Modeling the Evolution of Helium Precipitates in Metal Tritides

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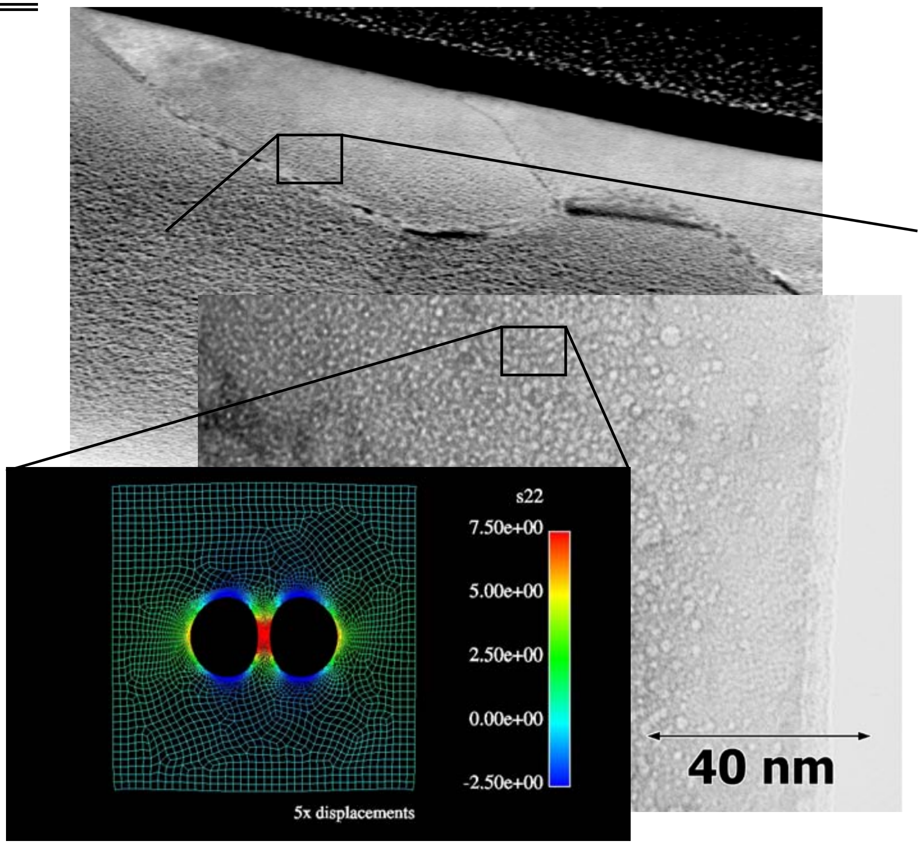
- Radioactive decay of tritium in metals creates high pressure, He-filled nano-bubbles.
  - TEM observed bubbles at 2 wks. (Thomas et al., Schober et al.)
- Bubble growth with age causes
  - material swelling
  - changes tritium retention
  - material fracture & He release.
- Outline of presentation:
  - Synopsis of model for Pd tritide
  - Differences for Er tritide (bubble shape, surface reactivity)



A continuum-scale model, assembled from published results, captures the *essential* physics.

- Bubble evolution is modeled as 4 distinct, separable stages:

  - Bubble Nucleation (homogeneous)

    Self-trapping (W.D. Wilson *et al*., 1981)
  - Bubble Growth

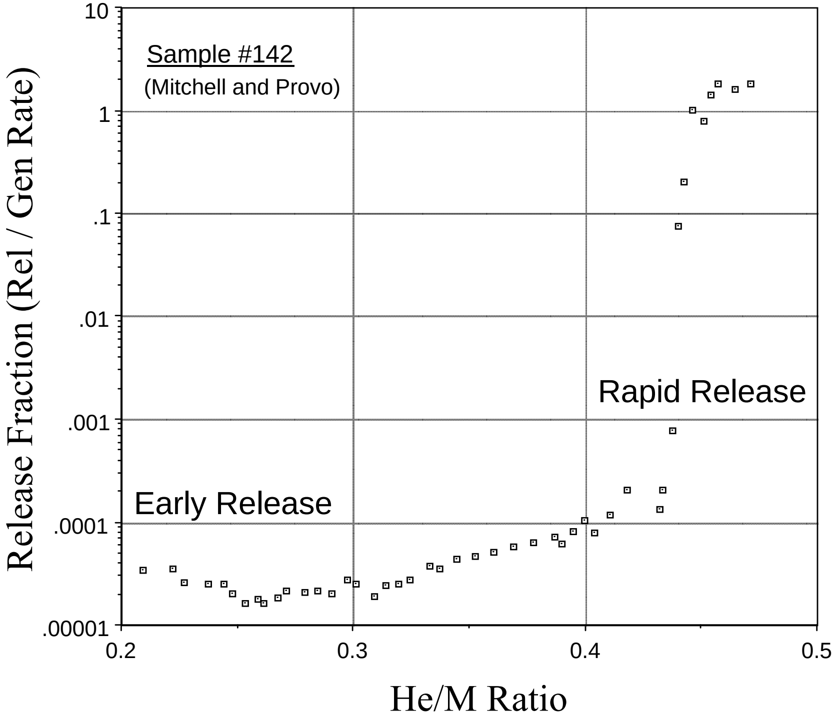
    Disloc. Loop Punching (H. Trinkhaus, 1983)
  - Inter-Bubble Fracture

    Blistering Criterion (J.H. Evans, 1977)
  - Linked-Bubble Network Generation

    Classical Percolation Theory

- The model is tested using predicted bubble density, size and pressure (& distribution), swelling, PCT shift, and He release behavior.

Typical He Release Spectrum: Zr Tritide



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Bubble nucleation occurs by self-trapping during a short pulse in mobile He concentration.

- Modeled using 3 components: mobile He, He-pairs, bubbles:

$$dc_1/dt = g - 2ps_1c_1^2 - ps_2c_1c_2 + 2q_2c_2 - ps_B(r)c_1c_B$$

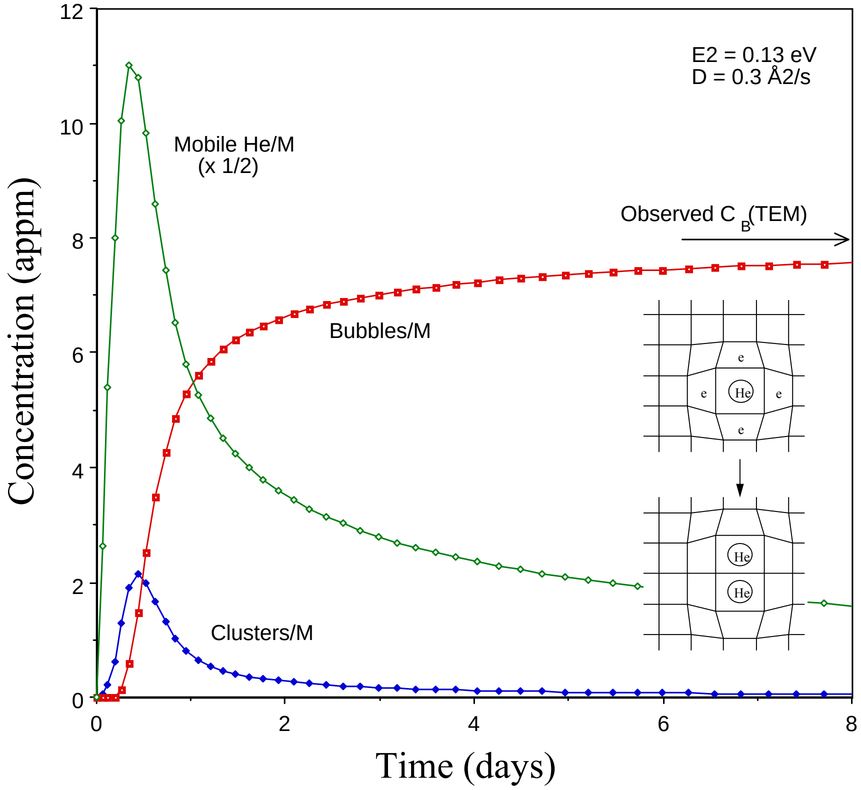
$$dc_2/dt = ps_1c_1^2 - q_2c_2 - ps_2c_1c_2$$

$$dc_B/dt = ps_2c_1c_2$$

generation rate, $g = \lambda(^3H/M)$

jump rate, $p = 12D_{He}/a^2$

pair dissoc. rate, $q_2 = 2pe^{-E_2/kT}$



- The mobile concentration drops as bubbles produce traps.

Using theoretical E_2 & E_3 and experimental D_{He} gives correct c_B.

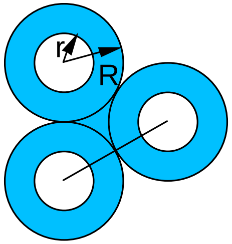
- Bubble nucleation is 90% complete in a 2 days.

A bubble's growth is determined by its He supply rate -- its tritium source volume.

- Bubble growth relations:
  - Mass conservation: $(r/R)^3 f_p = (v_{He}/v_{MH})(He/M)$

    (v=molar volume, f_p=.64 for random array packing)
  - Dislocation loop-punching: $p = 2\gamma/r + \mu b/r(1+\varepsilon)$

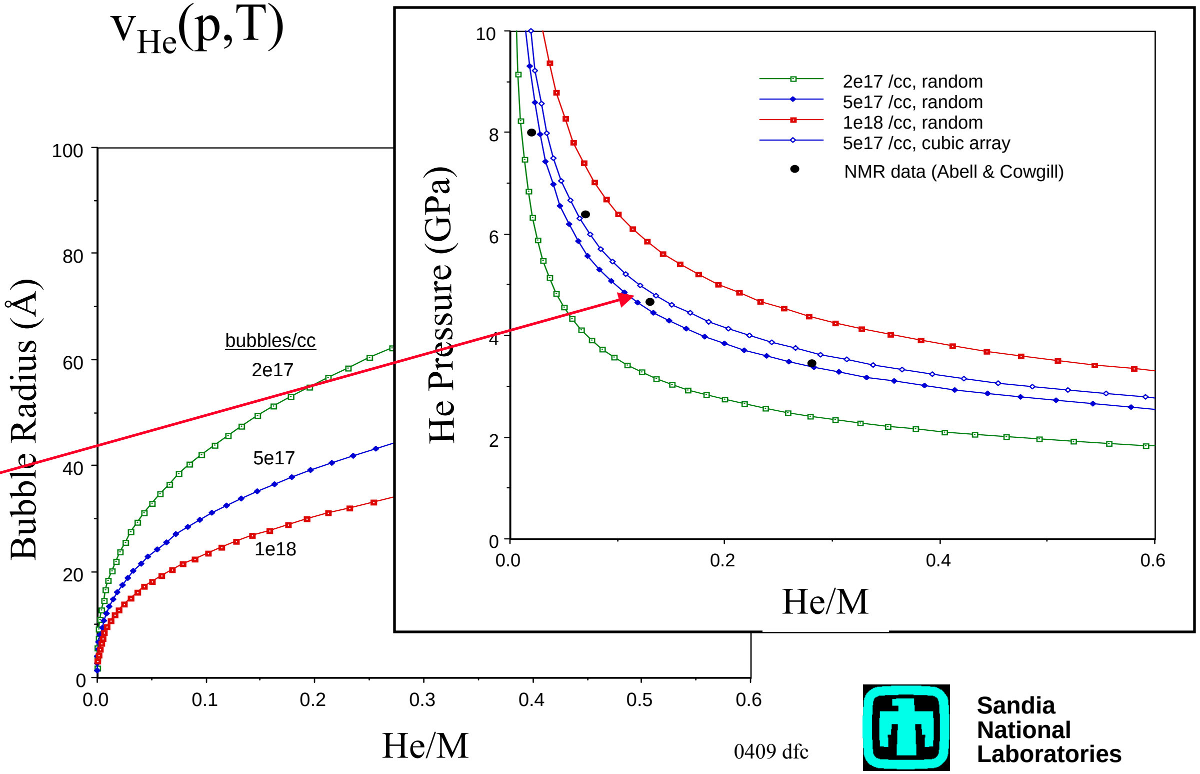
    (γ=surface energy, μ=shear modulus, b=Burgers vector)
  - Bulk He EOS: $v_{He}(p,T)$



Array of Spherical Source Volumes

- For a given bubble spacing R: At each He/M there is a unique r, p, v_{He}:

Modeled bubble pressures agree with p_{Av} deduced by NMR.



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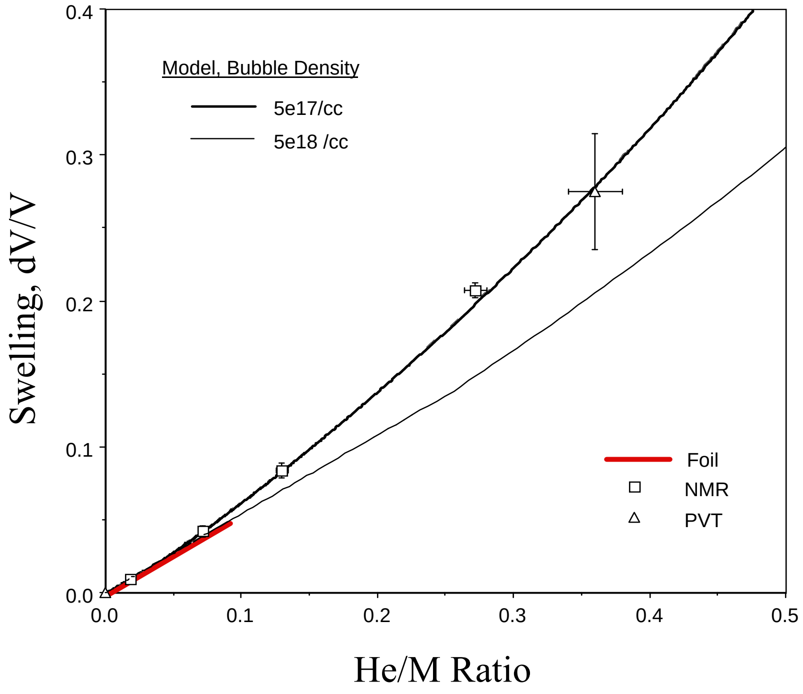
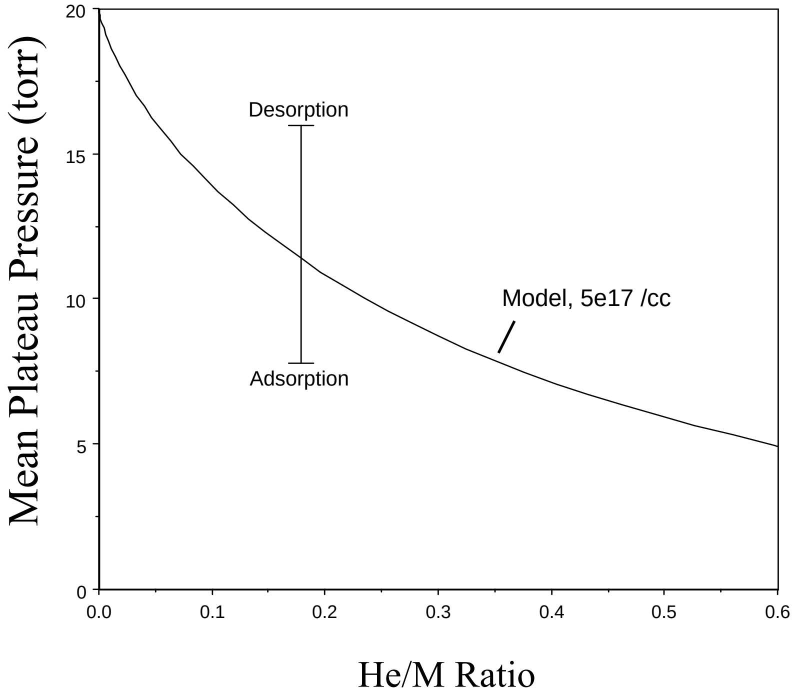
The bubbles cause swelling and lattice stress, which produces a shift in the hydride PCT.

Volume occupied by He bubbles:
$dV/V = (v_{He}/v_{MH})(He/M)$

Plateau $p_H = p_o\exp(-2\sigma_{hy}v_H/R_gT)$,
hydrostatic stress, $\sigma_{hy} = p_{He}(dV/V)$

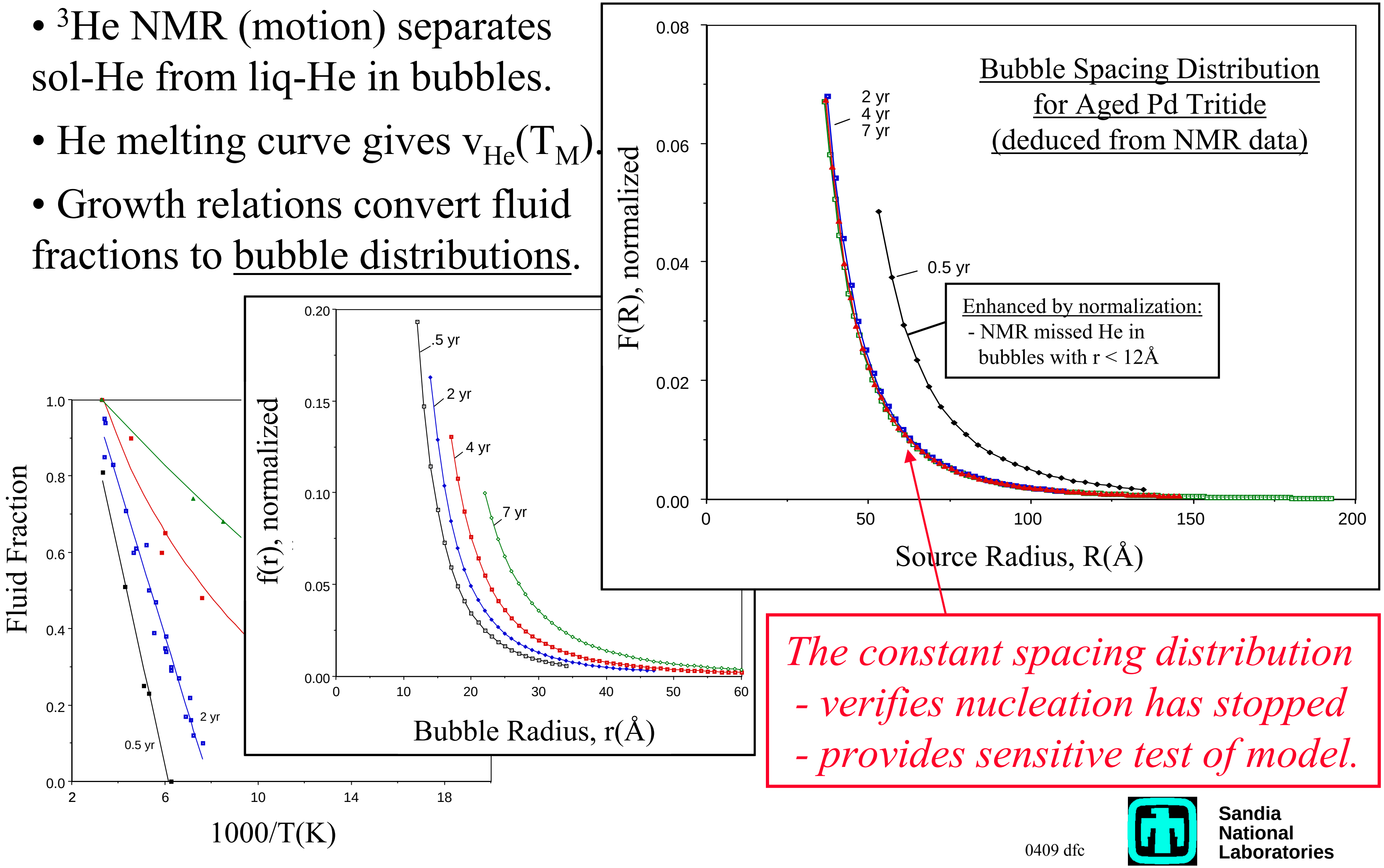




Swelling and PCT behavior are consistent with the lower bubble density found by TEM (Thomas et al., 1983), not higher (Thiebaut et al., 2000).

The bubble spacing distribution can be deduced from ^{3}He NMR data and the growth relations.

- ^{3}He NMR (motion) separates sol-He from liq-He in bubbles.
- He melting curve gives $v_{He}(T_M)$.
- Growth relations convert fluid fractions to bubble distributions.



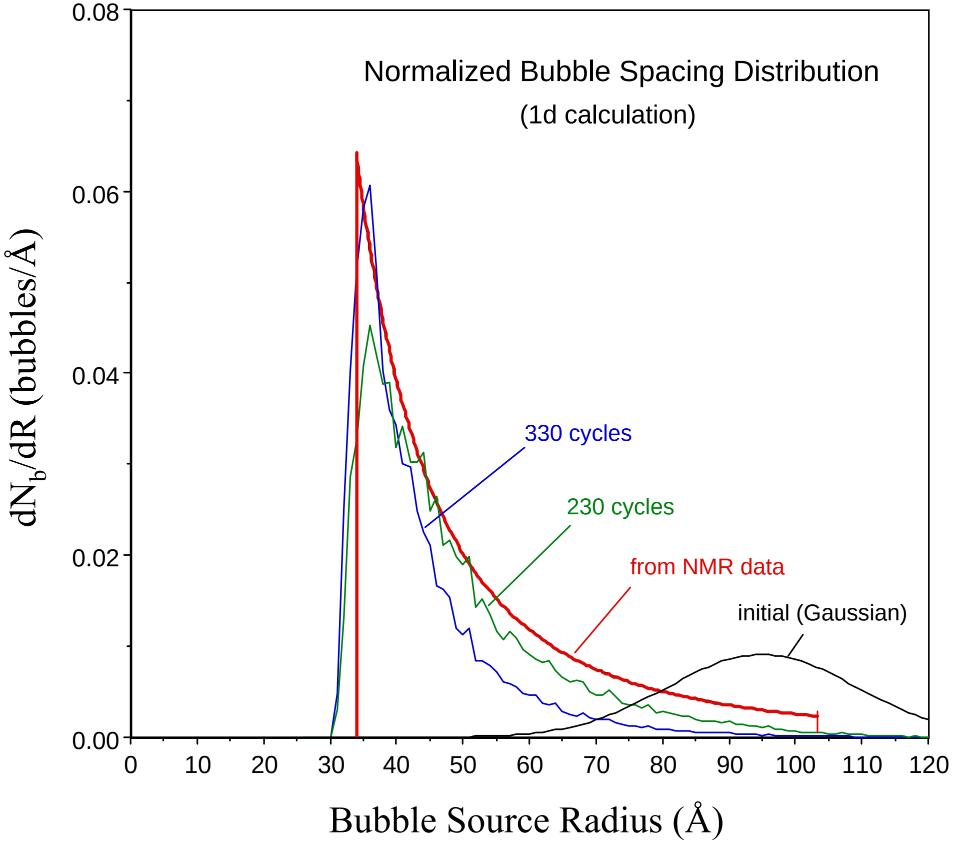
Bubble Spacing Distribution
for Aged Pd Tritide
(deduced from NMR data)

Enhanced by normalization:
- NMR missed He in bubbles with r < 12Å

The constant spacing distribution
- verifies nucleation has stopped
- provides sensitive test of model.

The shape of this bubble spacing distribution results from nucleation dynamics.

- Geometric effect: Repeated sub-division of larger bubble-free regions
  - weighted by probability for self-trapping c_m^2
  - randomly located within region of high, uniform c_m
- Peaking increases with sub-division cycle and stops when c_m becomes sufficiently low.
- Result is independent of initial trap distribution (for low c_{trap}).
  - *Inhomogeneous defect-nucl. bubbles experience "fill-in"*.



Inter-bubble fracture results in Rapid Helium Release.

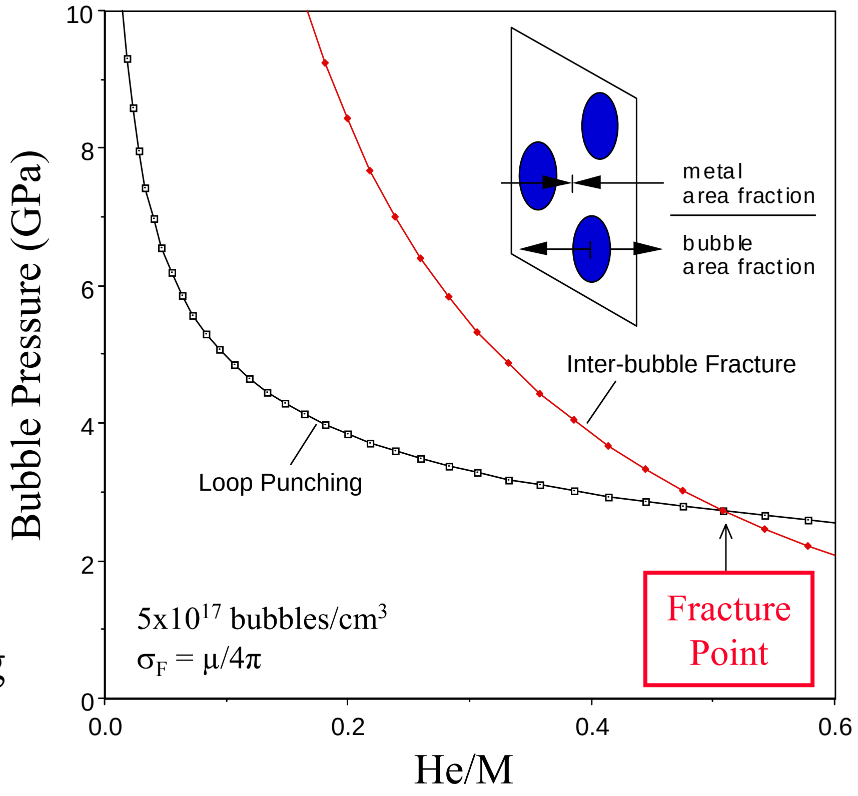
- As the bubbles grow, tension on the inter-bubble ligament increases.
- Evans' fracture criterion:

  For plane through adjacent bubbles, fracture occurs when:

  p_{LP} (bubble area) > σ_F (metal area)

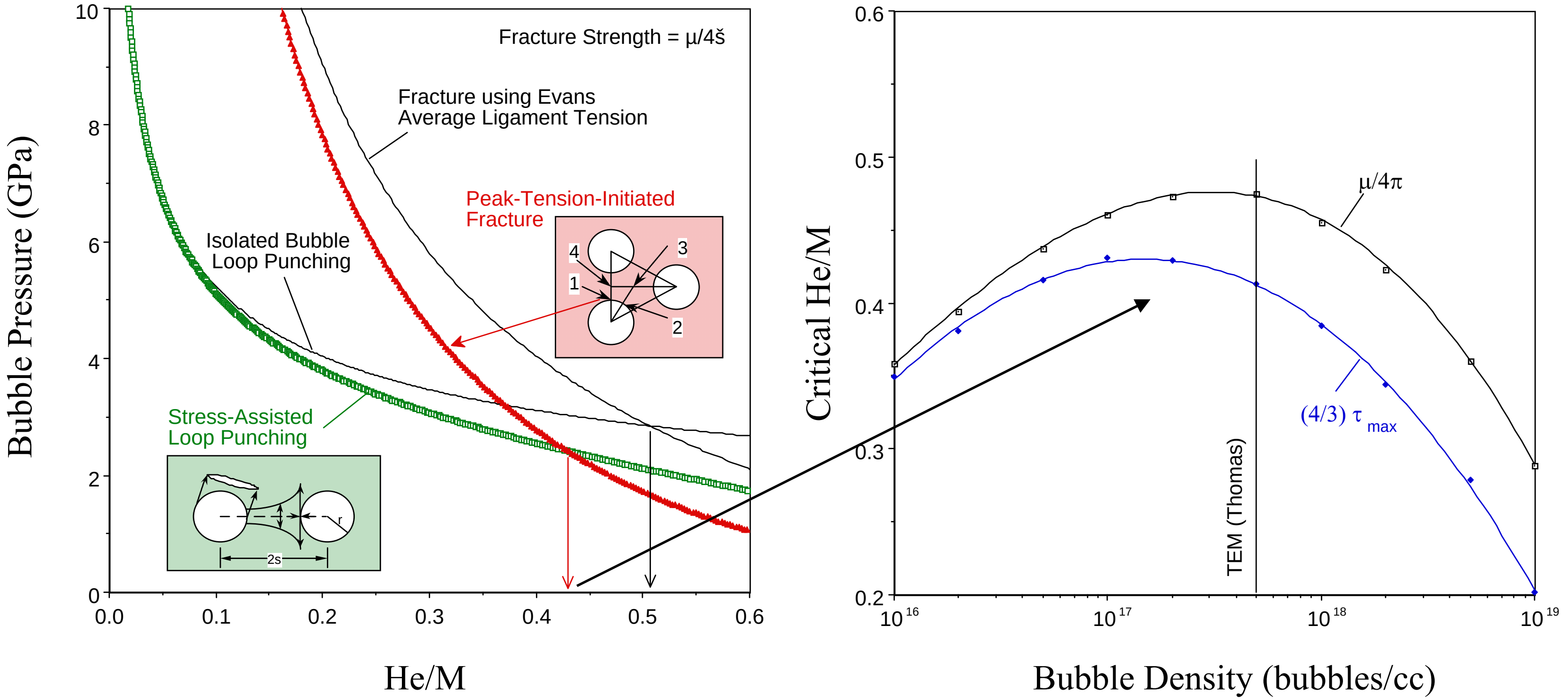
  (σ_F = fracture strength ≈ $\mu/4\pi$)
- Valid when neighboring ligaments fracture simultaneously (surrounding lattice provides no support).

Rapid release should occur when bubbles at mean bubble density undergo inter-bubble fracture.



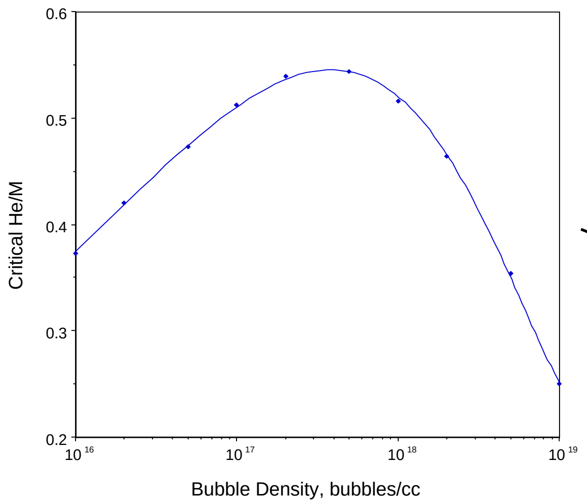
- Both curves are modified by local stresses due to bubble interactions.

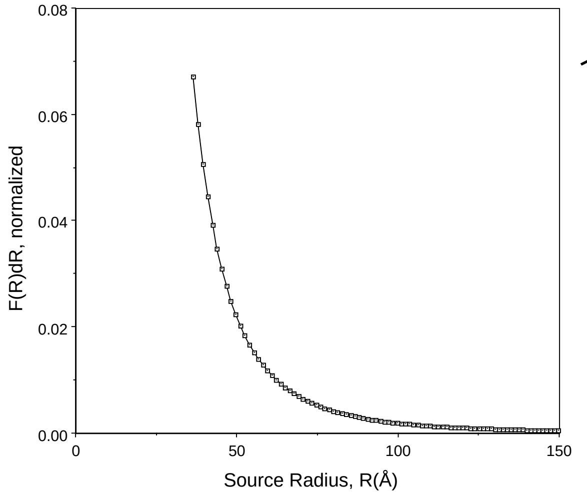
The Critical He/M is reduced by bubble interactions and depends on bubble density.

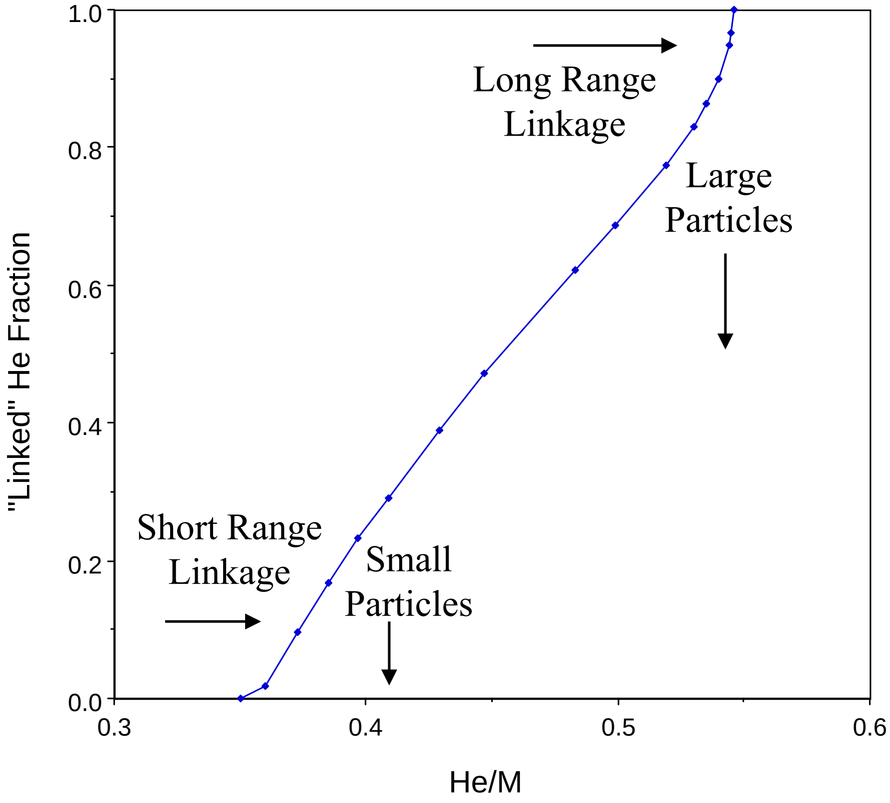


- Optimum bubble density for high Crit. He/M depends on fracture strength.
- Increasing the bubble density *reduces* the critical age.
    - Regions with high bubble density begin linkage first.

Combining the critical He/M curve with the bubble spacing distribution gives fractional bubble linkage.





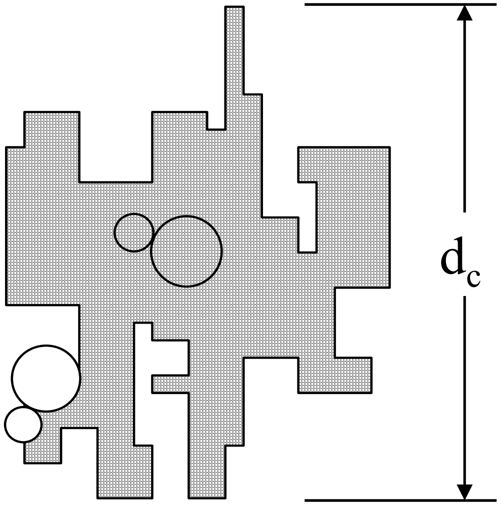


- The long-range linkage needed for He release from large particles requires higher He/M.

The *diameter* of linked-bubble clusters is calculated from Classical Percolation Theory.

- A cluster of linked-bubbles can be described as a cluster of adjacent (linked) sites.
- For site occupancy = ρ (fraction of sites linked), the volume fraction v for touching spheres centered on the sites is $v=f_p\rho$.

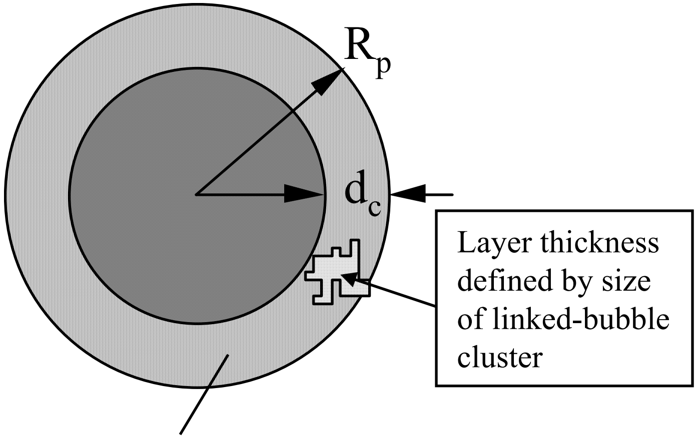
  (Large bubbles are considered as groups of small bubbles (sites) with packing fraction $f_p=1$.)
- At $\rho=\rho_c$, percolation threshold, the cluster is infinite with a critical volume fraction $v_c=f_p\rho_c$.
- For $\rho<\rho_c$, dimensional invariants relate v to d_c:
  - the #sites in average cluster, $s(\rho) \propto 1/(\rho_c-\rho)^{j+1}$
  - the cluster size, $d_c \propto s^{1/D}$, (D=fractal dimension).



Dimensional Invariants

	2d	3d
v_c	0.45	0.15
j	11/18	11/16
D	1.9	2.5

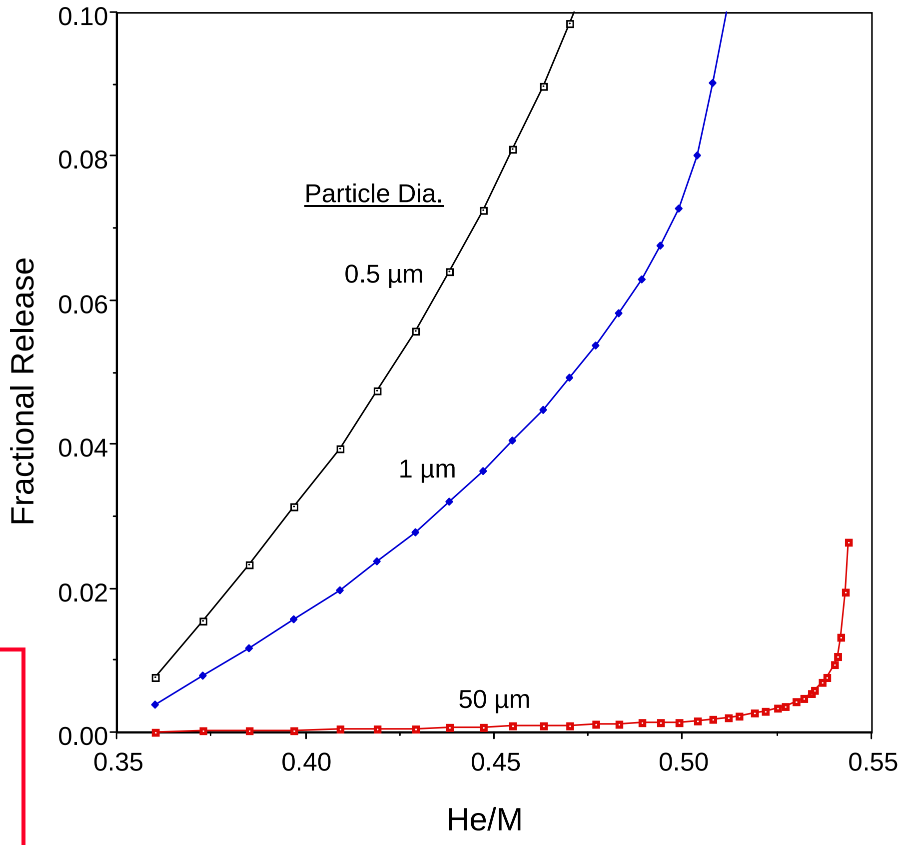
Fractional release is determined by the particle's volume fraction with clusters intersecting surface.



Layer thickness defined by size of linked-bubble cluster

- Integration over linked-volume fraction within d_c-thick layer gives quantity of He released.

• For small particles and thin films, this layer becomes a significant He fraction at younger age, lowering the "effective" Critical He/M.



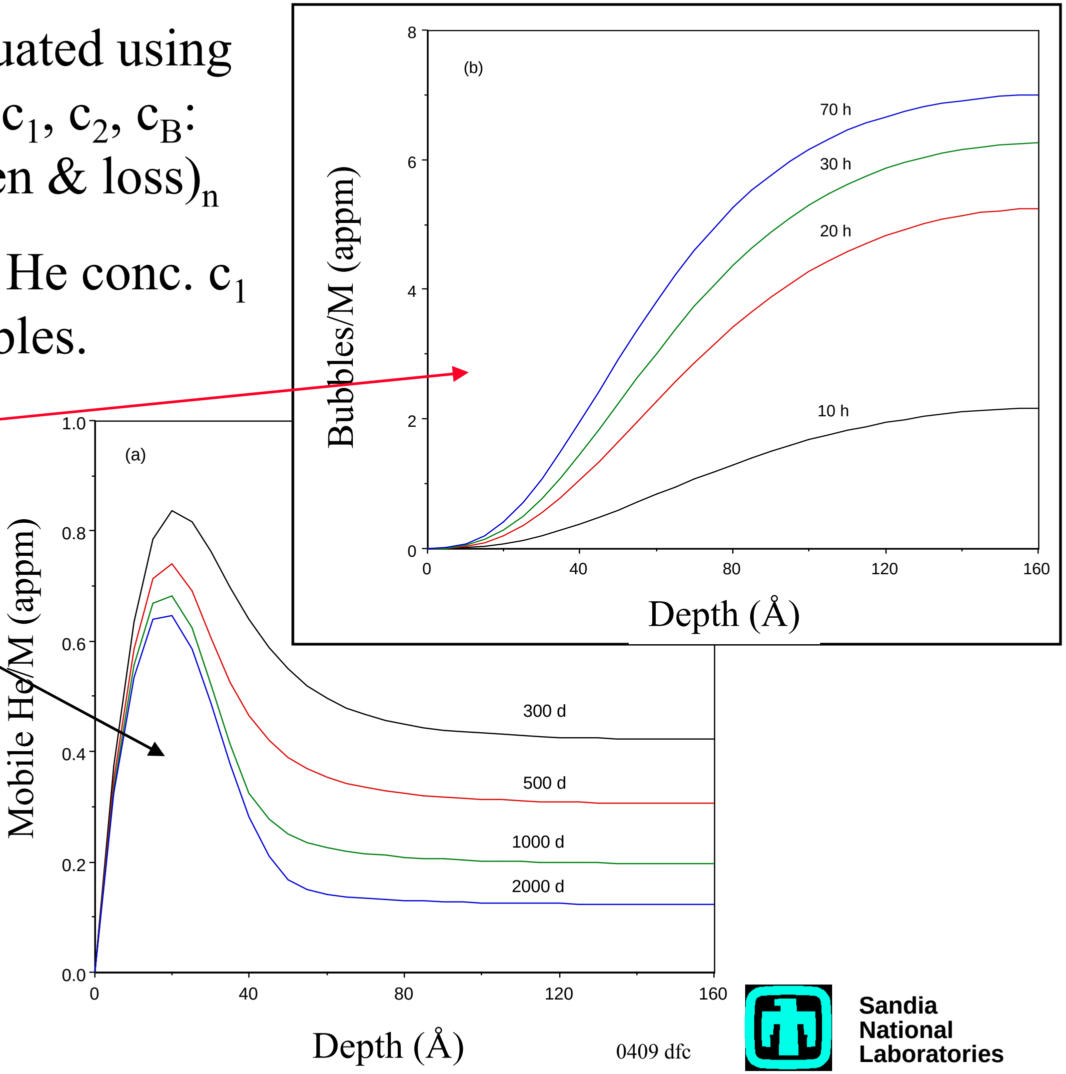
Early He release results from He generated near surfaces and surface-connected porosity.

- Bubble nucleation is evaluated using coupled diffusion eqs. for c_1, c_2, c_B:
  $$dc_n/dt = -D_n\, d^2c_n/dx^2 + (\text{gen \& loss})_n$$
- Near surfaces, the mobile He conc. c_1 is too low to nucleate bubbles.

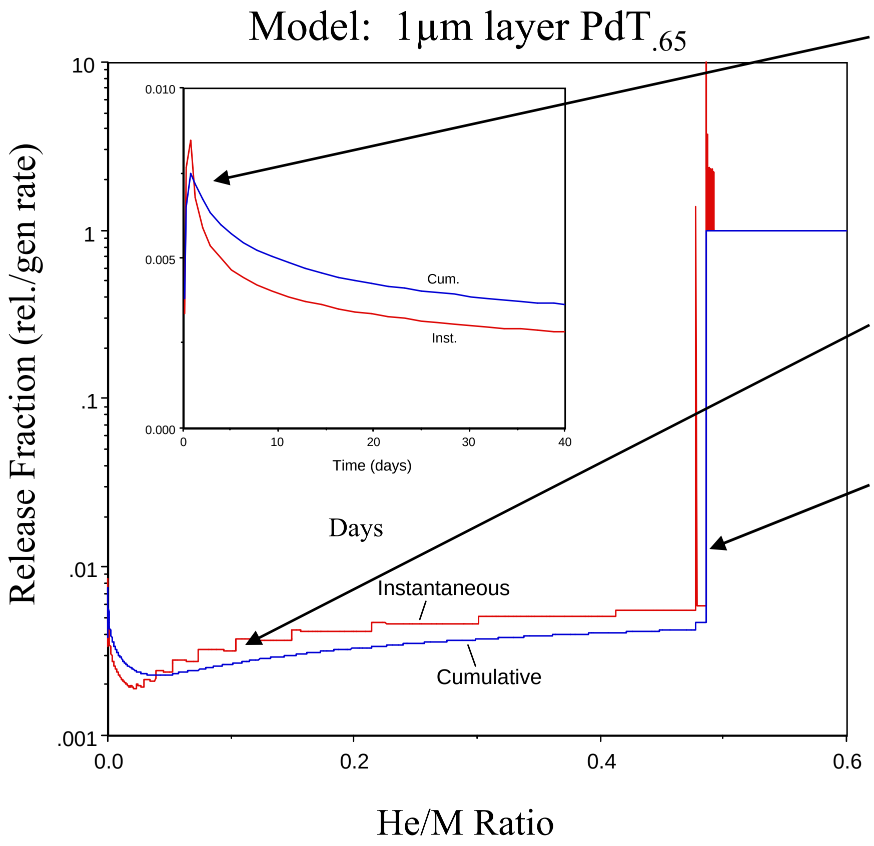
“Denuded zone” $x_d \approx R$ (bubble half-spacing).

- Escape of He generated in this region produces the Early Release Fraction:

$$\mathrm{ERF} = \left[\begin{array}{l} x_d/L\text{, layer} \\ 3x_d/R_p\text{, sphere} \end{array}\right.$$



The model produces a He release spectrum with all the characteristics of observed release.


Model: 1µm layer $PdT_{.65}$

- High initial release until bubbles become large enough to compete with nearby surfaces or grain boundary pipelines.
- Low, slowly increasing ERF with the breach of a few near-surface bubbles.
- Sharp onset of rapid release with the creation of an interconnected bubble network.
  - Inter-bubble fracture causes release rate to exceed generation rate until network is complete.

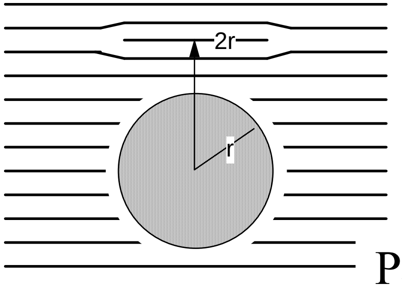
Model Summary and Testing:

- *Bubble Nucleation* by He self-trapping using theoretical He pairing energies and measured effective D_{He} gives
  - bubble density and denuded zone in agreement with TEM
  - correct Early Release Fraction and initial drop
  - explanation of Bubble Spacing Distribution deduced by NMR.
- *Bubble Growth* by dislocation loop punching gives
  - correct Bubble Pressure, Swelling, and PCT shift with age
  - evolution of bubble distribution in agreement with NMR.
- *Bubble Linking* by inter-bubble fracture using the average bubble density gives Critical He/M observed for large grain material.
- *Linked-bubble network growth* by percolation gives
  - lower Critical He/M found for small particles and thin films
  - typical thermal effects.

The model shows how the He release spectrum from an aging tritide is controlled by the bubble spacing distribution.

The bubble shape and growth process depend on the tritide's mechanical properties.

- Dislocation loop punching

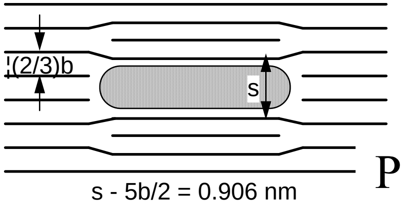


Surface Energy

Strain Energy

$$P_{LP} = 2\gamma/r + \mu b/r$$

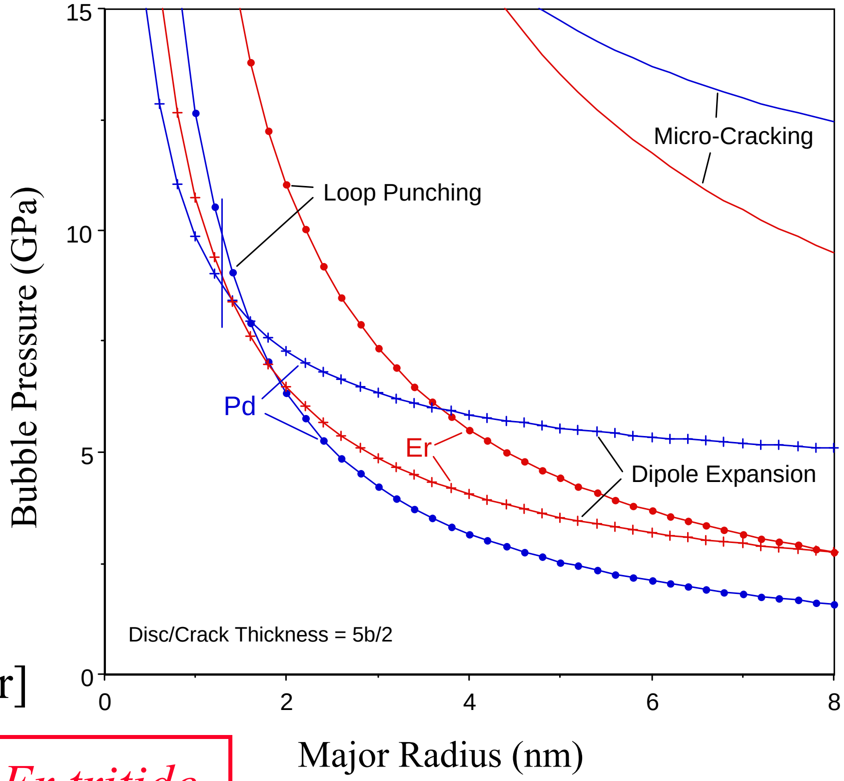
- Dislocation dipole expansion



$$P_{DE} \approx 2\gamma/s + \mu b/(2r+b)$$

- Micro-crack growth requires higher pressures: $P_{\mu C} = 2\gamma/s + \pi\mu s/[2(1-\nu)r]$

Tritide	γ(GPa-nm)	μ(GPa)	b(nm)	γ/μb
Pd	1.54	33.6	.2852	0.16
Er	0.637	57.4	.3623	0.03

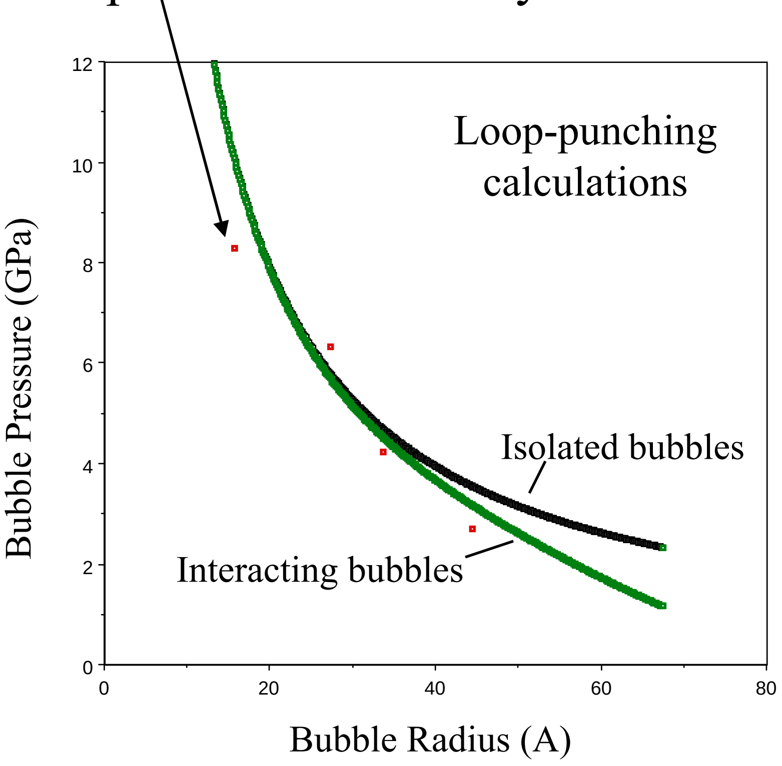


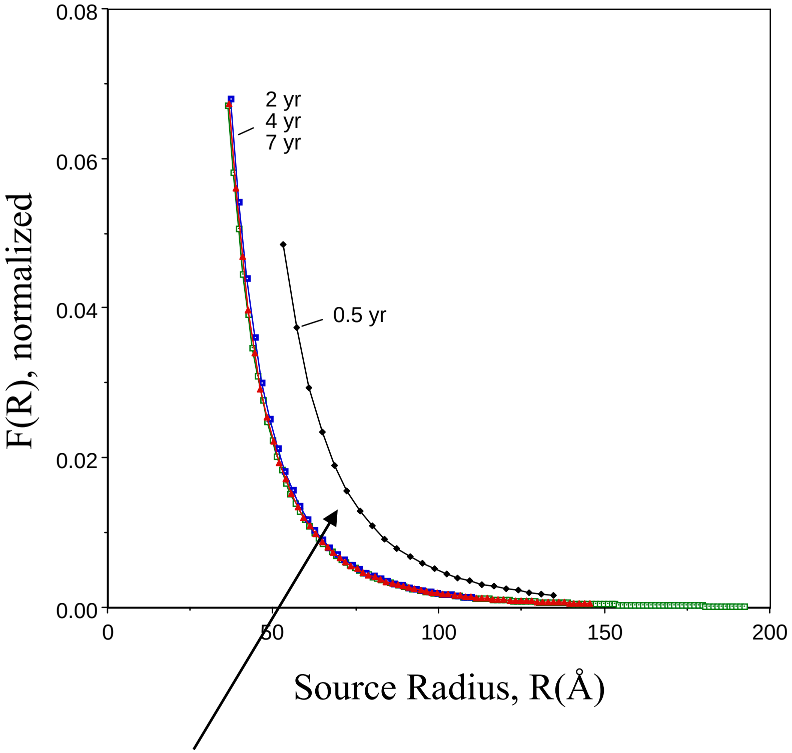
The low surface energy (low γ/μb) for Er tritide results in thin, disk-shaped bubbles.

Dislocation dipoles are also favored early in life for Pd tritide.

- This mechanism will lower the computed bubble pressure at 0.5 yr
  - from 10 to 8 GPa,

  and produce better agreement with the pressure deduced by NMR.





- It will also change the bubble spacing distribution computed for the 0.5 yr sample.

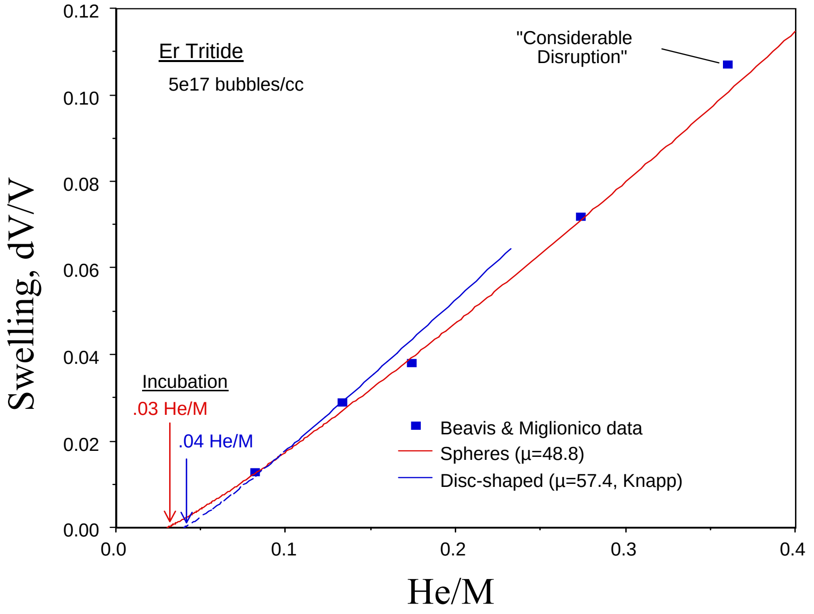
Observed bulk ErT_x swelling and lattice dilation can both be explained by dipole growth.

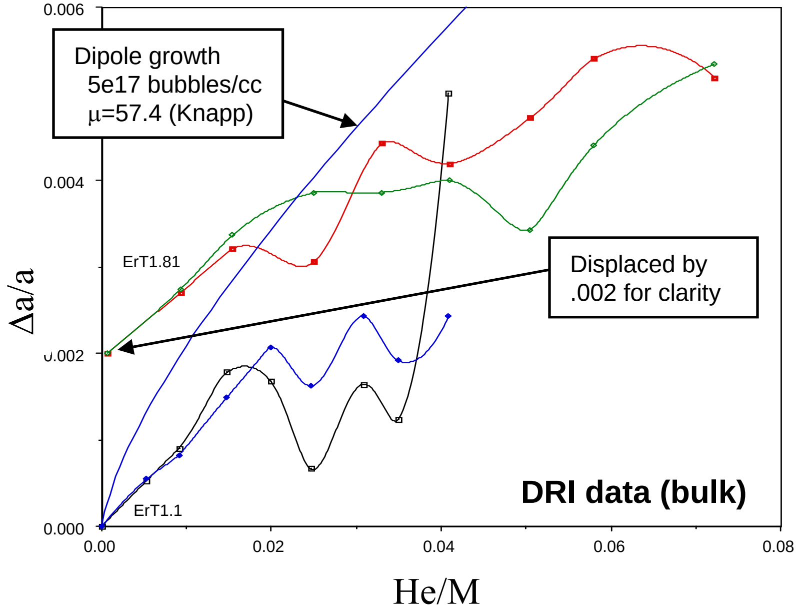
- For either growth mechanism, swelling can be fitted by varying the bubble density and adding an initial incubation period.

- A rapidly-growing lattice parameter supports the dipole process.

At .04 He/Er, Loops: $\Delta a/a \approx .0004$

Dipoles: $\Delta a/a \approx .006$



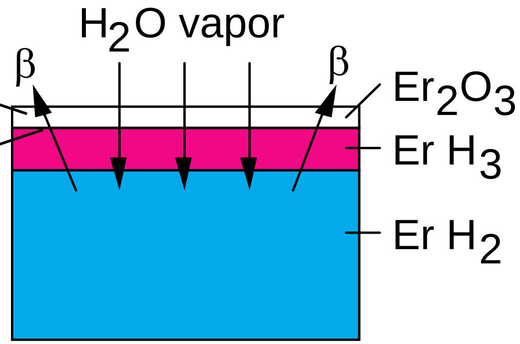


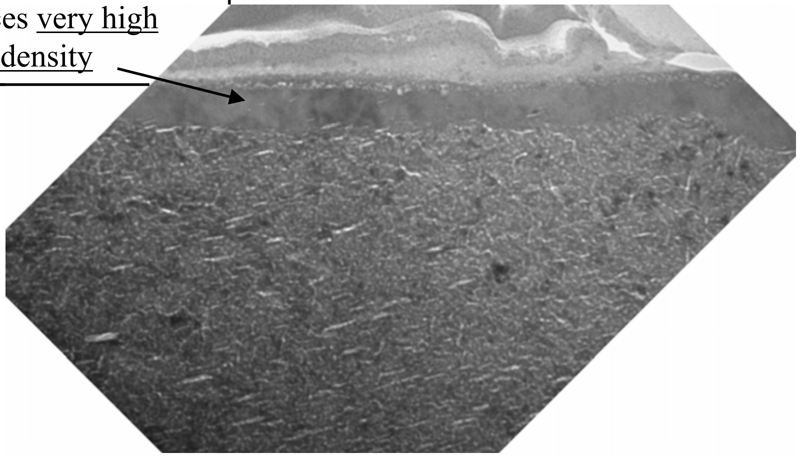
- Swelling incubation and Δa/a oscillations may be due to linkage of neighboring disks which should begin around 0.02 He/M.

Early release from Er films may be reduced by air-modified surface layers.

- Without near-surface layers, early release is high:
  ERF $\approx 1/(n_B)^{1/3}L$
  $\approx .01$ for 5e17 bubbles/cc.
- Near-surface impurities reduce the tritium concentration in this critical range and *lowers the ERF*.
- Ambient exposure may generate a temporary tri-hydride layer -- which can raise the n_B and *shorten the He escape depth*.
- Rapid oxidation with background H_2O vapor releases near-surface bubbles and *complicates testing*.

Beta activity breaks bonds
  - assists OH^- diffusion thru oxide
  - keeps interface active
OH^- reaction produces
  - oxide growth
  - stable tri-hydride layer, immobilizing new He
Bakeout frees He to diffuse
  - rapid self-trapping produces <u>very high bubble density</u>

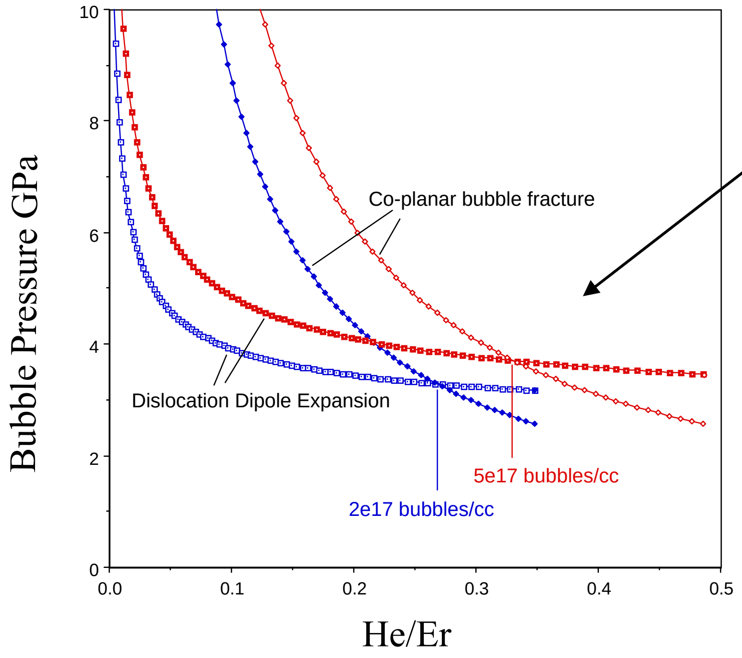




TEM by P. Kotula, SNL

Summary: The Nano-bubble Evolution Model can be modified for differences in tritide systems.

	Pd Tritide	Er Tritide Films
Bubble Nucleation	He self-trapping	At defects w/fill-in
Early Release	From λ_{escape}	Surface layer effects
Bubble Growth	Loop-punching	Disloc. dipole expansion
Bubble Linkage	Inter-sphere fracture	"Co-planar" disk fracture?
Rapid Release	3d network percolation	$2d^+$ network percolation?



SEM by G. Moore, SNL