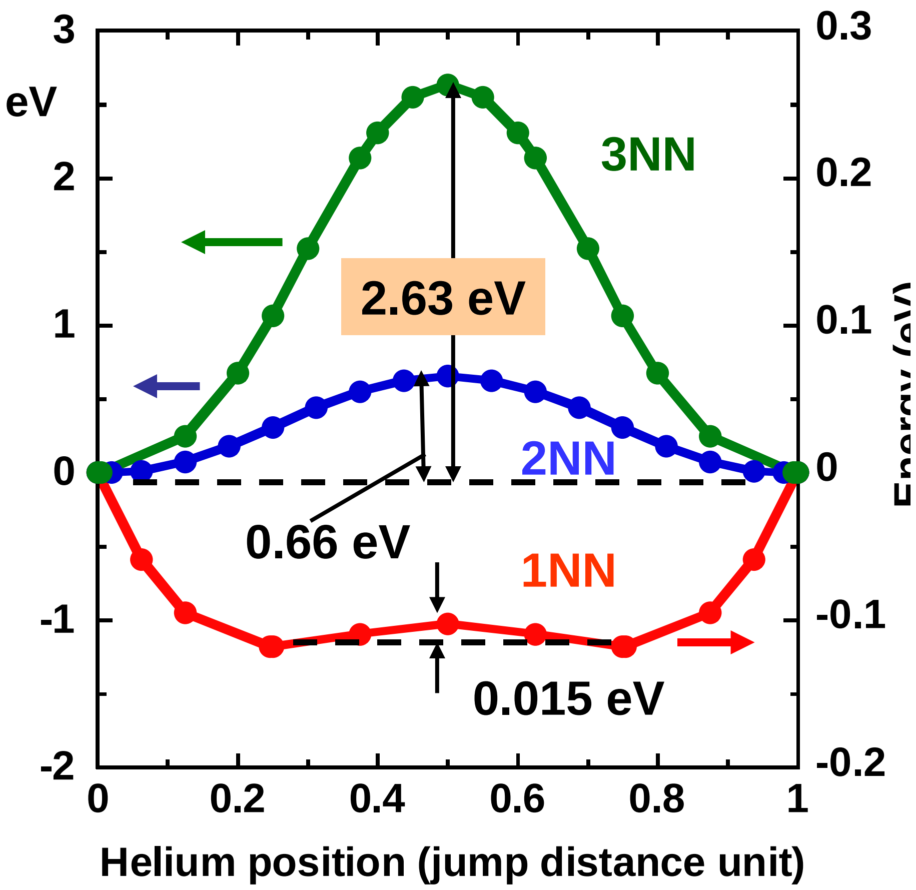


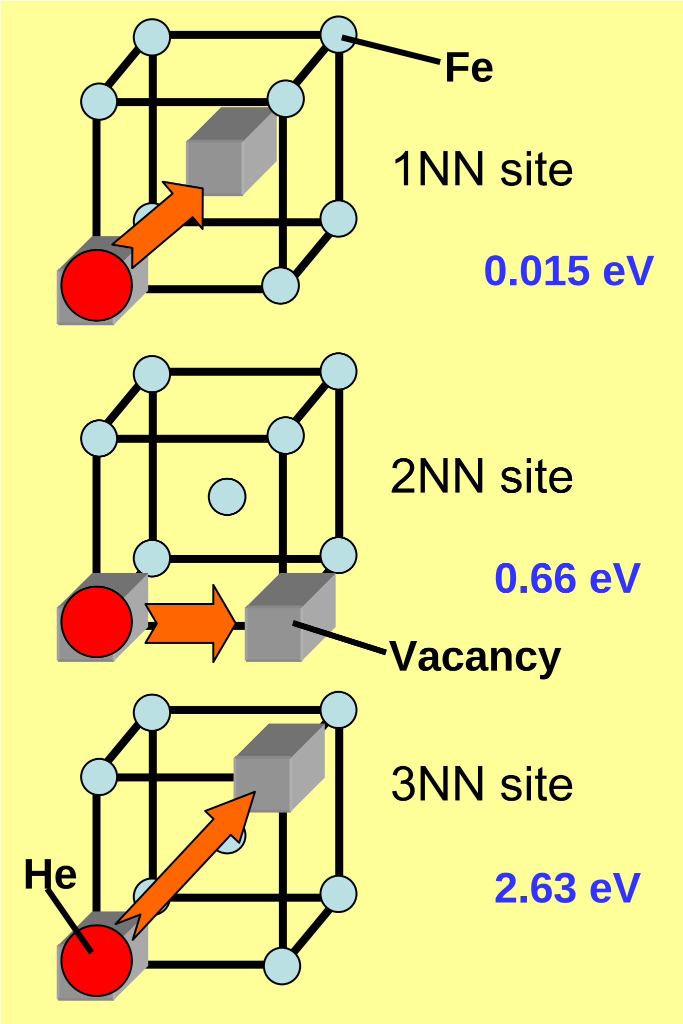
Helium density quickly approaches the loop-punching limit of He/Vac. = 2

Courtesy of Prof. Morishita & Phil. Mag. 87 (2007) 1139

He migration via vacancy mechanism: activation energy is close to vacancy migration energy

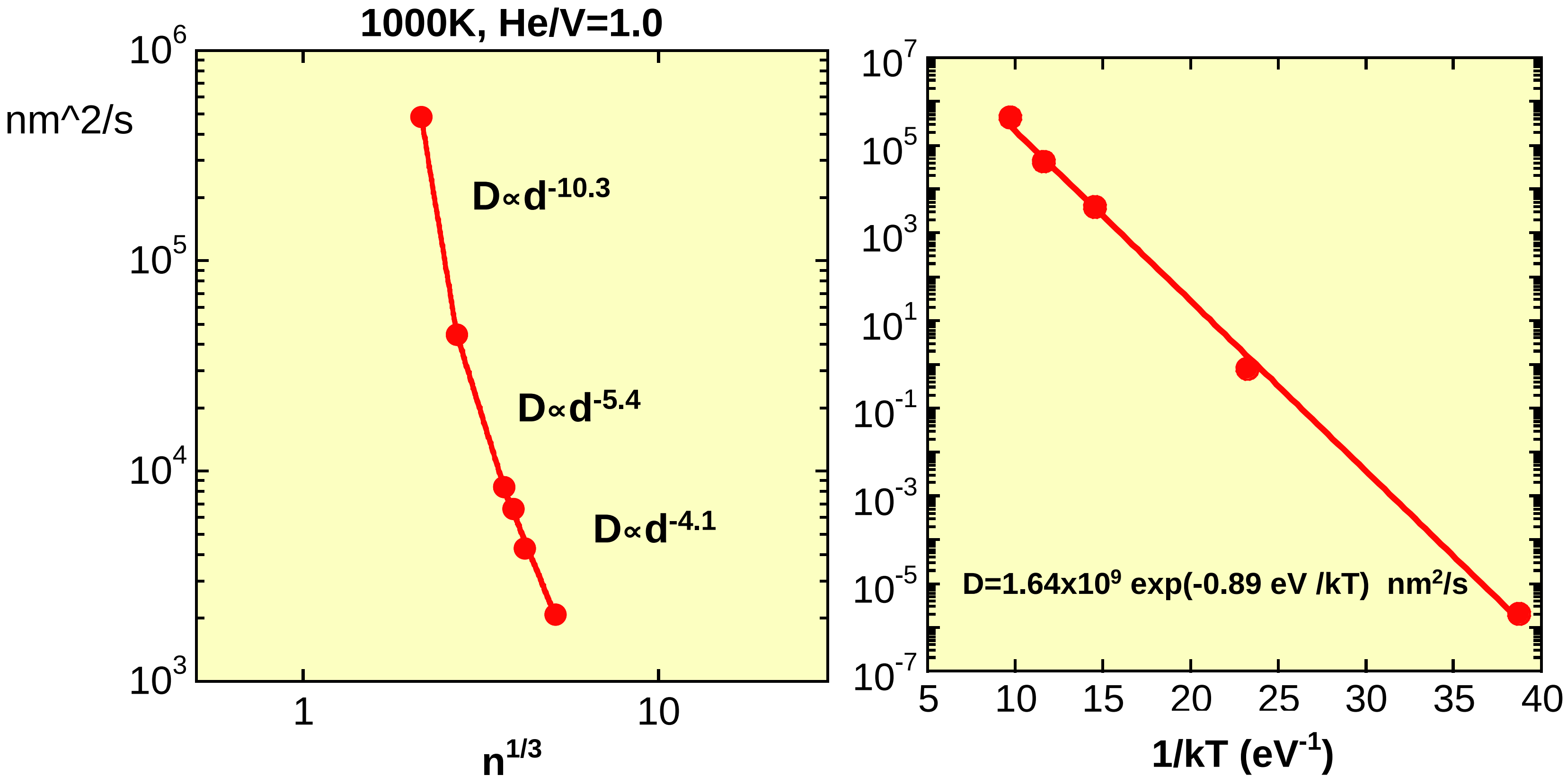
Courtesy of Prof. Morishita, Kyoto Univ.





Mobility of Helium-Vacancy Clusters

Courtesy of Prof. Morishita, Kyoto Univ.



Theory predicts a size dependence of D ∝ d^-4 for surface diffusion and D ∝ d^-3 for volume diffusion, where d is the bubble diameter. n is the number of vacancies in cluster.

Starting assumptions for helium bubble evolution model

- Mean-field assumption for the rate coefficients: every bubble has the same environment
- Helium is produced uniformly in space and time
- Only V, SIA, and He-V species diffuse, and migration of He-V is rate controlling
- Diffusion is strictly random: no long-range interaction between diffusing He and bubble
- Radiation-induced re-solution of helium bubbles may occur
- Impurity segregation to bubble surface or surface stress may result in interface controlled kinetics

Bubble that form by one substitutional Helium at a time

Monomer equation for He in solution

$$\frac{dN_1}{dt} = G - 16\pi r_1 D N_1^2 - 4\pi D N_1 \sum_{i=2}^{\infty} r_i N_i$$

Dimer equation for He bubble nuclei

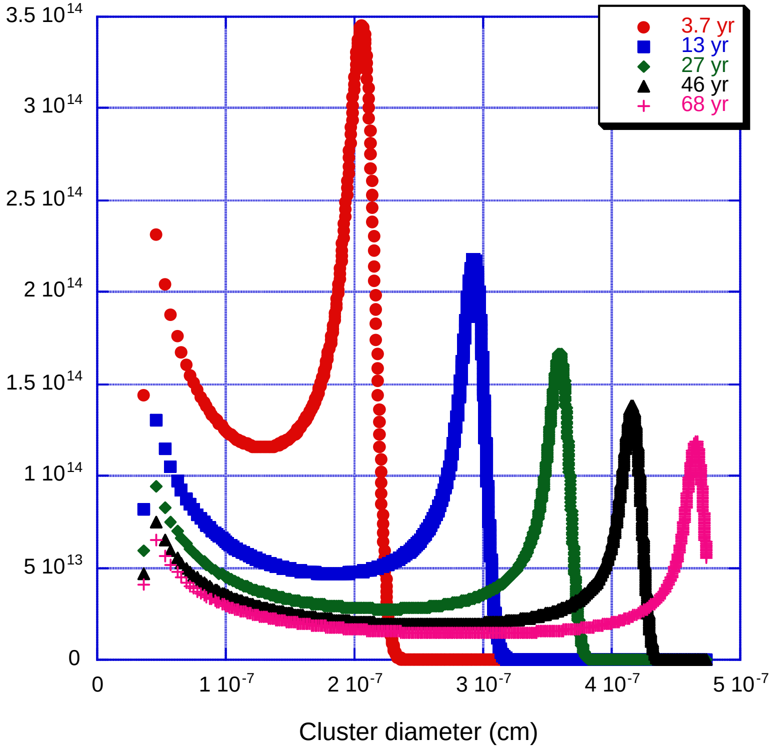
$$\frac{dN_2}{dt} = 8\pi r_1 D N_1^2 - 4\pi D N_1 r_2 N_2$$

……………………………

i-mer equation for bubbles containing i He Atoms and i Vacancies.

$$\frac{dN_i}{dt} = 4\pi D N_1 r_{i-1} N_{i-1} - 4\pi D N_1 r_i N_i$$

Case for Pu: He generation is constant at 40 appm/year



Model confirms peaked bubble size distribution as seen in TEM observations.
But observed size distributions are wider, indicating significant materials heterogeneities.

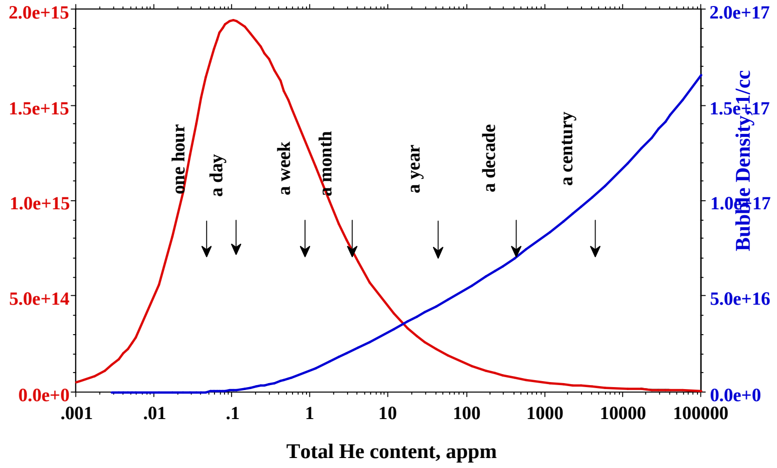
Stochastic effects of Helium generation and local environment spread out the nucleation burst

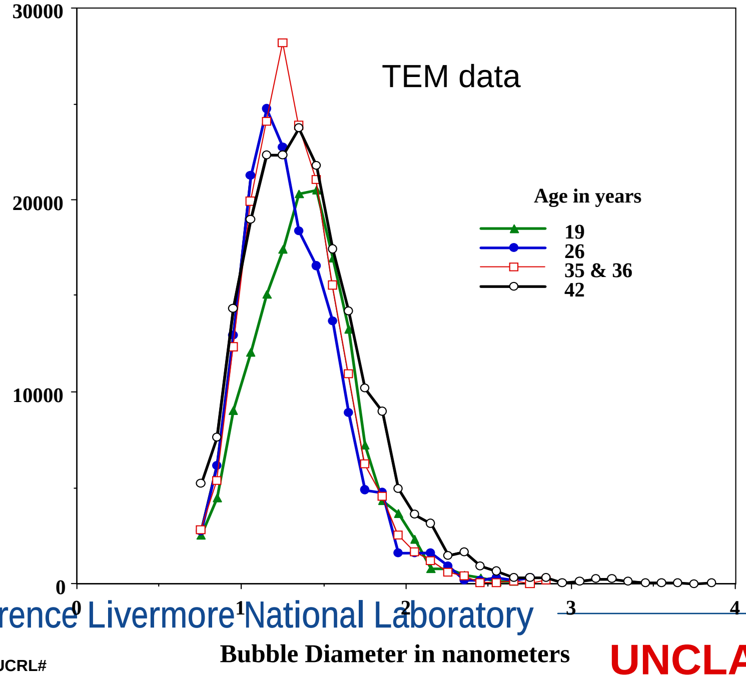
Bonilla, Carpio, Neu, Wolfer

Physica D 222 (2006) 131

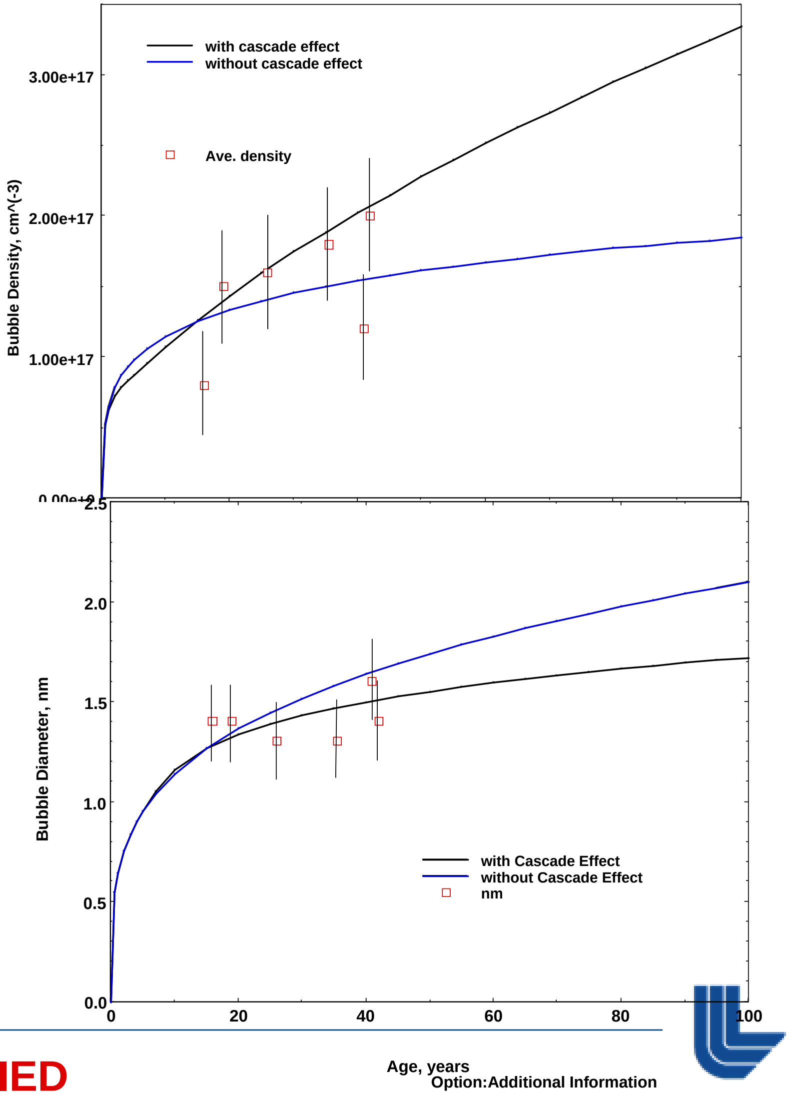
QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Helium bubble evolution in Pu: almost instant nucleation, not much growth beyond 1.5 nm, but steady increase in bubble density.



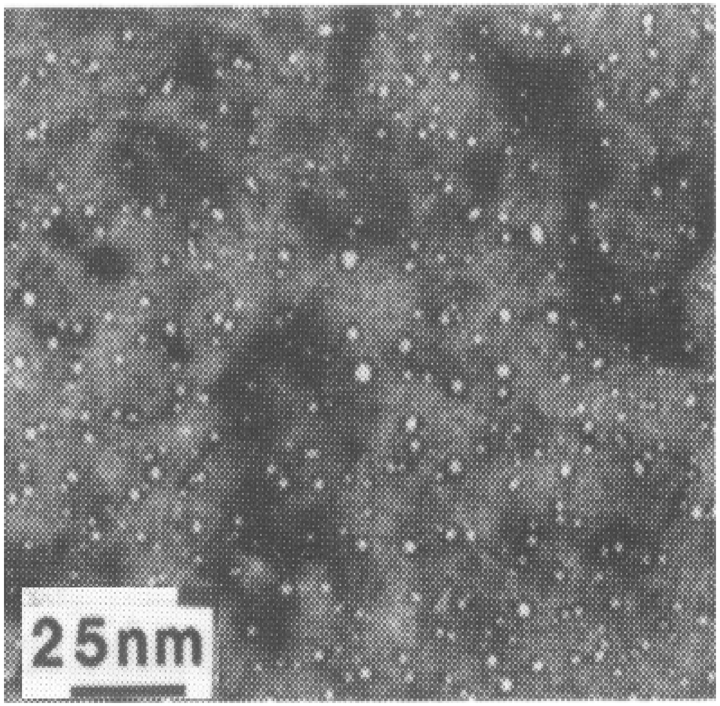


Best fit gives He migration energy: 0.72 eV



Hydrogen and Helium storage in HFIR-irradiated USPCA containing 4×10^{17} cm^{-3} "helium-filled cavities" to 34 dpa at 400ºC

Tanaka et al., 1988



JP-12 experiment

Specimens were irradiated in an aluminum gas-gapped assembly,filled with helium and **never touching water.**

After 13 years of storage in a dry canister, the gas contents of two specimens were measured.

2979 and 3012 appm He

3864 and 3790 appm H

Bubbles seem to reach terminal size with 2 nm diameter

Helium attrition from large bubbles by radiation effects ?

Possible Mechanisms:

1) ***Collision cascade from nearby U-recoils (85 keV) destroy bubble and disperse Helium atoms.***

   To match data, the efficiency has to be high: up to 5000 energized Pu atoms have to disperse the helium in a bubble ! MD simulations contradict it.

2) ***High energy α flux expels He atoms at the rate of He diffusion to bubble.***

   α-range in Pu: 10 μm

   A 1.5 nm bubble is hit once every 5 days, and an average energy of 30 eV is deposited to 150 He atoms.

   The gas temperature rises to 2200 K . It takes 30 ps to cool.

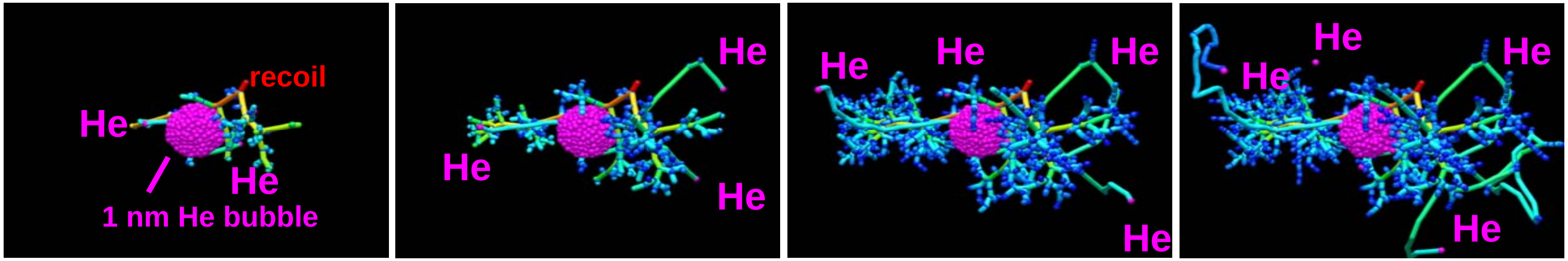
   If one He atom is dissolved in 9 α-hits or in 45 days, then He capture is balanced by loss.

   Process scales with $3R^2/32$.

Cascade-induced Helium mixing is too inefficient to explain termination of bubble growth

A. Kubota, unpublished results

20-keV Cu recoil in Cu with a 1-nm diameter He bubble producing 4 ejected He.



0.045 ps: 20 keV early cascade track producing 2 He energetic recoils.

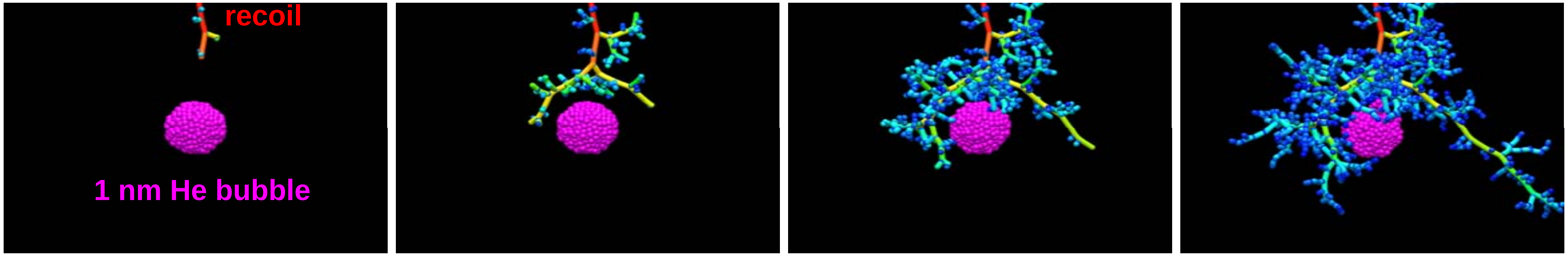
0.077 ps: 20 keV early cascade track, 3rd He recoil produced.

0.14 ps: Full cascade bloom, 4th He recoil produced.

0.37 ps: Larger overlap between cascade bloom and bubble to produce secondary He.

20000 eV
3500 eV
630 eV
112 eV
20 eV

20-keV Cu recoil in Cu with a 1-nm diameter He bubble producing no ejected He.



0.031 ps: 20 keV early cascade track directed towards He bubble.

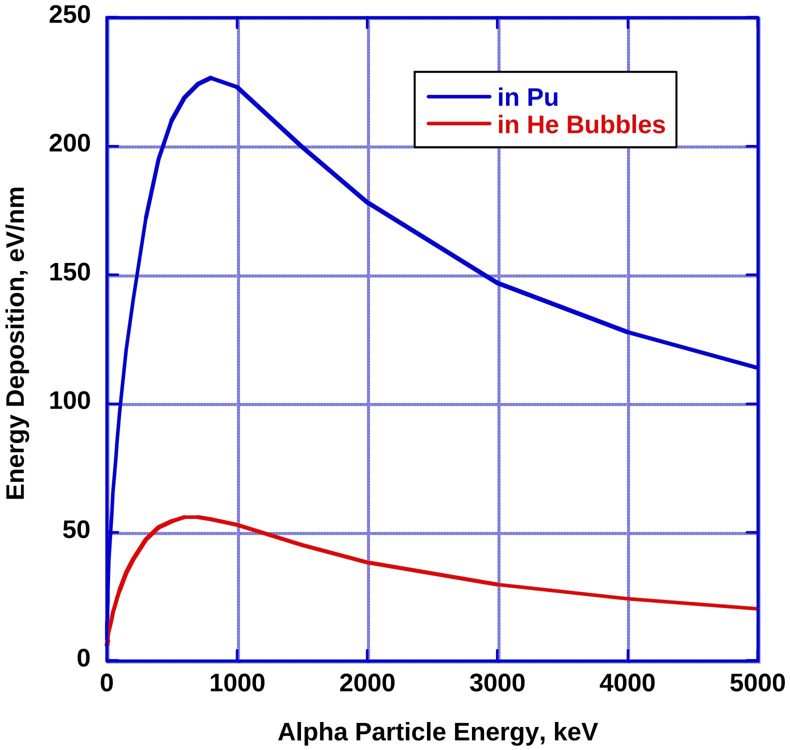
0.051 ps: Cascade branching occurs before reaching the bubble.

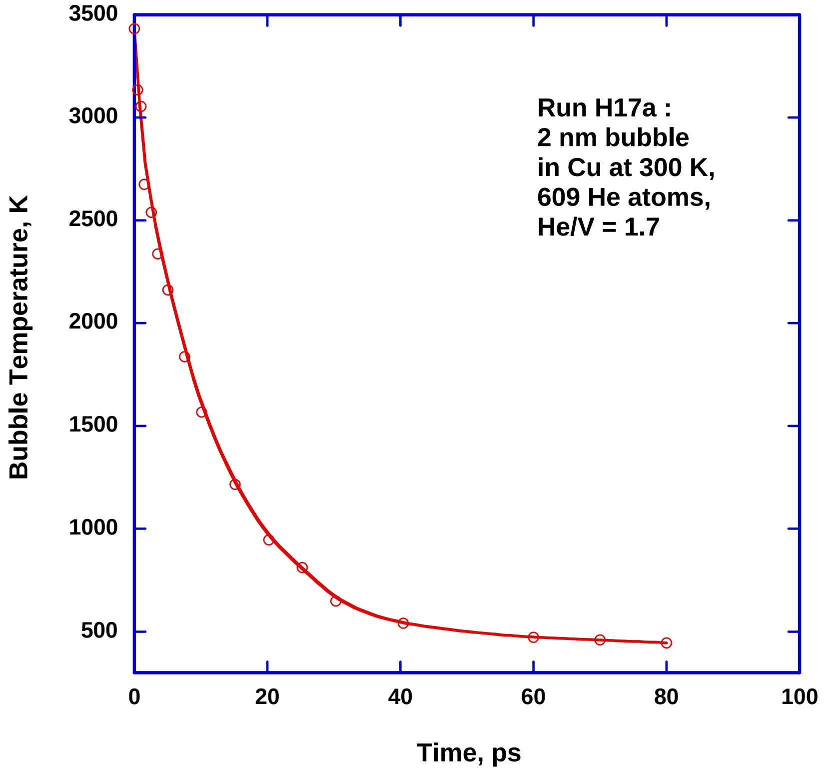
0.88 ps: Cascade continues around the bubble.

0.43 ps: Full cascade bloom with no ejected He.

QuickTime™ and a
Cinepak decompressor
are needed to see this picture.

Bubble Heating from Electronic Stopping of α's





Pressure-induced termination of bubble growth ?

Proposed Mechanisms:

1) **High stress field around bubble repels approaching He-V defect.**
2) **Surface stress creates an activation barrier for He-V defect.**
3) **Impurity segregation creates a surface activation barrier.**
4) **He-V absorption restricted to surface ledges.**

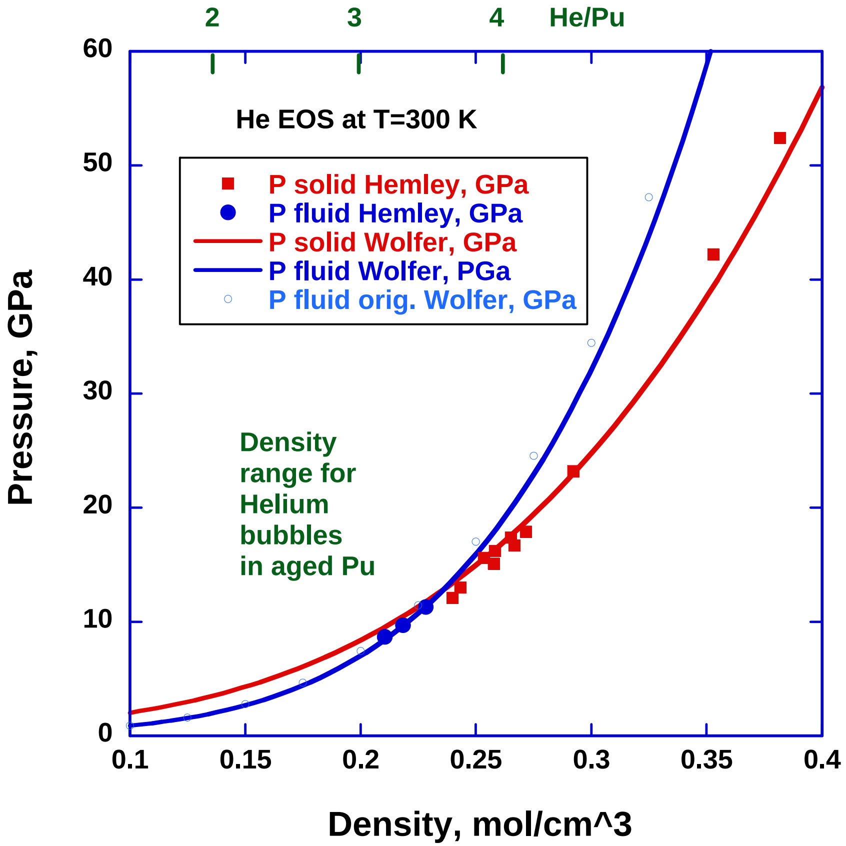
These mechanisms are difficult to quantify.

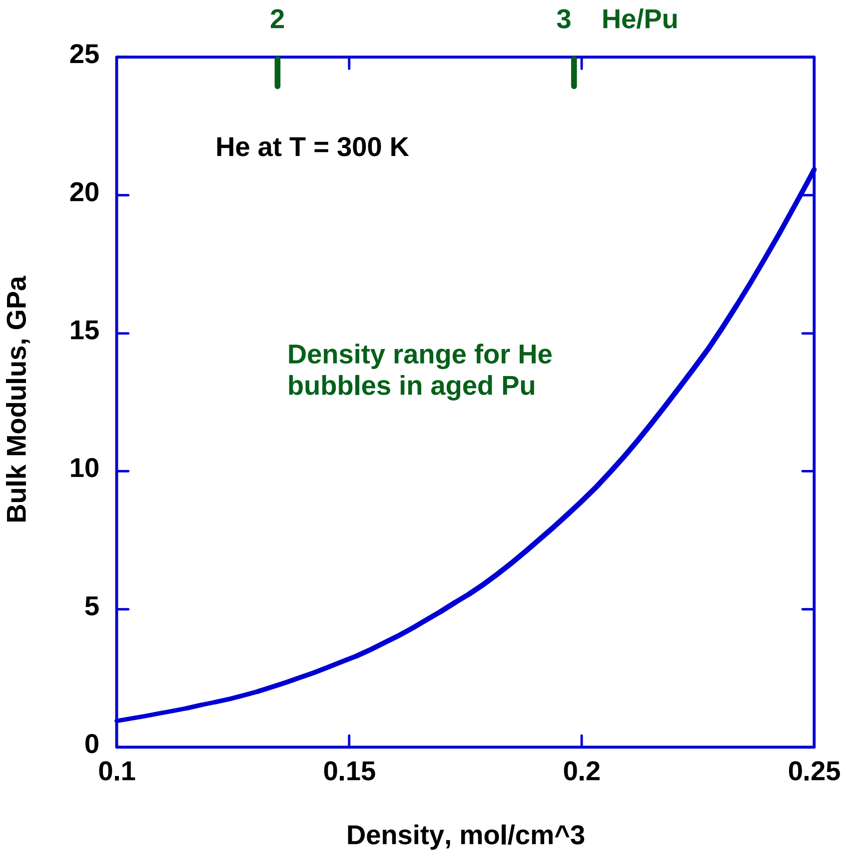
Mechanism 1 is unlikely: Hydrostatic stress around bubble is somewhat attractive and bubble is softer than matrix.

Mechanism 2 appears possible if He-V defect has large, negative relaxation volume (First-principle calculations in progress).

Mechanism 3 and 4 are not supported by TEM observations.

Helium bubbles in aged Pu are almost solid helium precipitates

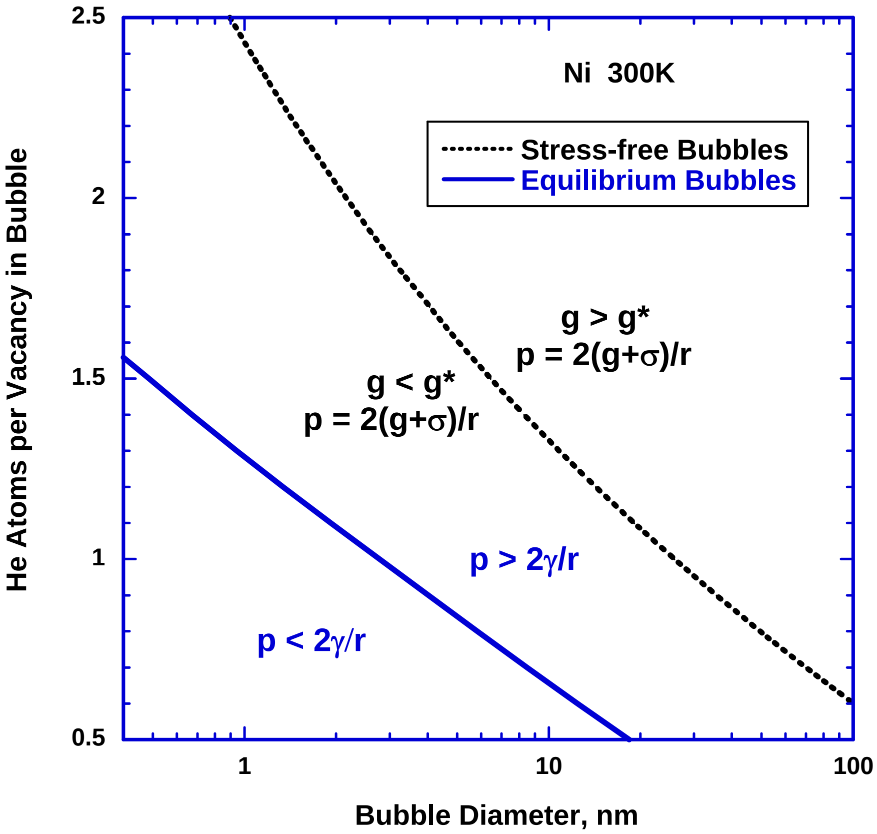




Bulk modulus of He in bubble < Bulk modulus of Pu

Therefore, He-V defect is attracted

Surface energy determines thermodynamic equilibrium and surface stress mechanical equilibrium



g^* is the surface stress

on a stress-free solid, $\varepsilon = 0$.

$\gamma(\varepsilon)$ is the surface energy at

surface strain ε.

Surface stress is

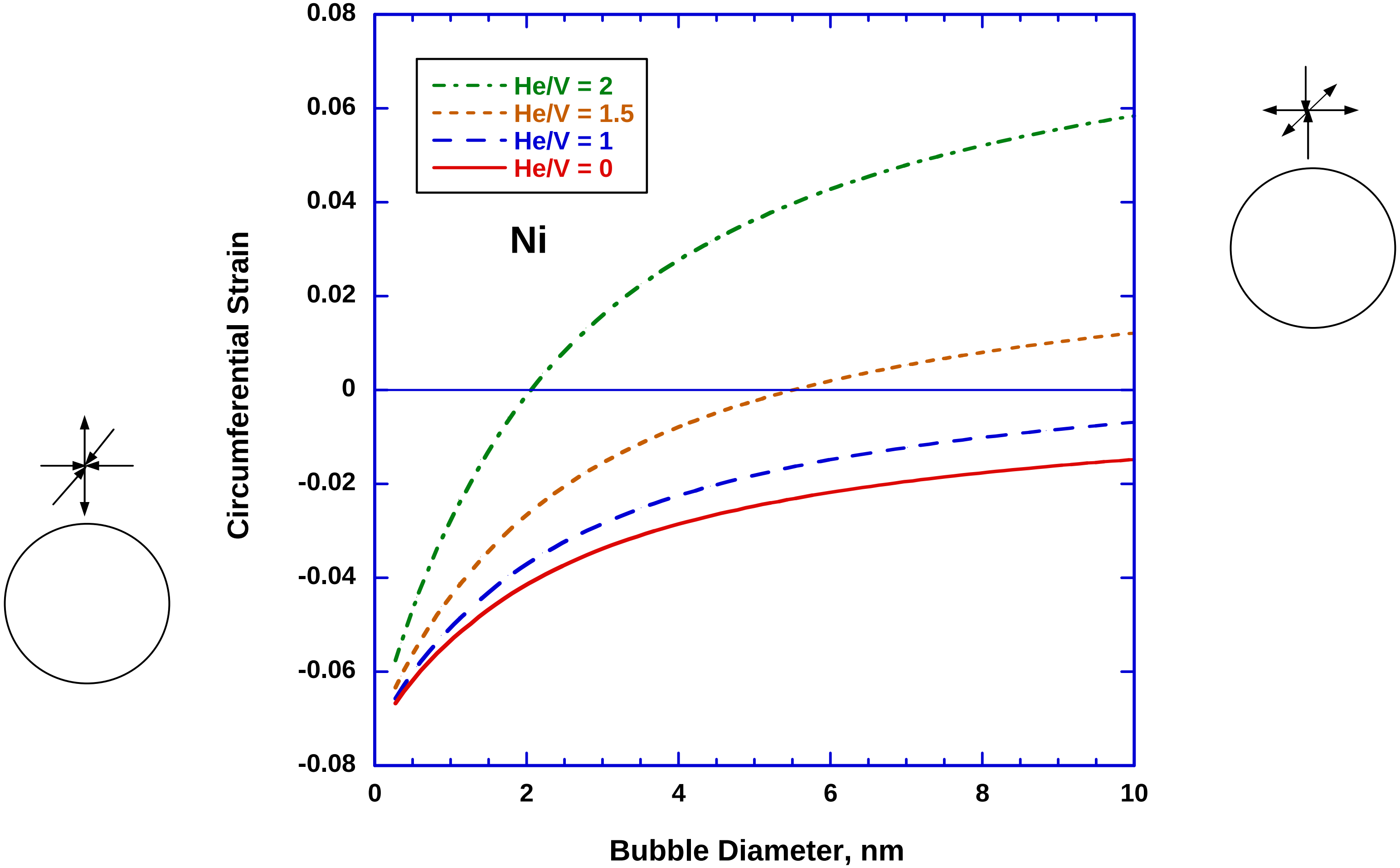
$$g(\varepsilon) = d\gamma(\varepsilon) / d\varepsilon$$

For bubbles with no stress field

$$p = 2g^*/ r , \sigma = 0.$$

Surface stress may create an activation barrier for He-V entry into bubble

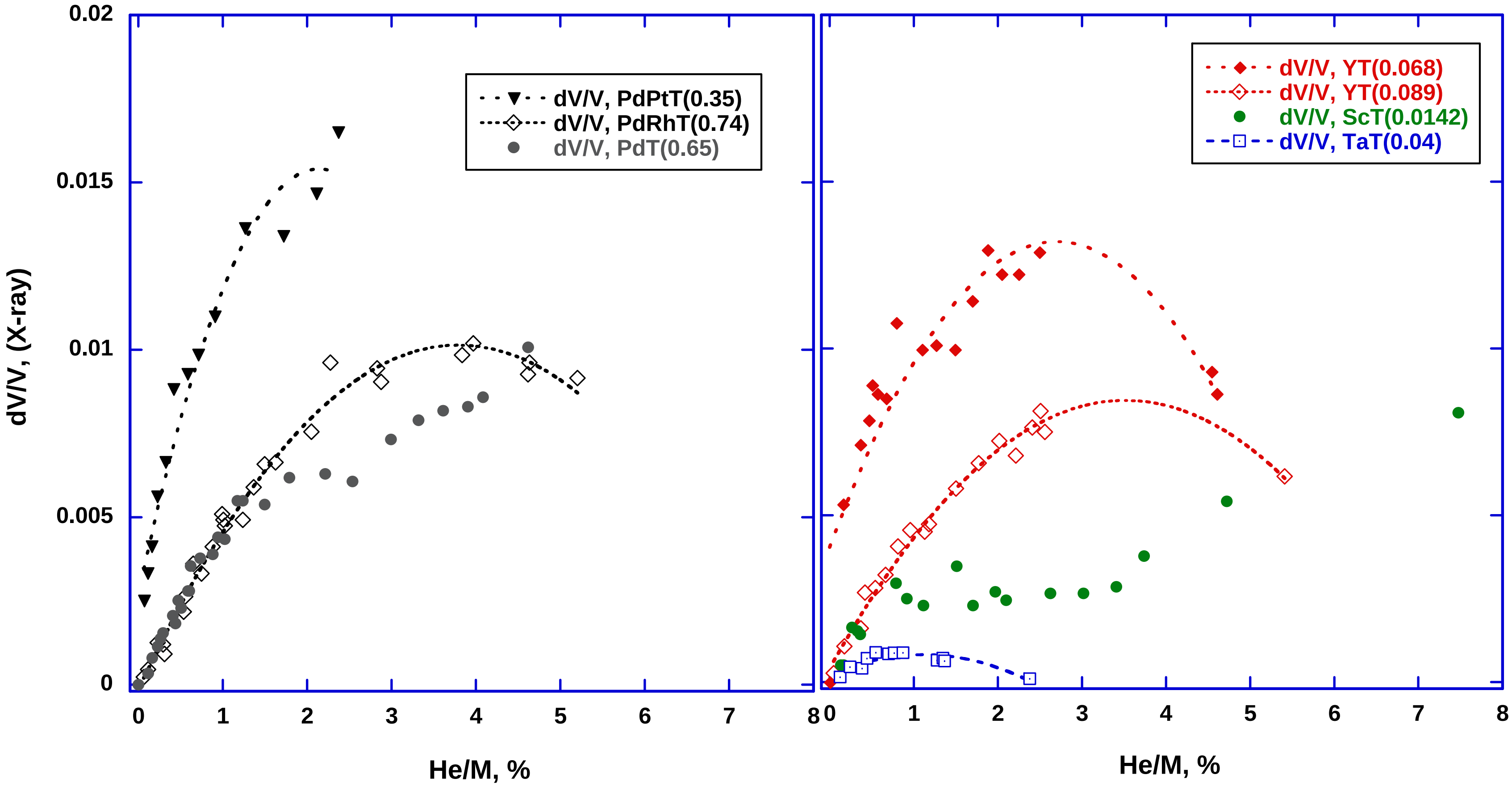
Only very high gas pressures can reverse the inward cavity relaxation caused by the surface stress



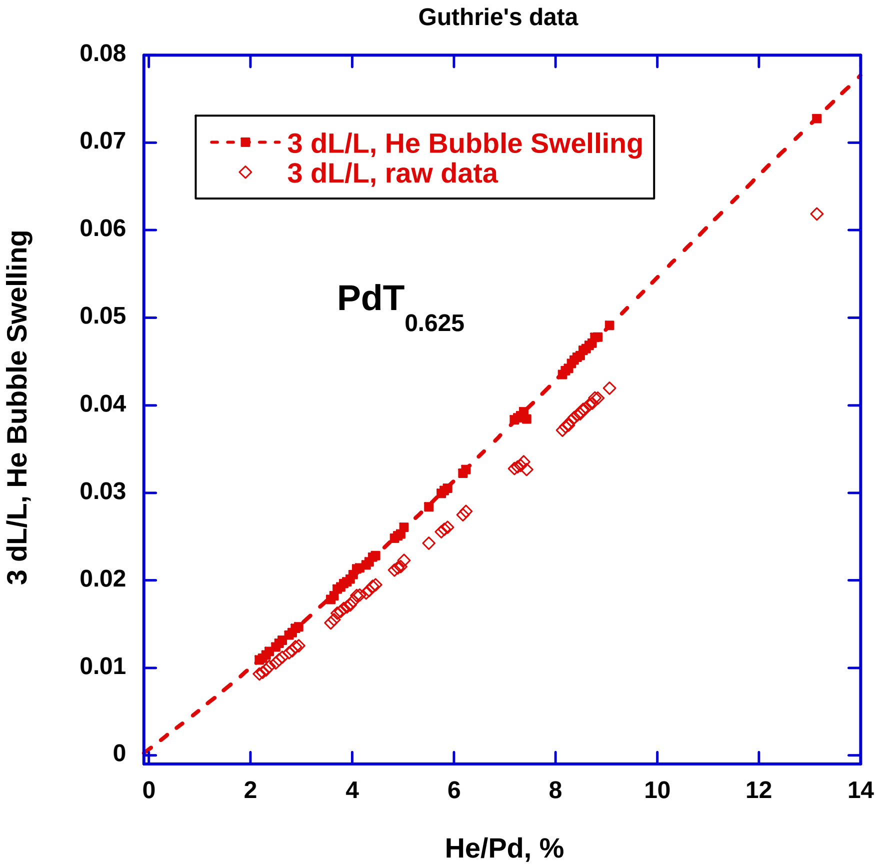
Lattice expansion from helium in metal tritides

Thiebaut et al. Phys. Rev. B 57 (1998) 10379

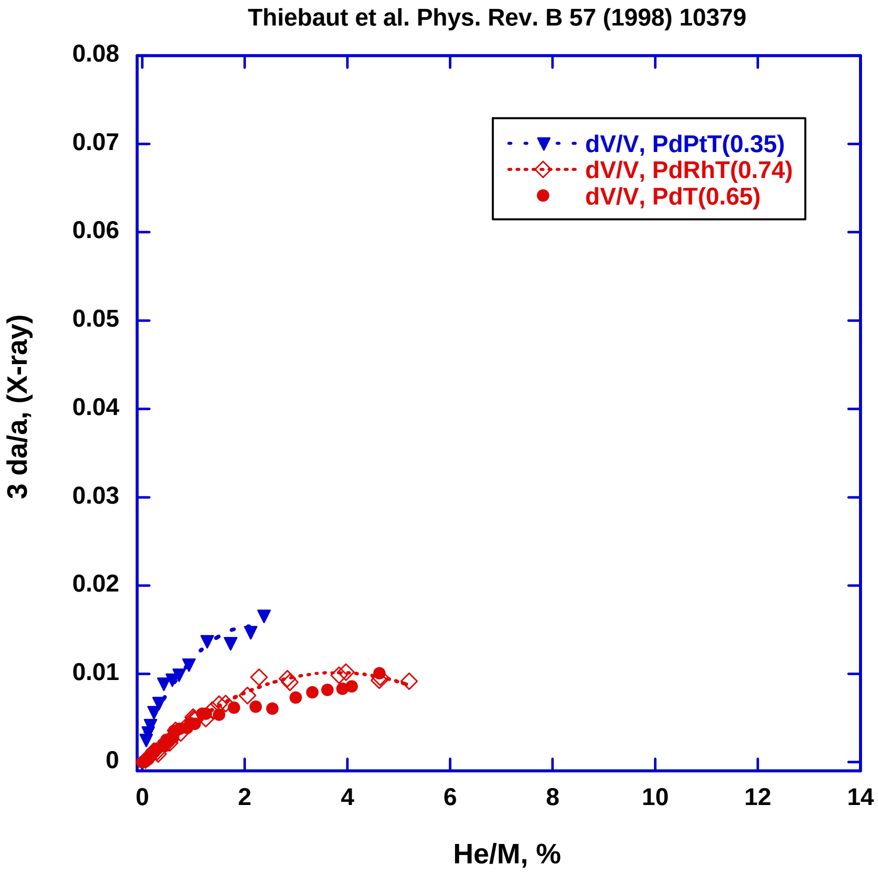
Prem et al. J. Alloys & Comp. 356-357 (2003) 683



Helium bubble swelling ≥ Helium-induced lattice dilation

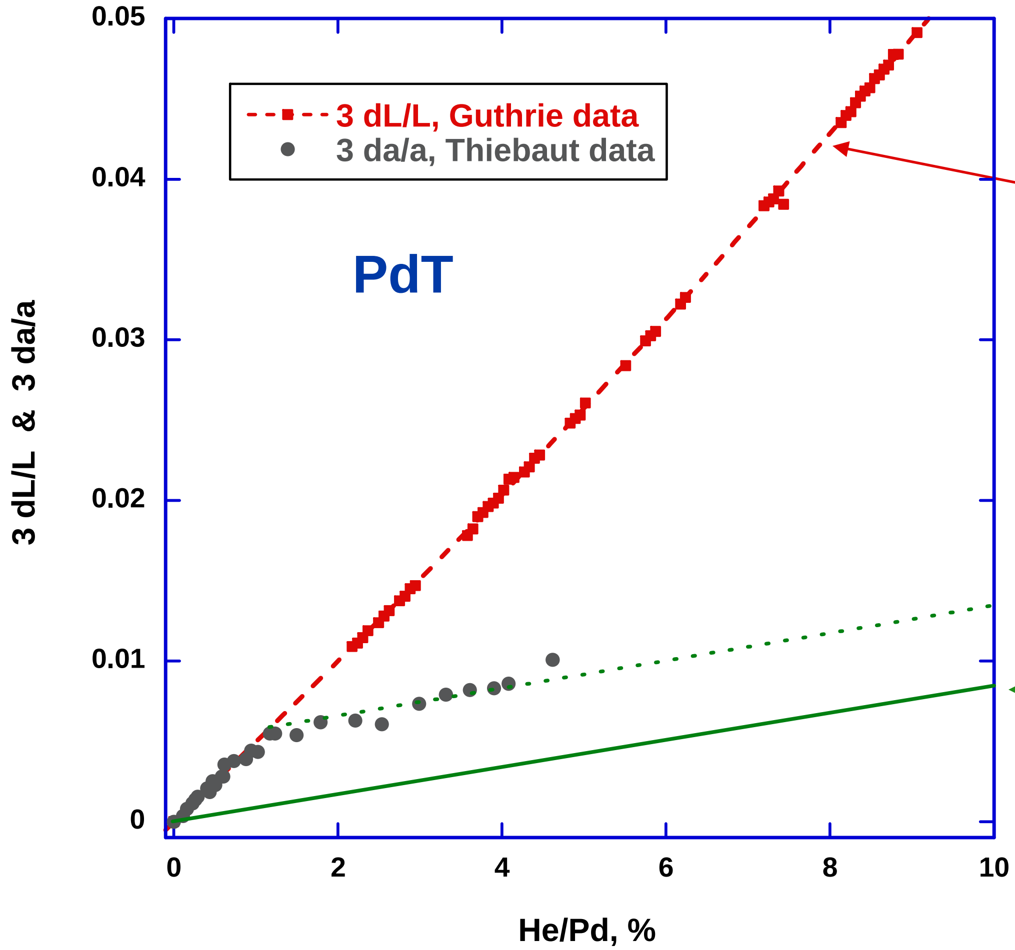


Slope implies He/Vac. = 2.29



Initial slope for PdT yields He/Vac. = 2.15

It appears that 1% He is in defects other than bubbles



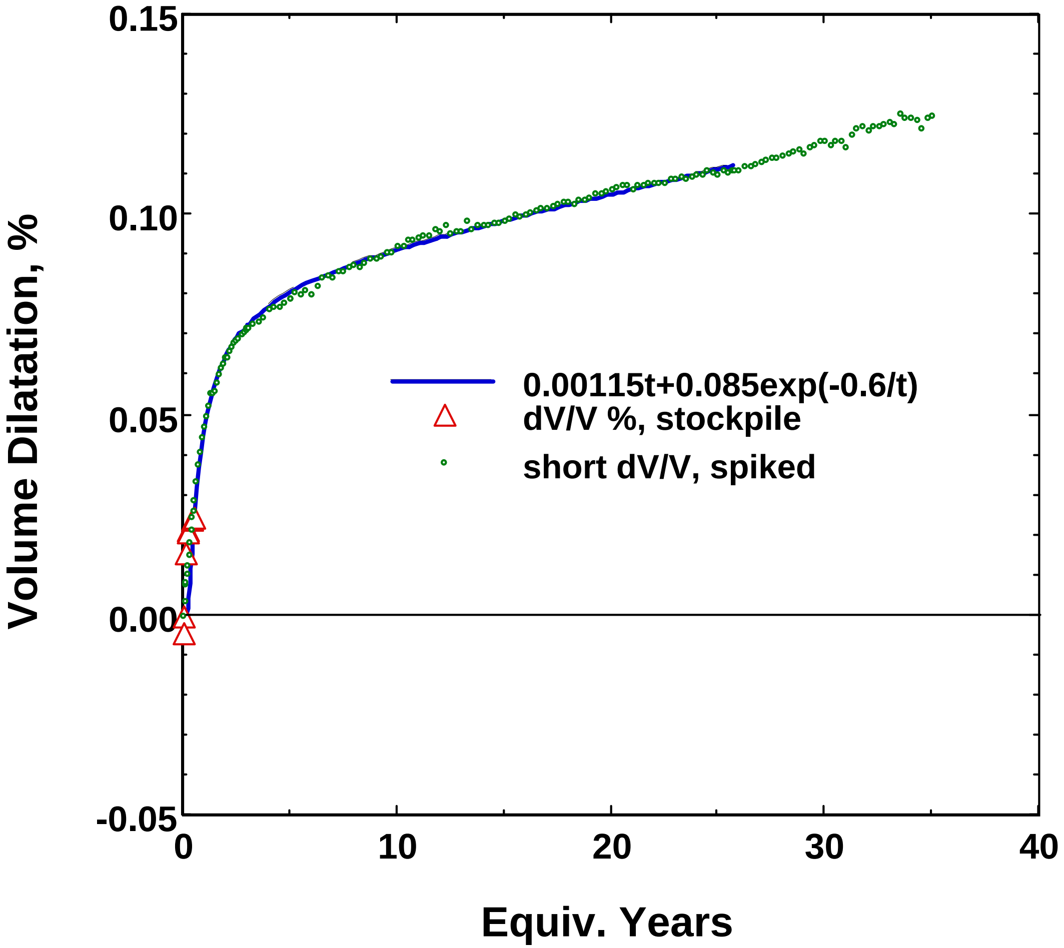
Helium Bubble Swelling

$$S = 3\frac{dL}{L_0} = \frac{He/Pd}{He/Vac.} \approx \frac{He/Pd}{2.29}$$

Lattice dilation caused by Helium bubbles

$$3\frac{da}{a_0} = \frac{(p-2g/r)S}{K_{He} + \frac{2(1-2\nu)}{3(1-\nu)}K_{Pd}(1-S)}$$

High precision dilatometry monitors dimensional changes in δ-Pu samples enriched with ^{238}Pu



10 equiv. Years = 400 appm He

Transient may be caused by Ga segregation

Linear increase is due to He and implies a He density of He/Vac. = 2.8 in bubbles.

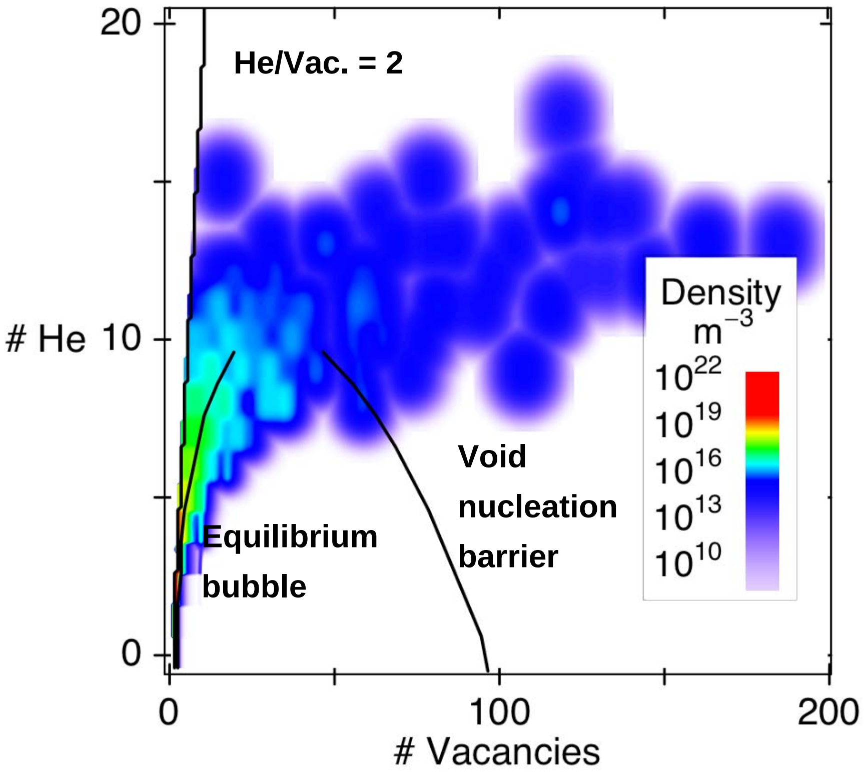
Positron lifetimes of 180-200 ps imply a density of He/Vac. = 2 to 3.

From Chung et al.,
J. Nucl. Matls. 355 (2006) 142

Combined Helium Bubble and Void Formation in Austenitic Steels Irradiated in HFIR-like Reactor

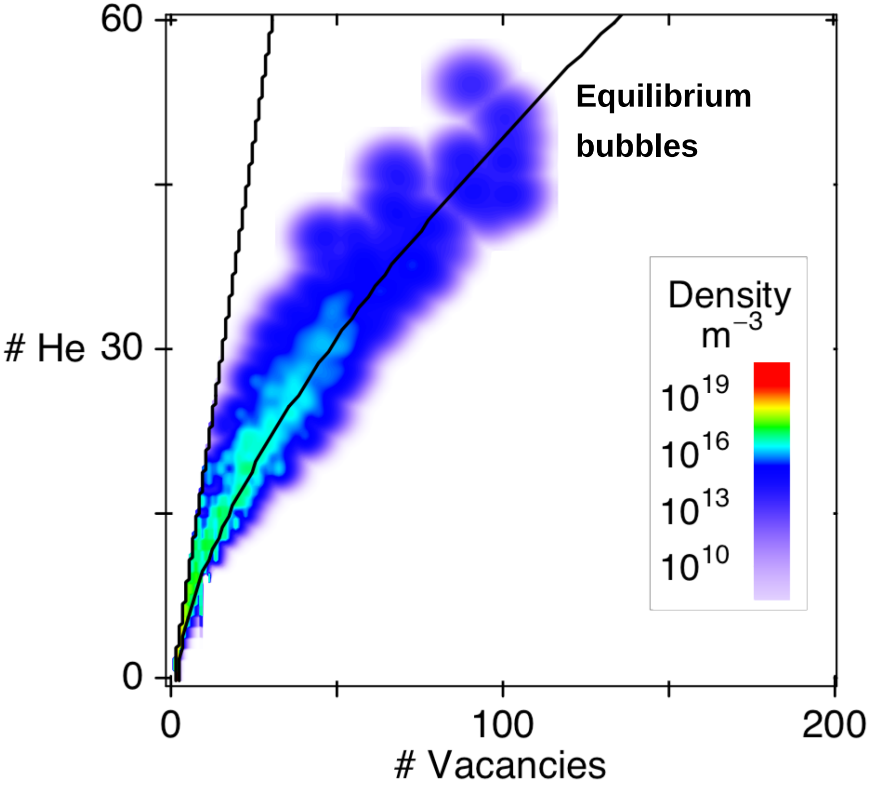
Surh, Sturgeon, Wolfer, submitted to J. Nucl. Mater.

at 500 °C



High pressure He bubbles coexist with voids

at 700 °C



Only equilibrium bubbles exist

Summary and Conclusions

- All metals can store Helium in the form of high-pressure bubbles or platelets
- Helium density in bubbles and other forms of precipitates (platelets) is from 2 to 3 He/Vac. when formed at temperatures below 0.4 T_M
- Bubbles produce dimensional increases that is greater than inferred from lattice parameter changes: $3\Delta L/L > 3\Delta a/a$
- Bubbles formed from nuclear transmutations seem to reach a terminal size
- Two possible mechanisms have emerged to explain terminal size that require further study
- Both dilatometry and x-ray diffraction experiments should be done on a wider variety of materials
- Helium bubbles formed in conjunction with voids also have He densities of about 2 He/Vac. when formed at $T \leq 0.4\ T_M$