

# **Modeling He Retention in Liquid Metals by Nano-Bubble Formation**

---

**Don Cowgill  
Sandia National Laboratories  
Livermore, CA 94550**

**ALPS/APEX Meeting, April 6-11, 2003**

## Outline:

- Physical mechanisms & equations
- Model for He nano-bubble formation in aging metal tritides
  - Modifications for bubbles in liquids
- Examples for He implantation in liquid Li, Sn, Ga



# We use a 1d finite-difference, diffusion code to calculate evolving concentration profiles.

- Coupled differential equations follow He *atom* and *bubble* concentrations as a function of depth and exposure time:

$$dc_n/dt = - D_n d^2c_n/dx^2 + (\text{Source terms})_n - (\text{Loss terms})_n$$

where  $c_n$  = concentration of bubbles with  $n$  atoms.

Source terms: for  $n=1$ , implant flux =  $\phi(x,t)^{\text{TRIM}}$

$n$ -species formation factors =  $c_1 c_{n-1}$  &  $c_{n+1} \exp(-E_{n+1}/kT)$

Loss terms:  $n$ -species dissociation factors =  $c_n \exp(-E_n/kT)$

$n$ -species promotion factors =  $c_1 c_n$

(Species formation and loss rates also involve attempt frequency and bubble size factors.)

*(This code accurately describes helium nano-bubble formation and growth in aging solid metal tritides.)*



# Model for Liquid Metals (cont.)

---

- The nano-bubble stability is determined by the liquid metal's surface tension  $\gamma$ :

$$\text{Binding energy of } n\text{-th He, } E_n = 4\pi [ (r_{n-1}^2 + r_1^2) - r_n^2 ] \gamma.$$

- The bubble pressure  $p_n$  and radius  $r_n$  are related by

$$p_n = 2\gamma/r_n.$$

- We assume spherical bubbles so that

$$V_{\text{bubble}} = (4/3)\pi r_n^3 = n v_a,$$

where  $v_a(p,T)$  is the He atomic volume as determined by the bulk He equation-of-state, corrected for bubble wall curvature effects (J. Nucl. Materials, 122 (1985) 565).

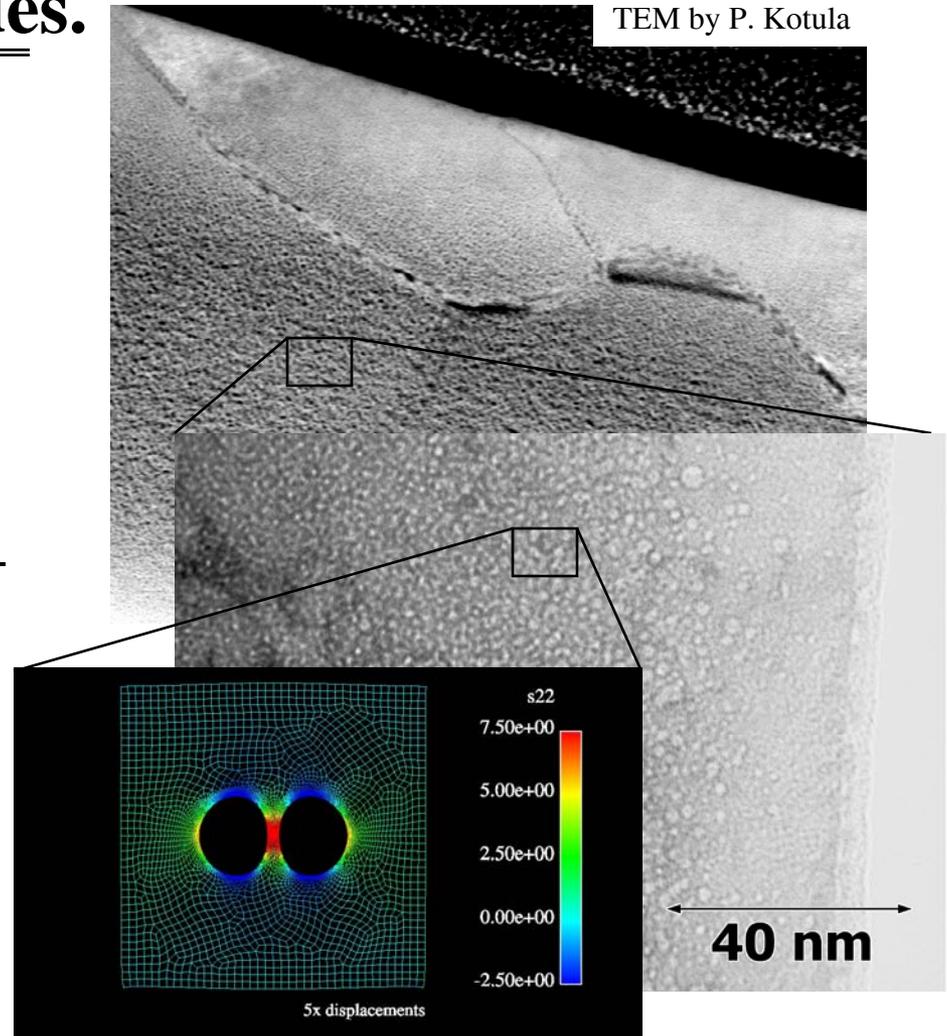
- Nano-bubble migration is included using the Stokes-Einstein equation for diffusion of sub-micron particles:

$$D_n = kT/6\pi\eta r_n.$$



# We follow an approach used to describe bubble evolution in metal tritides.

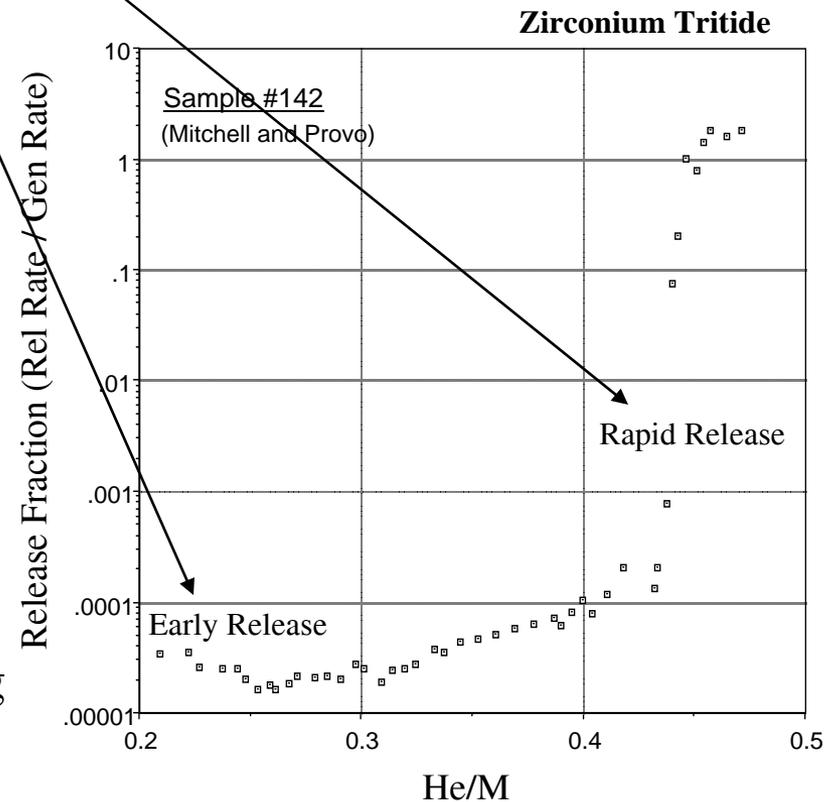
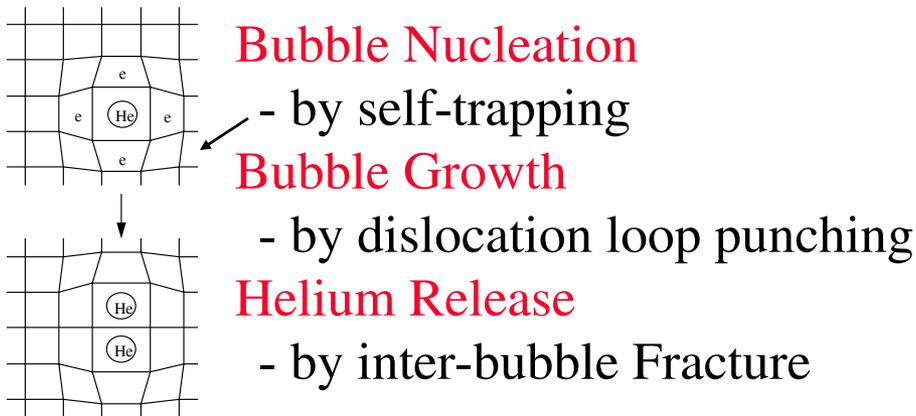
- Radioactive decay of tritium in metals creates high pressure, Helium-filled nano-bubbles.
- Bubble growth with age causes material swelling and changes in tritium retention characteristics.
- Bubble interactions produce high-stress regions which
  - modify bubble growth,
  - cause bulk material fracture.
- He is released rapidly when the inter-connected bubble network generates a pathway to the surface.



Finite Element Calculation by P. Klein

# Goal for aging tritides: Model retention of $^3\text{He}$ generated by tritium decay.

- Treat all stages of He Release: Early, Rapid, & transition between.
- Uses an analytic formulation sufficient to capture the *essential physics*.
  - Atomistic detail is added, as needed, for “fine-tuning”.
- Nano-bubble evolution is modeled as three distinct, separable stages:



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

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

$$dc_m/dt = g - 2ps_1c_m^2 - ps_2c_m c_2 + 2q_2c_2 - ps_b(r)c_m c_b$$

$$dc_2/dt = ps_1c_m^2 - q_2c_2 - ps_2c_m c_2$$

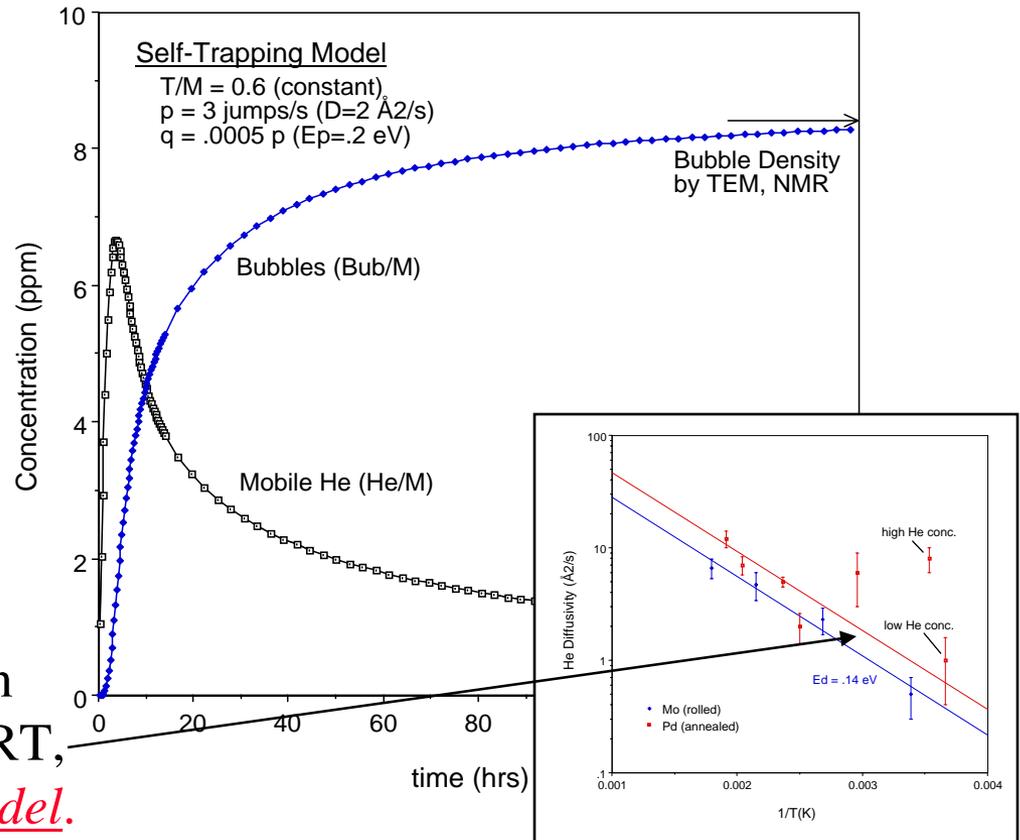
$$dc_b/dt = ps_2c_m c_2$$

generation rate,  $g = \lambda(T/M)$

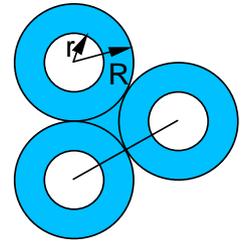
jump rate,  $p = 12D/a^2$

pair dissociation rate,  $q_2 = pe^{-E_2/kT}$

- Recent He implant/re-emission experiment gives  $D \approx 2 \text{ \AA}^2/\text{s}$  at RT, confirming the self-trapping model.



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

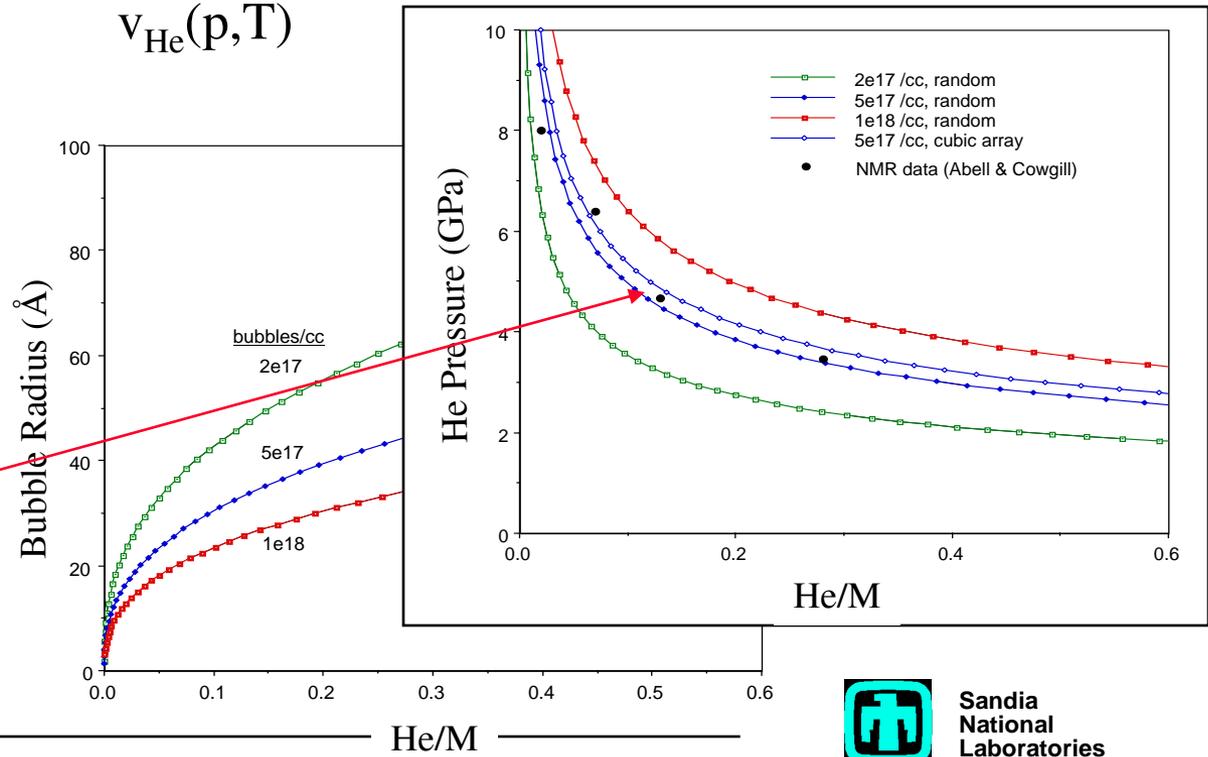


Array of Spherical Source Volumes

- Constitutive relations for bubble growth:
  - Mass conservation:  $(r/R)^3 f_p = (v_{He}/v_{MH})(He/M)$   
( $v$ =molar volume,  $f_p=.64$  for random array packing)
  - Loop-punching:  $p = 2\gamma/r + \mu b/r(1+\epsilon)$   
( $\gamma$ =surface energy,  $\mu$ =shear modulus,  $b$ =Burgers vector)
  - Bulk He EOS:  $v_{He}(p,T)$

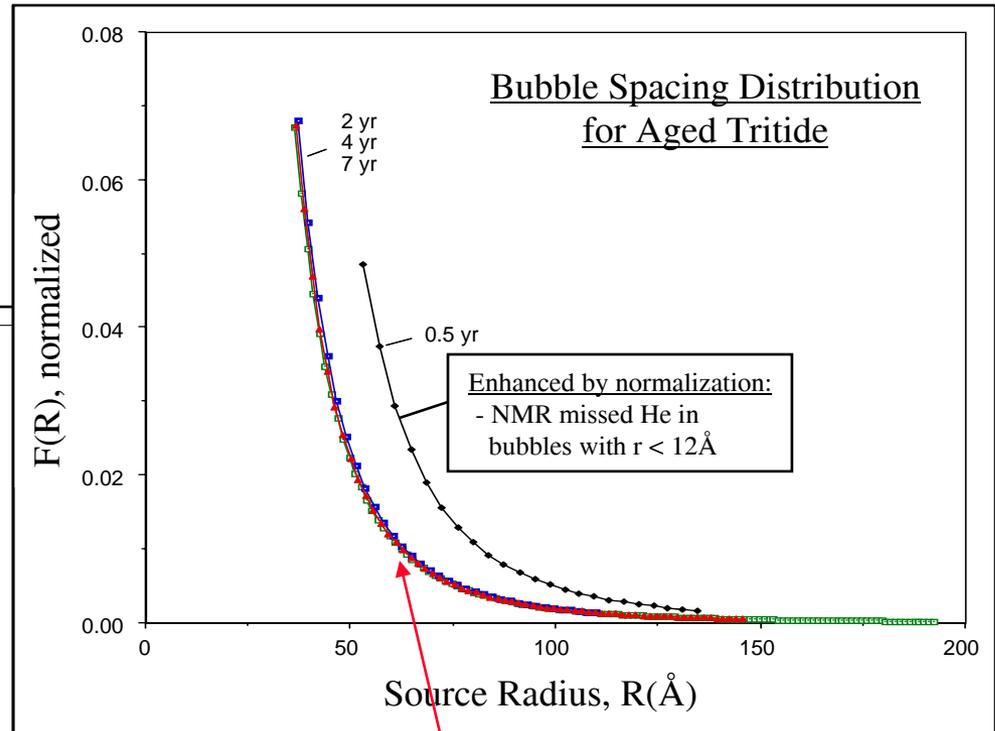
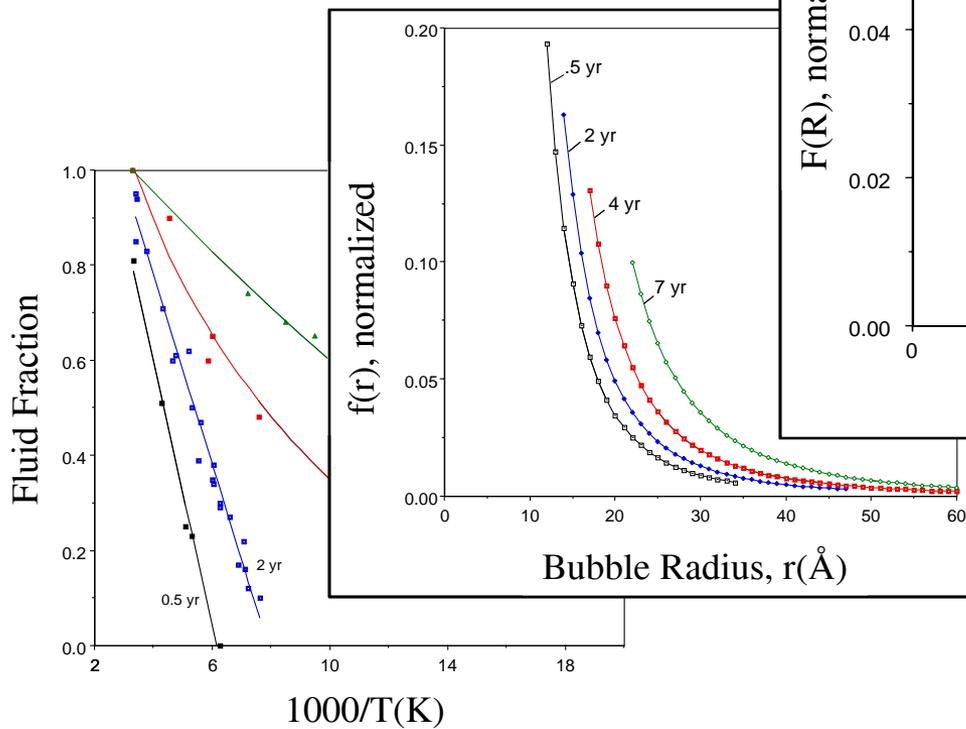
- For a given bubble spacing  $R$ : At each  $He/M$  there is a unique  $r$ ,  $p$ ,  $v_{He}$ :

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



# The distribution of bubble spacings is needed to evaluate bubble-bubble interactions.

- $^3\text{He}$  NMR (motion) separates sol-He from liq-He in bubbles.
- Growth relations convert fluid fractions to bubble distributions.



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



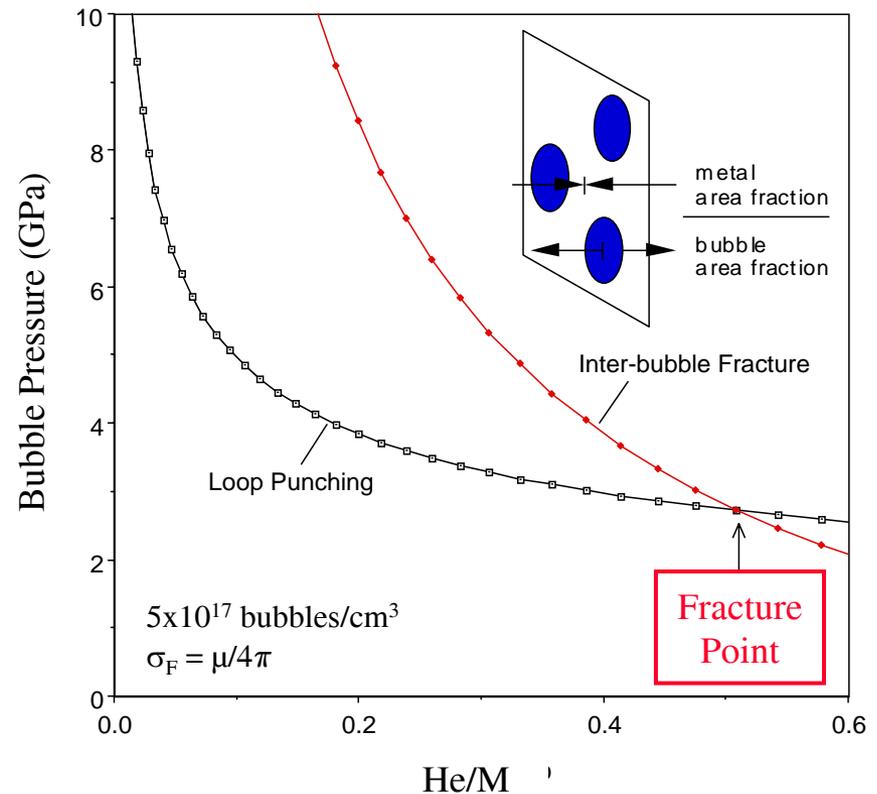
# Inter-bubble fracture produces Rapid Helium Release.

- As bubbles grow, tension on the inter-bubble ligament increases.
- Evans' fracture criterion:  
\_\_\_\_\_ (Uses average ligament stress)

For plane through adjacent bubbles,  
fracture occurs when:

$$p_{LP} \text{ (bubble area)} > \sigma_F \text{ (metal area)}$$
$$(\sigma_F = \text{fracture strength} \approx \mu/4\pi)$$

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



# Bubble nucleation is lower near surfaces.

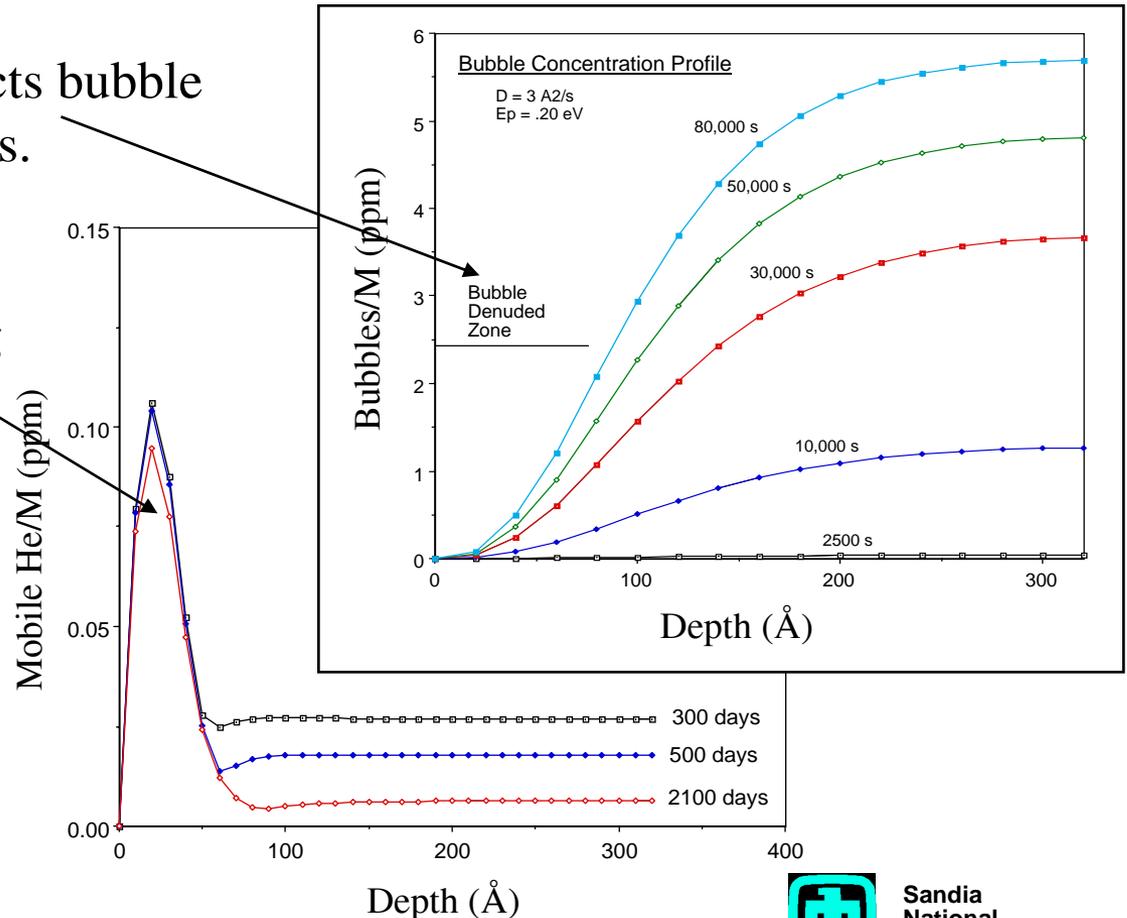
- Modeled using coupled diffusion equations for concentrations  $c_n$ :

$$dc_n/dt = -D_n d^2c_n/dx^2 + (\text{generation terms})_n - (\text{promotion, dissociation terms})_n$$

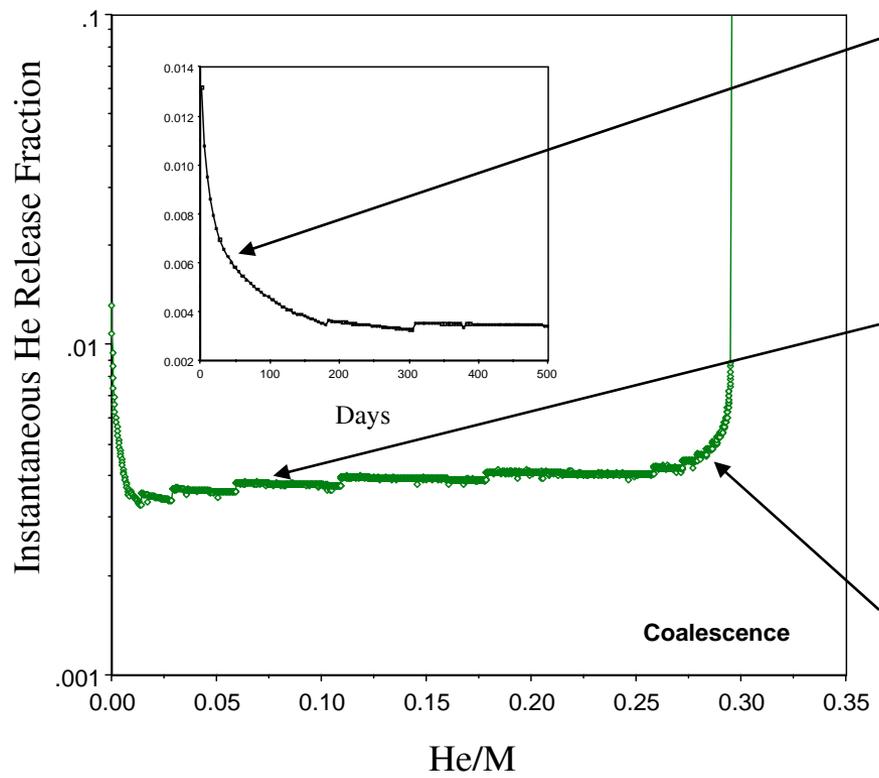
- Model correctly predicts bubble denuded zone thickness.

- Mobile He remains plentiful near releasing surfaces and pipes.

*This high mobile He concentration contributes the Early He Release.*



# The computed He release for solid tritides has all the characteristics of observed release.



- Initially, release is high until bubbles become large enough to compete with nearby surface or GB pipeline.
- Mobile He near surfaces & GB's produce the Early Release Fraction.
  - Slowly increases with “breach” of near-surface bubbles.
- Rapid Release occurs when bubble network becomes interconnected.
  - Depends on mechanism details.

*Model shows how material parameters affect each part of release spectrum.*

# Modeling differences for He implantation in Liquid Metals:

---

- The nano-bubble stability is determined by the liquid metal's surface tension  $\gamma$ :

$$\text{Binding energy of } n\text{-th He, } E_n = 4\pi [ (r_{n-1}^2 + r_1^2) - r_n^2 ] \gamma.$$

- The bubble pressure  $p_n$  and radius  $r_n$  are related by

$$p_n = 2\gamma/r_n.$$

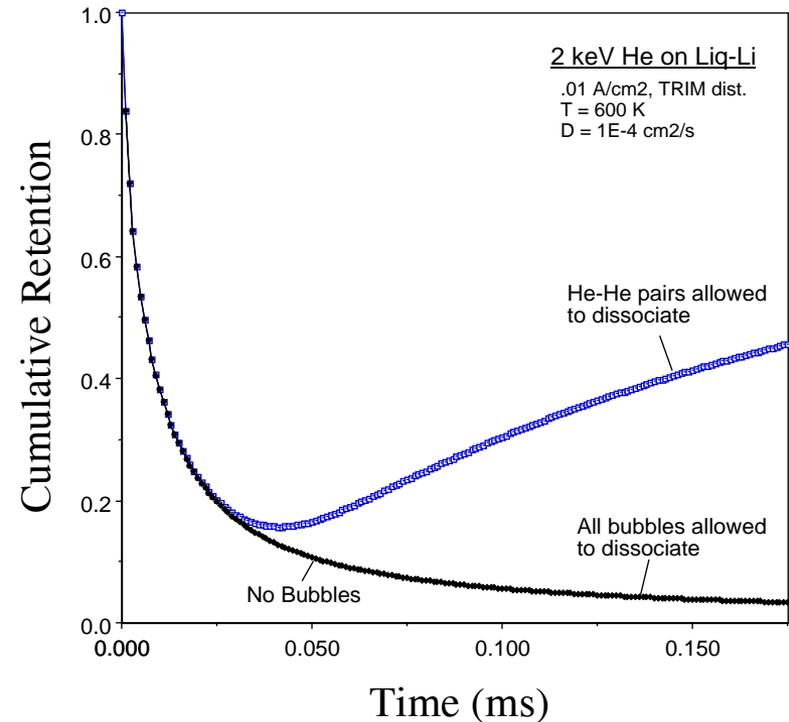
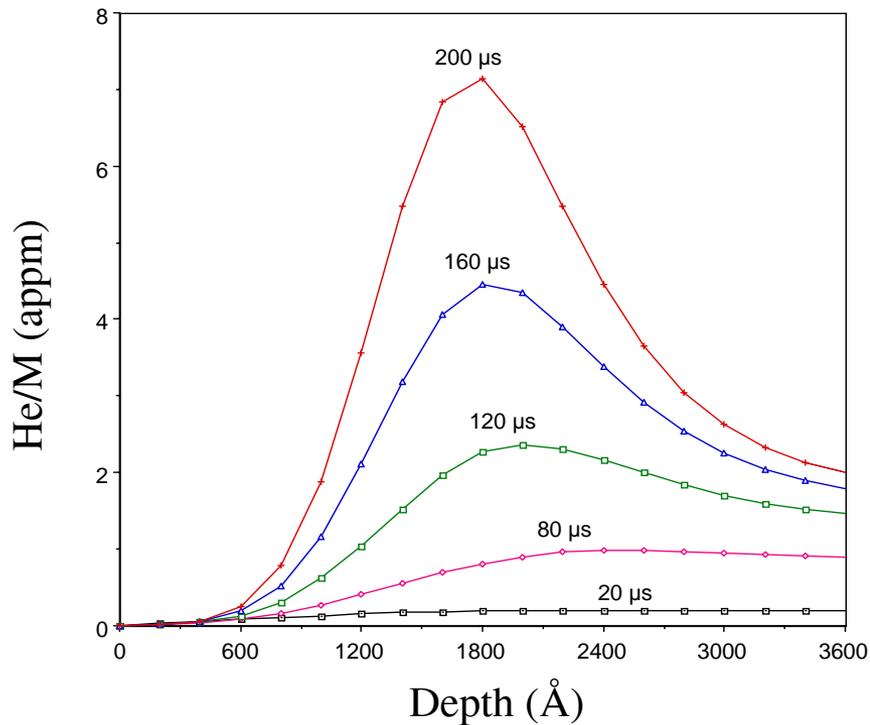
- Nano-bubble migration is included using the Stokes-Einstein equation for diffusion of sub-micron particles:

$$D_n = kT/6\pi\eta r_n.$$

- Bubble coalescence can occur and may be of major importance.



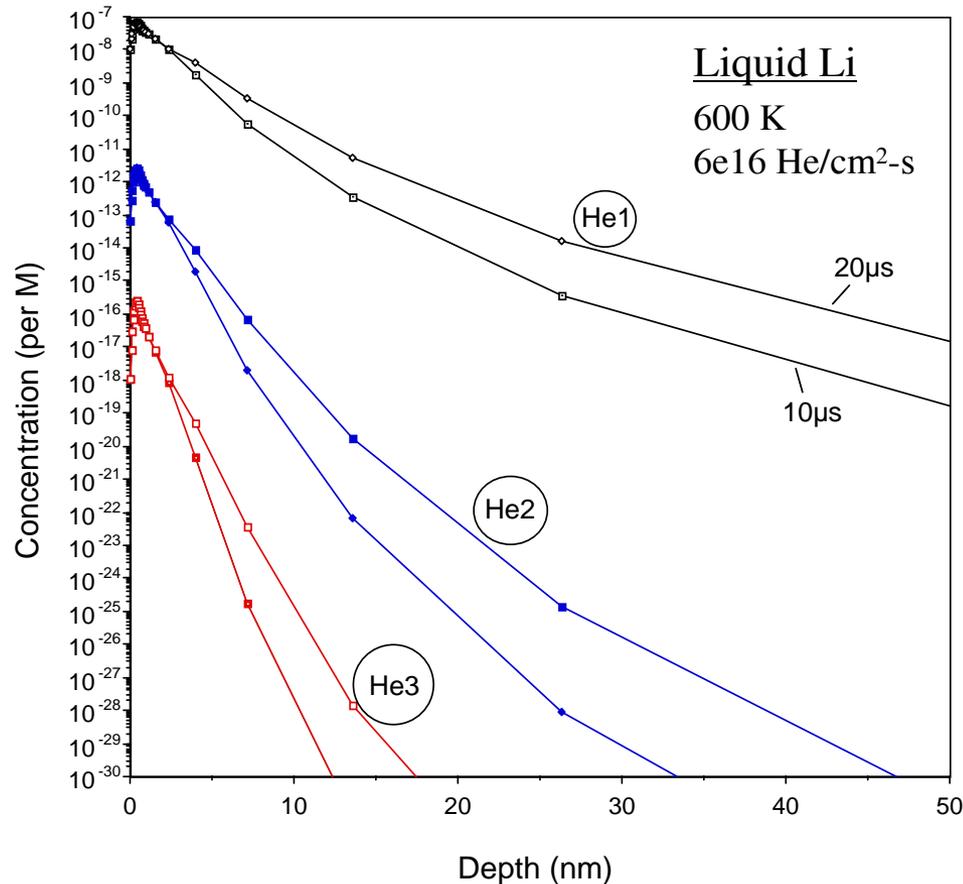
# Results show high plasma fluxes can produce the He concentrations needed to generate bubbles.



- The bubble formation is strongly flux dependent.
- A significant He fraction will be retained after 50 μs  
*-- only if bubbles are formed and retained.*



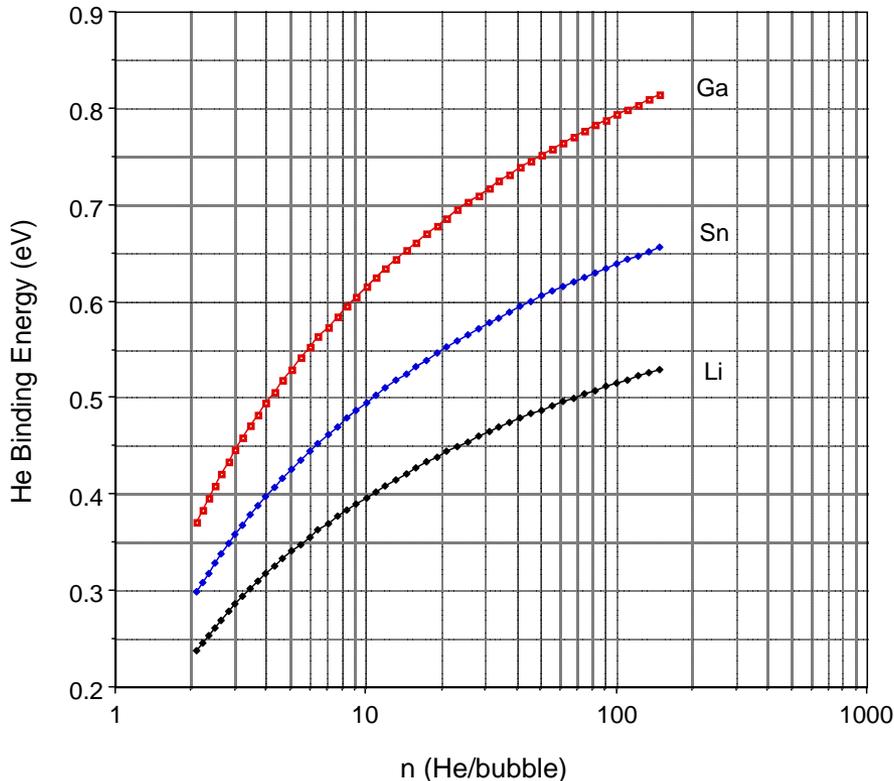
# Computed profiles show bubble concentrations drop several orders for each $\delta n=1$ increase in size.



- High surface concentrations drive atomic He and small bubbles deep into the fluid.
- The release rate is significantly slower for He in larger bubbles.

*He retention is limited by bubble dissociation, not bubble migration.*

# The rapid dissociation of small bubbles is due to a low He binding energy to the bubble.



- Production of large stable bubbles requires:  
species promotion > dissociation  
or  $s_n c_1 > n \exp(-E_n/kT)$ ,  
 $s_n$  = bubble surface area  
 $c_1$  = atomic He concentration.
- At .01 A/cm<sup>2</sup>, 600 K,  $c_1 \sim 10$  appm;  
which requires  
 $E_n \geq 0.4$  eV.
- The promotion rate increases with  
 $c_1$  or He flux.

*A larger surface tension will enhance bubble populations in Sn and Ga.*

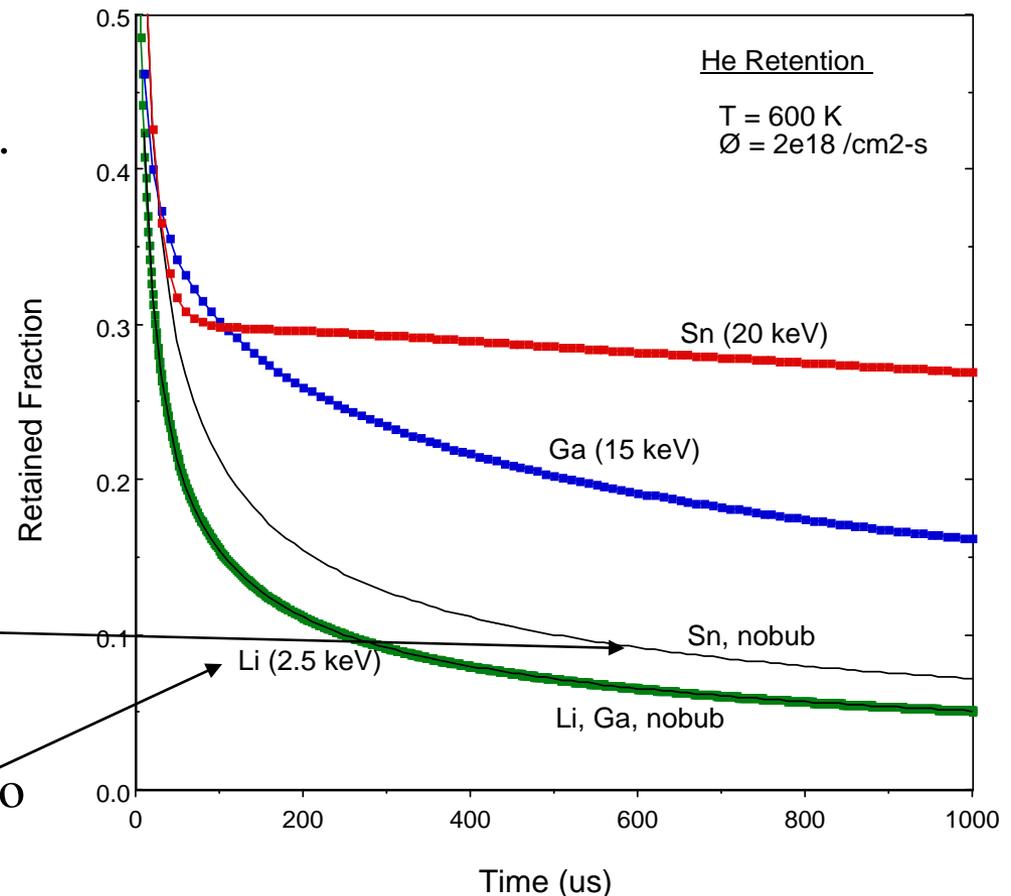
# Early high flux results showed both Sn and Ga will pump He if implanted deep enough.

- Calculation is for same He implant depth in each metal and high He flux ( $0.3 \text{ A/cm}^2$ ).

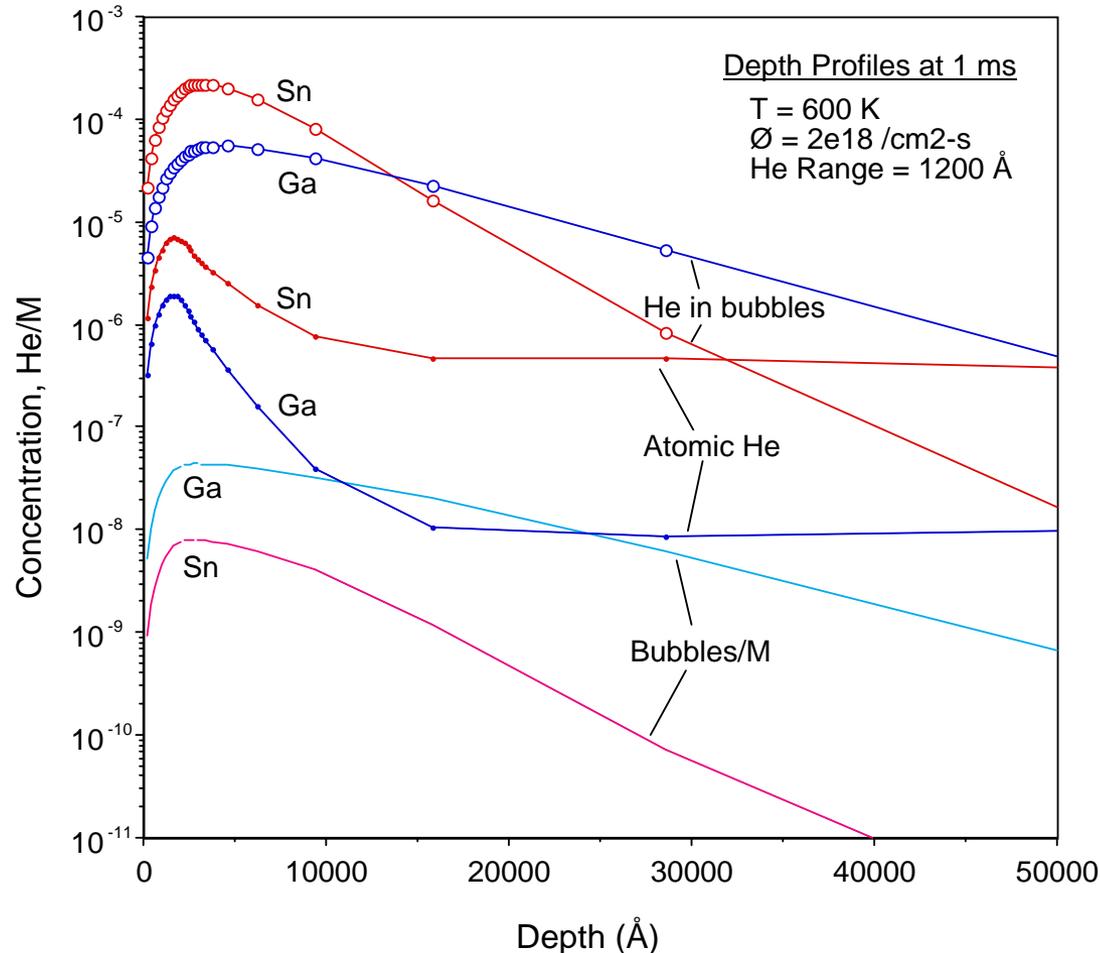
- Parameters used in model:

	$D(10^{-4}\text{cm}^2/\text{s})$	$\gamma(\text{GPa}\cdot\text{\AA})$
Li	1.0	3.8
Sn	0.5	5.3
Ga	1.0	7.2

- Without bubble formation, He diffusivity is only effect.
- In Li, bubbles still remain too small to be stable.

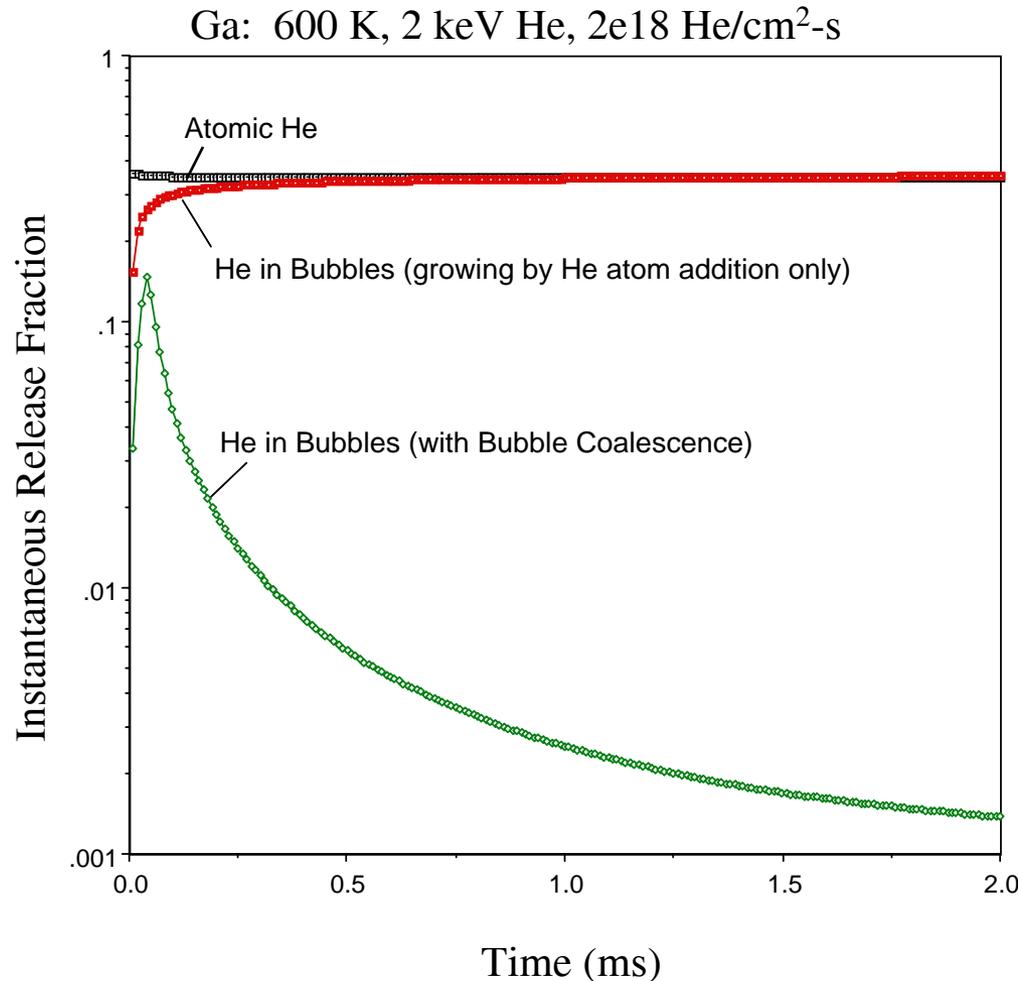


# At these equivalent implant depths, profiles show most of the He is retained in bubbles .



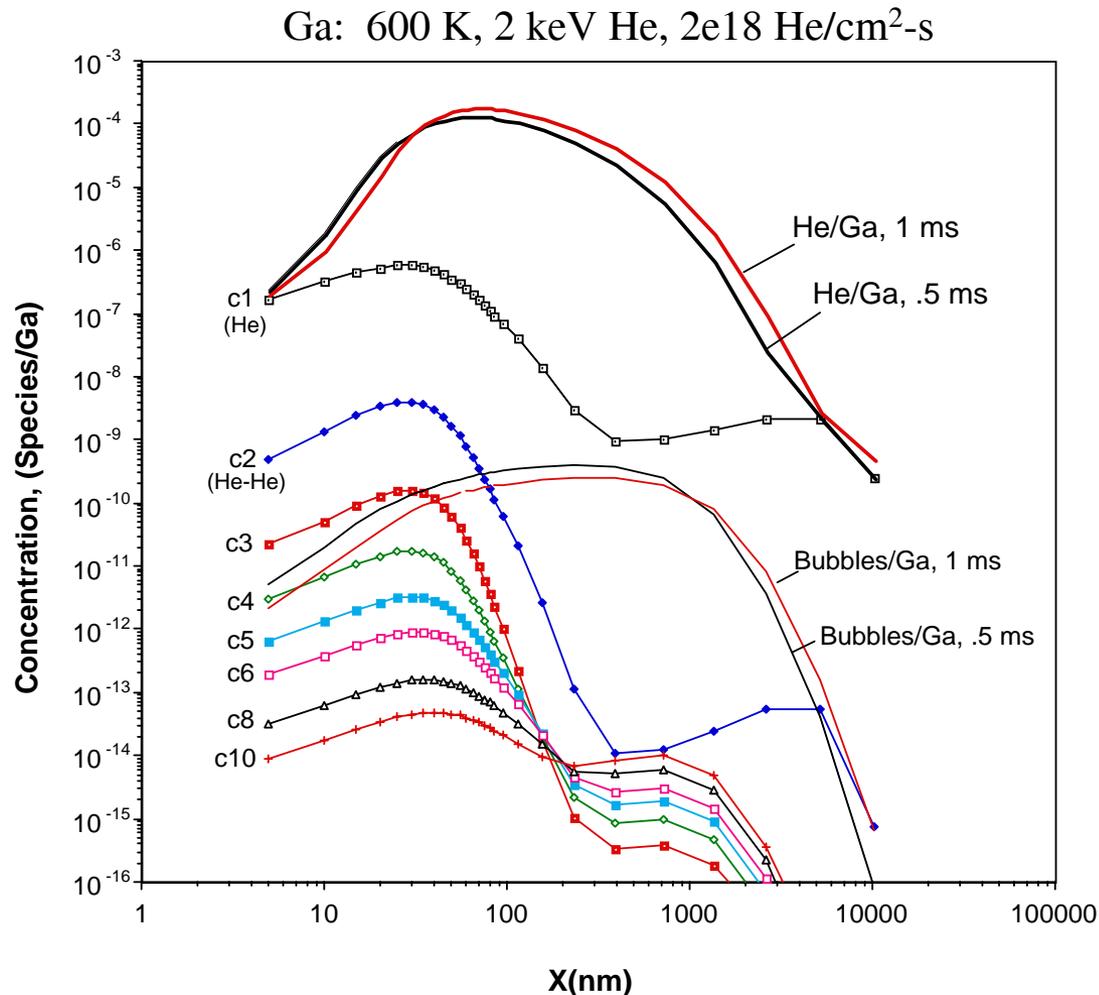
- Concentrations of atomic He are much lower than the “He in bubbles”.
- Ga has more bubbles, due to higher binding E.
- Sn has larger bubbles, due to slower migration and more time to grow.

# Recently added “small bubble coalescence” significantly reduces the He release rate.



- Calculations up to this point have allowed bubbles to grow by addition of only one He atom at a time.
- The improvement allows mobile small bubbles ( $n \leq 6$ ) to coalesce with themselves and larger bubbles.
- The result may still underestimate pumping by not allowing larger bubbles to coalesce, but this is a rare occurrence.

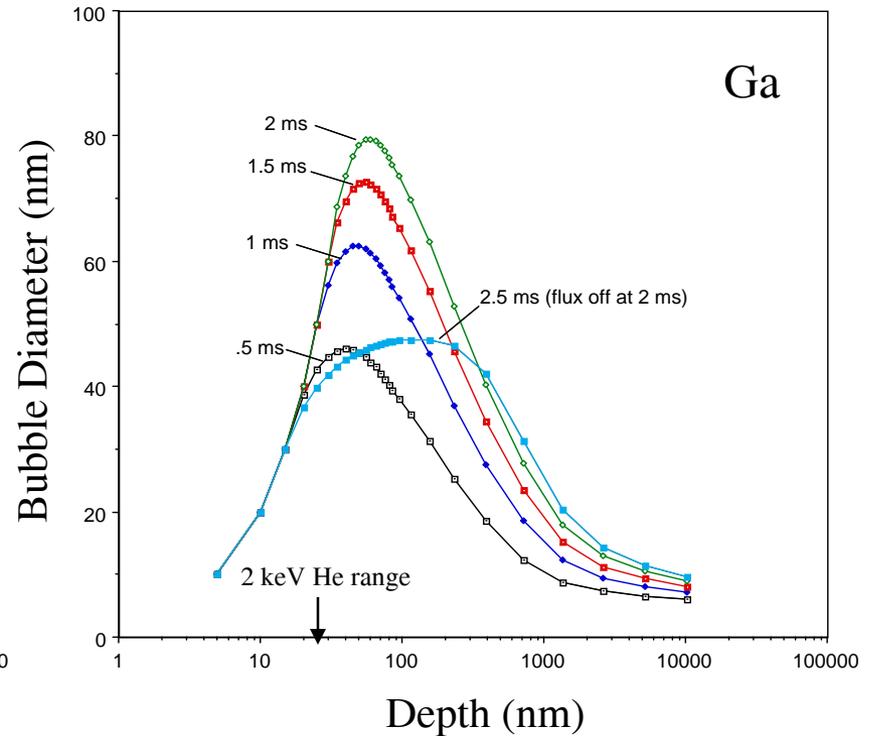
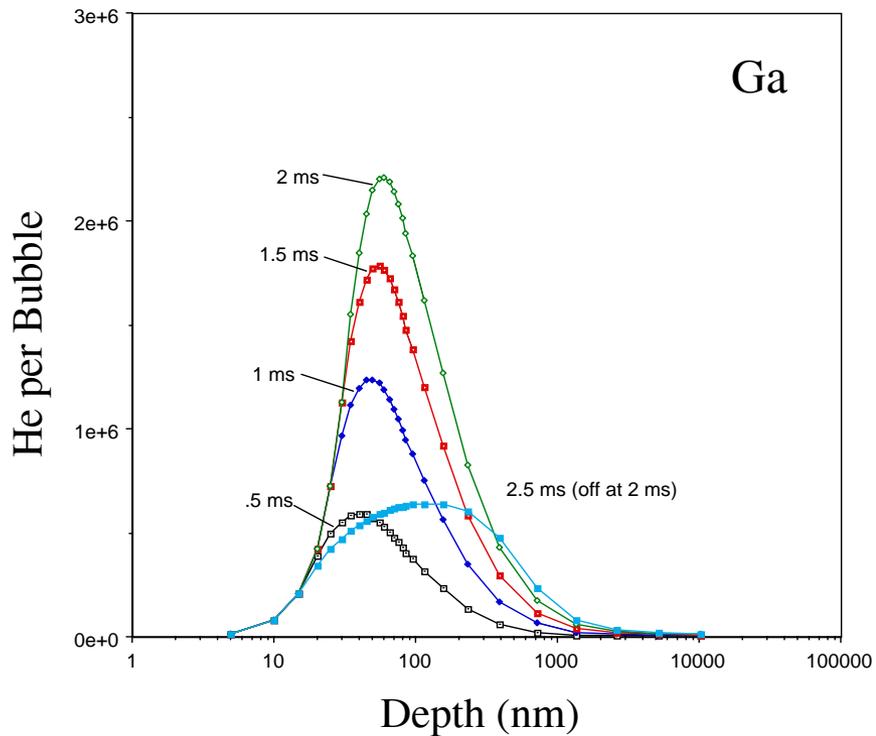
# With coalescence, concentrations of small bubbles remain low, but large bubbles become plentiful.



- The larger bubbles are immobile so their coalescence is rare.
- The He/M concentration continues to grow with exposure time.

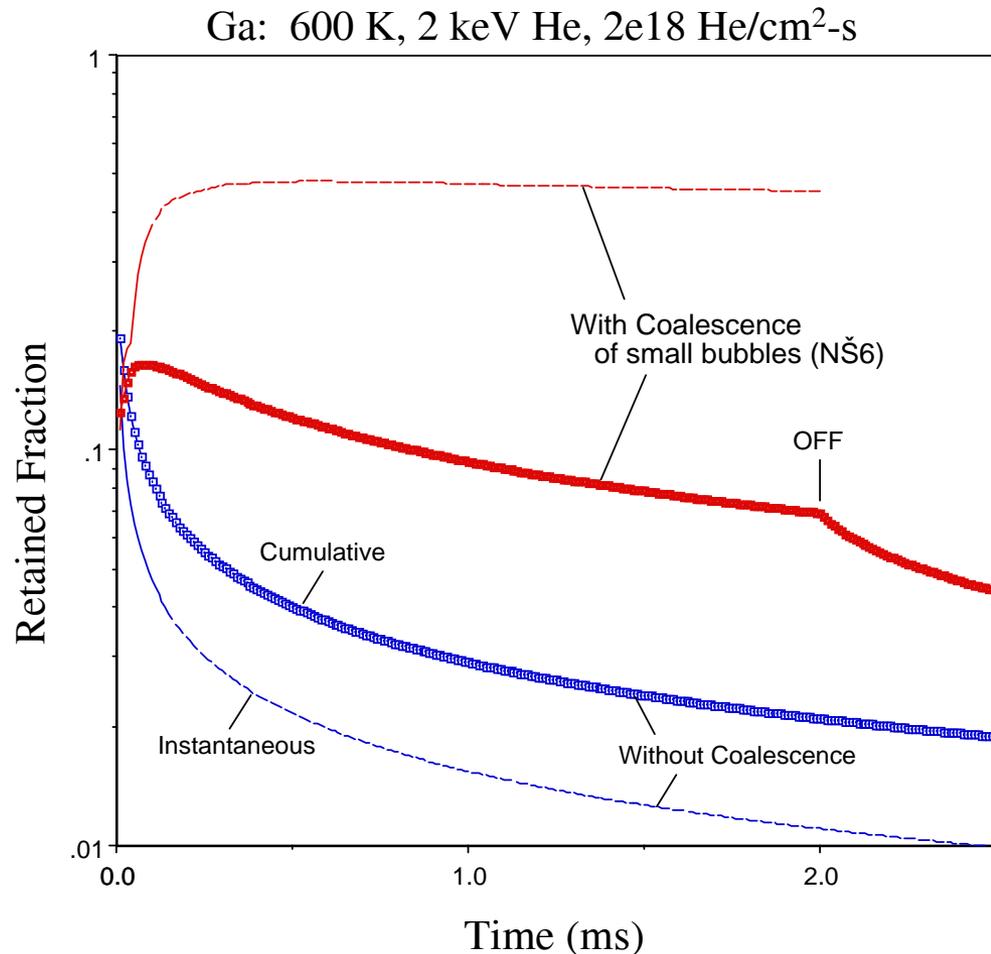


# The large bubbles are produced well beyond the He implant range.



- These large bubbles are relatively immobile.
- Their continued growth during long exposures will likely cause metal ejection.

# In summary, a high He flux can produce stable bubbles and high He retention in liquid metals.



- A high flux is needed to grow bubbles faster than they dissociate.
- Bubble stability increases with surface tension from Li to Sn to Ga.
- Bubble coalescence leads to continued growth with exposure -- likely causing metal ejection for  $t > 1$  sec.
- Release is slow after flux is terminated.