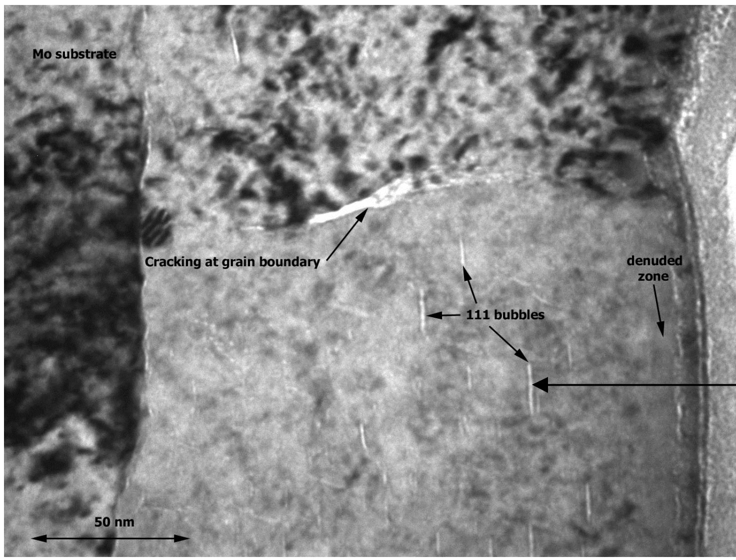
SAND2007-4057C

Physics of He Platelets in Metal Tritides

Don Cowgill, SNL, Livermore CA USA

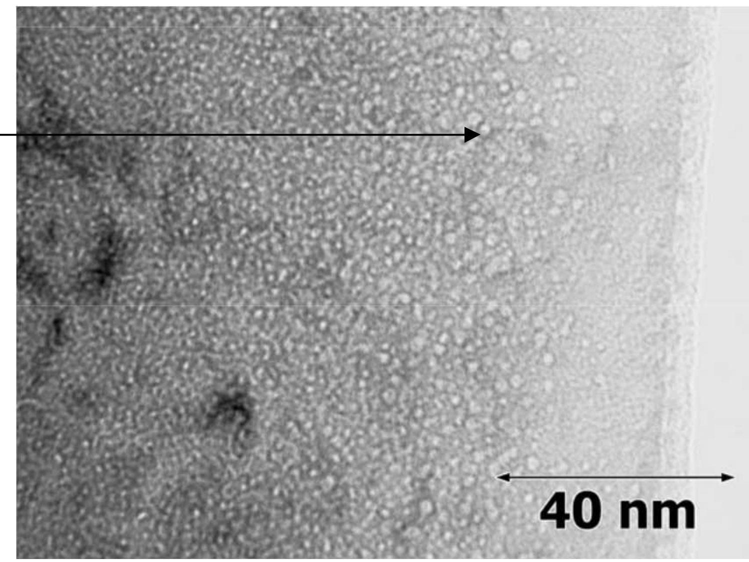
IHISM Workshop, St. Petersburg, Russia, 2-6 July 2007

What causes the bubble shape difference?



Pd tritide

Er tritide



TEM images by Brewer, Gelles, & Kotula

<u>Outline</u>

- Platelet stability and growth
- Pd vs Er system
- Model testing with XRD data
- Percolation of Interbubble Fracture
- Other materials & future efforts

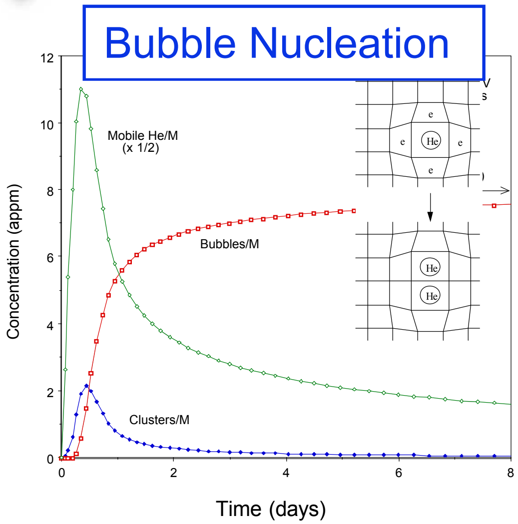
> *"In the spirit of a workshop, this is work in progress."*

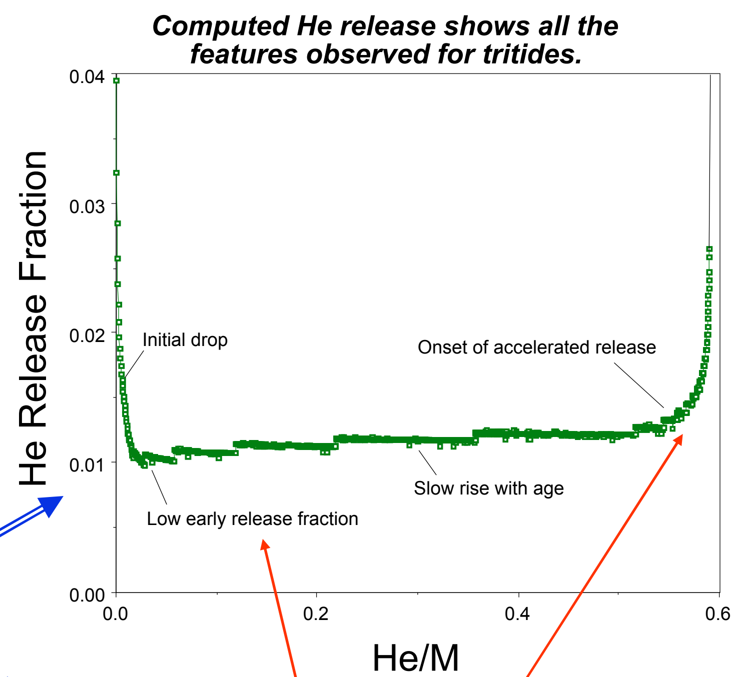
0706 dfc

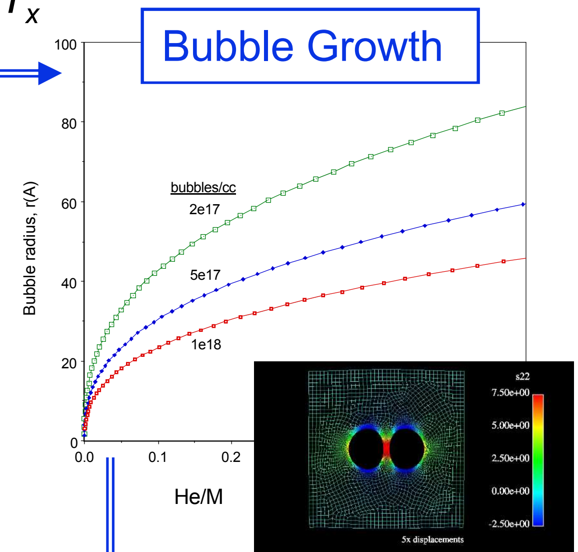
Sandia National Laboratories

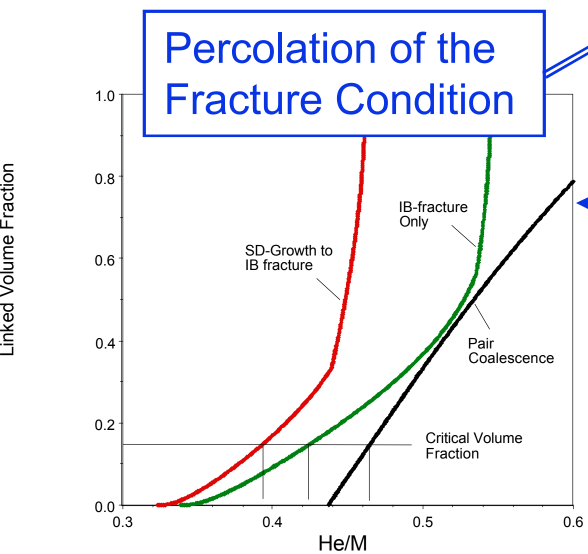
The evolution of He bubbles/platelets is captured in a continuum-scale model.

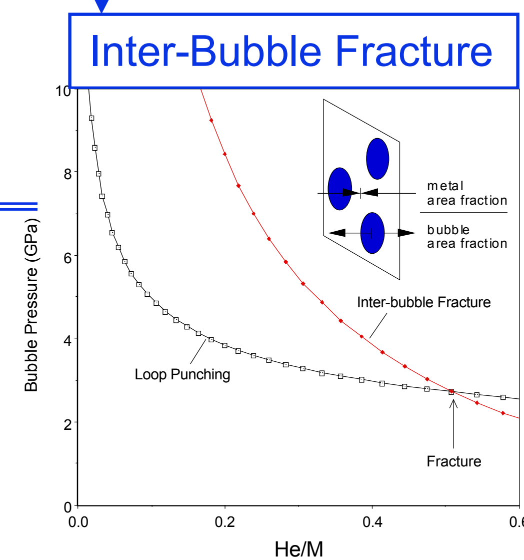
Behavior of spherical bubbles in PdT_x











The He release spectrum is critically dependent on the bubble shape and spacing distribution.

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

- Model using 3 components: mobile He, He-pairs, "bubbles":

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

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

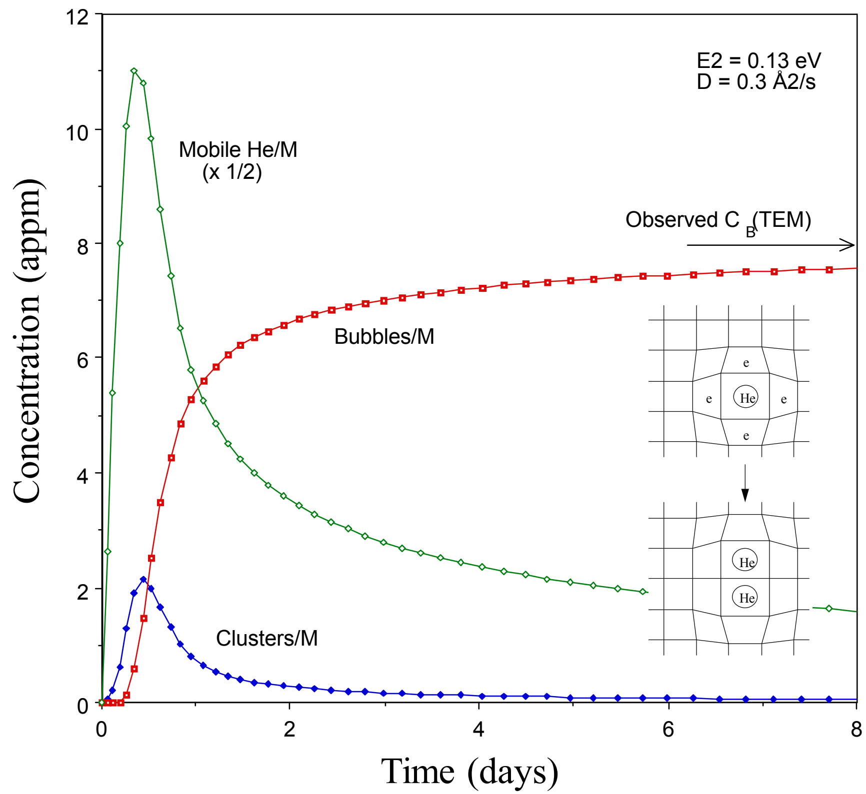
$$dc_B/dt = ps_2c_1c_2$$

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.

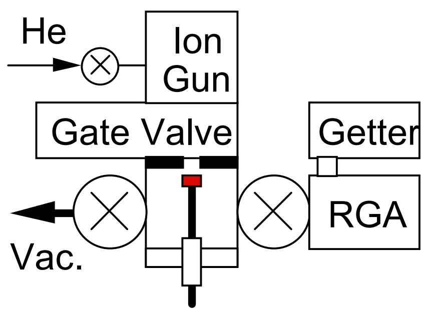


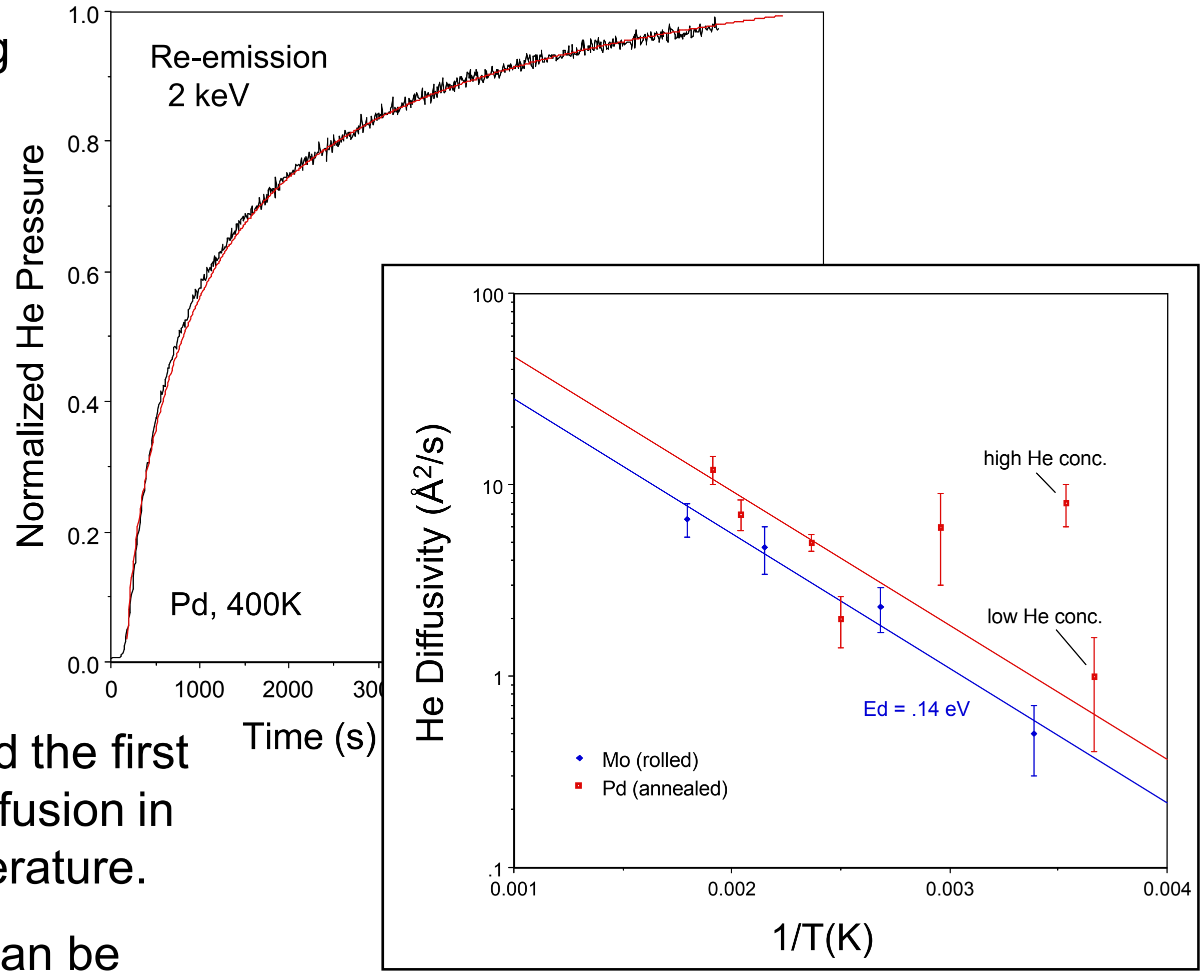
Using theoretical E_2 and experimental D_{He} gives correct c_B.

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

Nucleation parameters are being measured by our He Implant/Re-emission technique.

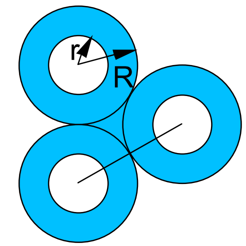
- He re-emission following a short implant pulse is fitted to the self-trapping model.





- This technique produced the first measurements of He diffusion in metals near room temperature.
- Self-trapping energies can be determined by varying the implant pulse characteristics.

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

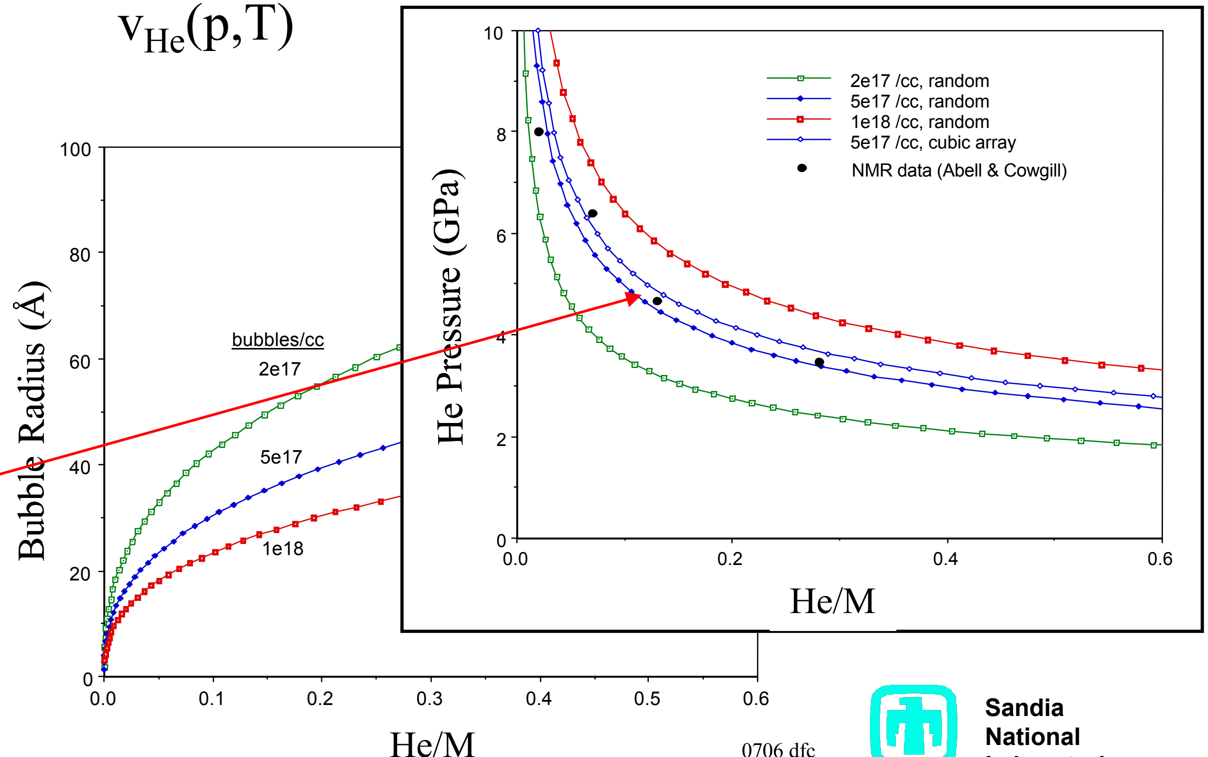


Array of Spherical Source Volumes

- 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: $v_{He}(p,T)$

- 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.

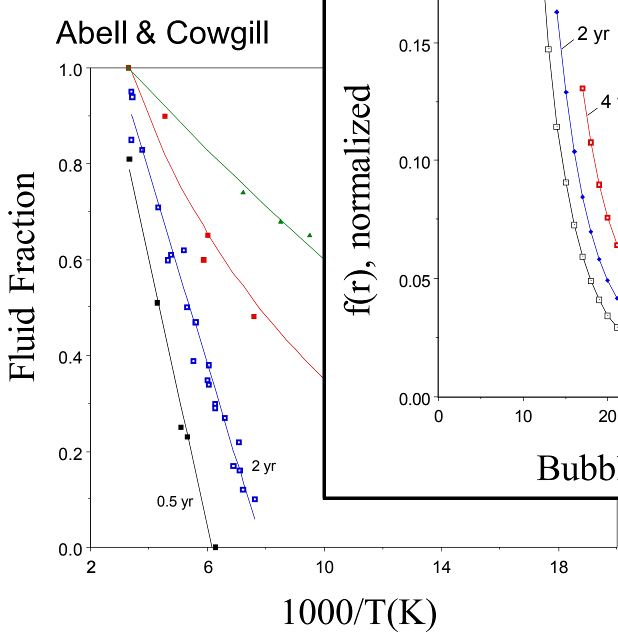


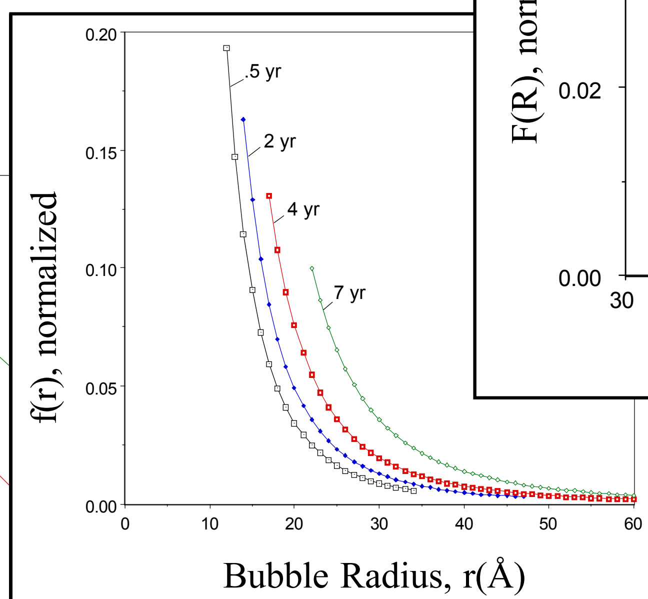
0706 dfc

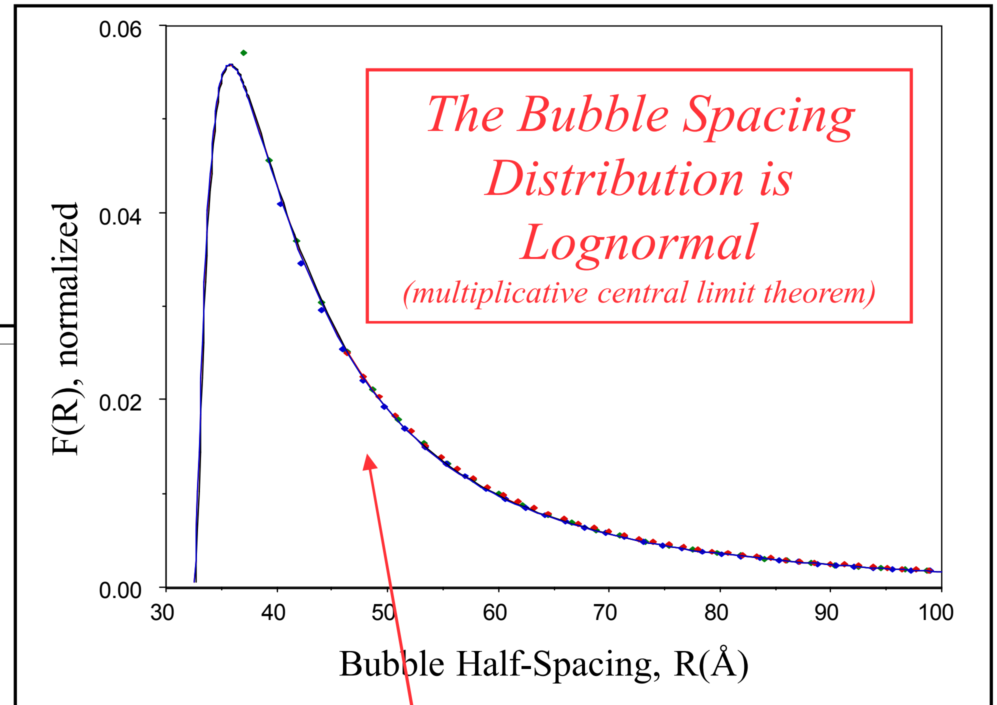
Sandia National Laboratories

The bubble spacing distribution in PdT_x has been determined by ^3He NMR.

- ^3He T_1 (motion) separates sol-He from liq-He in bubbles.
- Growth relations convert fluid fractions to <u>bubble distributions</u>.





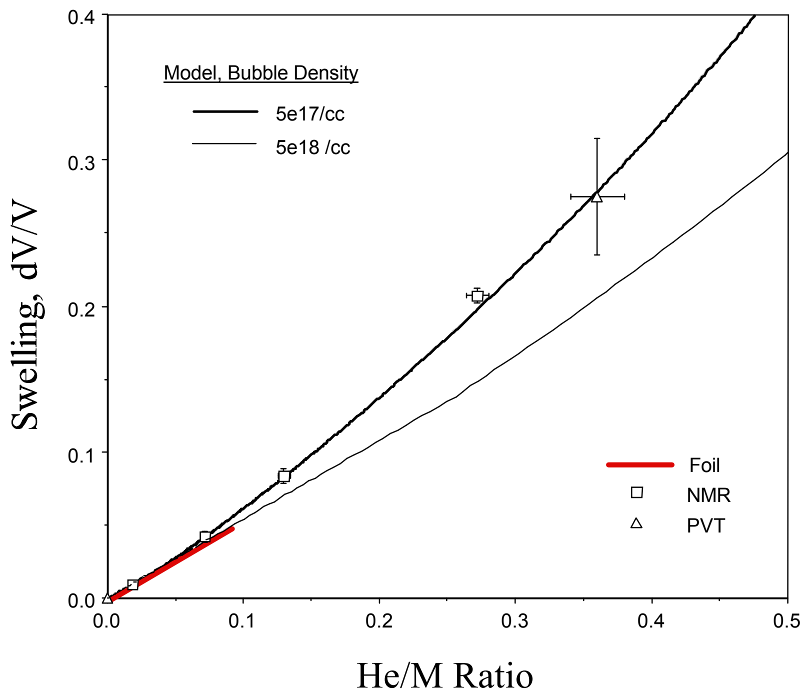


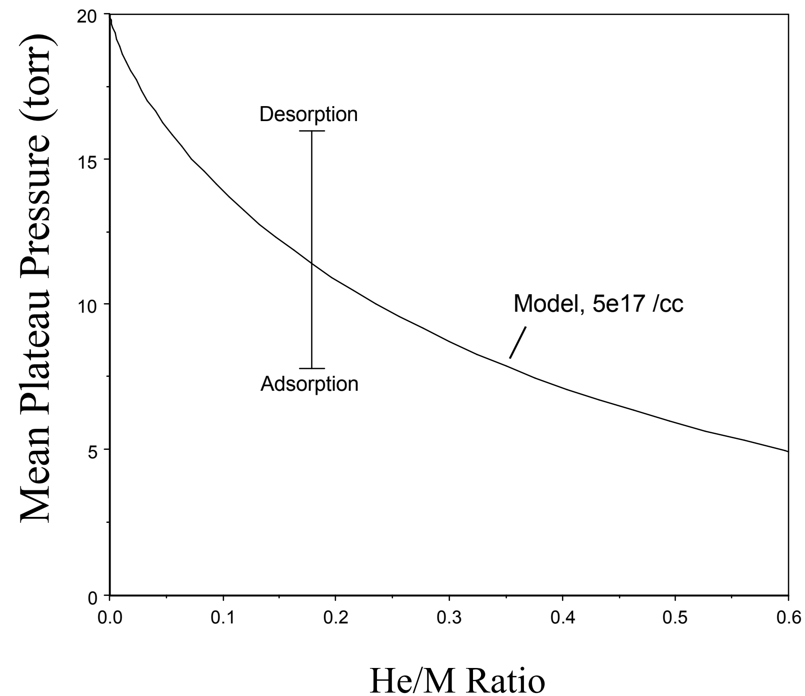
The constant spacing distribution
- verifies nucleation has stopped
- provides a sensitive test of the nucleation and growth models.

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

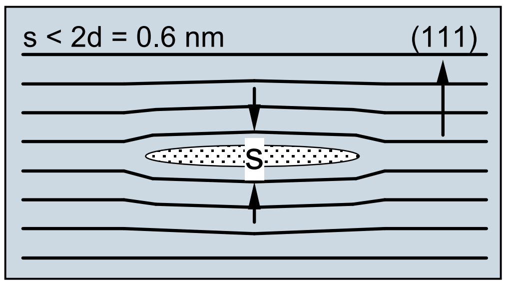




Swelling and PCT behavior are consistent with the lower bubble density found by TEM (Thomas et al., 1983), not higher (Thiebaut et al., 2000).

The bubbles in fcc materials likely evolve from nano-cracks.

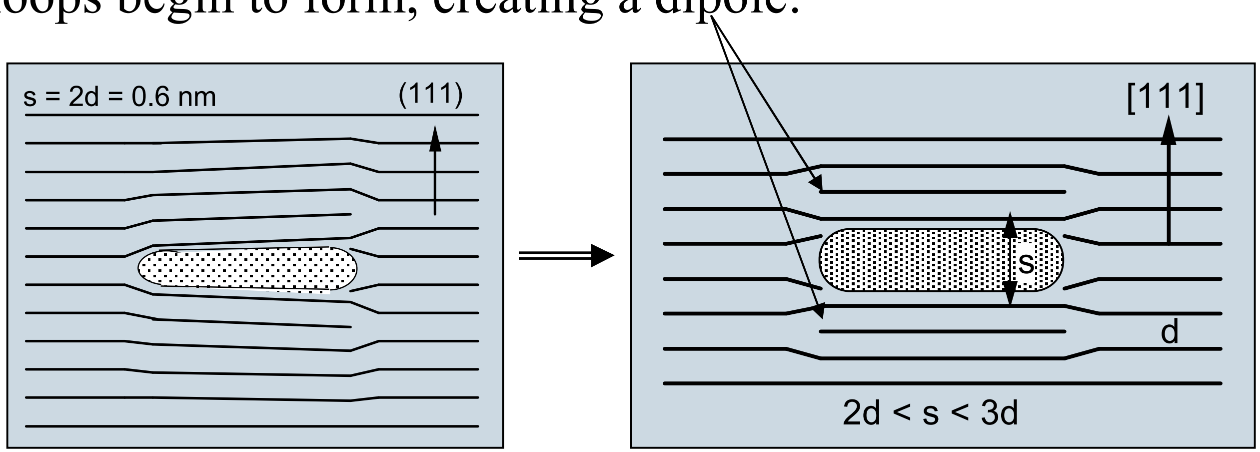
- He atoms accumulate in “relatively open” spaces between (111) planes, where they open Griffith-like nano-cracks:



HR-TEM of n-crack in PdT by Thiebaut

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

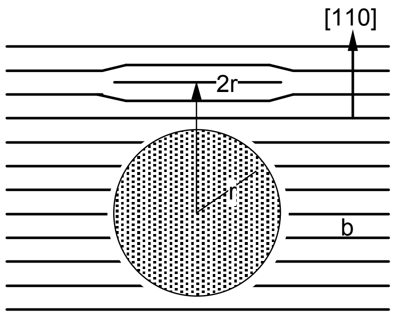
- When the crack opens to s=2d, dislocation loops begin to form, creating a dipole:



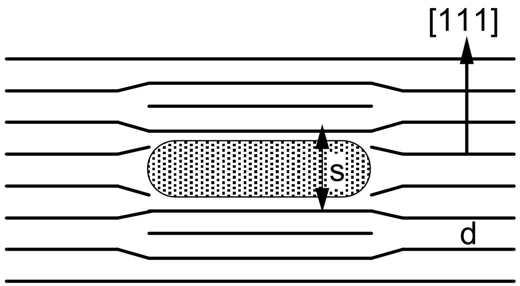
[110] view

The He pressure within the precipitate has components due to surface and strain energies.

Spherical bubbles grow by "dislocation loop punching"



Platelets can grow by "dislocation dipole expansion"



Surface Energy: $p_e\, dV = \gamma\, dA$

$p_e\, \pi r^2\, b = \gamma\, 2\pi r\, b$
$p_e = 2\gamma/r$

$p_e\, \pi[(r+b)^2-r^2]\, s = \gamma\, 2\pi[(r+b)^2-r^2+(r+b)s-rs]$
$p_e = (2\gamma/s)\, [(2r+b+s)/(2r+b)]$

Lattice Strain: stress = μ strain

$p_s\, \pi r^2 = \mu\, [(b/2)/d]\, 2\pi rd$
$p_s = \mu b/r$

$p_s\, \pi[(r+b)^2-r^2] = \mu\, [(d/2)/b]\, 2\pi[(r+b)-r]b$
$p_s = \mu d/(2r+b)$

Bubble Pressure: $p = p_e + p_s$

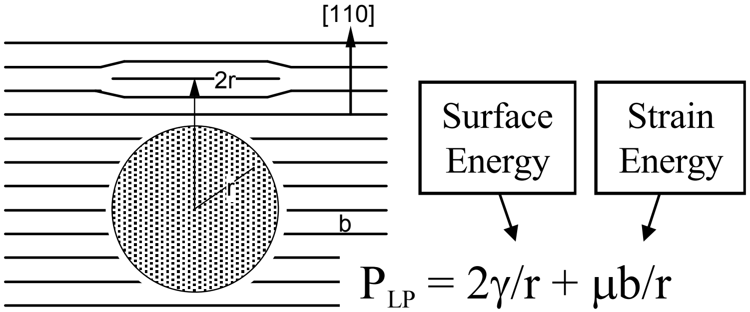
$p_{lp} = 2\gamma/r + \mu b/r$

$p_{de} = (2\gamma/s)\, [(2r+b+s)/(2r+b)] + \mu d/(2r+b)$
$p_{de} = 2\gamma/s + \mu d/2r$, at large r

Sandia National Laboratories

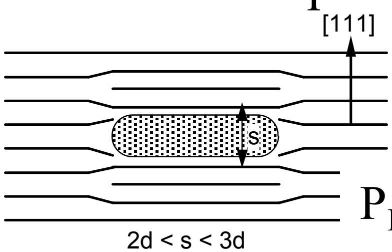
The bubble shape and growth process depend on the tritide's mechanical properties.

- Dislocation loop punching



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

- Dislocation dipole expansion

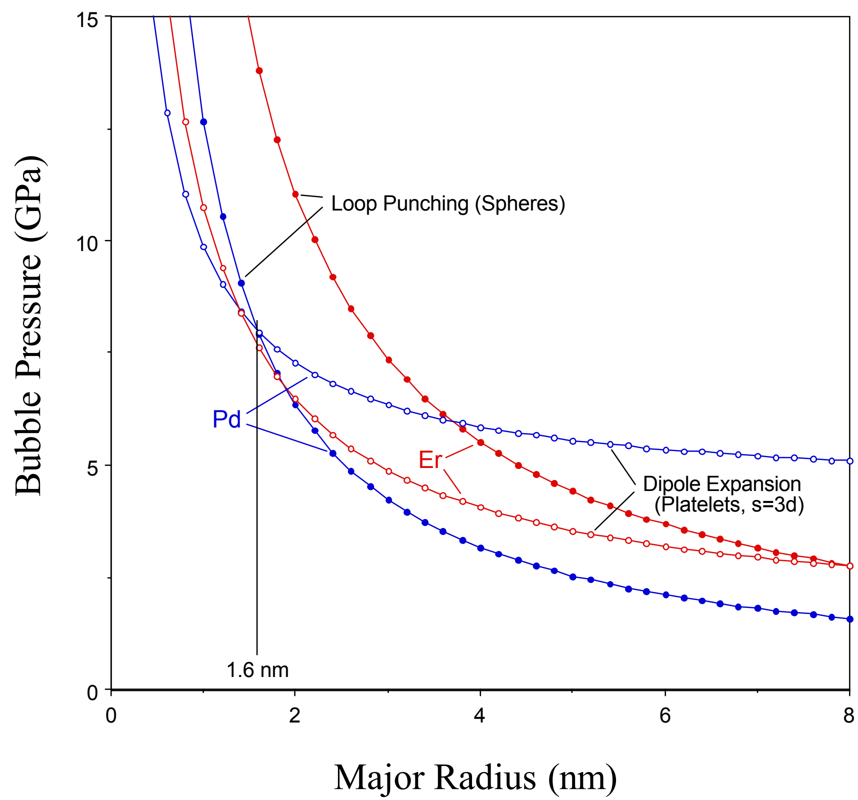


$P_{DE} \approx 2\gamma/s + \mu d/(2r+b)$

- Thin, disk-shaped bubbles are caused by a low surface energy (low $\gamma/\mu b$).

Note: Platelets are also the preferred shape in *young Pd tritide (<50 days)*.

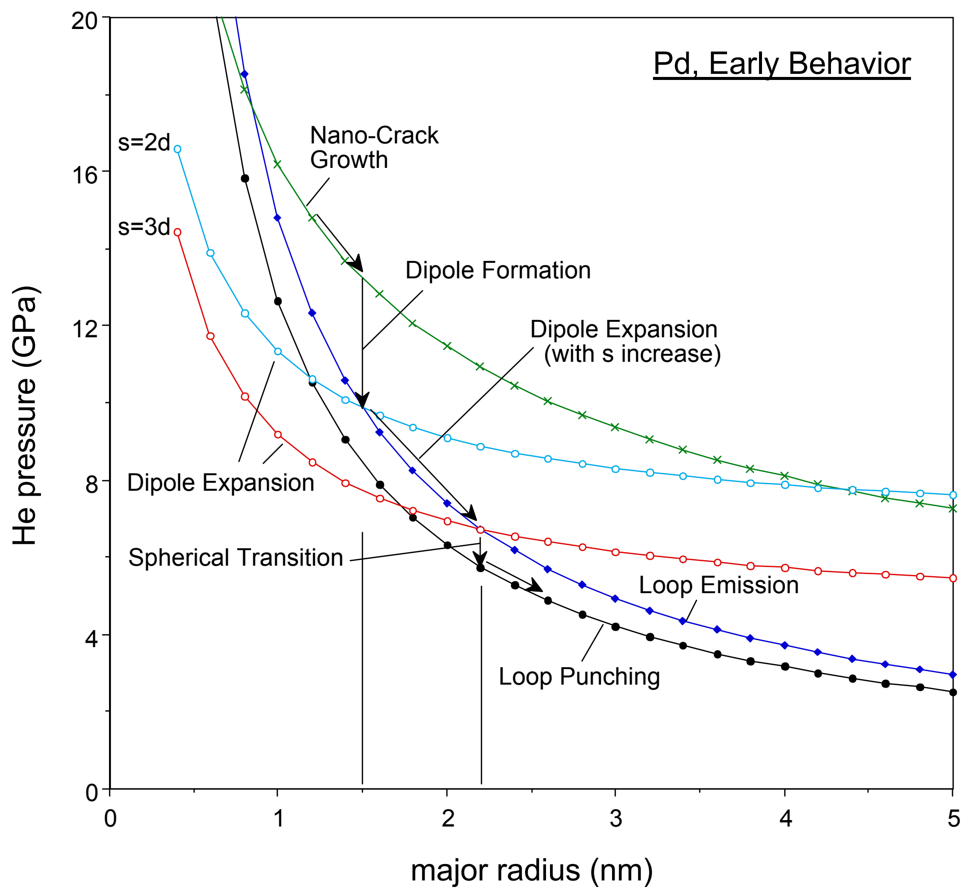
Tritide	γ(GPa-nm)	μ(GPa)	b(nm)	γ/μb
Pd	1.54	33.6	.2852	0.16
Er	0.637	57.4	.3623	0.03



Sandia National Laboratories

The early growth of bubbles in PdT appears to have several stages.

1. He atoms collect in (111) planes and open nano-cracks (Griffith):
   $P_{nC} = 4\gamma/s, \quad s = 4[\gamma(1-\nu)r/\pi\mu]^{1/2}$.
2. Dislocation dipoles form when the nano-crack gap reaches s=2d.
3. Platelet pressures drop as their thicknesses increase to s≈2.5d.
4. The platelets expand radially until s=3d, where the dipole escapes.
5. [110] loops are emitted as the platelets transition to spheres.
6. Spherical bubbles continue to grow by normal loop-punching.



Sandia National Laboratories

Testing of pressure formulation is provided by lattice dilation data on aged tritides.

- Tensile stress created by the precipitates produces a positive da/a.

- Spherical bubbles at Loop Punching pressure:

  Hydrostatic tensile stress balances bubble pressure

  $p_{LP}(\Delta V/V) = B^*(3\ da/a)_{LP}$, B^* = bulk modulus of aged material

  where $\Delta V/V = (4/3)\ \pi r^3\ n_B$, n_B = bubbles/cm^3

$$(da/a)_{LP} = [1/3B^*]\ p_{LP}(\Delta V/V)$$

- Platelets at Dipole Expansion pressure:

  [111] tensile stress balances platelet pressure, 4 components

  Projection along [100] cubic axes = $1/3^{1/2}$

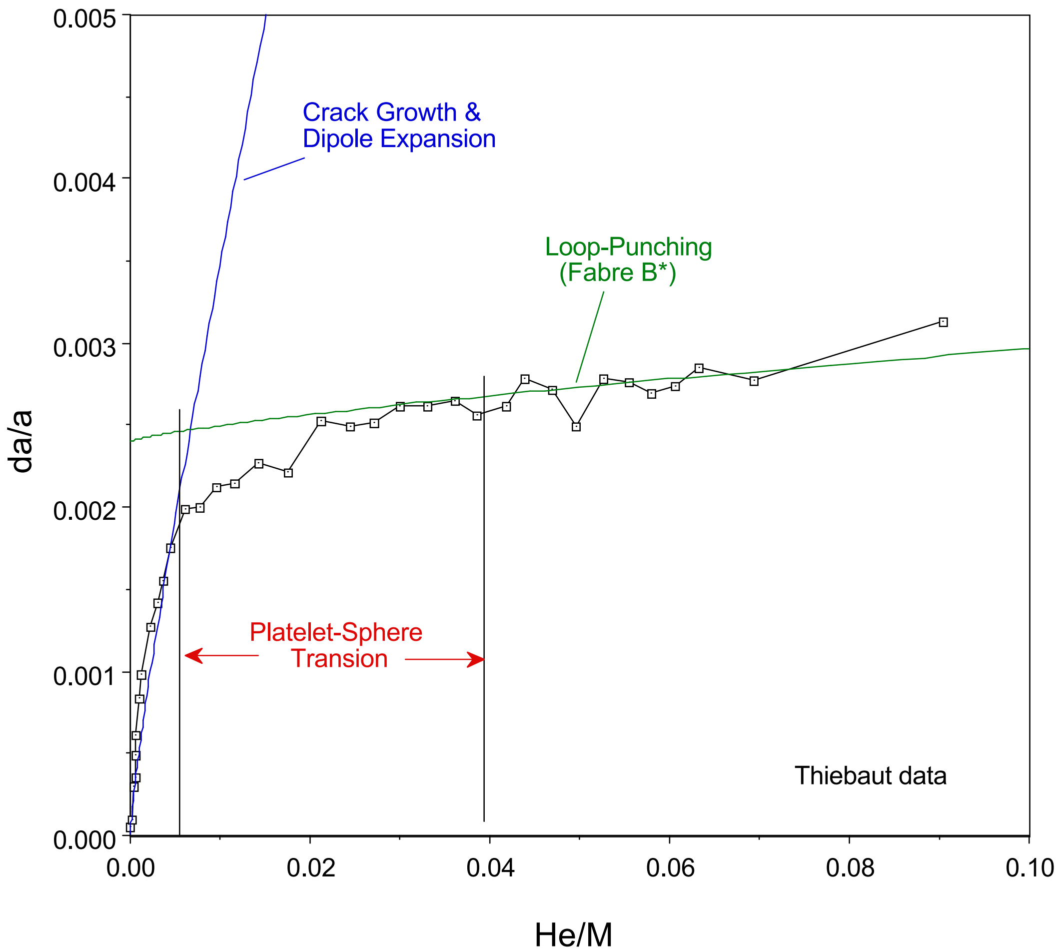
  $p_{DE}(\Delta A/A)\ 4/3^{1/2} = E^*(da/a)_{DE}$, E^* = Young's modulus of aged material

  where $\Delta A/A = \pi r^2\ (n_B/4)^{2/3}$, n_B=bubbles/cm^3

$$(da/a)_{DE} = [4/3^{1/2}E^*]\ p_{DE}(\Delta A/A)$$

Sandia National Laboratories

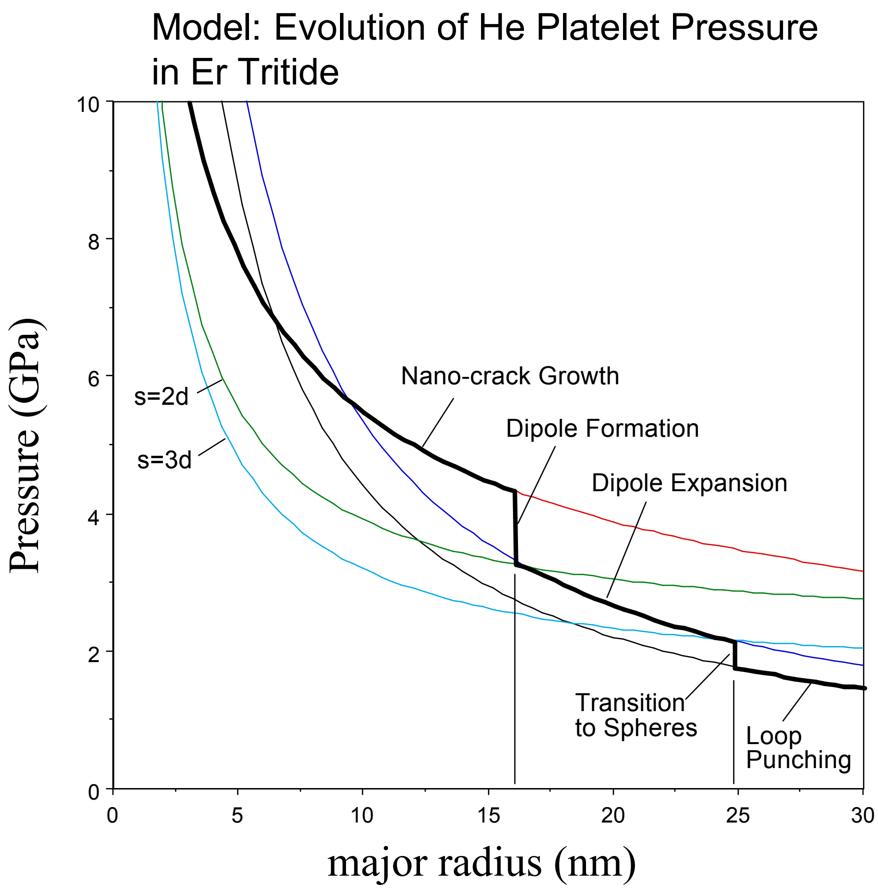
Lattice dilation "details" of PdT appear to support the existence of multiple stages.



- Initial Griffith crack growth at high pressure will produce an even rise.
- The bubble volume increases by 8X during the transition from platelets to spheres.
- Emitted dislocations must remain trapped between "bubbles".
  - Bubble source volumes remain constant!)

Sandia National Laboratories

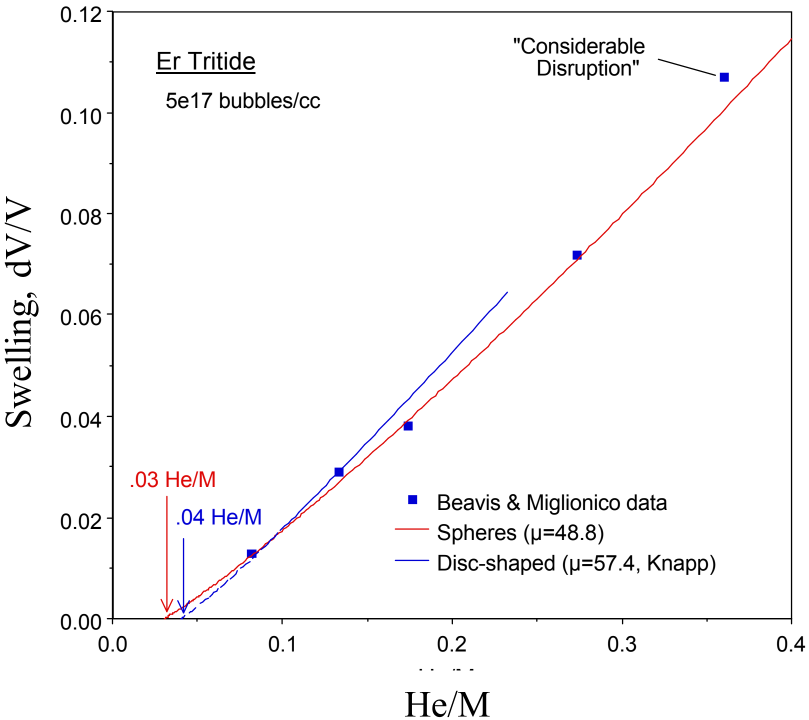
The He precipitates in Er tritide remain 2-dimensional platelets throughout life.

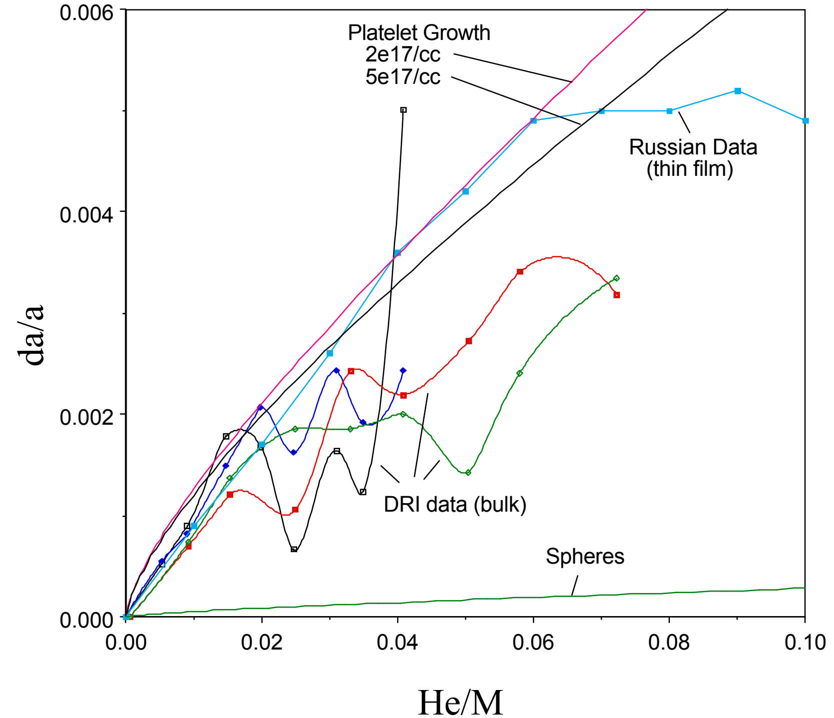


- He pressure decreases as the nano-crack opens.
  - He becomes liquid at ~ 12 GPa.
- When the crack width reaches 2d, a dislocation dipole begins to form, causing a drop in pressure.
- The pressure decreases further as the completed dipole expands and its width increases to 3d.
- Linking of the platelets will occur prior to their spherical transition.
  - At r ≈ 25 nm, the co-planar platelet area >1 (area projections overlap).

Lattice dilation is significantly greater for platelets.

- Swelling data can be fitted by either growth mechanism; but the *initial incubation period is not consistent with loop punching.*

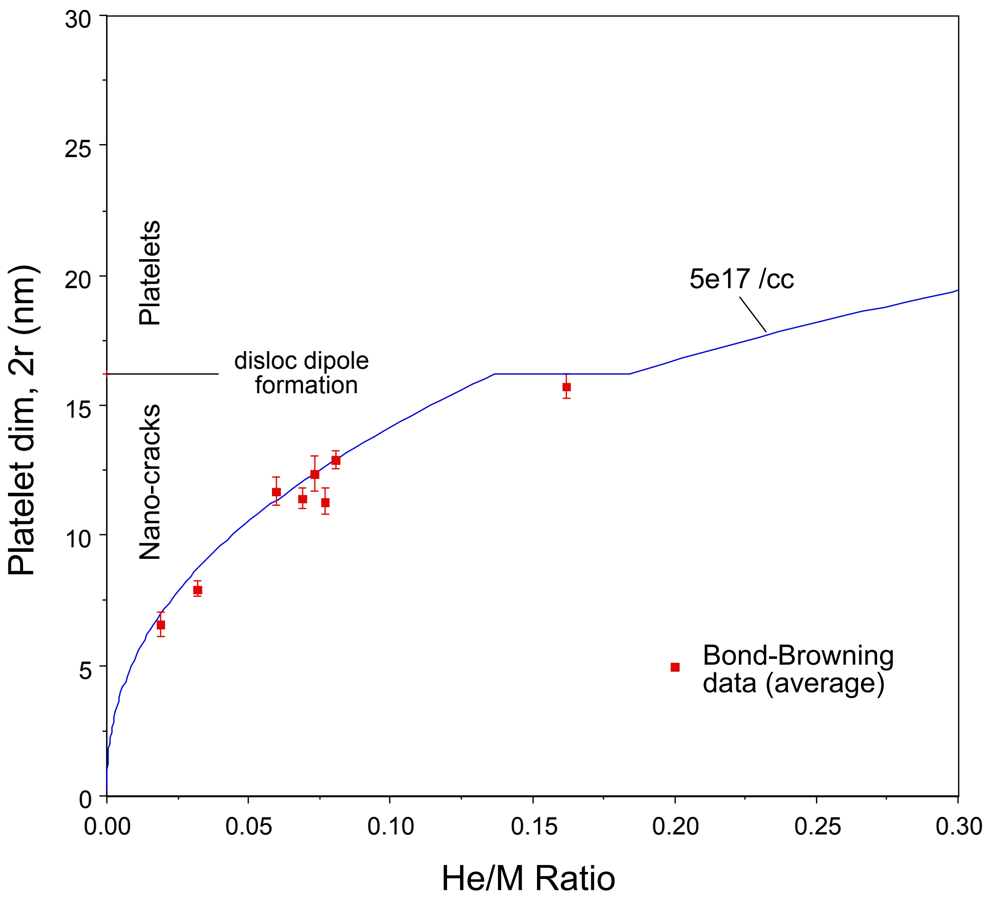




- Platelets produce greater lattice strain and can account for the rapidly increasing lattice parameter.

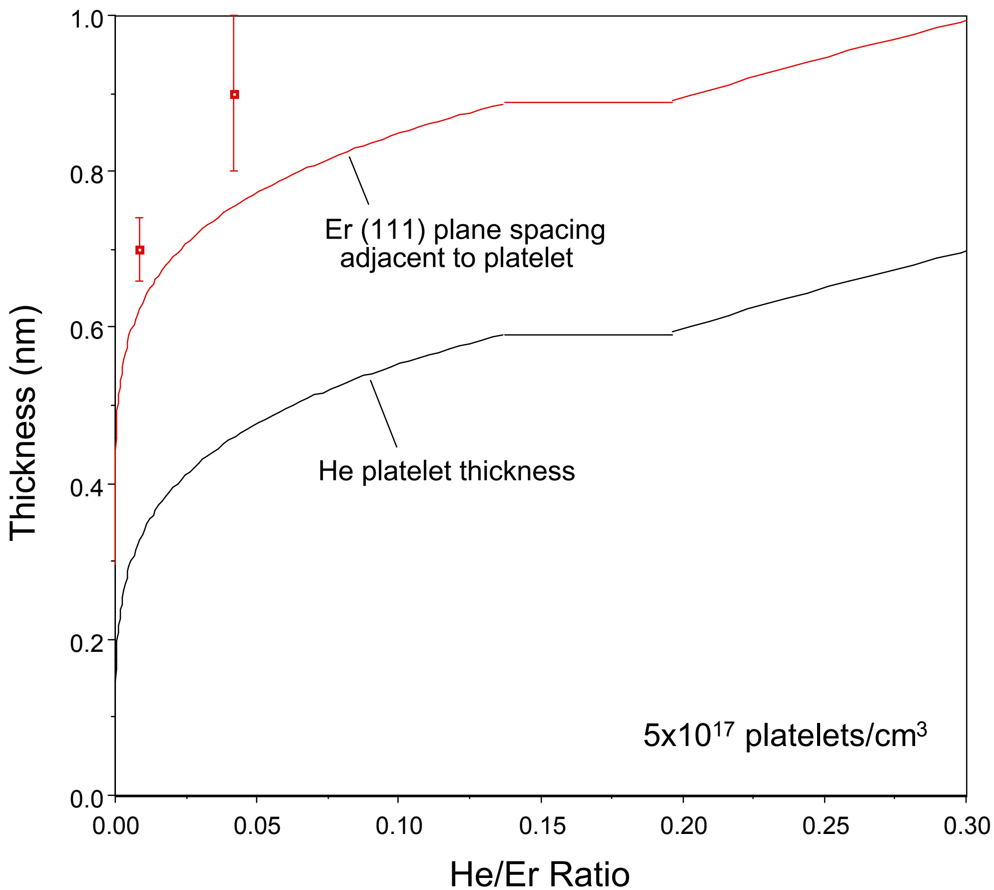
Sandia National Laboratories

Model accounts for the platelet growth observed by Bond & Browning.



- Model calculation for an average platelet density of 5×10^{17} platelets/cm^3.
  - Pd tritide bubble density!
- Here, platelet interactions are assumed negligible.
  - We must revisit this!
- For Er tritide, rapid He release occurs around 0.3 He/Er, when the average platelet is 20 nm.

The platelet thickness is nearly constant, but is should increase slowly with age.



- Predicted thickness appears slightly less than the TEM determination?
  - Need more data.
  - X-ray diffraction?
- Accurate measurement of the platelet thickness and density can provide a determination of the surface energy:

$$\gamma = \frac{\pi \mu s^2}{4(1-\nu)\, r}$$

The bubble shape condition appears to hold for precipitates in fcc, hex, and bcc materials.

Material	γ(GPa-nm)	μ(GPa)	b(nm)	$2\gamma/\mu b$	shape
ErT	0.637	57.4	.3623 fcc	.061	platelets
ScT	0.954	54.0	.3382 fcc	.104	early platelets, then?
TiT	1.39	76.2	.3111 fcc	.117	platelets & elongated?
Ni	1.72	76.5	.2490 fcc	.180	spheres?
ZrT	1.48	32.6	.3522 fcc	.258	spheres
PdT	1.54	33.6	.2852 fcc	.322	spheres
Be	1.10	146	.359 hex	.051	platelets
Ti-α	1.39	40.1	.291 hex	.238	platelets
W	2.22	158	.273 bcc	.103	platelets
V-α	1.95	47.4	.263 bcc	.312	spheres
Nb-α	1.90	38.2	.285 bcc	.350	spheres

- Surface energy/strain energy ratio for spherical bubbles
- Platelets are prefered for small r, where $s/2r > 2\gamma/\mu b$.

Work on platelet structures is continuing.

- Thin (111) platelet bubbles can be associated with nano-cracks or dislocation dipole structures.

- Additional theoretical work is examining
  - formulations of platelet characteristics
  - linking of platelets by inter-platelet fracture

- Continued testing should examine
  - the bubble pressure and spacing distribution in young Pd tritide (in spherical transion stage).
  - bubble shapes in other materials (e.g. SiC).
  - bubble shapes in implanted materials.

- TEM and XRD studies in selected materials are needed to characterize bubble shapes and transition points.

For spherical bubbles, Rapid He Release is modeled using a ligament fracture criterion.

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

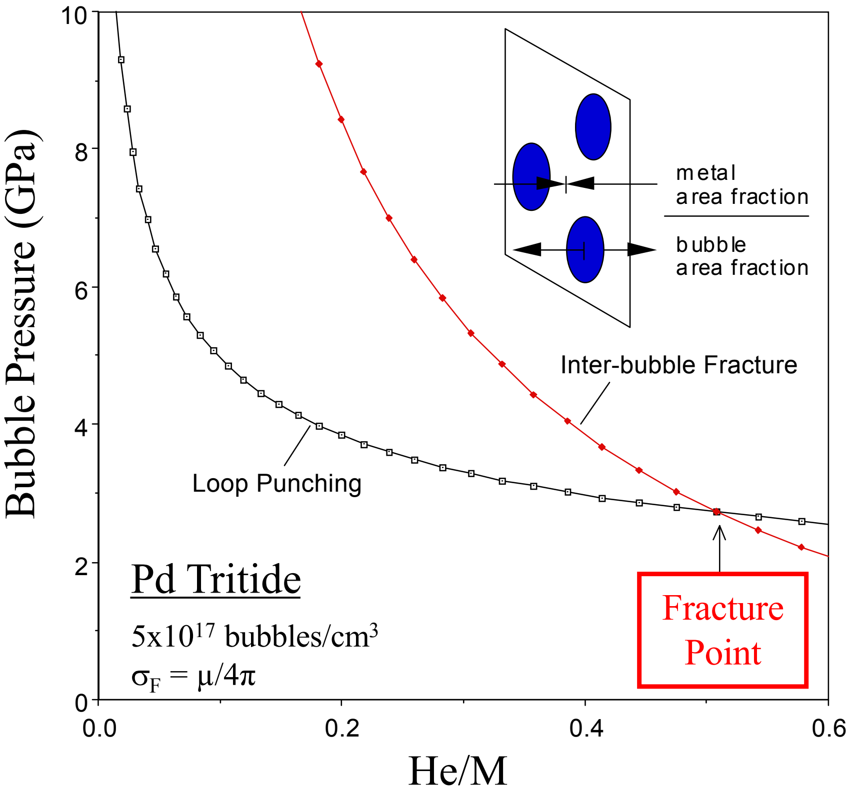
  For plane through adjacent bubbles, fracture occurs when:

  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.

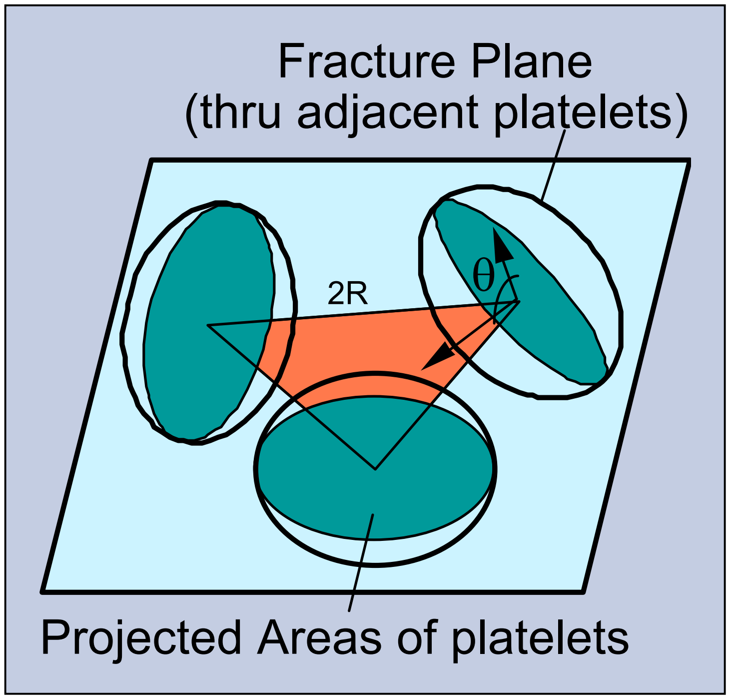
Sandia National Laboratories

Inter-platelet fracture can be modeled using platelet area projections in the fracture plane.

- Equating stresses on the ligament between 3 adjacent platelets:

$$p_S \text{ (projected platelet area)} = \sigma_F \text{ (projected metal area)}$$

$$(p_F - 2\gamma/s)\,(\pi r^2/2)\cos\theta = \sigma_F\,[3^{1/3}R^2 - (\pi r^2/2)\cos\theta]$$

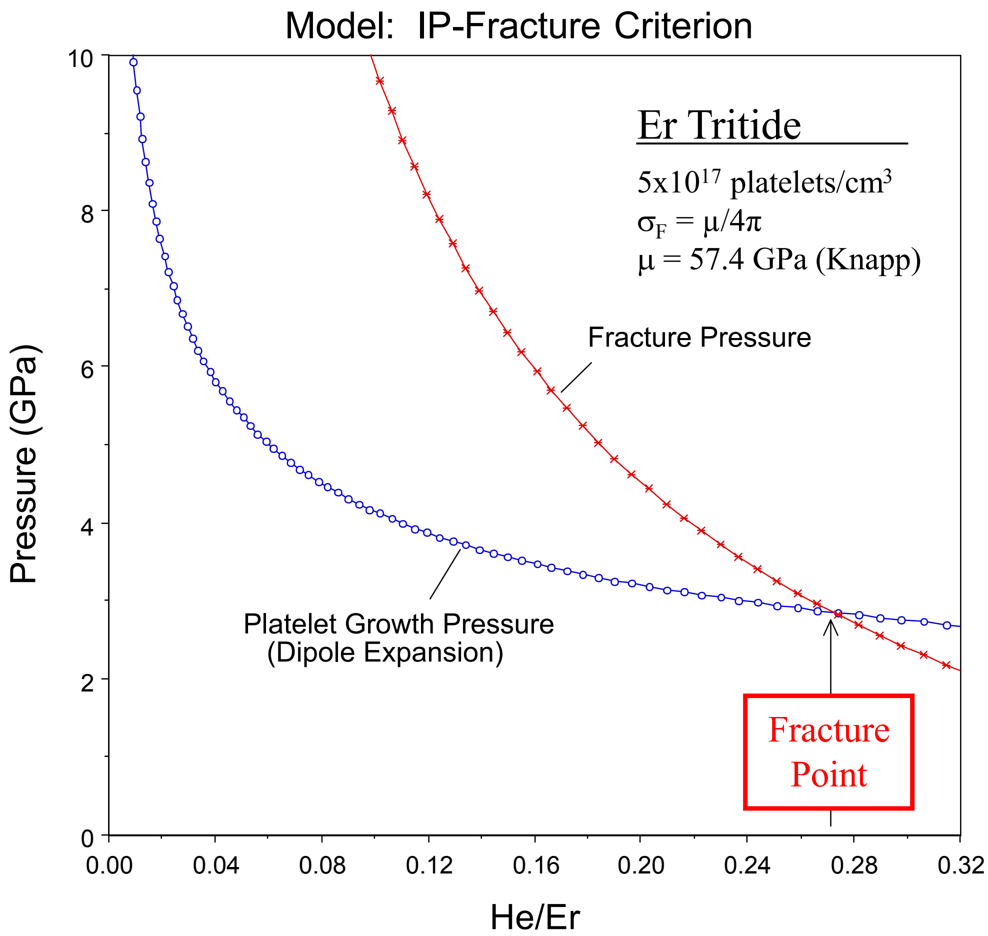


- θ = Platelet angle in the fracture plane.
- Relative angle between platelets is zero or angle between [111] directions, 70.529°.
- Averaging areas using (100), (110), (111) principle planes, considering the frequency in each geometry, gives $< \cos\theta > = 0.4755$.
- IP-Fracture criterion:

$$p_F = 2\gamma/s + \sigma_F\,\{\,[\pi r^2 n_P^{2/3} < \cos\theta >]^{-1} - 1\,\}.$$

Sandia National Laboratories

The pressure for inter-platelet fracture drops below that for platelet growth at 0.27 He/Er.

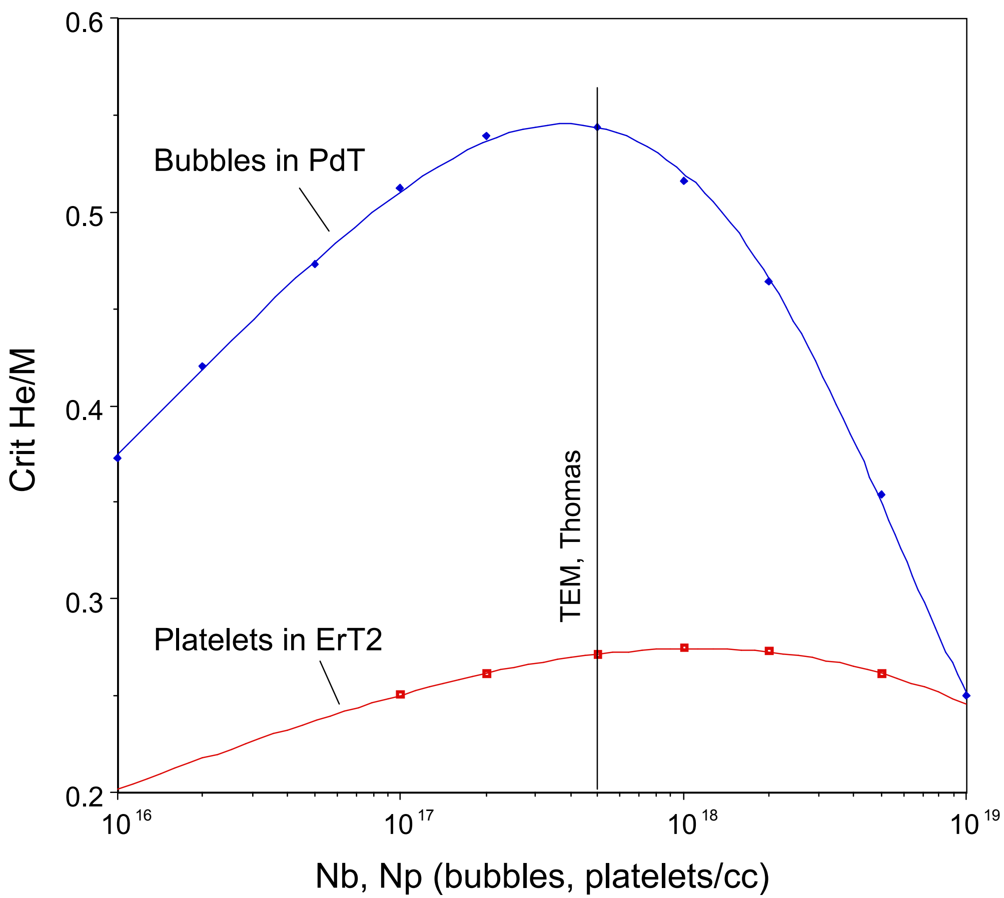


- This fracture condition depends on platelet density and fracture strength σ_F.
- Rapid He release will occur when this condition extends over several platelet spacings

  -- when platelets at the mean density undergo IP-fracture.

Sandia National Laboratories

Dependence of the Crit He/M on "bubble" density is weaker for platelets.



- The optimum density appears slightly higher for Er platelets, compared to Pd bubbles.
- For spherical bubbles in PdT, regions with high bubble density begin linkage first.
- By contrast, the ligaments between platelets in ErT_2 should all fracture at about the same time -
  - producing a more abrupt transion to Rapid Release.

Work on platelet structures is continuing.

- Thin (111) platelet bubbles can be associated with nano-cracks or dislocation dipole structures.

- Additional theoretical work is examining
  - formulations of platelet characteristics
  - linking of platelets by inter-platelet fracture

- Continued testing should examine
  - the bubble pressure and spacing distribution in young Pd tritide (in spherical transion stage).
  - bubble shapes in other materials (e.g. SiC).
  - bubble shapes in implanted materials.

- TEM and XRD studies in selected materials are needed to characterize bubble shapes and transition points.