

Voids

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Dislocation loop energy in FCC alloys

- For an FCC crystal we can typically see two loop types:

- Faulted:

$$E_L^f = 2\pi r_L \Gamma + \pi r_L^2 \gamma_{SFE}$$



Writing in terms of materials constants we get:

$$E_L^f = \frac{2}{3} \frac{1}{(1-v)} \mu b^2 r_L \left[\ln \frac{4r_L}{r_0} - 2 \right] + \pi r_L^2 \gamma_{SFE}$$

\uparrow
Poisson's
ratio ≈ 0.3

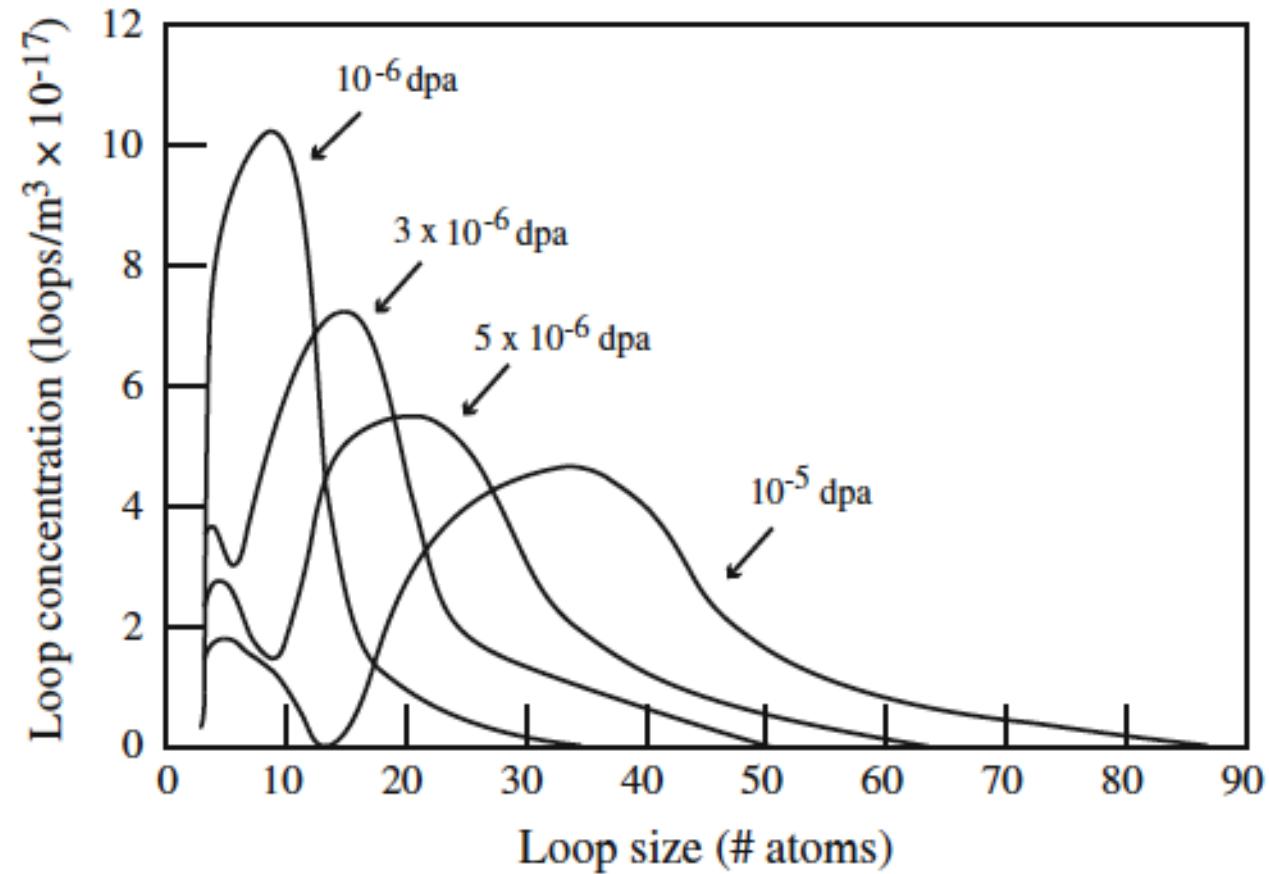
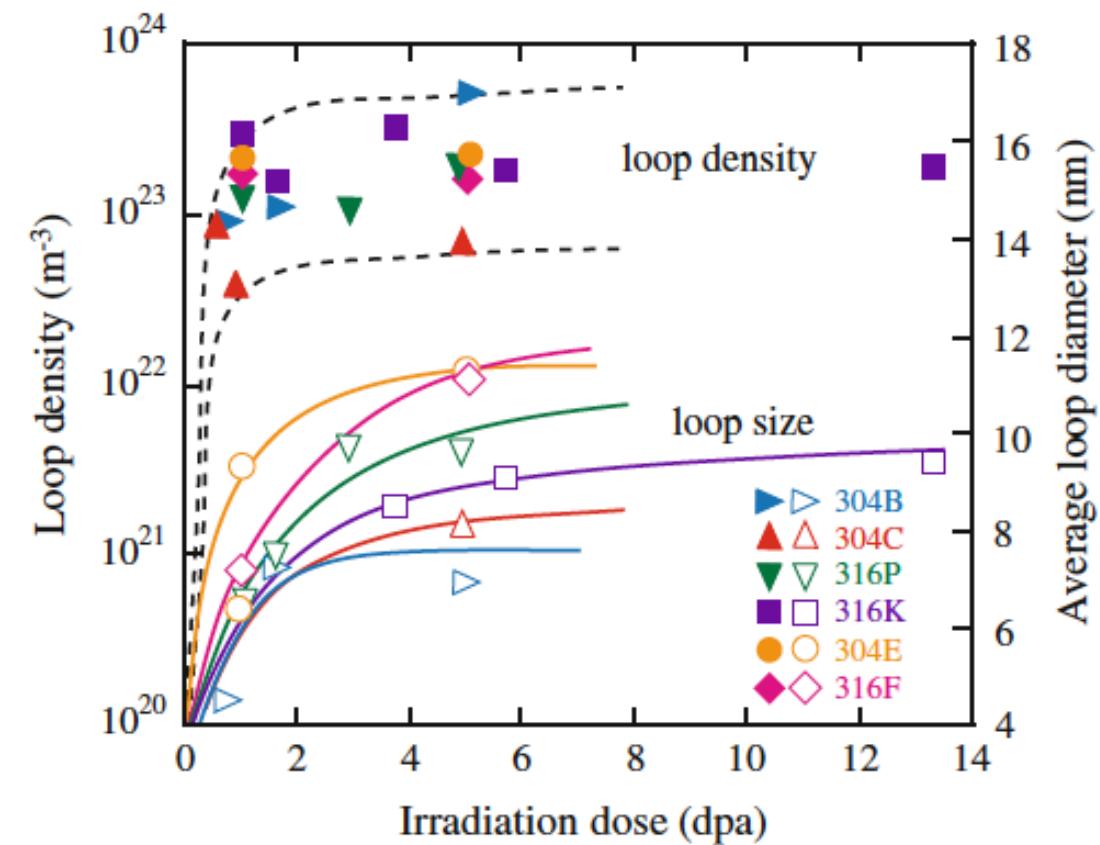
- Perfect:

(no stacking fault)

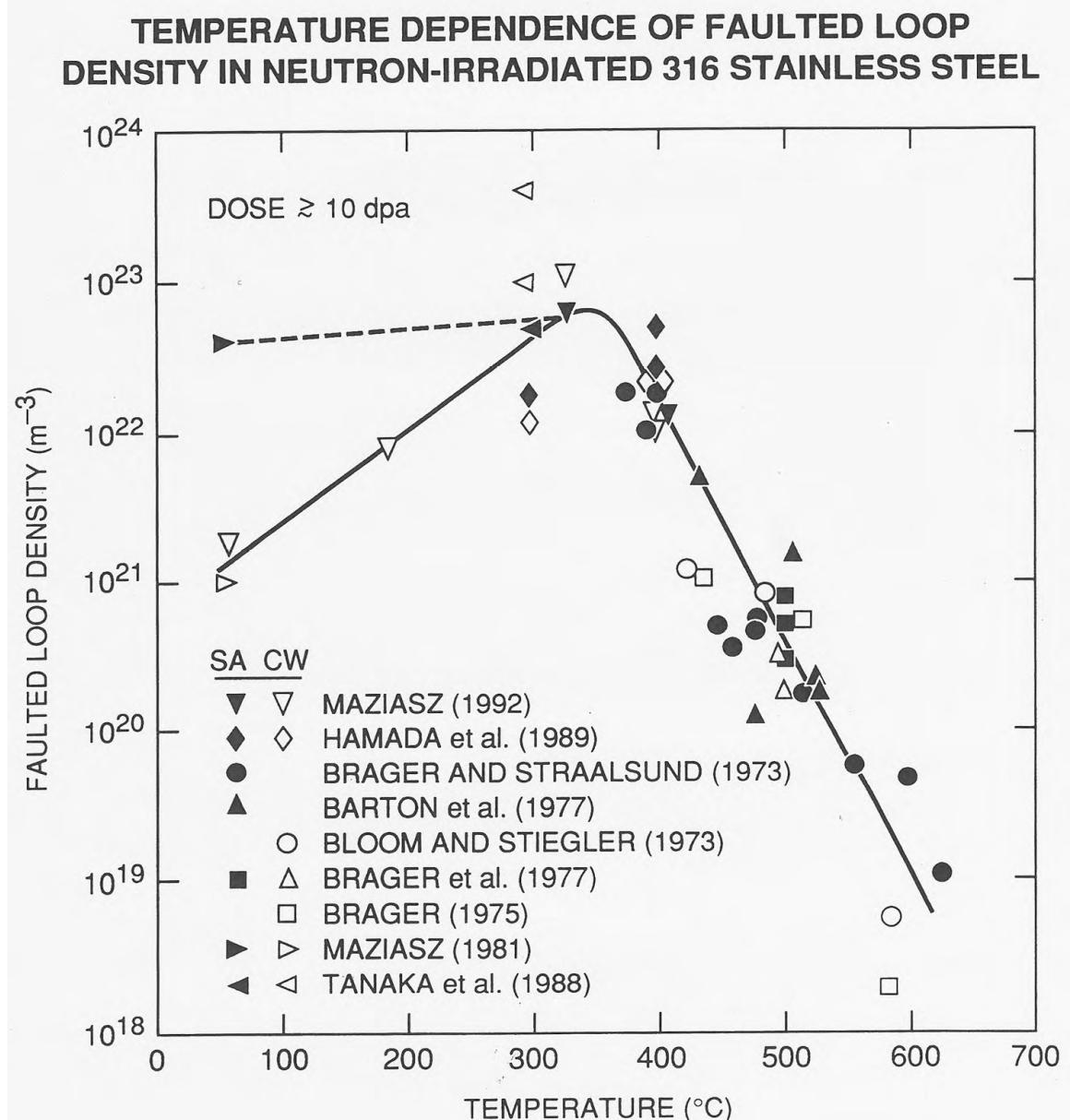
$$E_L^p = \left[\frac{2}{3} \frac{1}{(1-v)} + \frac{1}{3} \left(\frac{2-v}{2(1-v)} \right) \right] \mu b^2 r_L \left[\ln \frac{4r_L}{r_0} - 2 \right]$$



Dose dependence



Temperature dependence



Zinkle, Maziasz & Stoller, JNM 206 (1993) 266



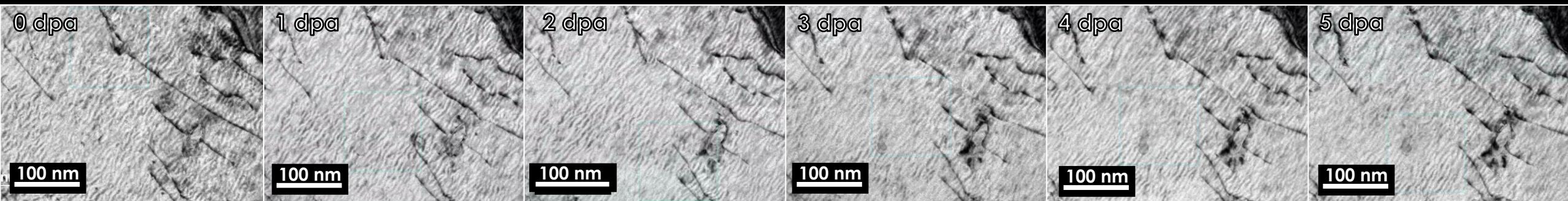
Image Stitching



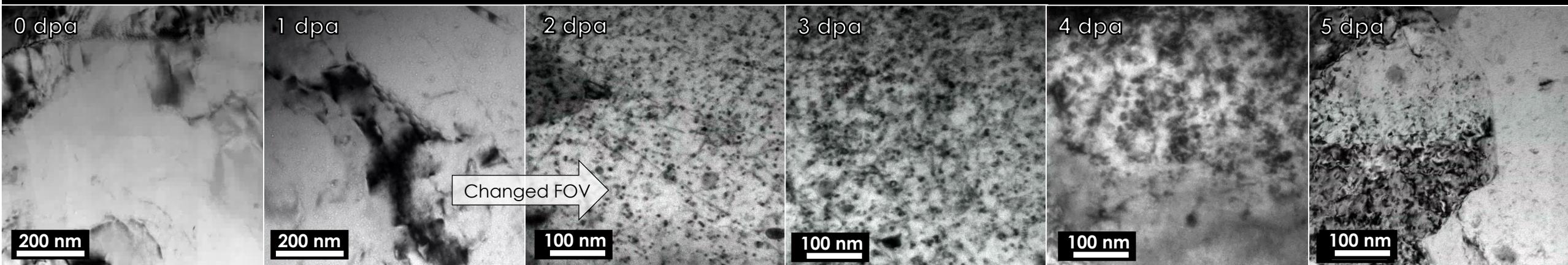
100 nm

In situ imaging conditions: [100] zone axis, $g = <110>$

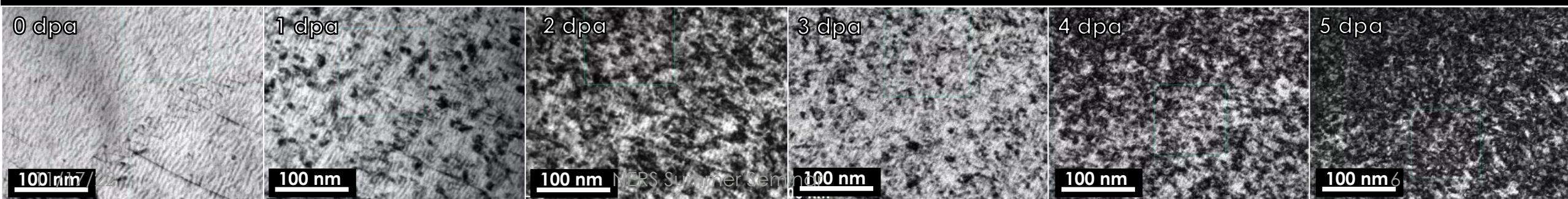
5 dpa



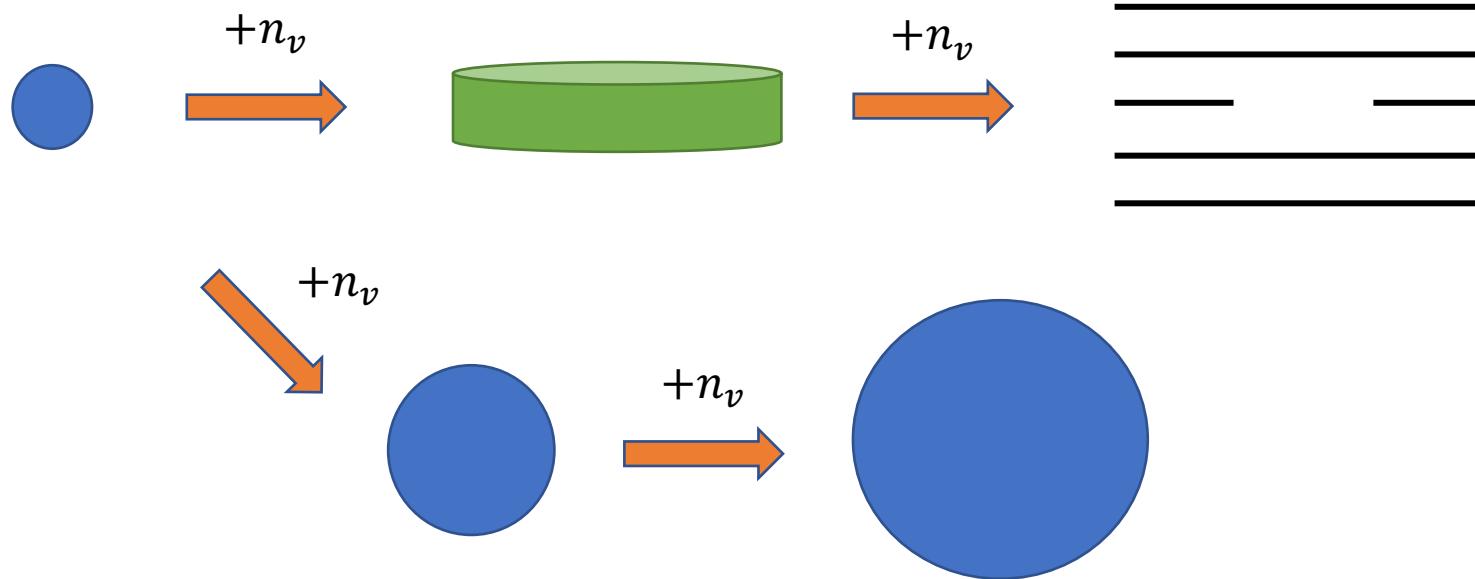
5 dpa + 1,000 appm He/dpa



5 dpa + 3,333 appm He/dpa



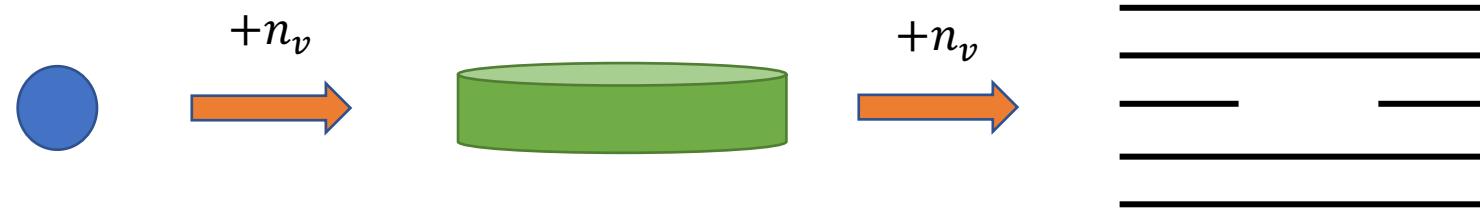
Now let's consider vacancy condensation



$$E_s = 4\pi r^2 \sigma \rightarrow E_c = 2\pi r^2 \sigma$$

- For the same n_v , $E_c > E_s$ meaning an activation energy is required to generate large spherical voids

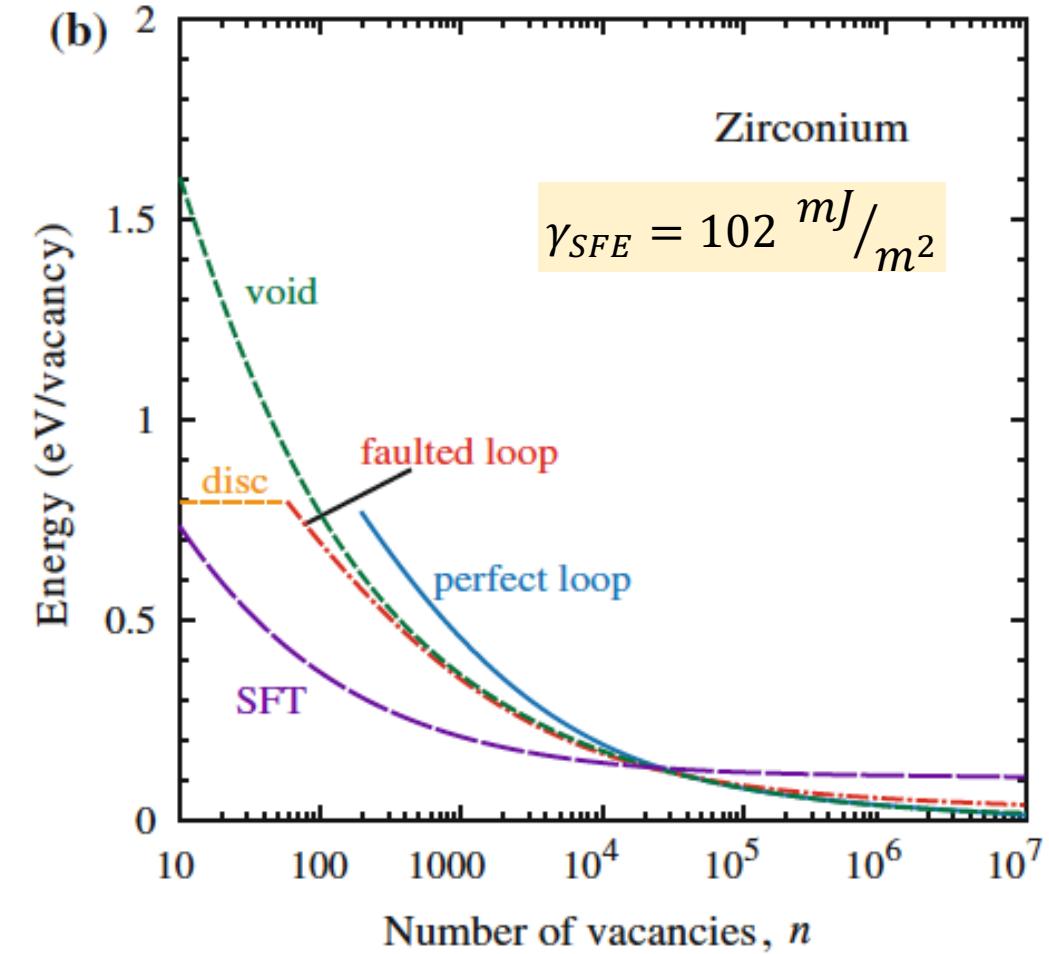
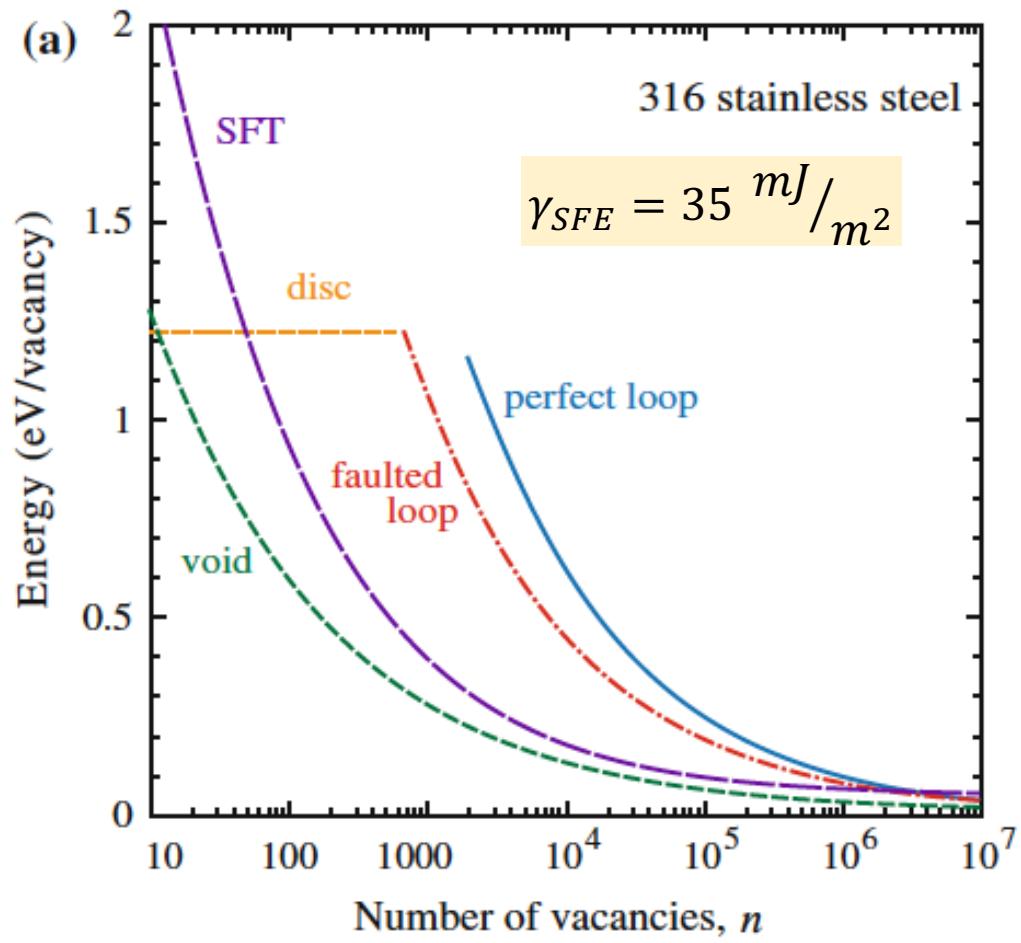
Now let's consider vacancy condensation



$$\therefore E_s = 4\pi r^2 \sigma \rightarrow E_c = 2\pi r^2 \sigma$$

- For the same n_v , $E_c > E_s$ meaning an activation energy is required to generate loops

Visualizing the energetics

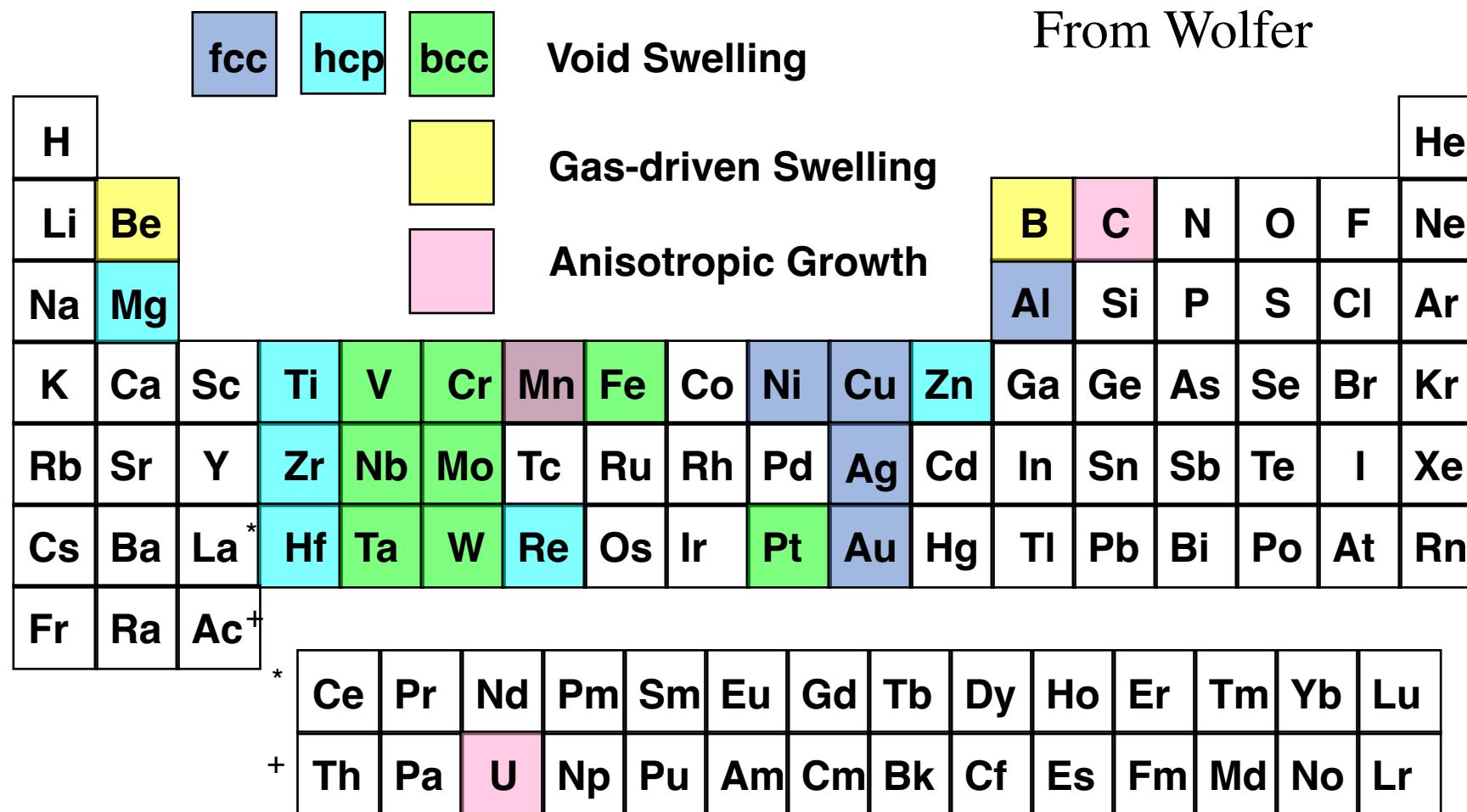


Voids formed in metals

- Voids form by vacancy condensation. Vacancies are supersaturated in irradiated metals.
- Void formation requires “bias” or preferential absorption of self-interstitials at dislocations or other sinks, relative to vacancies
 - V - I recombination is an “unbiased” process since it removes vacancies and interstitials at the same rate
 - Cavities are unbiased sinks for point defects
 - Because of dislocation bias, slightly more interstitials (~20%) are absorbed by dislocations, leaving a slight excess of vacancies to first nucleate and then grow voids.
- These processes are very sensitive to gas pressure in the cavity
 - A void has no gas (in practice, could have very low levels of gas atoms)
 - Impurity atoms within the metal (e.g., O, N) and He produced by (n,a) reactions or by direct implantation are the principal radiation-produced gases that can be trapped by cavities.



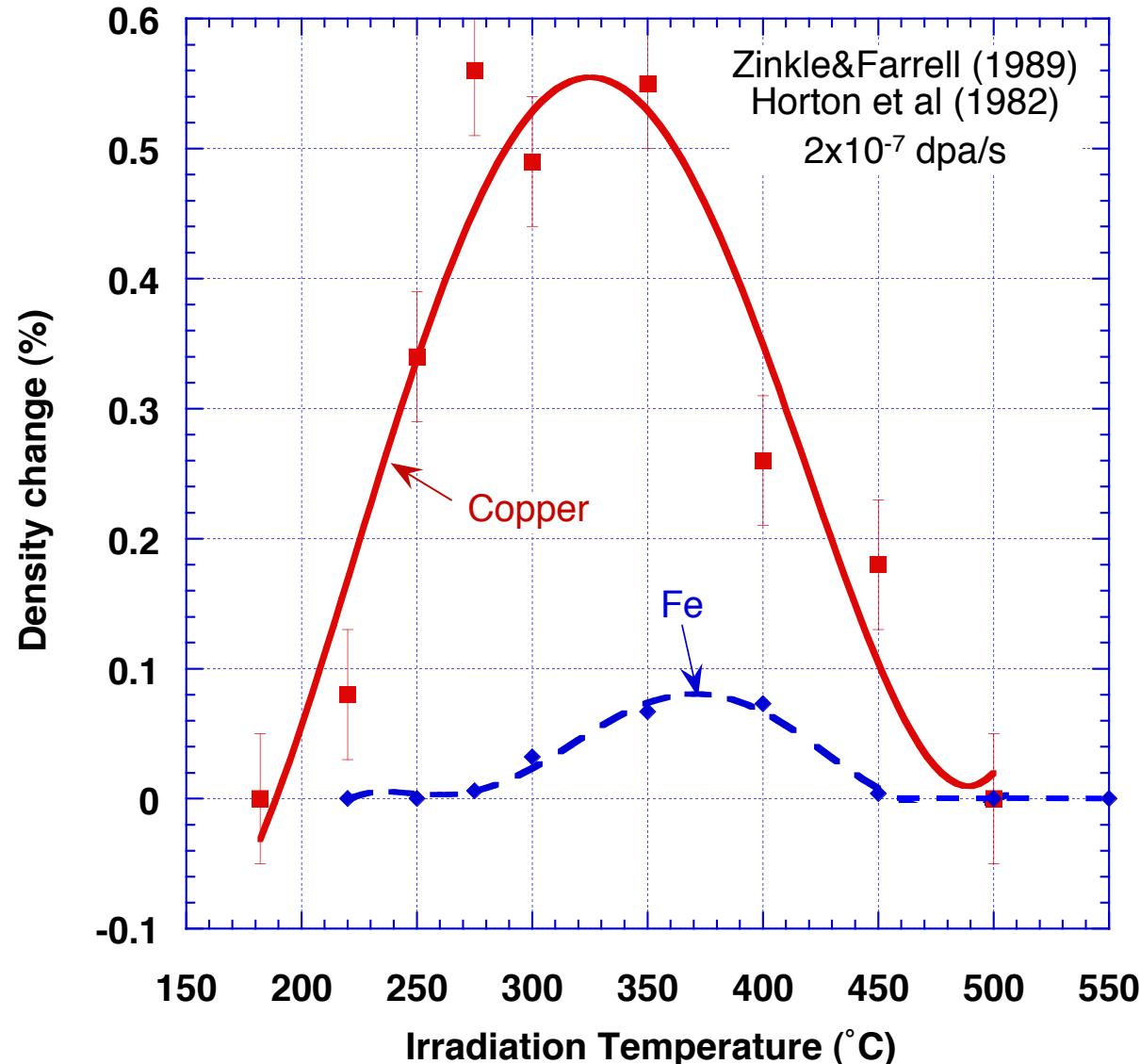
Effect of materials variables on void growth



No Element Tested Has Ever Failed to Swell

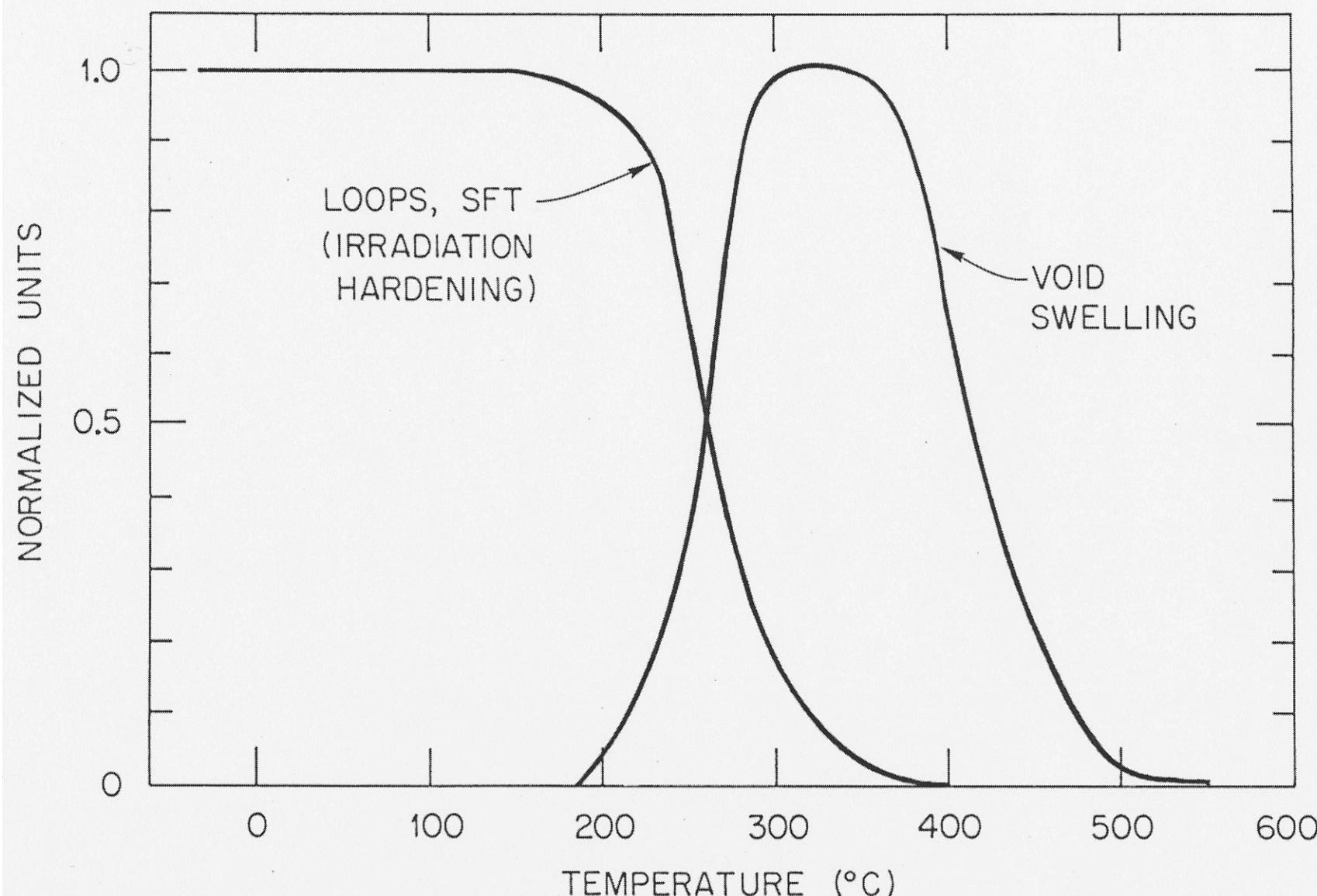


Comparison of Temperature-Dependent Void Swelling in Neutron Irradiated Cu and Fe at 1 dpa



Void swelling is typically of concern for irradiation temperatures between ~ 0.3 and $\sim 0.6 T_M$

Temperature dependence for void swelling involves balance between recombination and vacancy emission

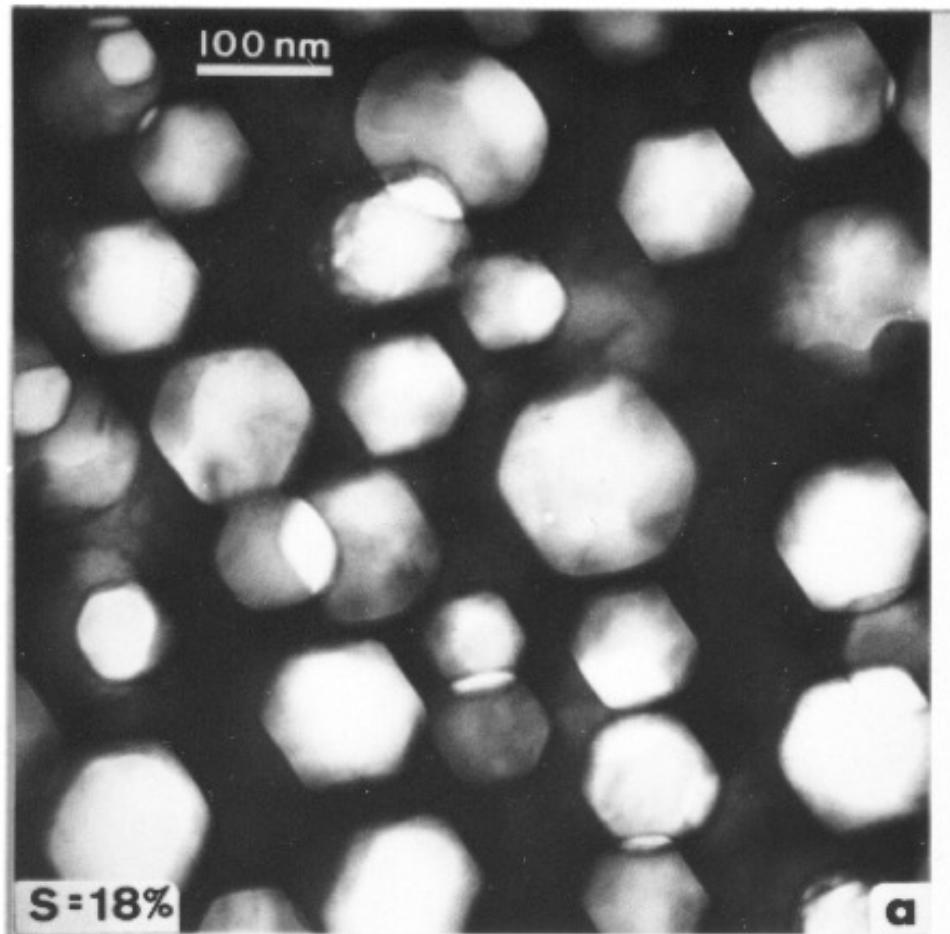


Zinkle, ASTM STP 1125 (1992) p. 813



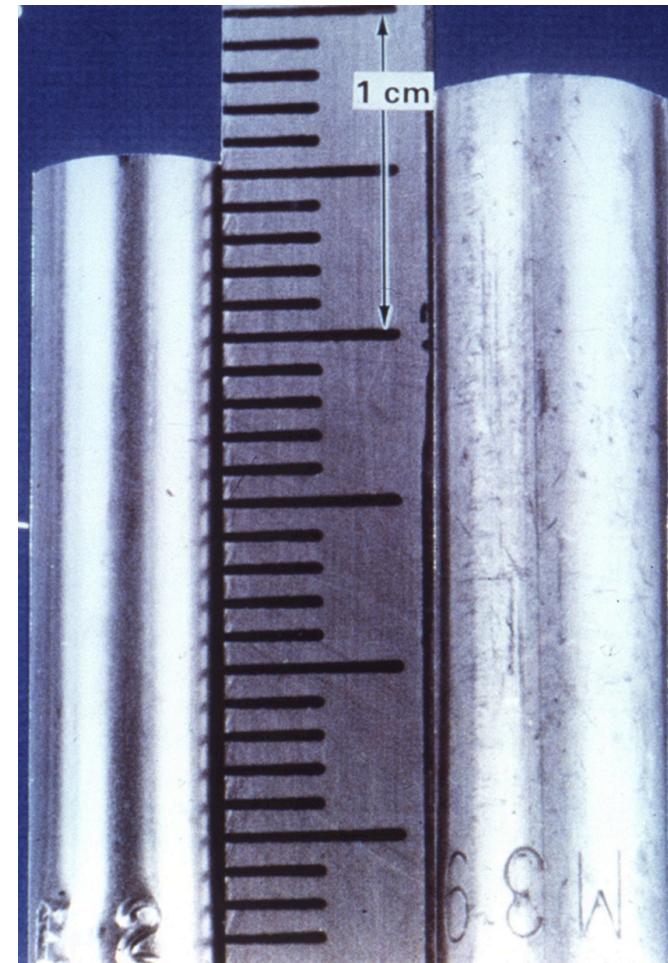
Physical effect of void formation in a material

ion-irradiated austenitic stainless steel
(625°C, 70 dpa)



N. Packan & K. Farrell, J. Nucl. Mater. 85&86 (1979) 677

neutron irradiated 20%CW 316 steel at
T=523°C, $1.5 \times 10^{23} \text{n/cm}^2$



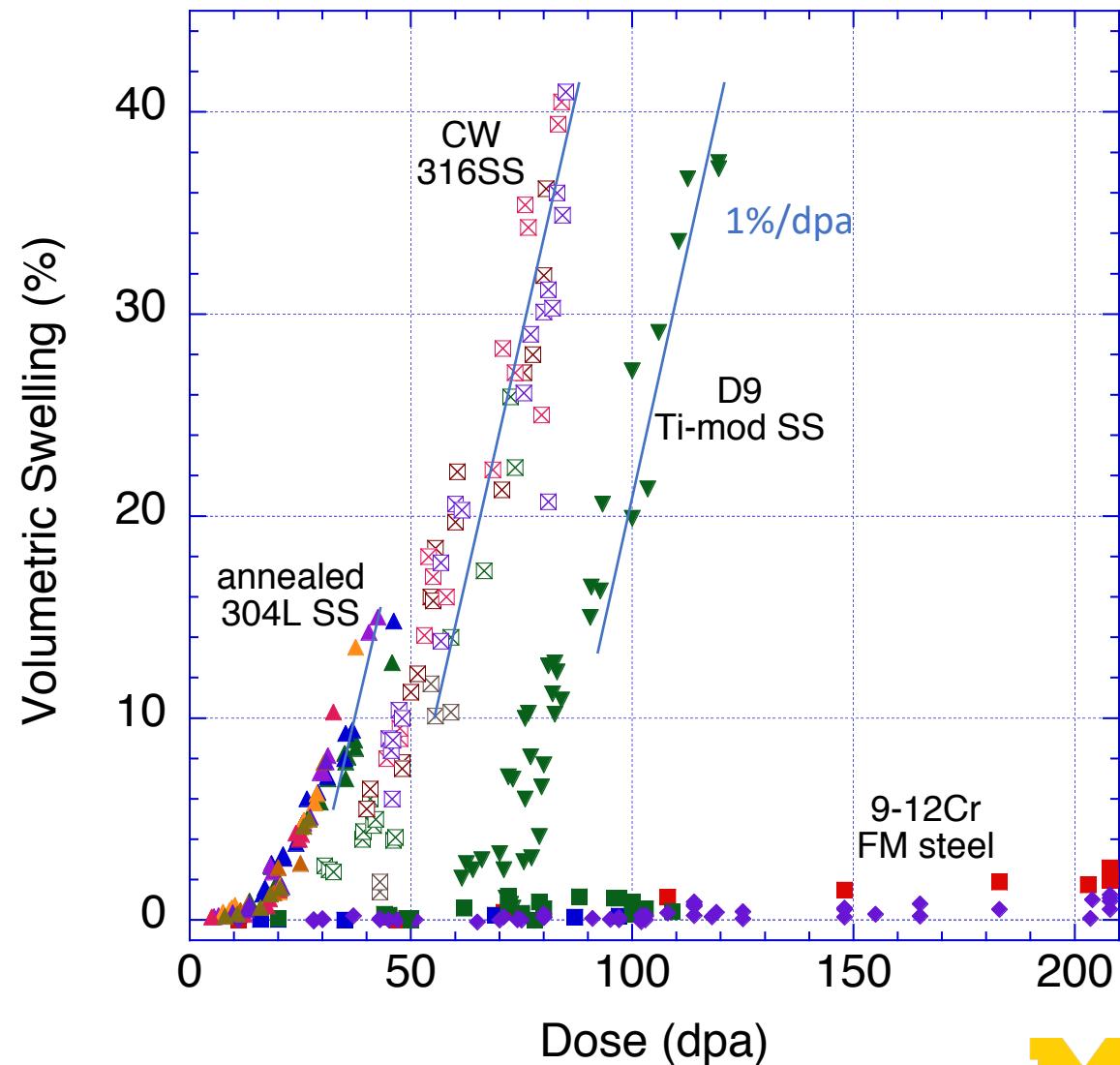
J.L. Straalsund et al., J. Nucl. Mater. 108&109
(1982) 299

Physical effect of void formation in a material

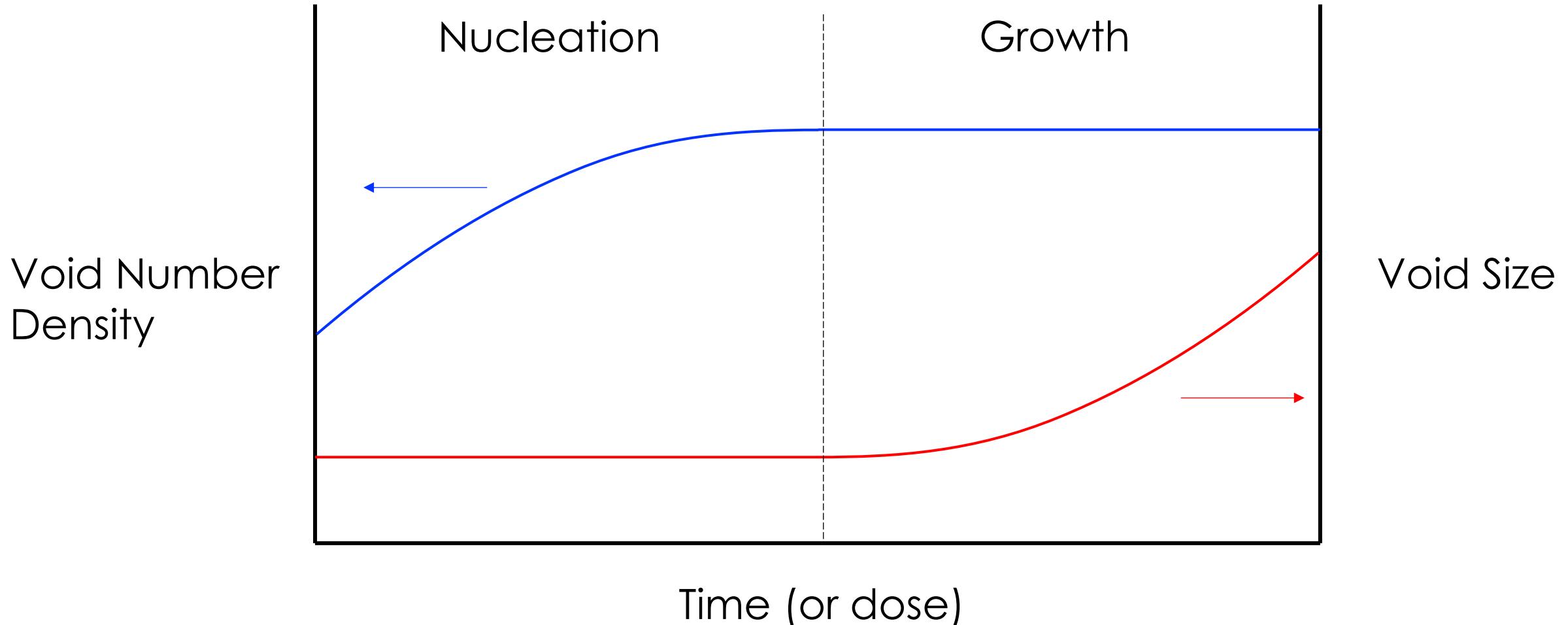
Dimensional changes >5-10 vol.% are unacceptable for typical engineering designs

E.g., linear dimensional change due thermal expansion in 316SS between room temperature and 500°C is:

$$DI = a\Delta T = 18 \times 10^6 / ^\circ C * 480^\circ C = 0.86\%$$



Nucleation vs. Growth



Void Nucleation Theory

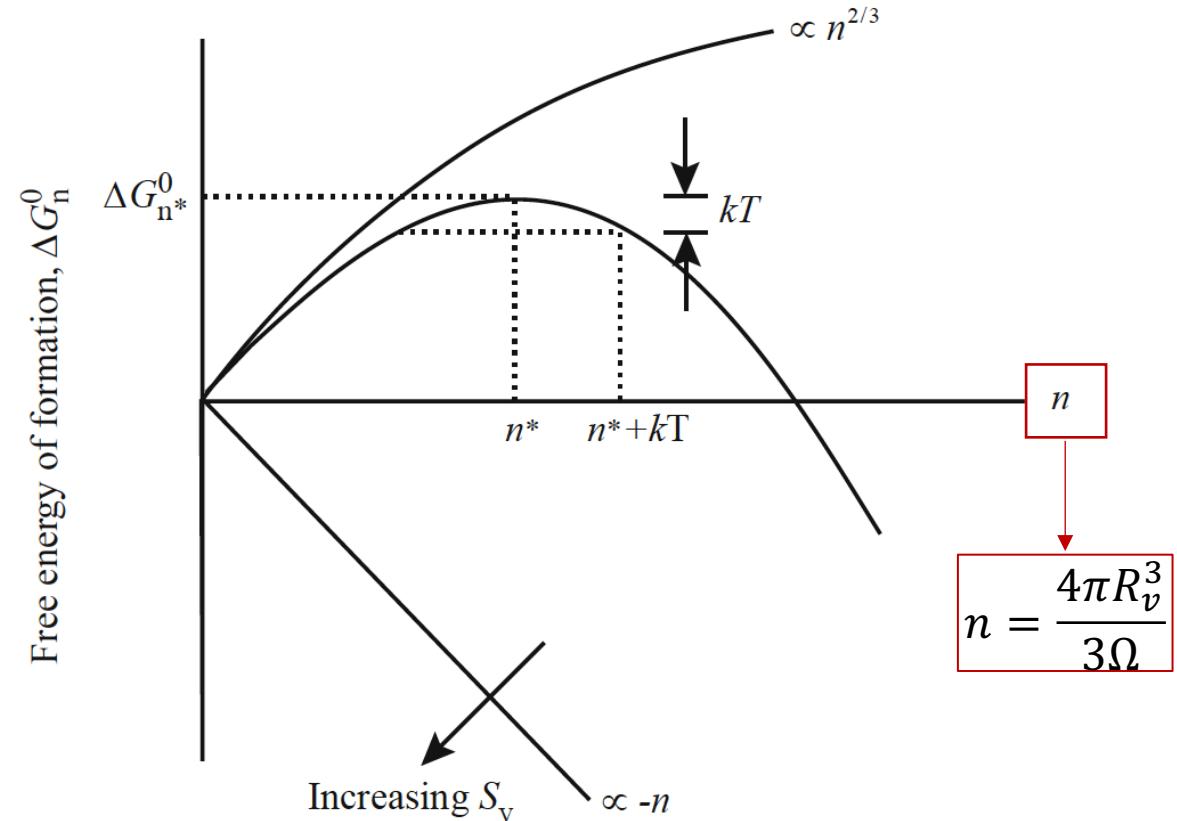
- The base driving force for void formation can simply be put as:

$$S_v = \frac{C_v}{C_v^0}$$



Void Nucleation Theory: Graphical depiction

$$E_s = 4\pi r^2 \sigma$$



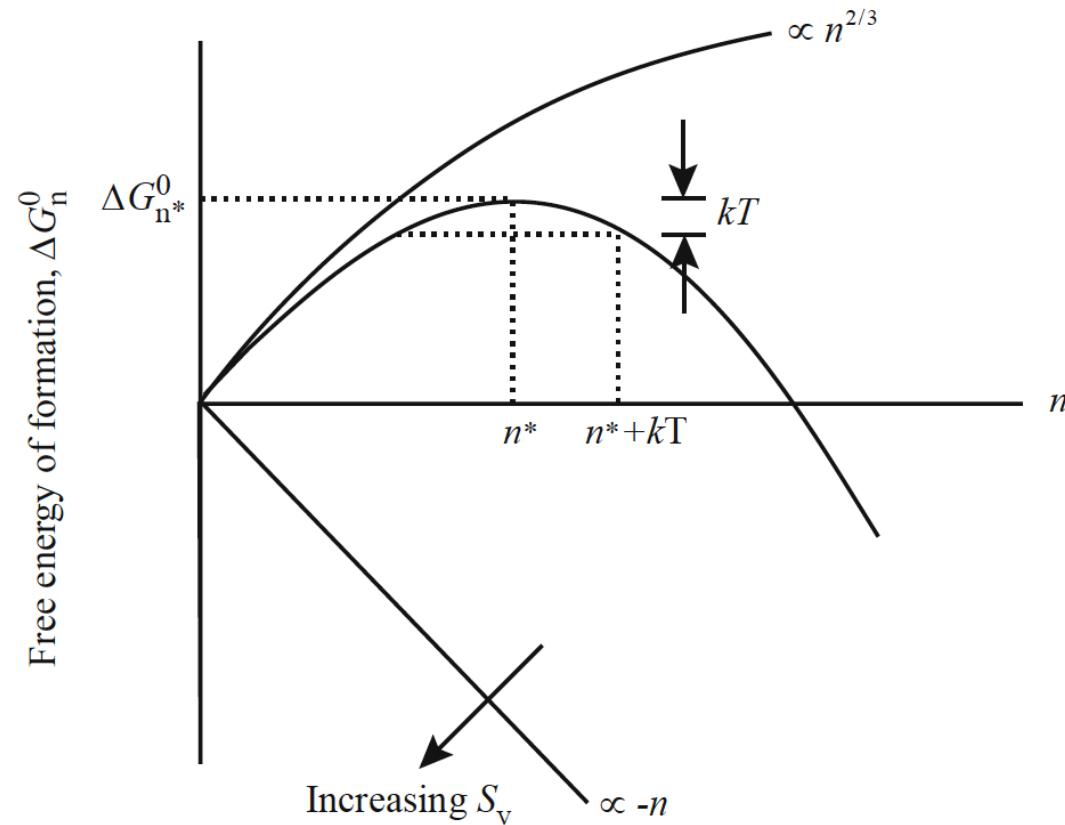
Full derivations and discussion in Was 8.1

Fig. 8.2 Schematic illustration of ΔG_n^0 , the free energy of formation of a spherical void consisting of n vacancies and the effect of thermal fluctuations on the critical size void embryo

Void Nucleation Theory: Graphical depiction

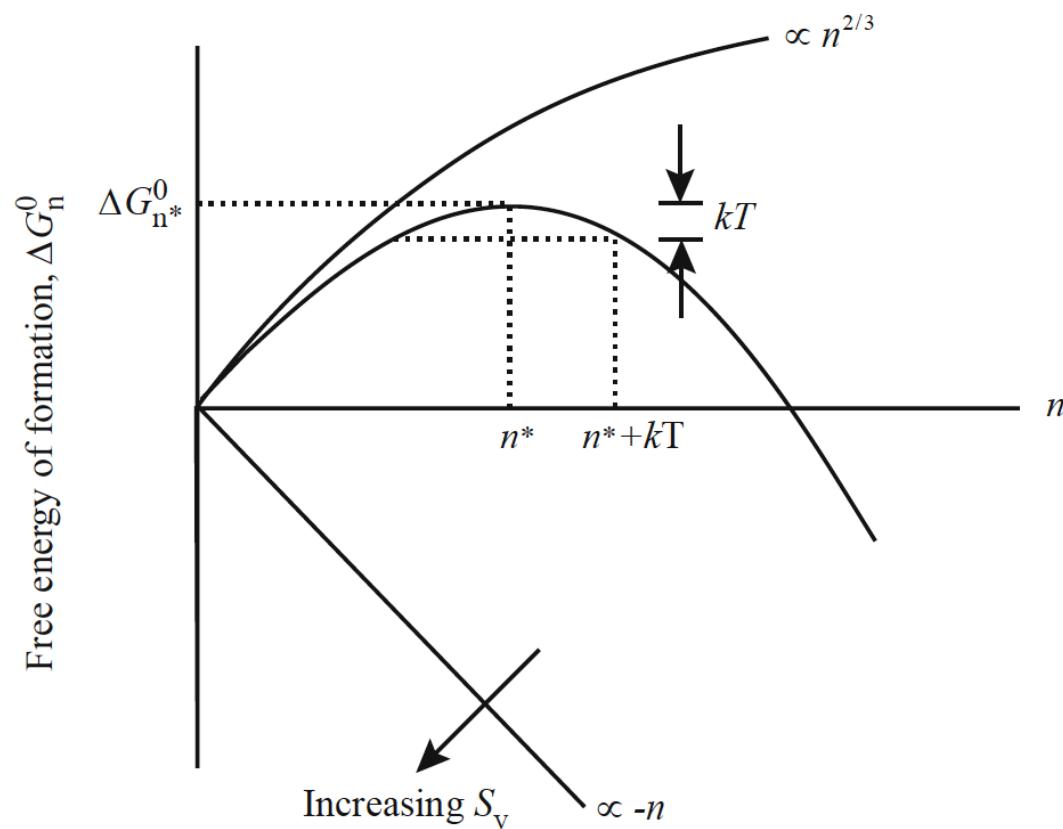
$$\Delta G_n^0 = -nkT \cdot \ln(S_v) + (36\pi\Omega^2)^{1/3} \gamma n^{2/3}$$

We can solve for n^* by:



Derivations and
discussion in Was 8.1

Void Nucleation Theory: Graphical depiction



Derivations and discussion in Was 8.1

- Homogeneous nucleation:

When supercritical particles are formed due to thermal fluctuations

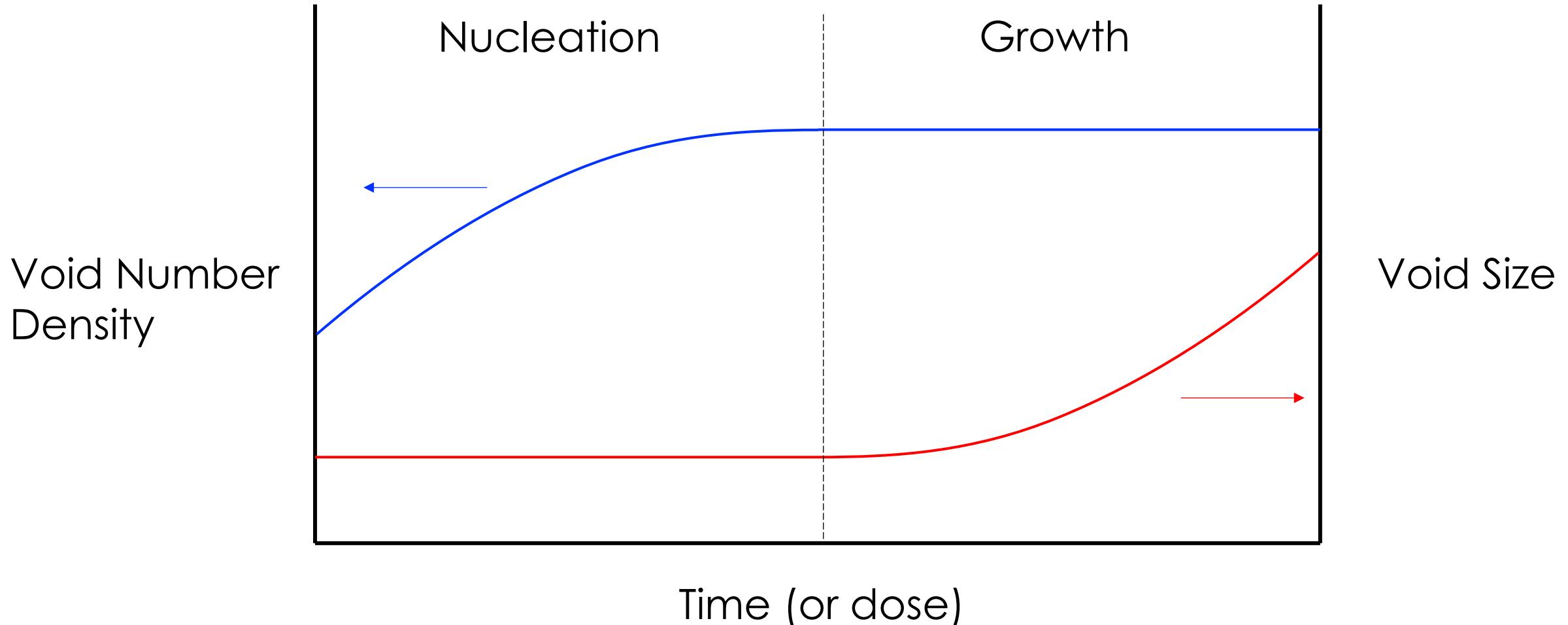
- Heterogeneous nucleation:

When external objects (surfaces, interfaces, impurities, defects, seeds) lower the barrier for nucleation

What happens to the graph with heterogeneous nucleation?



Nucleation vs. Growth



Lecture Break

A single cow can belch and fart up to 115 L of methane per day.
How many megaliters of methane does WI cows release in a year?



Void Nucleation Rate

- Nucleation of ν_j on one particular kind of attractive sites (e.g. compressive stress field around a dislocation). The following assumptions are made:
 1. The lattice is in thermal and dynamic equilibrium, which are minimally affected by displacement and thermal spikes
 2. Mono-vacancies and solvent mono-interstitials are the only mobile point defects present (gas atoms are neglected)
 3. The defects obey dilute solution thermodynamics
 4. A steady state concentration of vacancies and interstitials exist
 5. Void growth rate is diffusion limited



Void Nucleation Rate

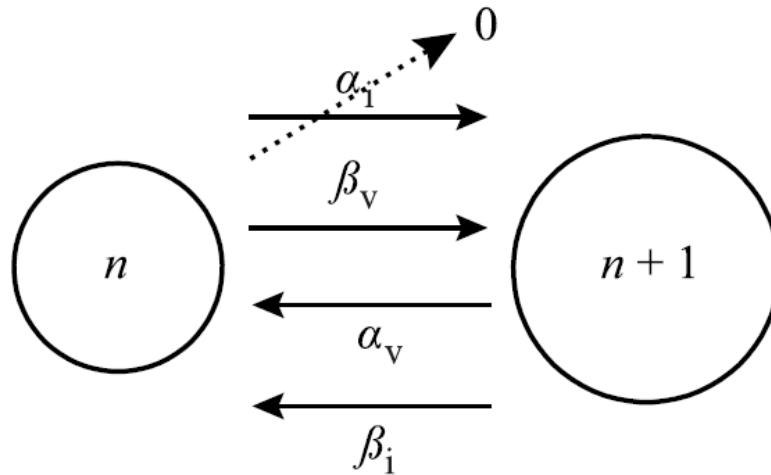
- Voids are three-dimensional clusters of vacancies formed by the following reactions
 1. **Cluster growth** by ν absorption: $\nu + \nu_j \rightarrow \nu_{j+1}$
 2. More generally, we consider **small cluster mobility**: $\nu_j + \nu_k \rightarrow \nu_{j+k}$
 3. **Cluster shrinkage** by ν emission: $\nu_j \rightarrow \nu_{j-1} + \nu$
 - Depends on equilibrium ν concentration at void surface - C_ν^0 from the rate of absorption of ν by cavities and also depends on the binding energy between the ν and the cluster
 4. **Cluster shrinkage** by i absorption: $\nu_j + i_k \rightarrow \nu_{j-k}$
 - Depends on i and i_k concentrations
 5. Growth by i emission is neglected, e.g. $C_i^0 \sim 0$



Void Nucleation Rate

- The flux between any two sized voids, say n and $n + 1$:

$$J_n = \beta_v(n)\rho(n) - p(n+1)(\alpha_v(n+1) + \beta_i(n+1))$$



- $\beta_v(n)\rho(n)$ = rate of v absorption by clusters of size n
- $\alpha_v(n+1)p(n+1)$ = rate of v emission by clusters of size $n + 1$
- $\beta_i(n+1)p(n+1)$ = rate of i absorption by clusters of size $n + 1$



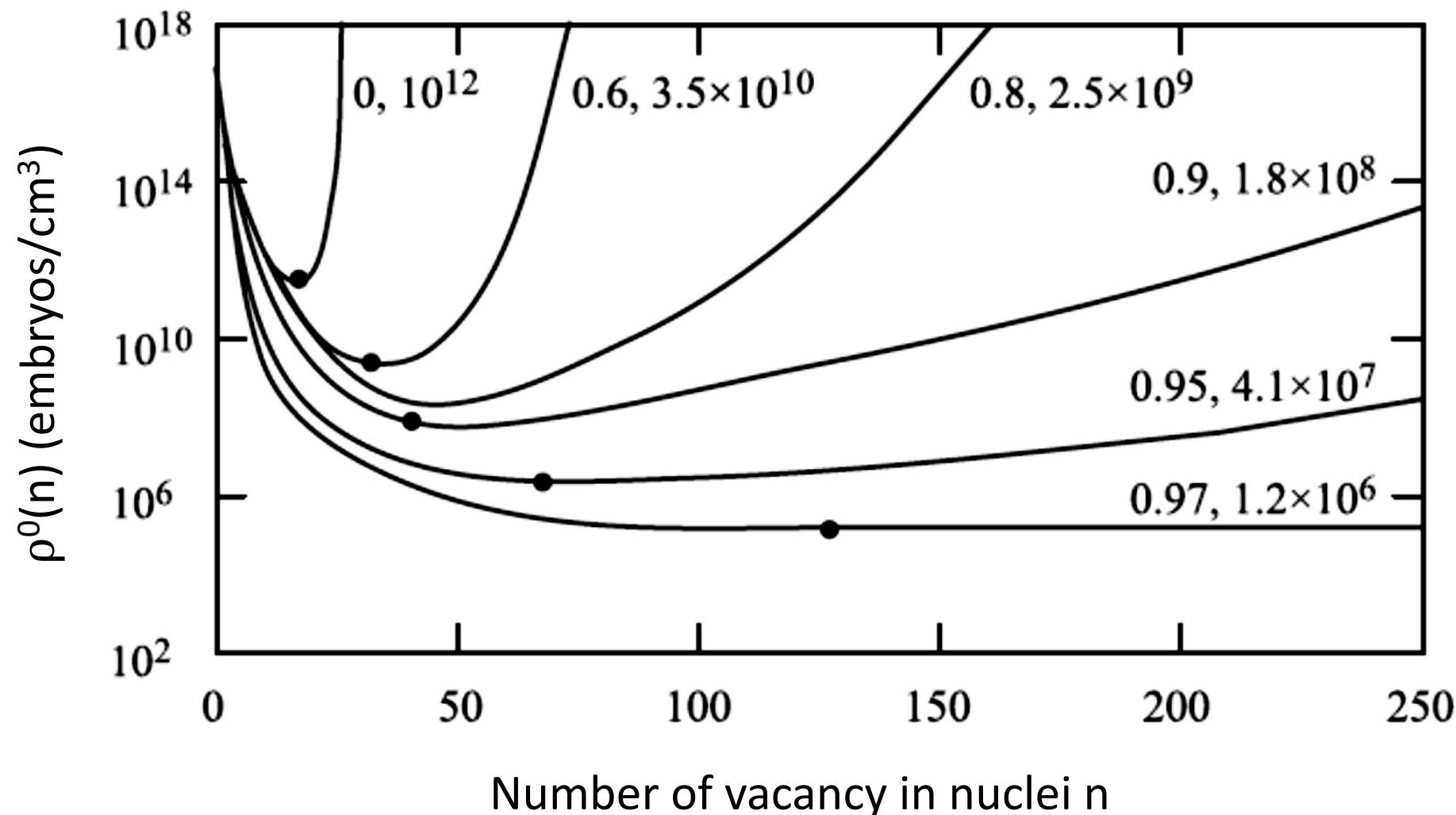
Void Nucleation Rate

- Lengthy derivation covered in Was 8.1.2
- For sake of simplicity, the # of void embryos can be written as:

$$\frac{\rho^0(n)}{C_v} = e^{\sum_{k=1}^{n-1} \ln \left(\frac{\sqrt[3]{\frac{k}{k+1}}}{\left(\frac{C_v^{eq}}{C_v} e^{\left(\frac{8\pi\gamma}{\xi\sqrt[3]{k+1}} - p \right) \frac{\Omega}{kT}} + \frac{D_i C_i}{D_v C_v} \right)} \right)}$$

- C_v^{eq}/C_v is the inverse of vacancy supersaturation S_v^{-1}
- $(D_i C_i)/(D_v C_v)$ is the arrival rate ratio between v and i
- γ is the surface energy of the cavity
- p is the gas pressure in the cavity ($p=0$ for voids!)





Void Nucleation Rate

- To obtain void nucleation as $(D_i C_i)/(D_v C_v)$ approaches 1 requires higher vacancy supersaturation
- Strong dependence of nucleation on vacancy supersaturation

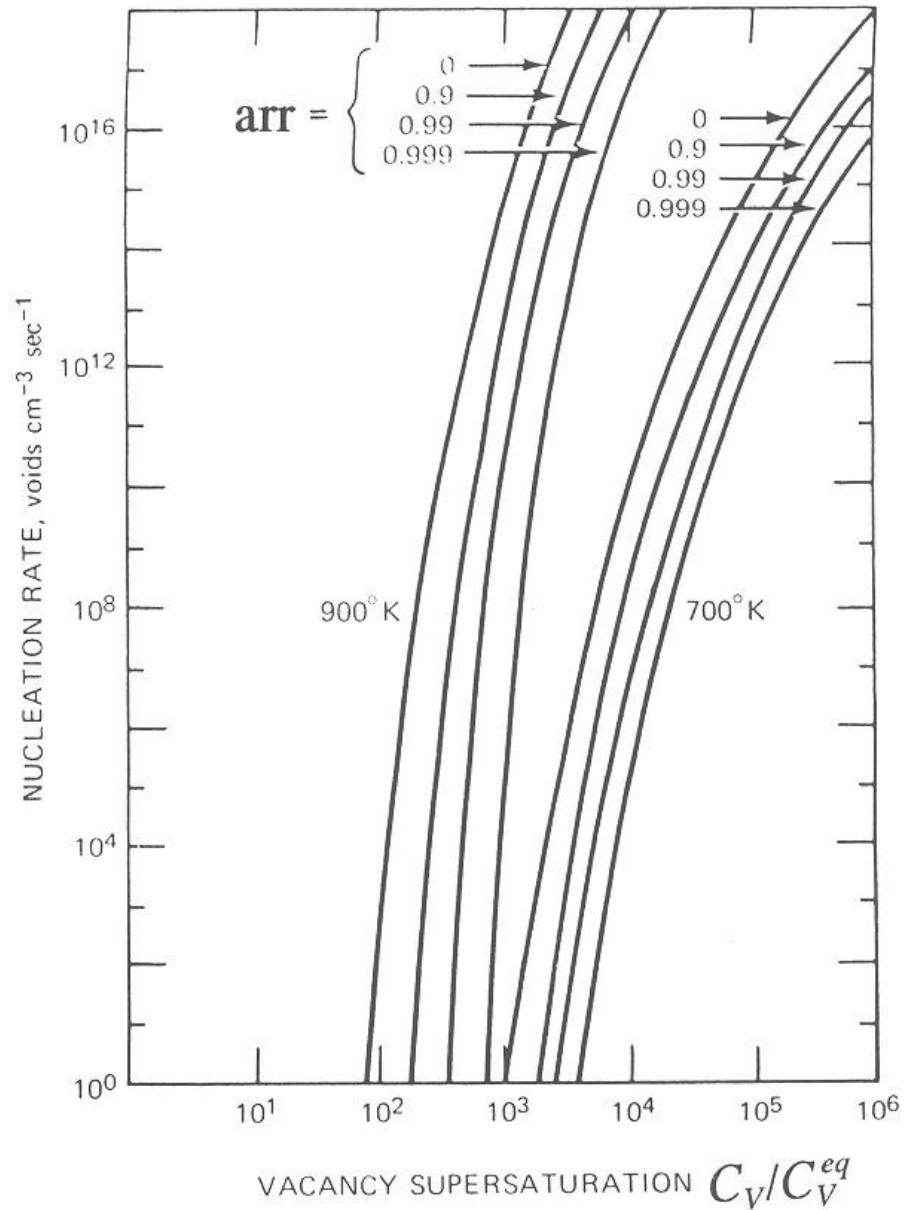
Typical results:

$$T = 700 \text{ K}; C_v/C_v^{eq} = 10^4$$

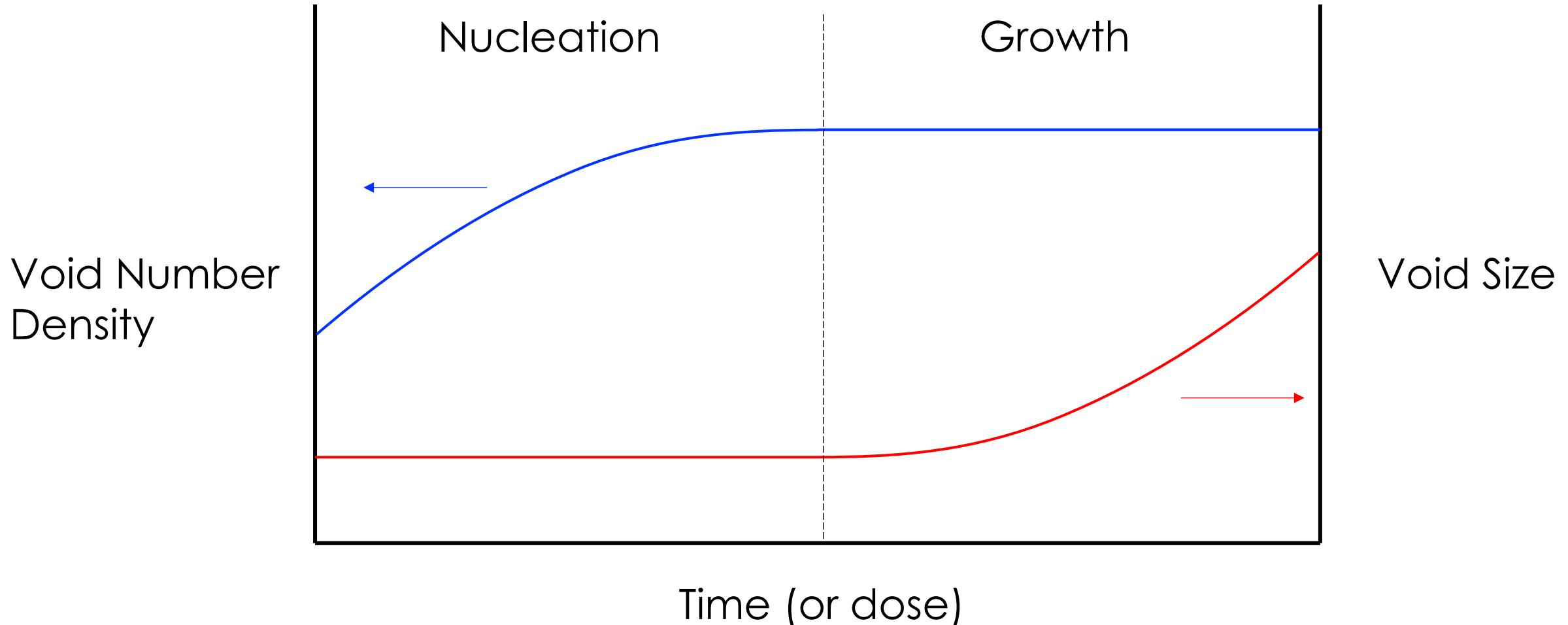
$$\text{arr} = (D_i C_i)/(D_v C_v) = 0.99$$

$$J \sim 10^8 \text{ voids nucleated}/\text{cm}^3/\text{s}$$

- After 1 year, 3×10^{15} voids/cm³
- The voids are small, about the critical size

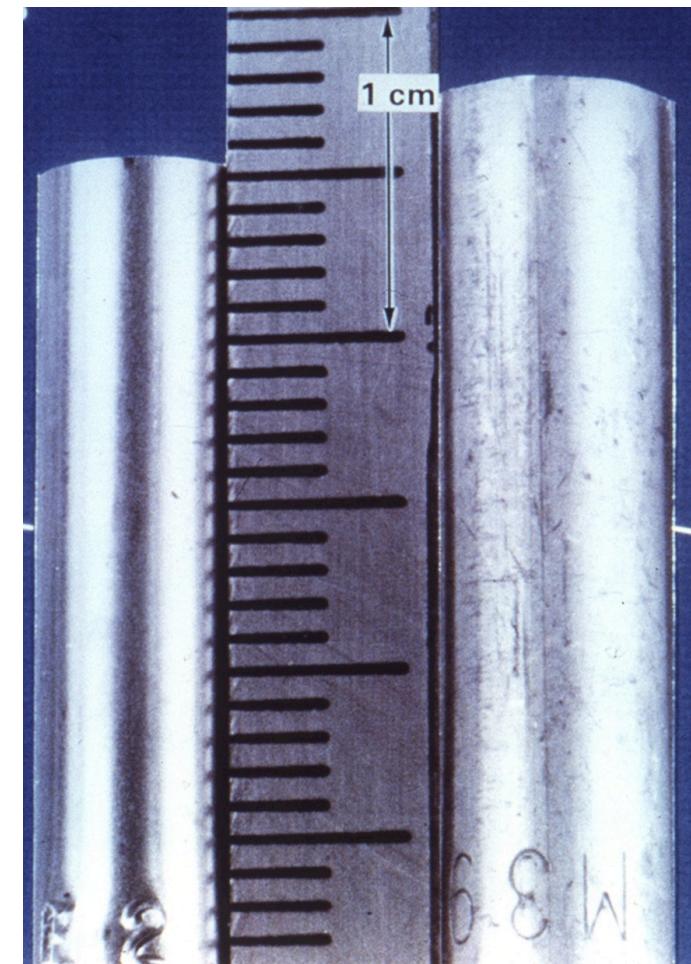


Nucleation vs. Growth



Void Growth

- During the **nucleation** period, the number density of cavities increases with time, but the sizes remain small
- During the **growth** period that follows, the number density stabilizes at a value of $N \text{ cm}^{-3}$ and the cavity size increases with time $R(t)$
- In most cases, we're interested in quantifying **swelling** either in the growth or nucleation stage:



Void Growth

- For void growth, we need to know the net flux of vacancies to a void embryo. The net rate is thus a combination of the fluxes of interstitials and vacancies to a void, where:



Void Growth

$$\frac{dV}{dt} = 4\pi R\Omega(D_v C_v - D_i C_i)$$



Void Growth

$$K_0 - K_{iv}C_iC_v - K_{vs}C_vC_s = 0$$

$$K_0 - K_{iv}C_iC_v - K_{is}C_iC_s = 0$$

Solving for C_i and C_v , we get the familiar solution of:

$$C_v = \frac{-K_{is}C_s}{2K_{iv}} + \left[\frac{K_0K_{is}}{K_{iv}K_{vs}} + \frac{K_{is}^2C_s^2}{4K_{iv}} \right]^{1/2}$$

$$C_i = \frac{-K_{vs}C_s}{2K_{iv}} + \left[\frac{K_0K_{vs}}{K_{iv}K_{is}} + \frac{K_{vs}^2C_s^2}{4K_{iv}} \right]^{1/2}$$



Void Growth



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Void Growth

Remember:

$$C_v = \frac{-K_{is}C_s}{2K_{iv}} + \left[\frac{K_0K_{is}}{K_{iv}K_{vs}} + \frac{K_{is}^2C_s^2}{4K_{iv}} \right]^{1/2}$$

$$C_i = \frac{-K_{vs}C_s}{2K_{iv}} + \left[\frac{K_0K_{vs}}{K_{iv}K_{is}} + \frac{K_{vs}^2C_s^2}{4K_{iv}} \right]^{1/2}$$

and

$$k_{jx}^2 = \frac{K_{jx}C_x}{D_j}$$



Void Growth

- With everything defined,

$$C_v = \frac{D_v(4\pi R\rho_v + z_vp_d)}{2K_{iv}}(\sqrt{1+\eta} - 1)$$

$$C_i = \frac{D_i(4\pi R\rho_v + z_ip_d)}{2K_{iv}}(\sqrt{1+\eta} - 1)$$

$$\eta = \frac{4K_0 K_{iv}}{D_i D_v (4\pi R\rho_v + z_vp_d)^2}$$

$$dR/dt = \dot{R} = \frac{\Omega}{R}(D_v(C_v - C_v^V) - D_i C_i)$$

- We can now rewrite the growth law as:



Void Growth

$$R \dot{R} = K_o \Omega \left(\frac{z_i - z_v}{z_v} \right) \frac{z_v \rho_d}{(4\pi R \rho_v + z_v \rho_d)(4\pi R \rho_v + z_i \rho_d)} F(\eta)$$

- The **first term** is the main dpa-rate effect on void growth
- The **second term** is the “bias” term: if $Z_i = Z_v$, void growth *is impossible*
- The **third term** is the sink-strength balance term. Void growth is eliminated if there are too many or too few dislocations. Optimum growth occurs when the void sink term ($4\pi R \rho_v$) and the dislocation sink term ($z_v \rho_d$) are equal.
- The **fourth term** contains the effect of point defect recombination:

$$F(\eta) = 2 \left(\sqrt{1 + \eta} - 1 \right) / \eta$$

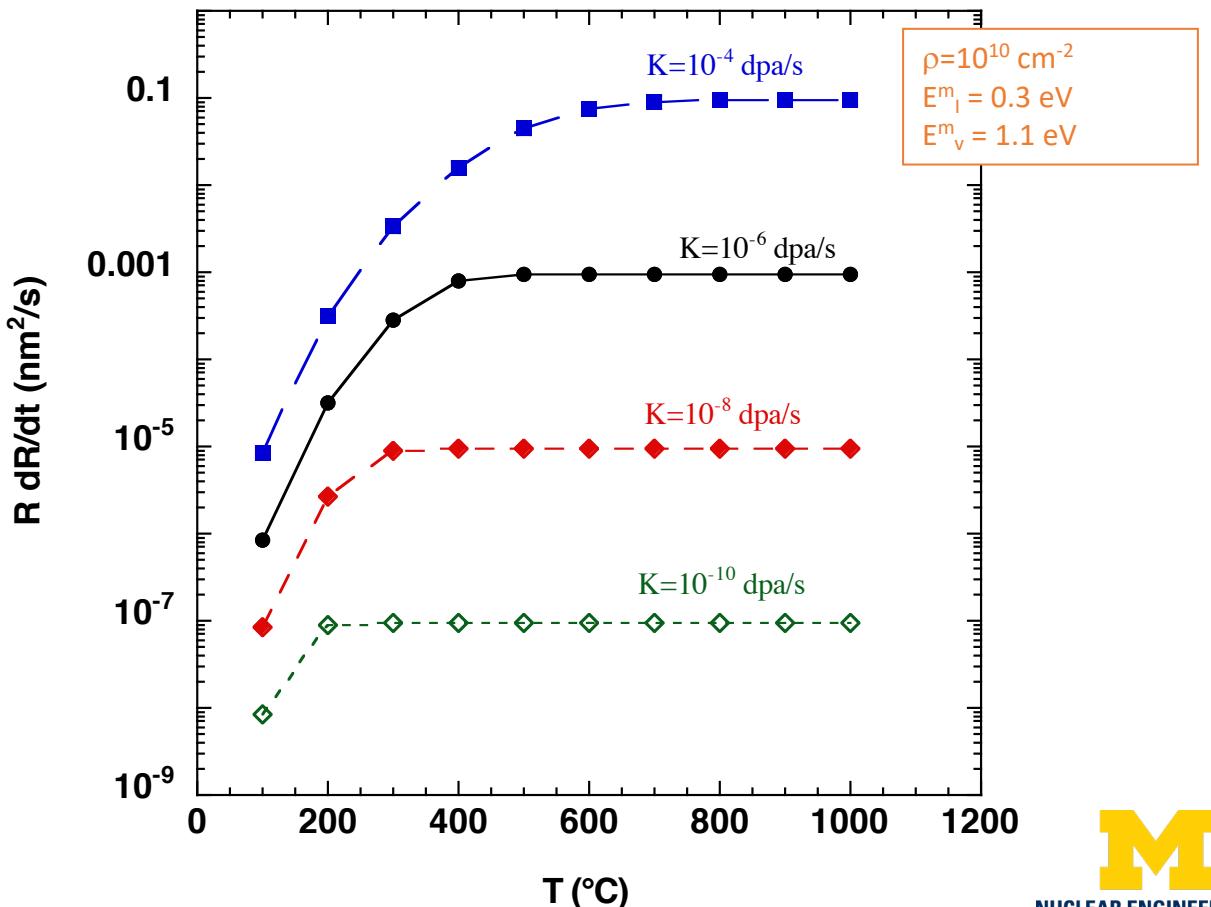
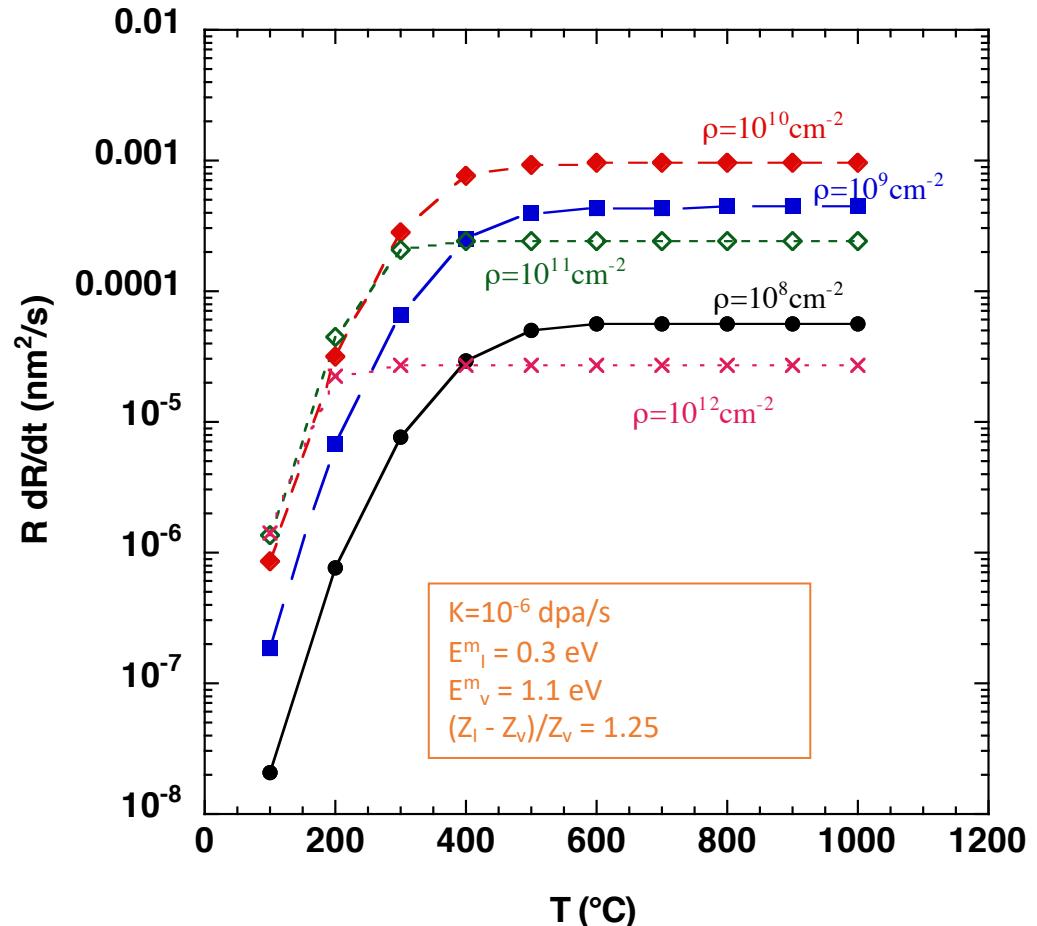
Since η decreases with increasing temperature and F decreases with increasing η :

- At high temperature, $F \rightarrow 1$ and recombination does not effect void growth
- At low temperature, $F \rightarrow 0$ and recombination prevents void growth.



Void Growth

$$R \dot{R} = K_o \Omega \left(\frac{z_i - z_v}{z_v} \right) \frac{z_v \rho_d}{(4\pi R \rho_v + z_v \rho_d)(4\pi R \rho_v + z_i \rho_d)} F(\eta)$$



Vacancy Thermal Emission

- The four factor formula does not account for C_v^0 , but at high temperatures this assumption is not valid. At very high temperatures, void growth ceases due to vacancies "boiling off", e.g. vacancy emission. If we repeat taking into account C_v^0 , we get:



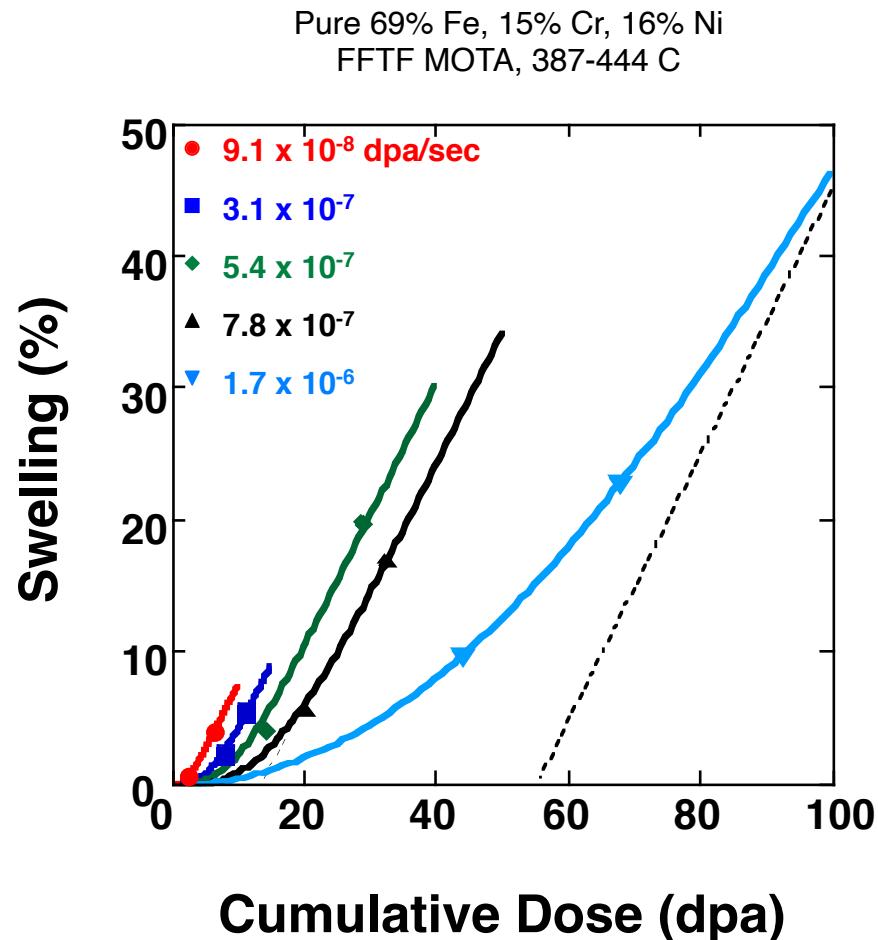
Dose, dose rate & temperature effects on swelling

- Theory predicts that void selling rate passes through a maximum with temperature. The maximum is $\sim 1/3$ the melting temperature of the metal (T_m K)
- The void growth model also includes the effect of dose rate and accumulated dose
- The dose rate effect means that void swelling at the same dose is different for ion or electron irradiation (high dose rates) compared to neutrons (low dose rate)
- The steady state swelling is roughly correlated to the damage:
- Or

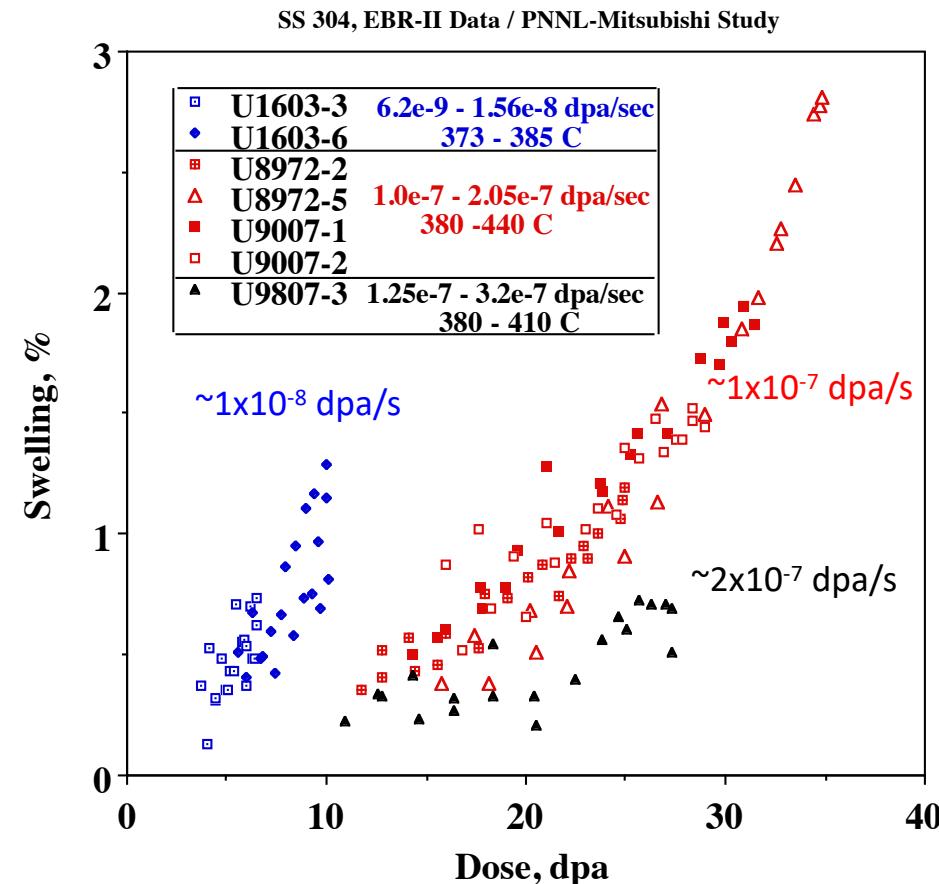


The onset of void swelling can be a strong function of the dose rate

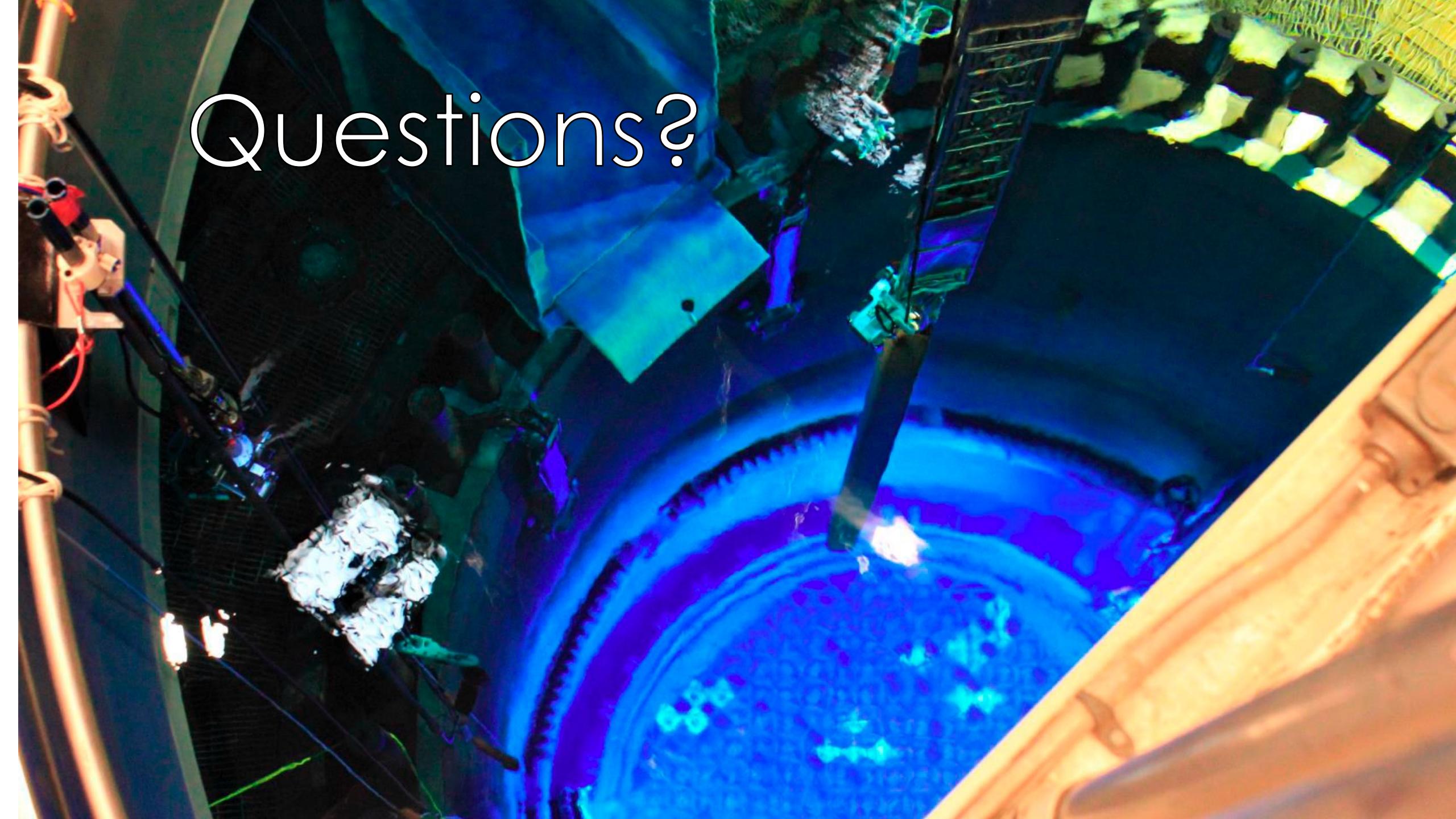
Okita et al.



Garner et al., PNNL



W.G. Wolfer, LLNL



Questions?