Loops + Voids

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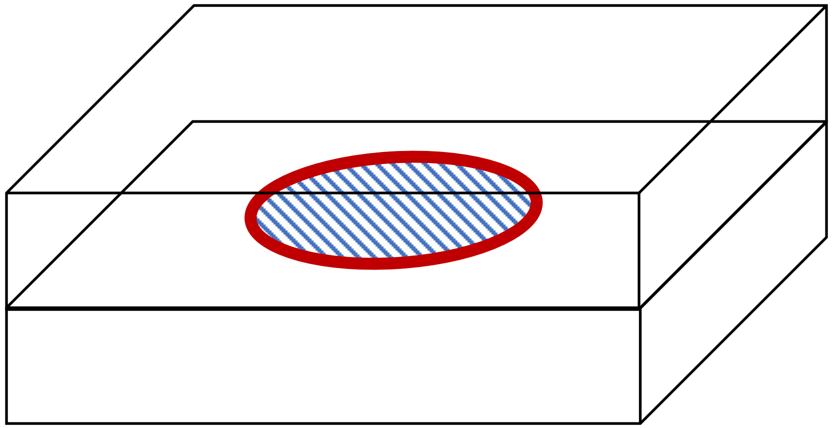
Dislocation loop energy in FCC alloys

- For FCC, we must consider both the energy created because of the loop and of the possible stacking fault:



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:

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

  - Perfect:

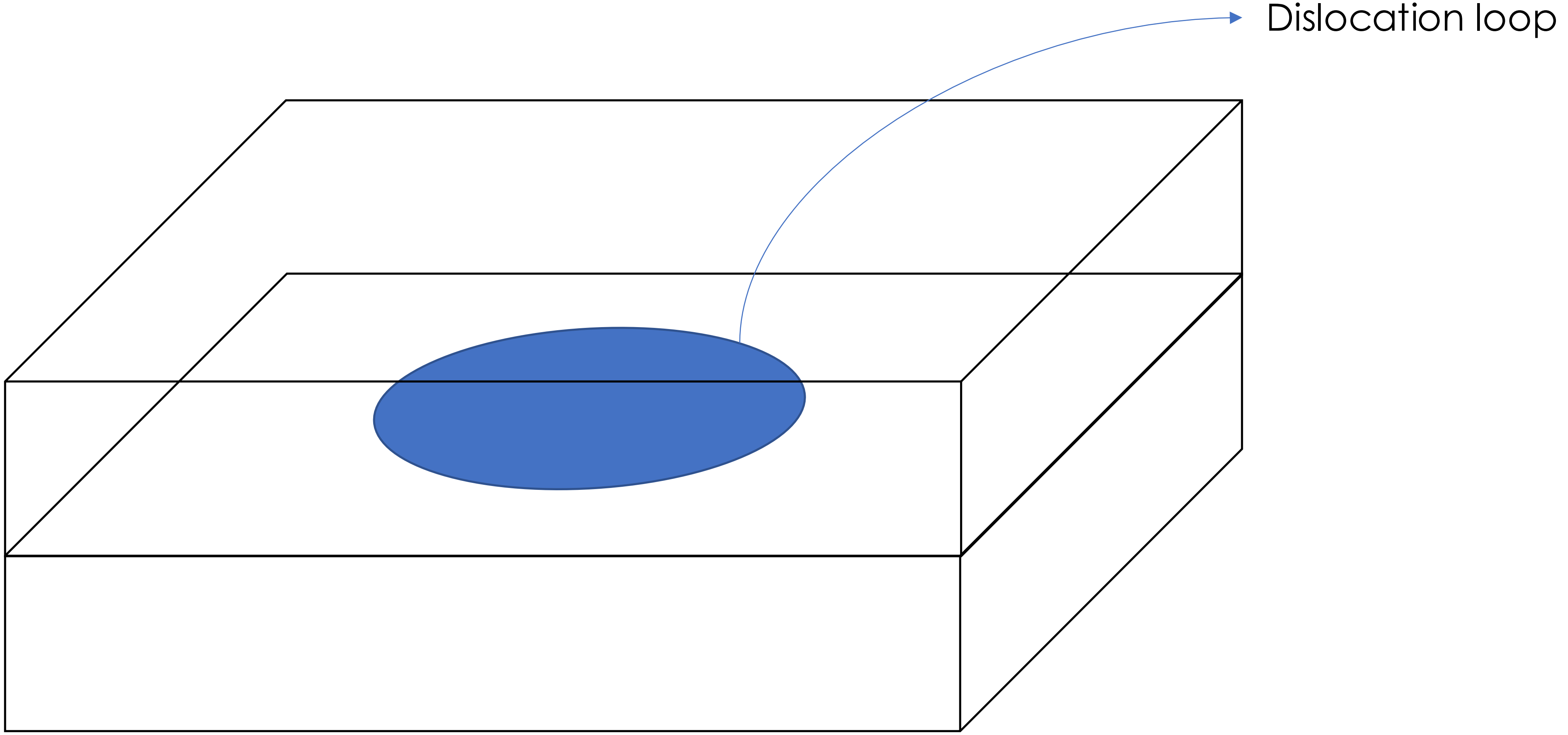
$$E_L^p = \left[\frac{2}{3}\frac{1}{(1-\upsilon)} + \frac{1}{3}\left(\frac{2-\upsilon}{2(1-\upsilon)}\right)\right]\mu b^2 r_L\left[ln\frac{4r_L}{r_0} - 2\right]$$

Dislocation loop energy in FCC alloys

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

Metal/Alloy	$\gamma\ (mJm^{-2})$	Reference
SS-304	21	Murr 1975, Hadji & Badji 2002
SS-316	42	Hadji & Badji 2002
Ni	128	Murr 1975
Ti	15	Conrad 1981
Al	166	Murr 1975
Zr	240	Murr 1975

A simple loop growth model

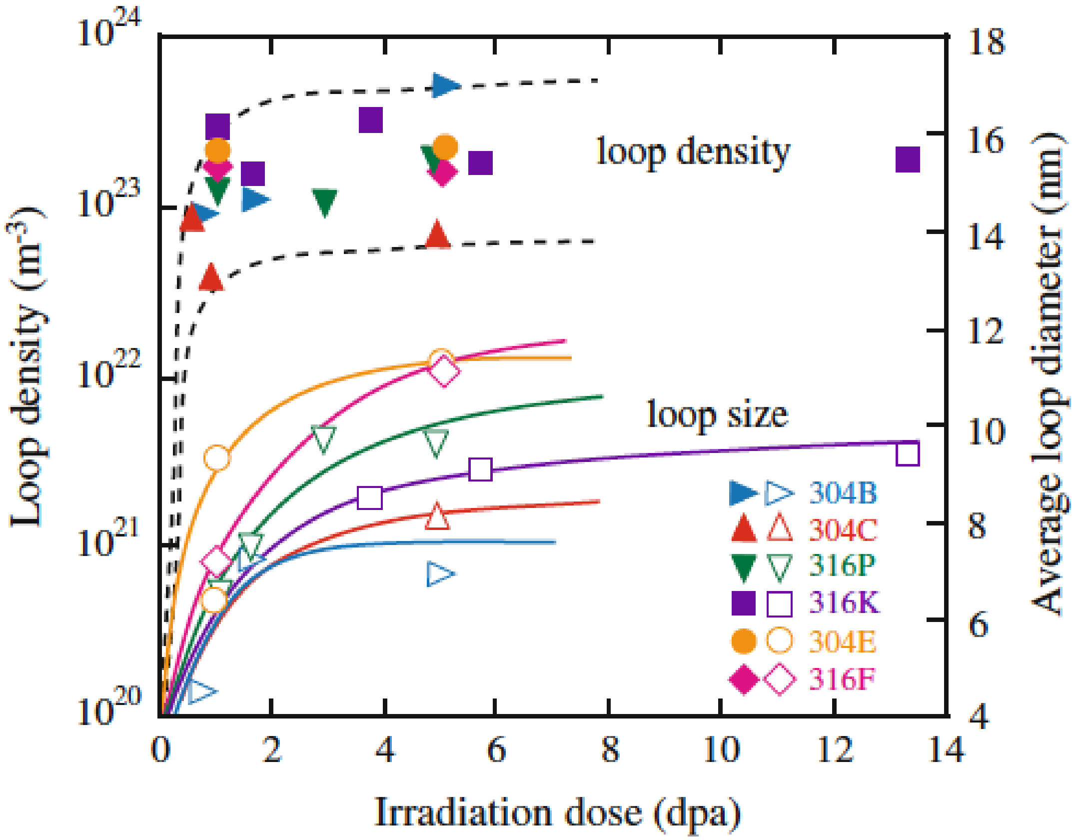


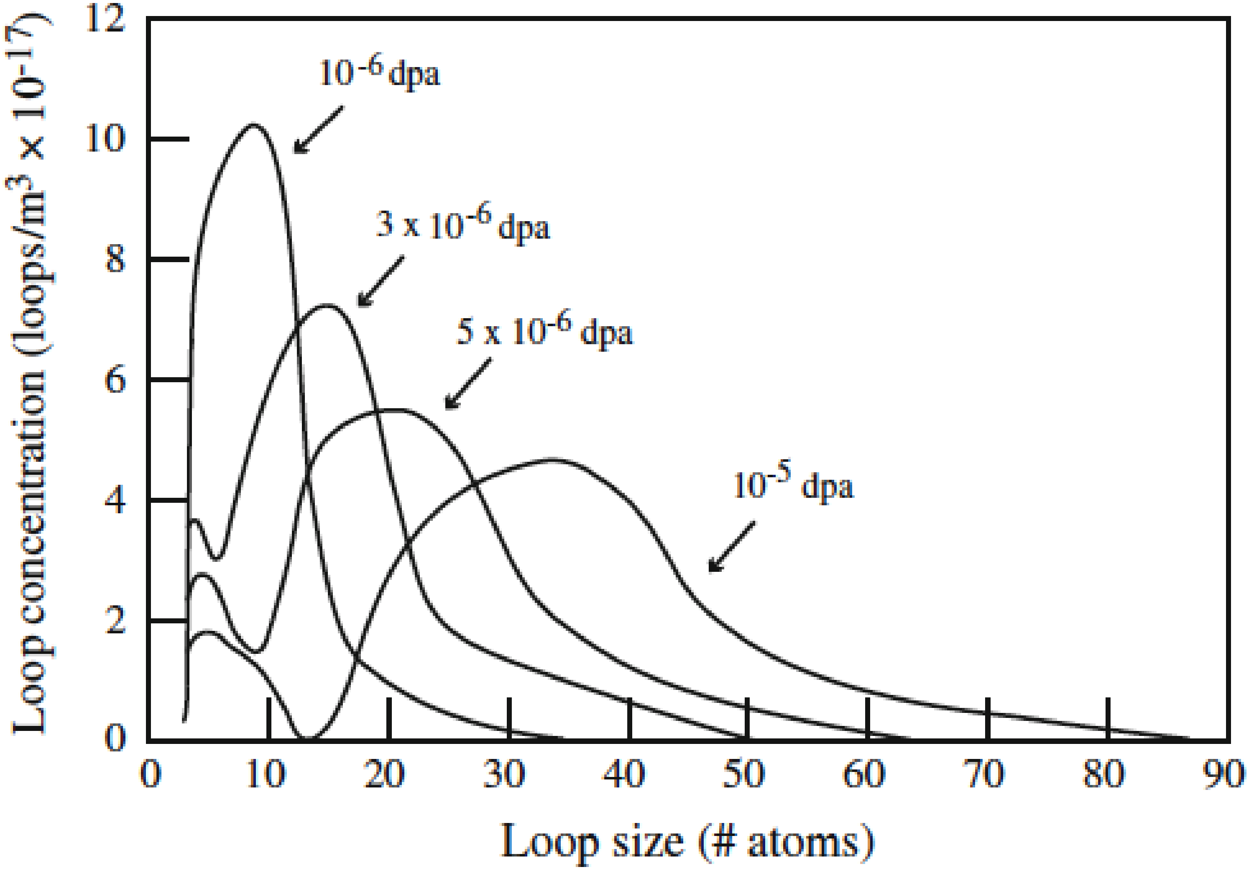
A simple loop growth model

$$\left(\frac{dr_L}{dt}\right)_v = \frac{1}{b}\left[D_v C_v - Z_i D_i C_i - D_s^v \exp\left(\frac{\tau b^2}{r_L k_b T}\right) + D_s^i exp\left(-\frac{\tau b^2}{r_L k_b T}\right)\right]$$

$$\left(\frac{dr_L}{dt}\right)_i = \frac{1}{b}\left[Z_i D_i C_i - D_v C_v - D_s^i \exp\left(\frac{\tau b^2}{r_L k_b T}\right) + D_s^v exp\left(-\frac{\tau b^2}{r_L k_b T}\right)\right]$$

Dose dependence





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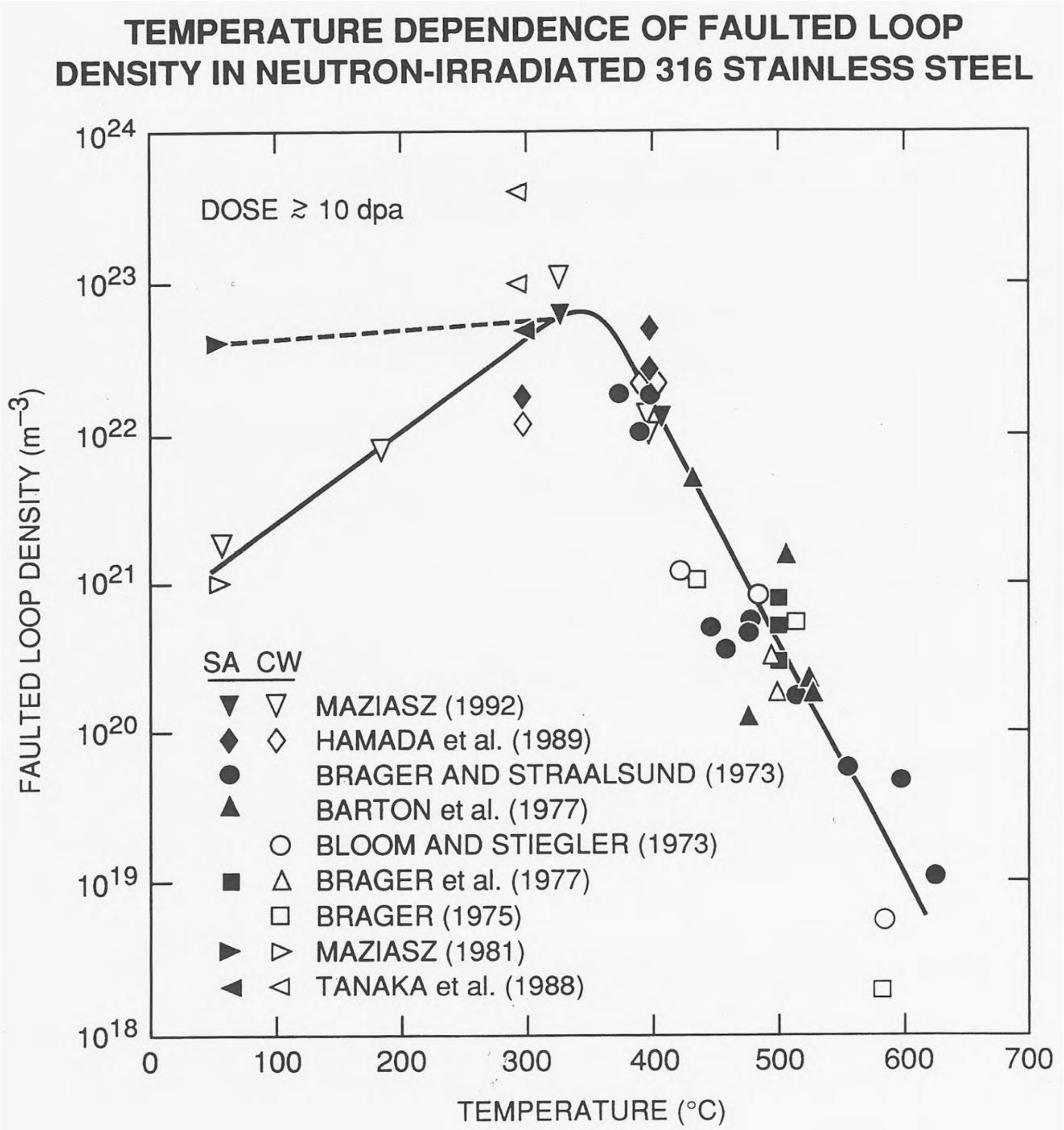
Temperature dependence



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

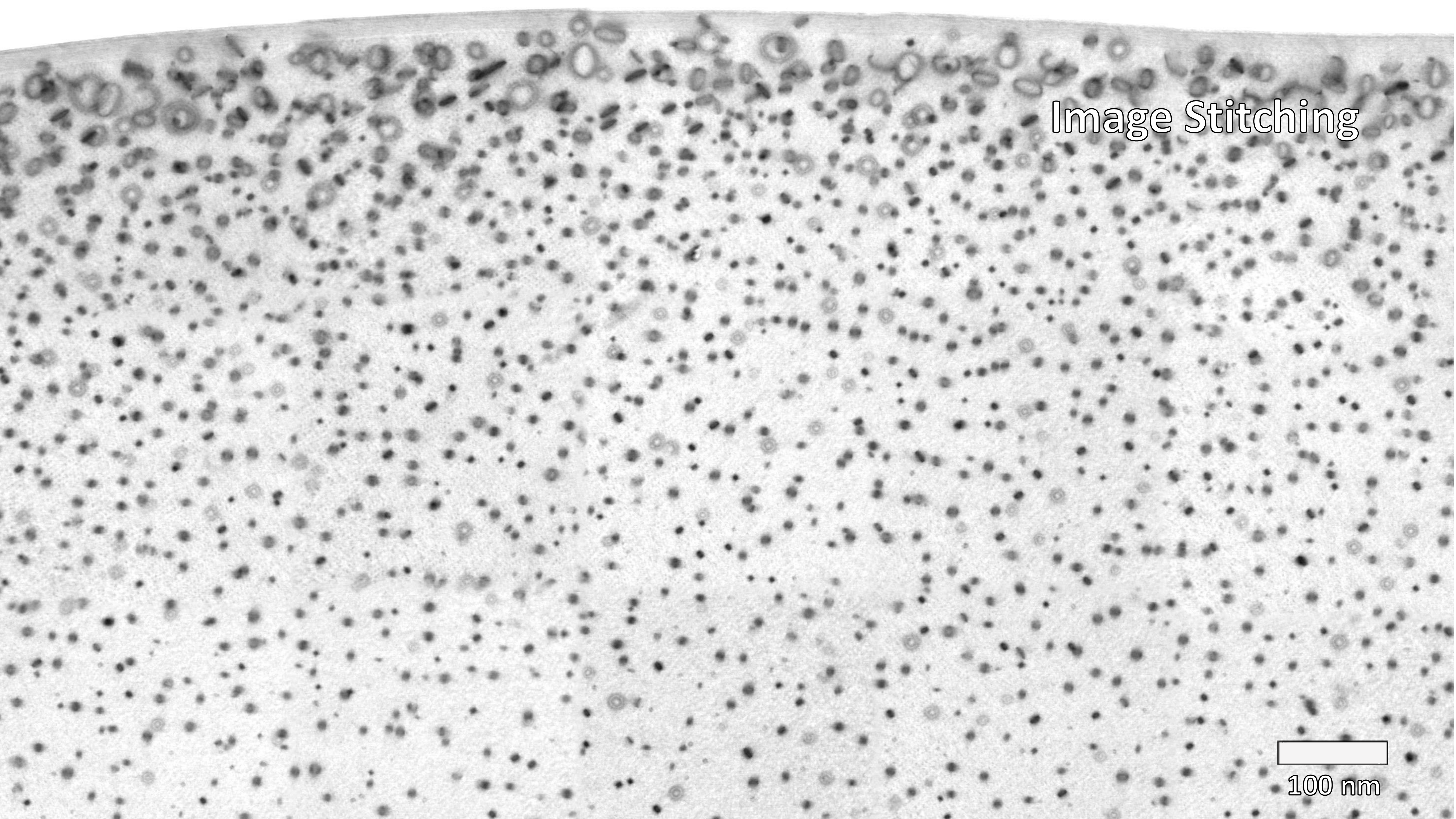
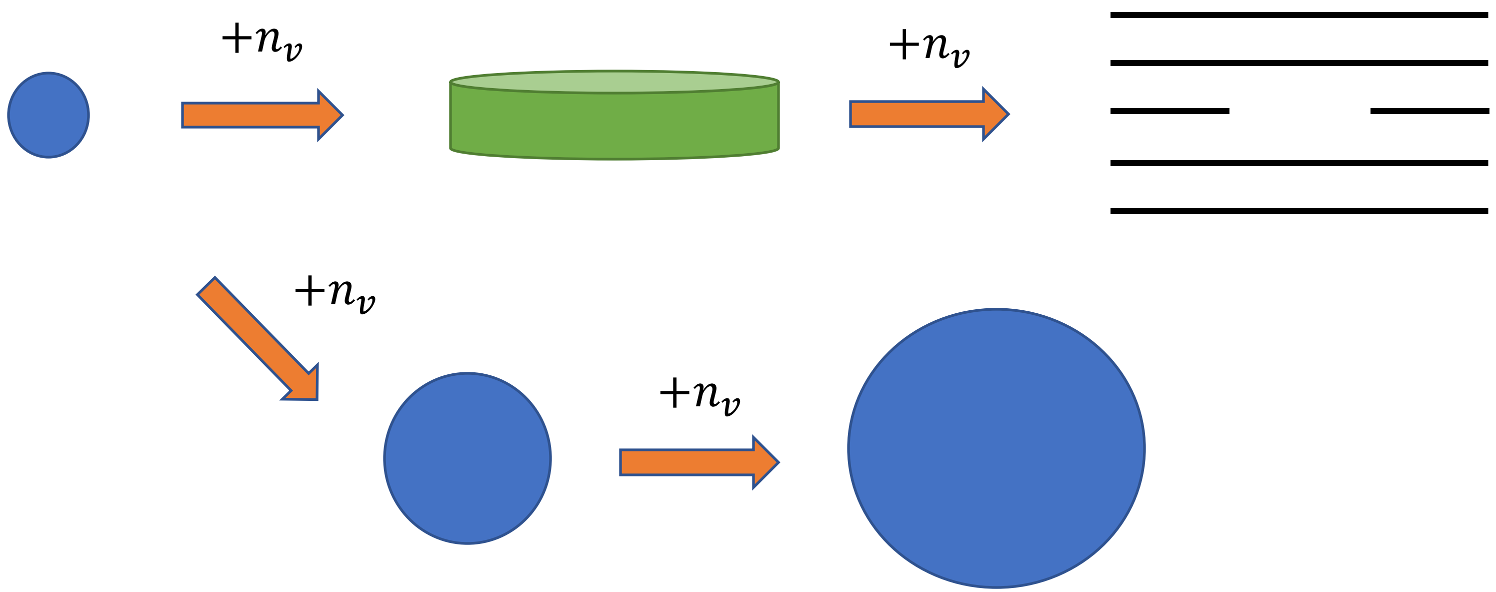


Image Stitching
100 nm

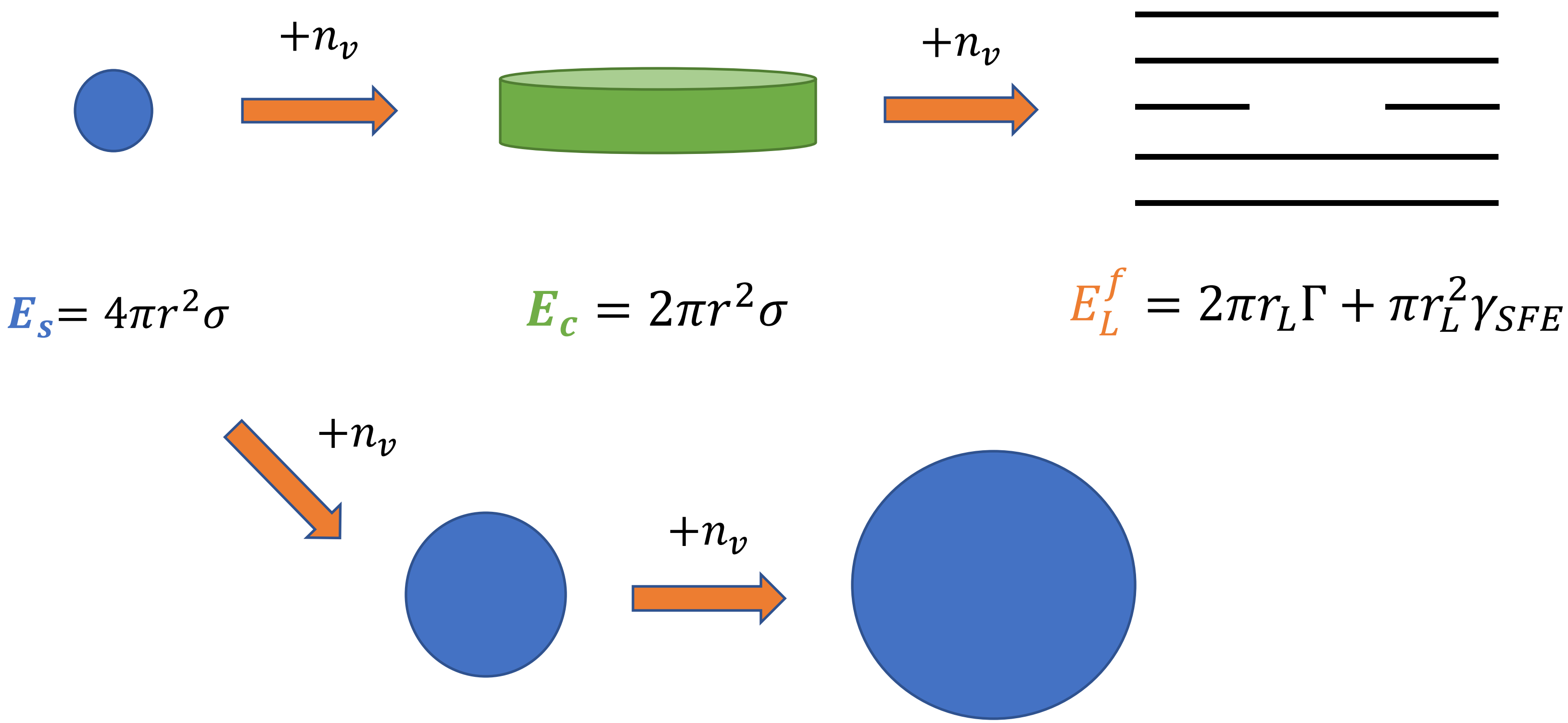
Now let's consider vacancy condensation



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

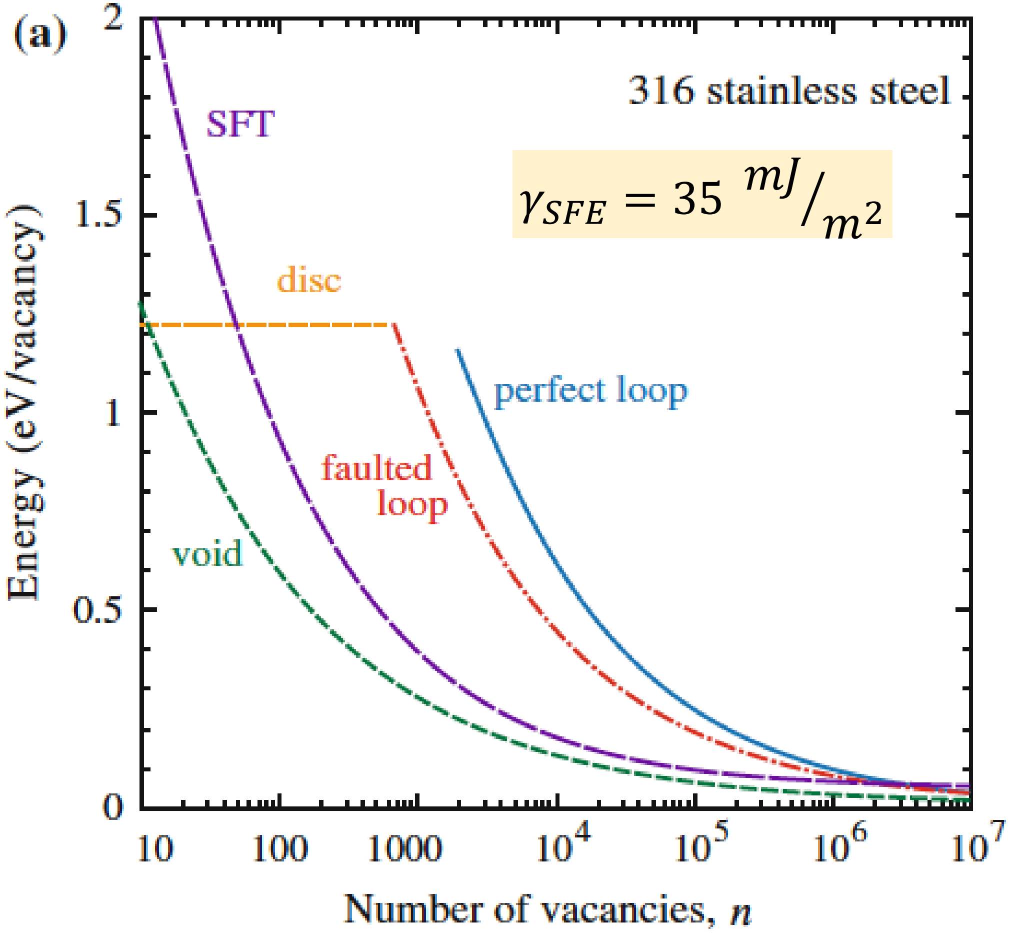
- For the same n_v, $E_C > E_s$ meaning an activation energy is required to generate large spherical voids

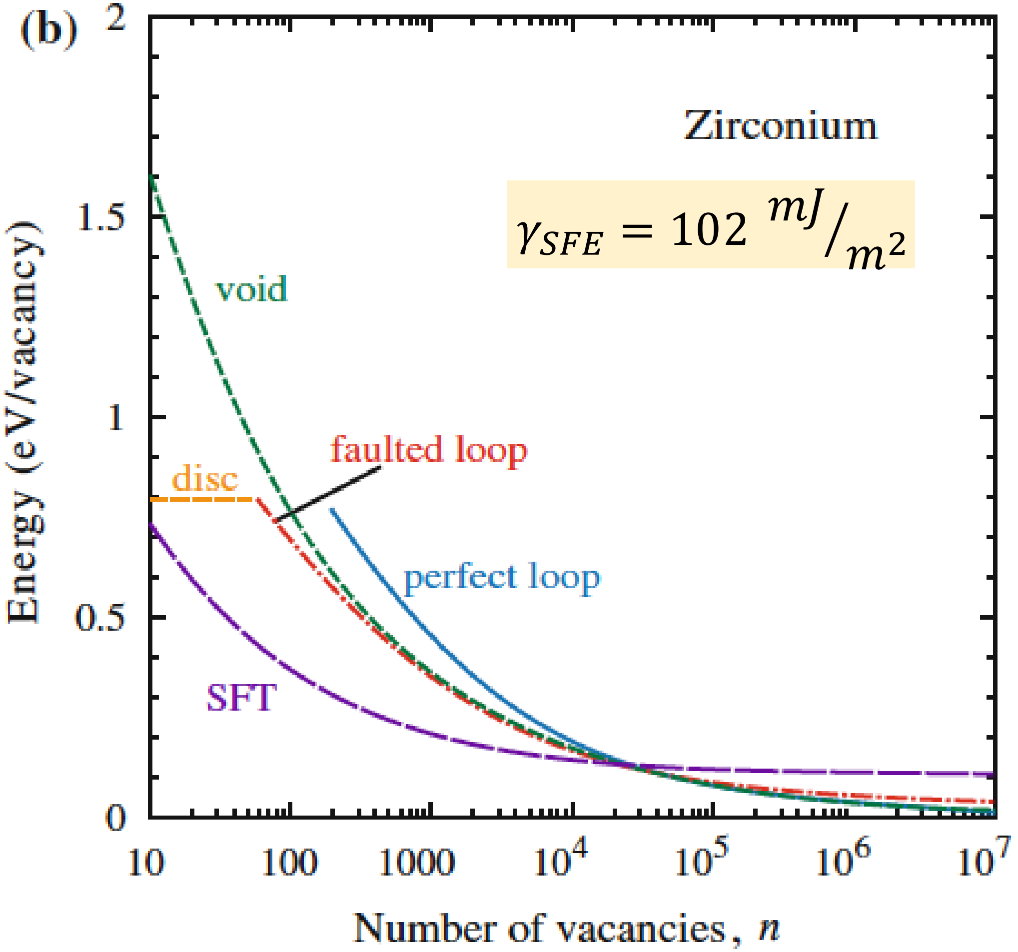
Now let's consider vacancy condensation



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

Visualizing the energetics





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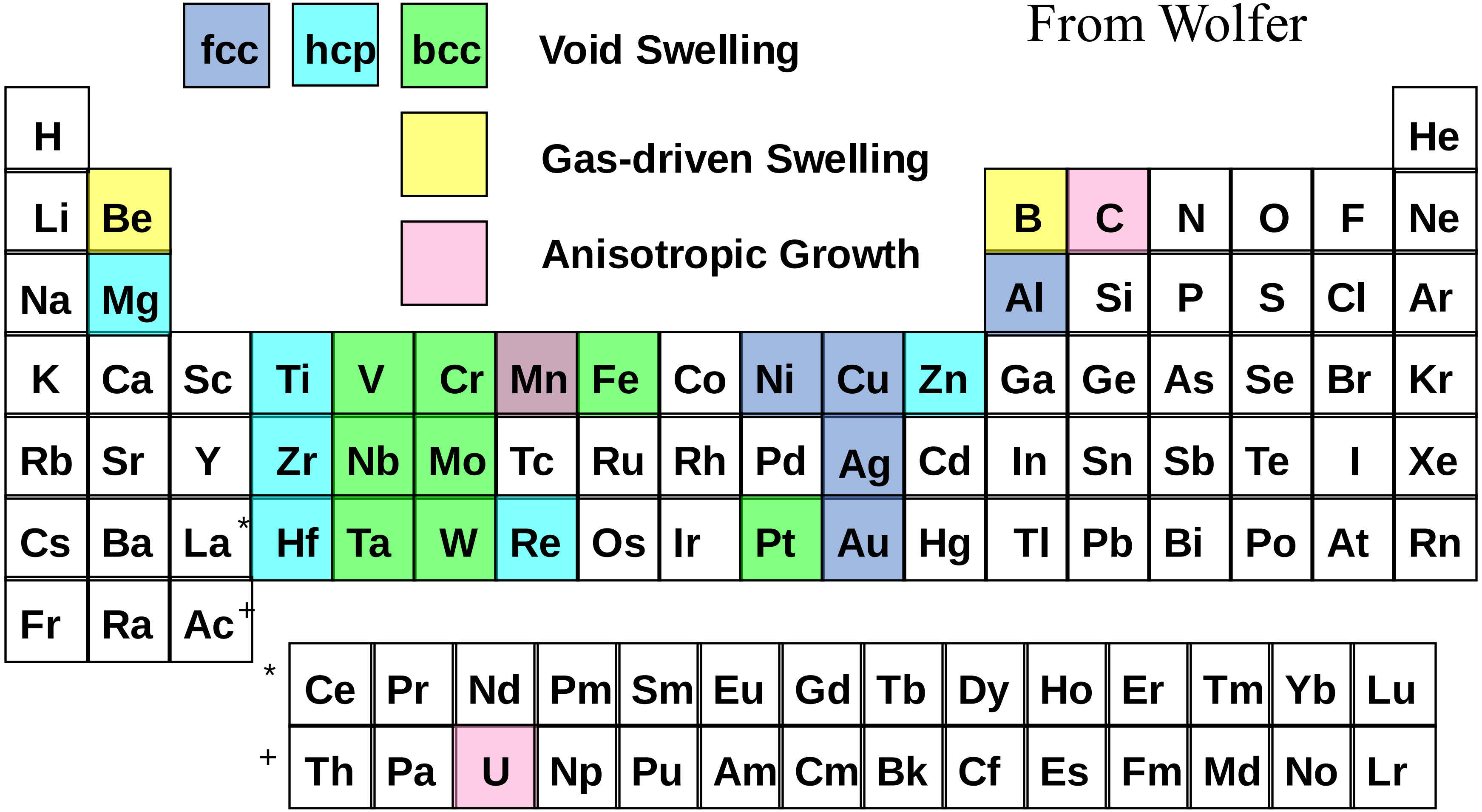
Voids formed in metals

- 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.

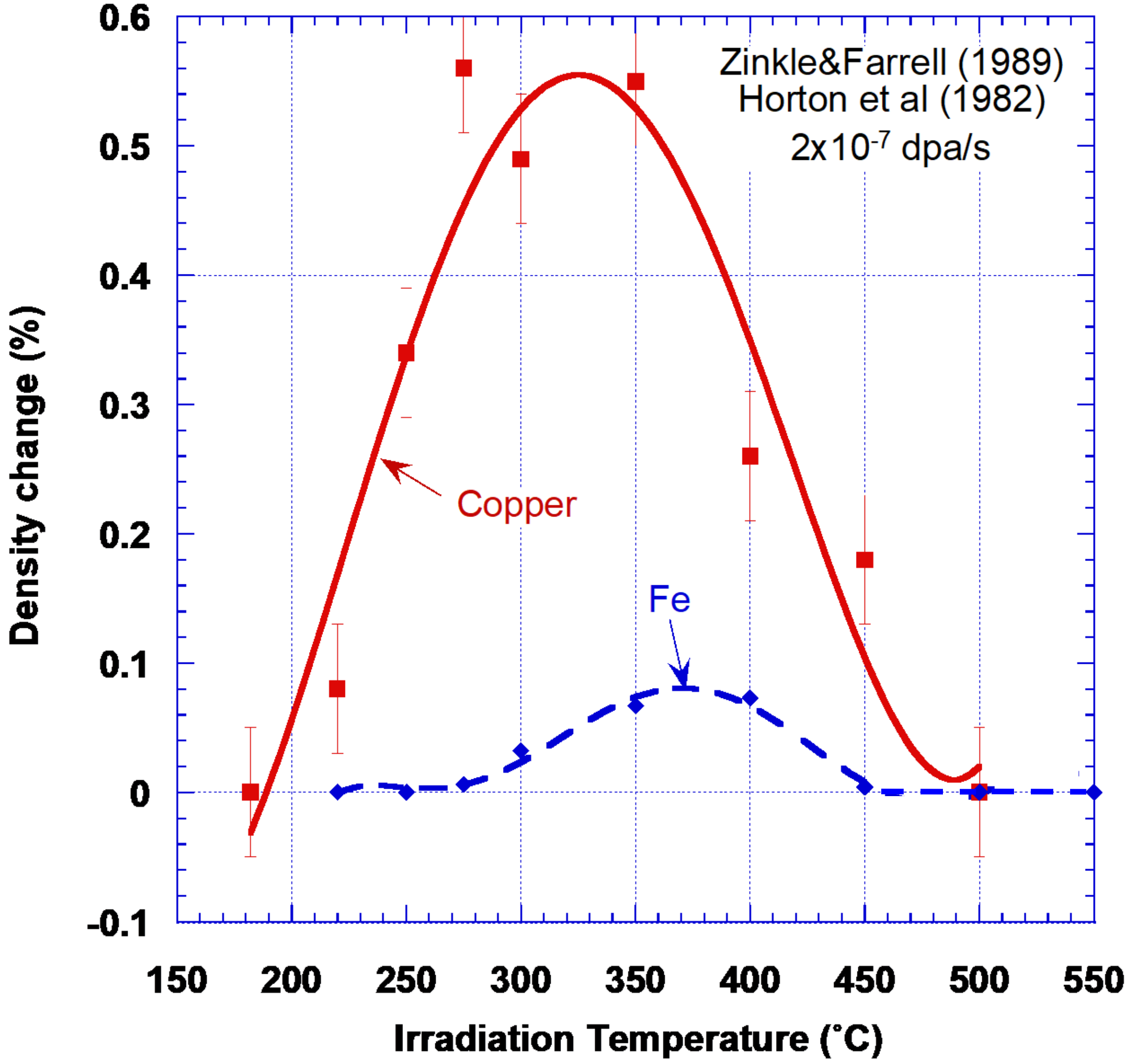
Effect of materials variables on void growth



From Wolfer

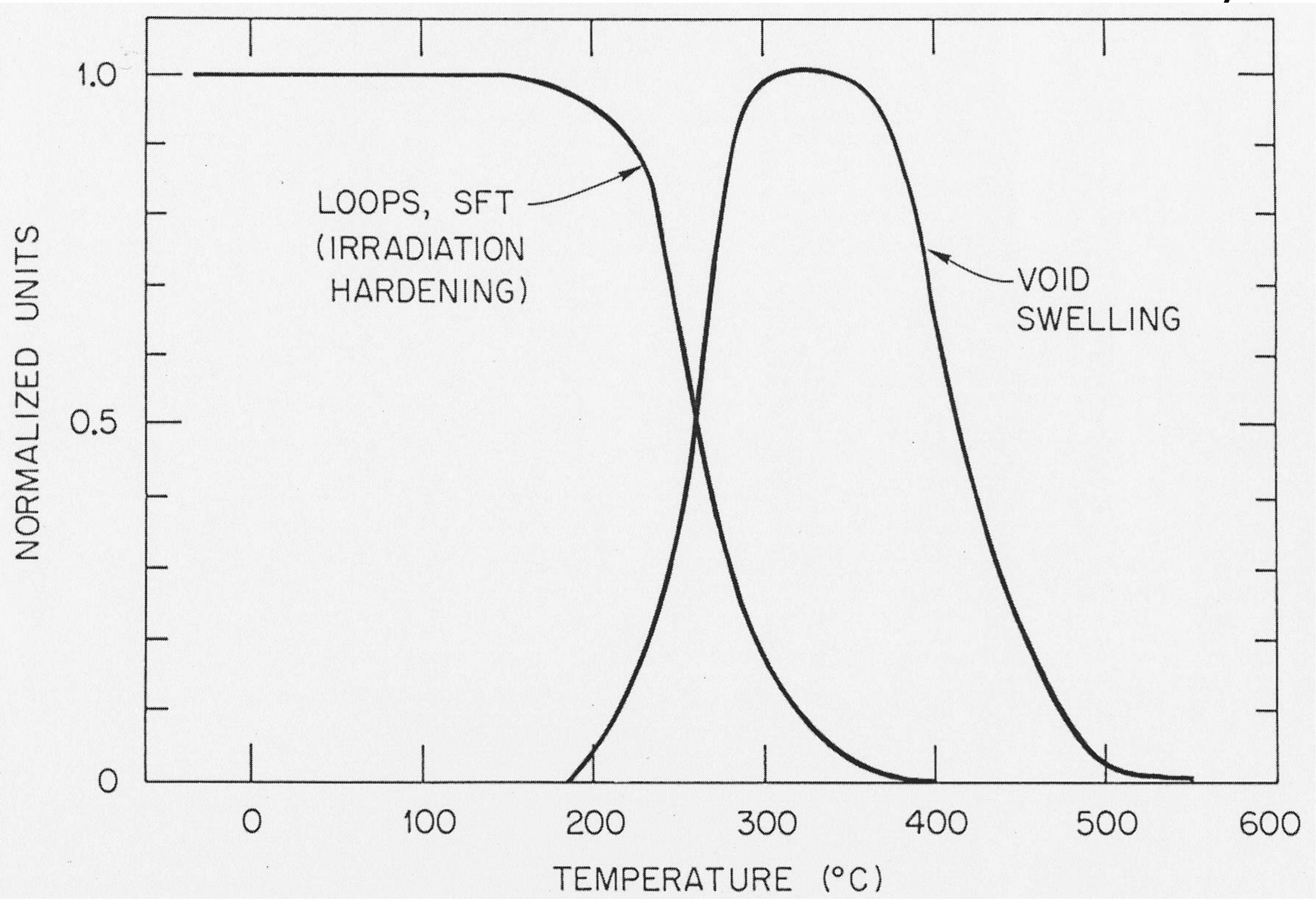
No Element Tested Has Ever Failed to Swell

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 ~0.6 T_M

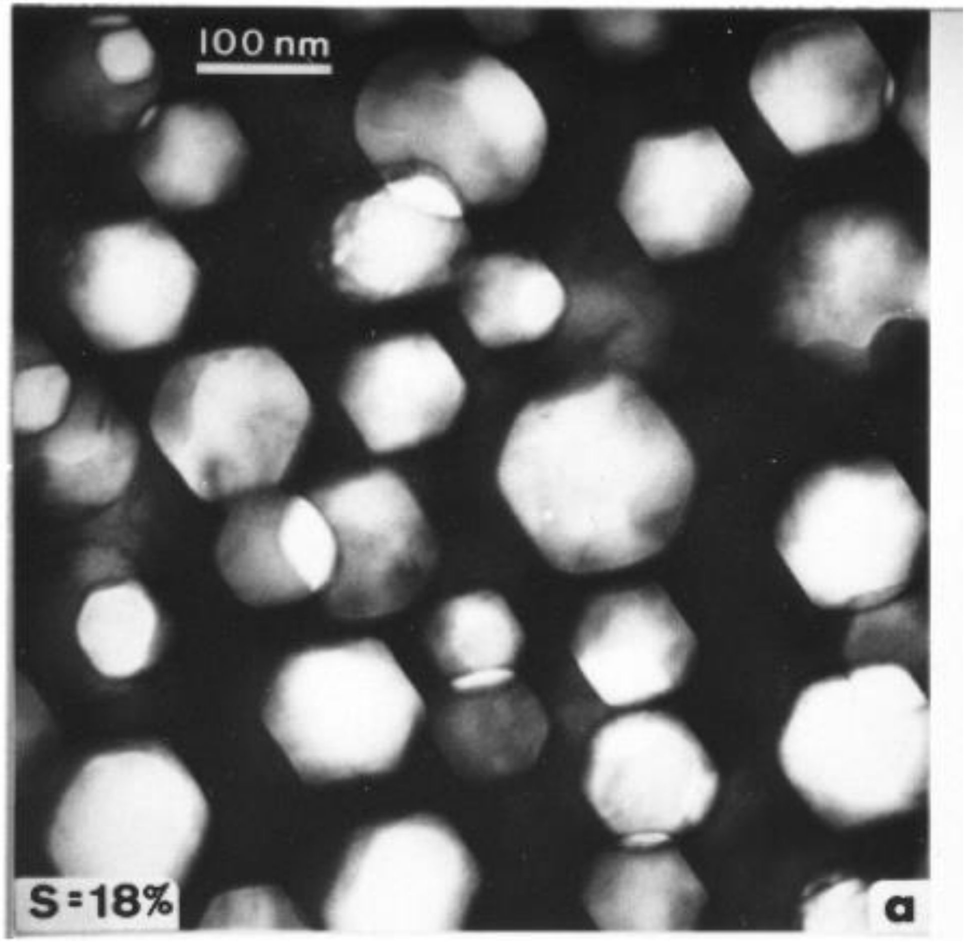
Temperature dependence for void swelling involves balance between recombination and vacancy emission



Zinkle, ASTM STP 1125 (1992) p. 813

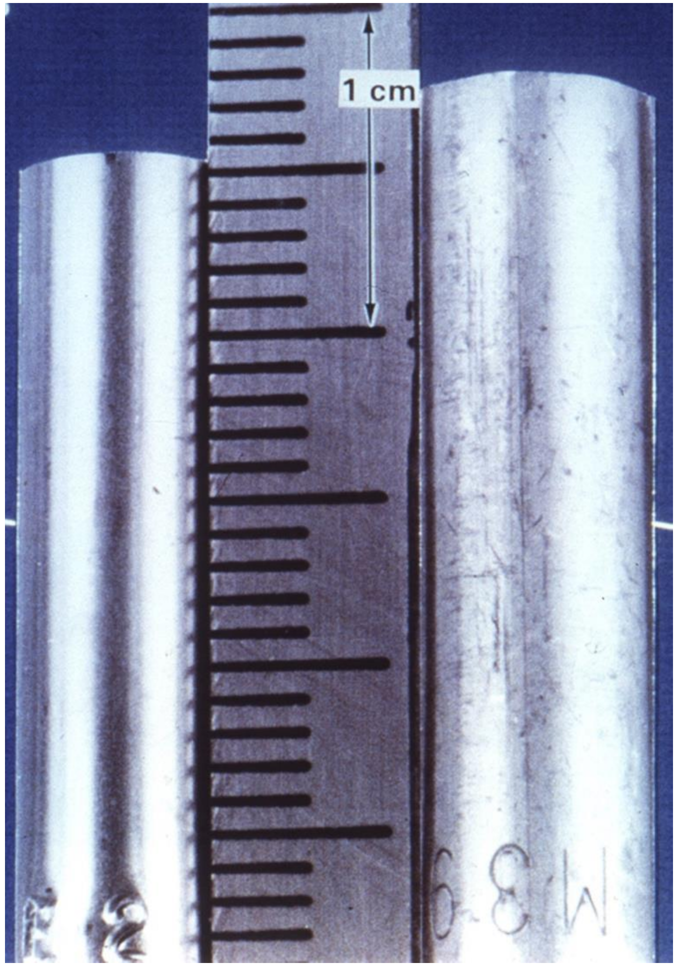
Physical effect of void formation in a material

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 $T=523^{0}C$, $1.5x10^{23} n/cm^2$



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

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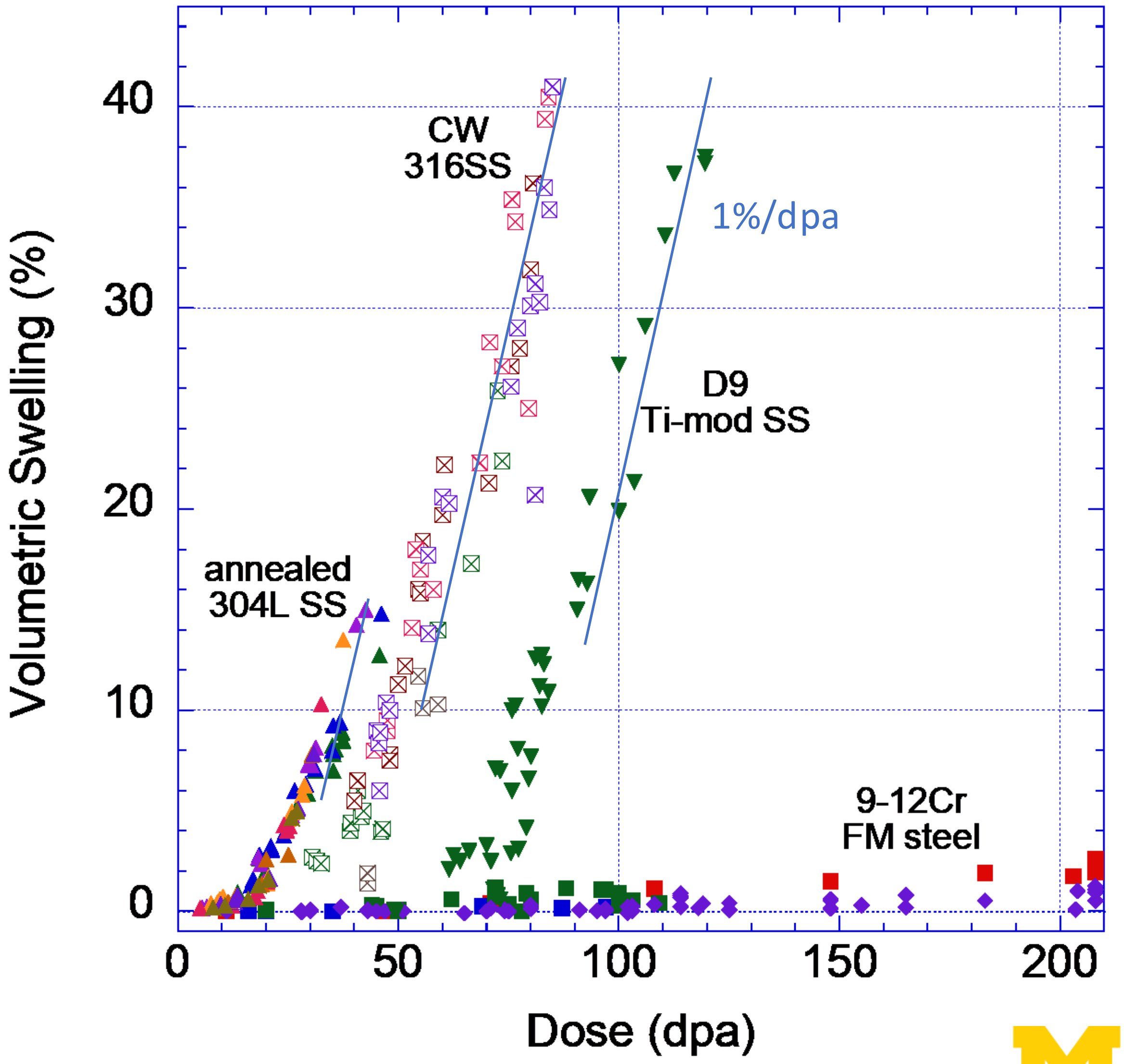
Physical effect of void formation in a material

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:

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



Zinkle & Was, Acta Mater. 61 (2013)

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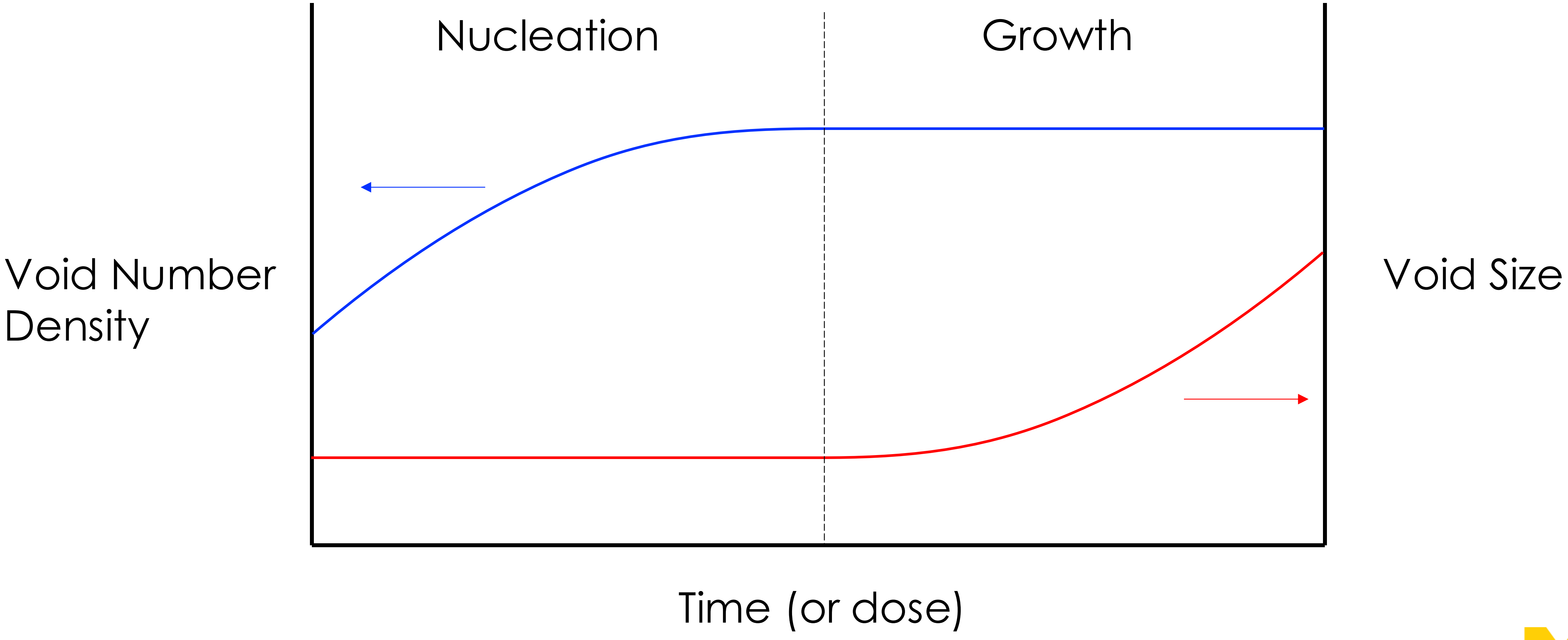
Half Time! – This pink elephant is in DeForest, Wisconsin. Based Google Maps how many miles is it from the ERB building at University of Wisconsin – Madison?

Nucleation vs. Growth



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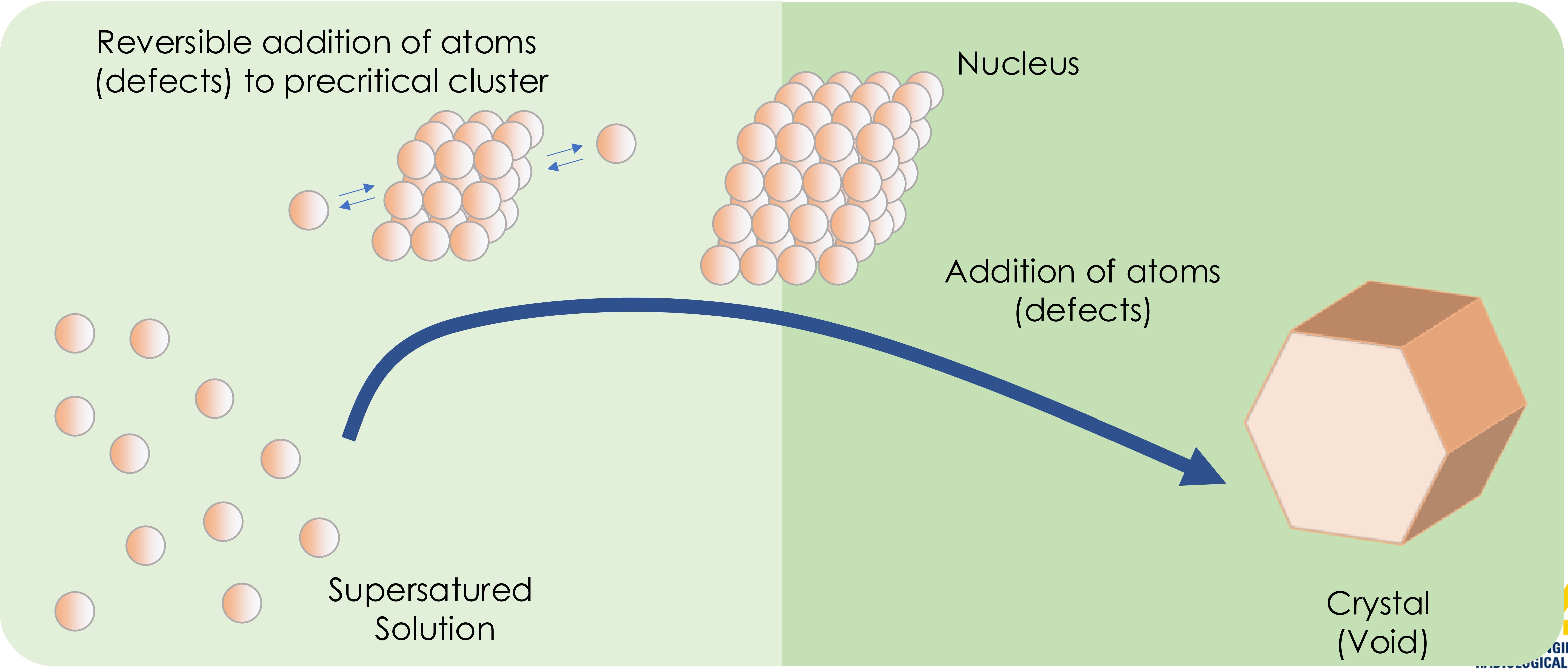
Nucleation

The nucleation theory used in nuclear materials is commonly the *classical pathway* description



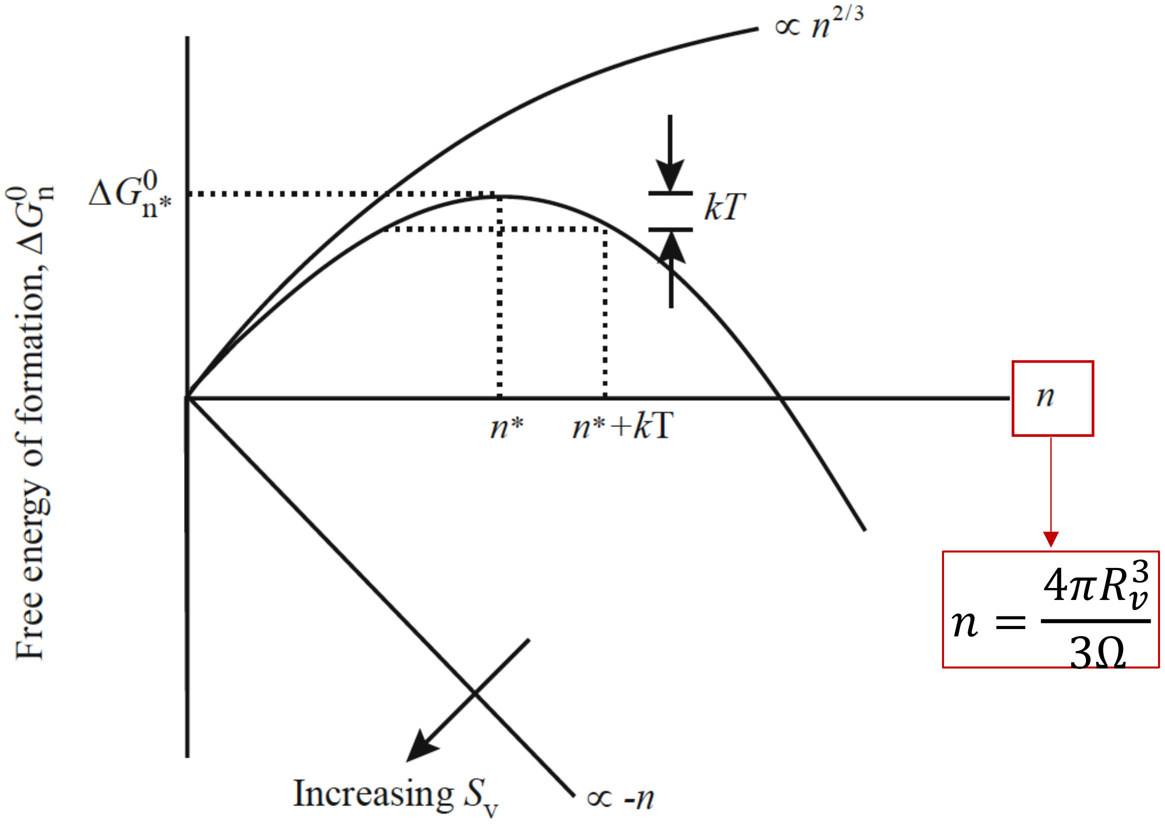
Void Nucleation Theory

- 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

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

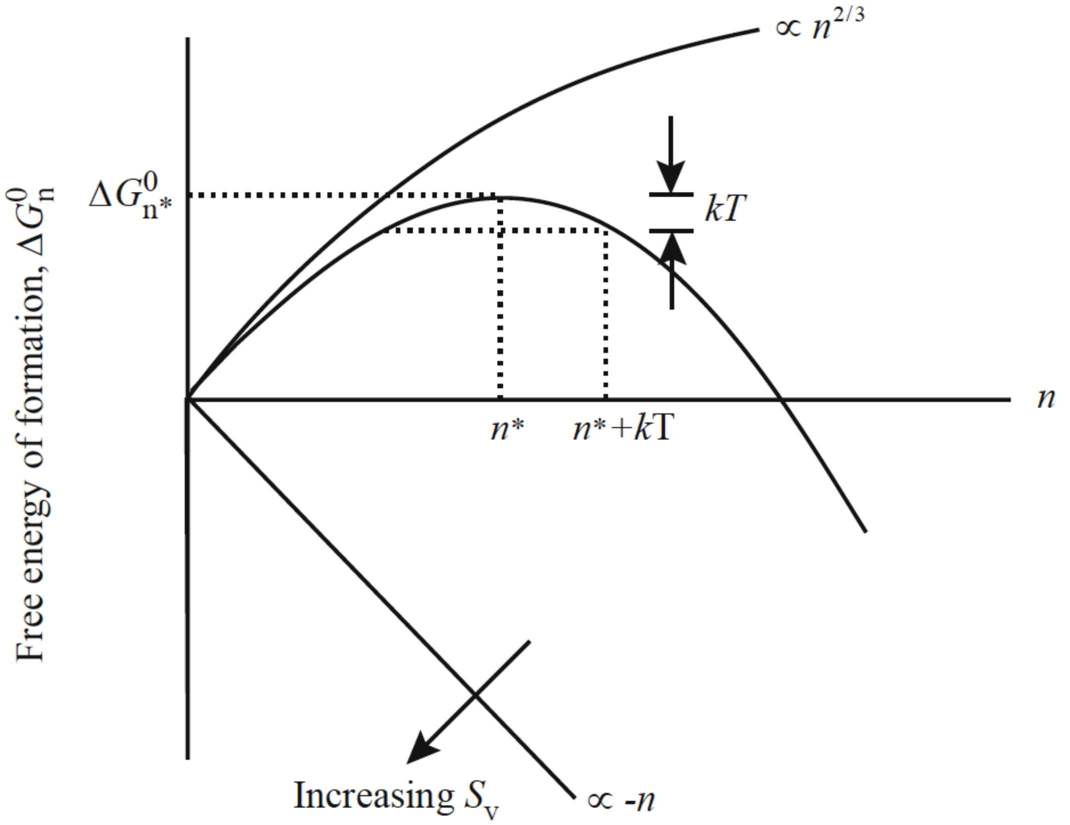


Full derivations and discussion in Was 8.1

Fig. 8.2 Schematic illustration of ΔG^0_n, 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

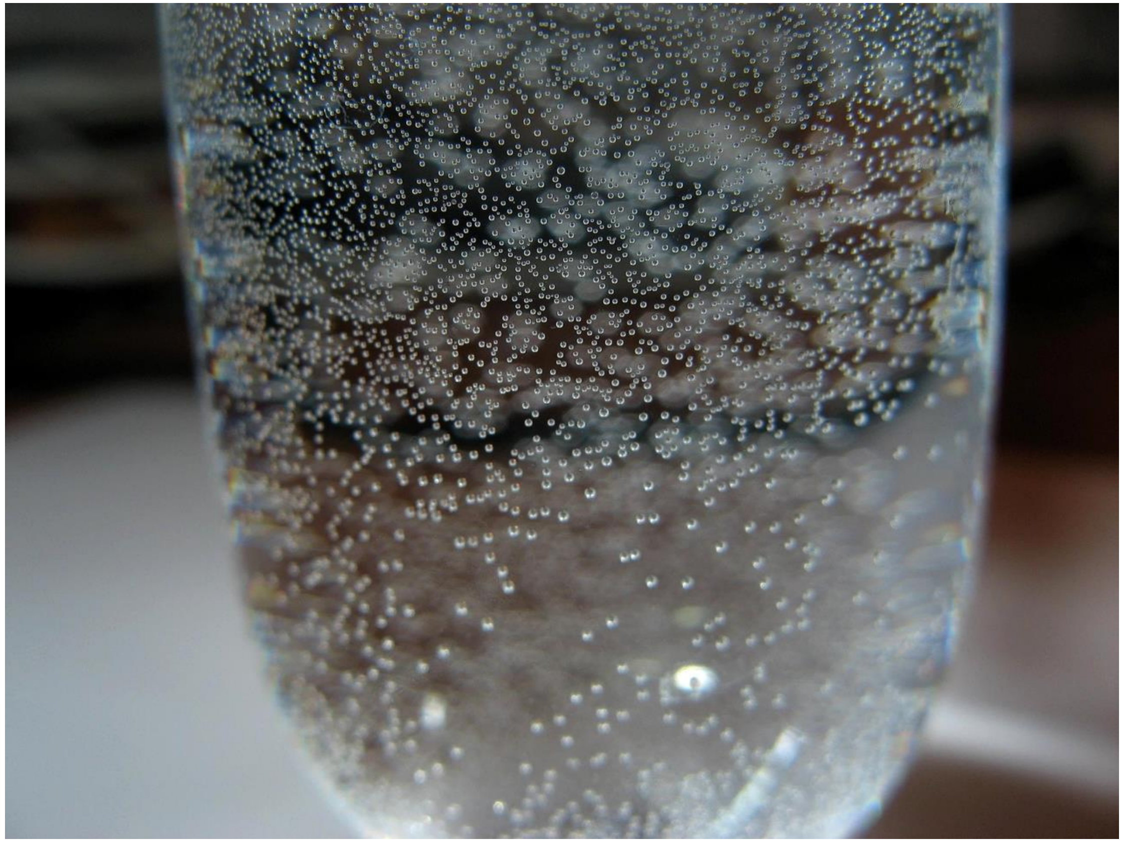
$$\Delta G_n^0 = -nkT \cdot \ln(S_v) + (36\pi\Omega^2)^{1/3}\gamma n^{2/3}$$



Derivations and discussion in Was 8.1

We can solve for n* by:

Void Nucleation Theory: Graphical depiction



- 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

Derivations and discussion in Was 8.1

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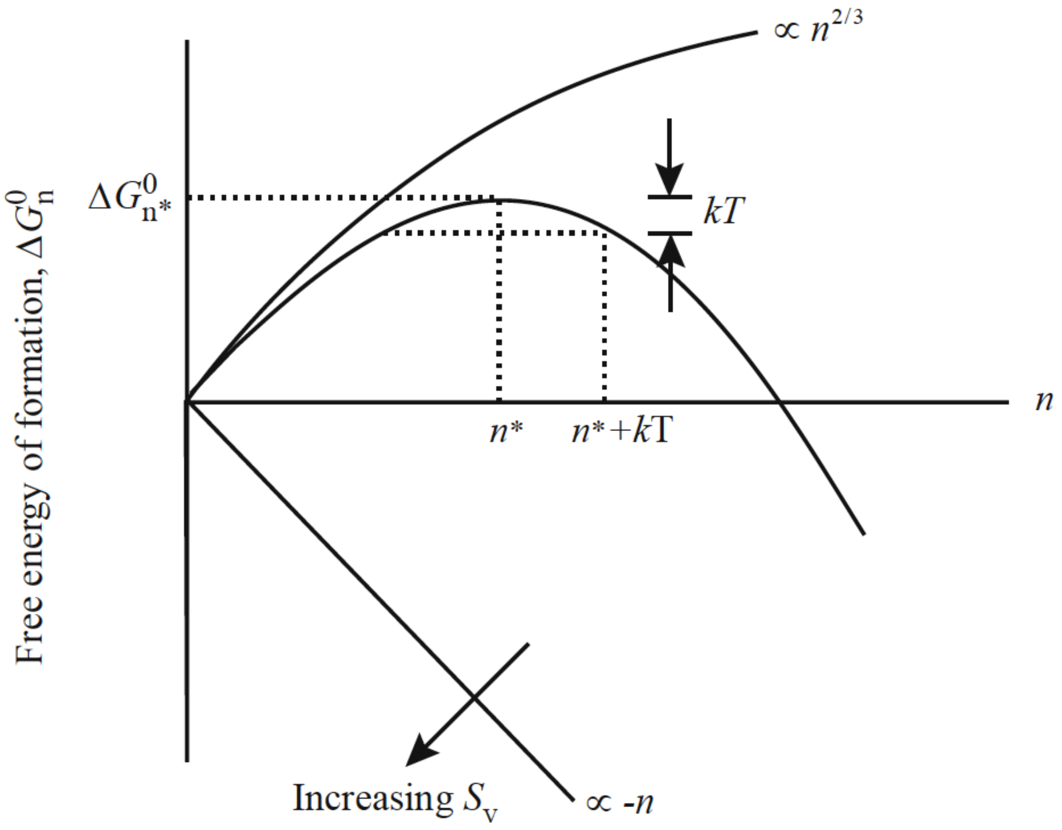
Void Nucleation Theory: Graphical depiction



- 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?

Derivations and discussion in Was 8.1

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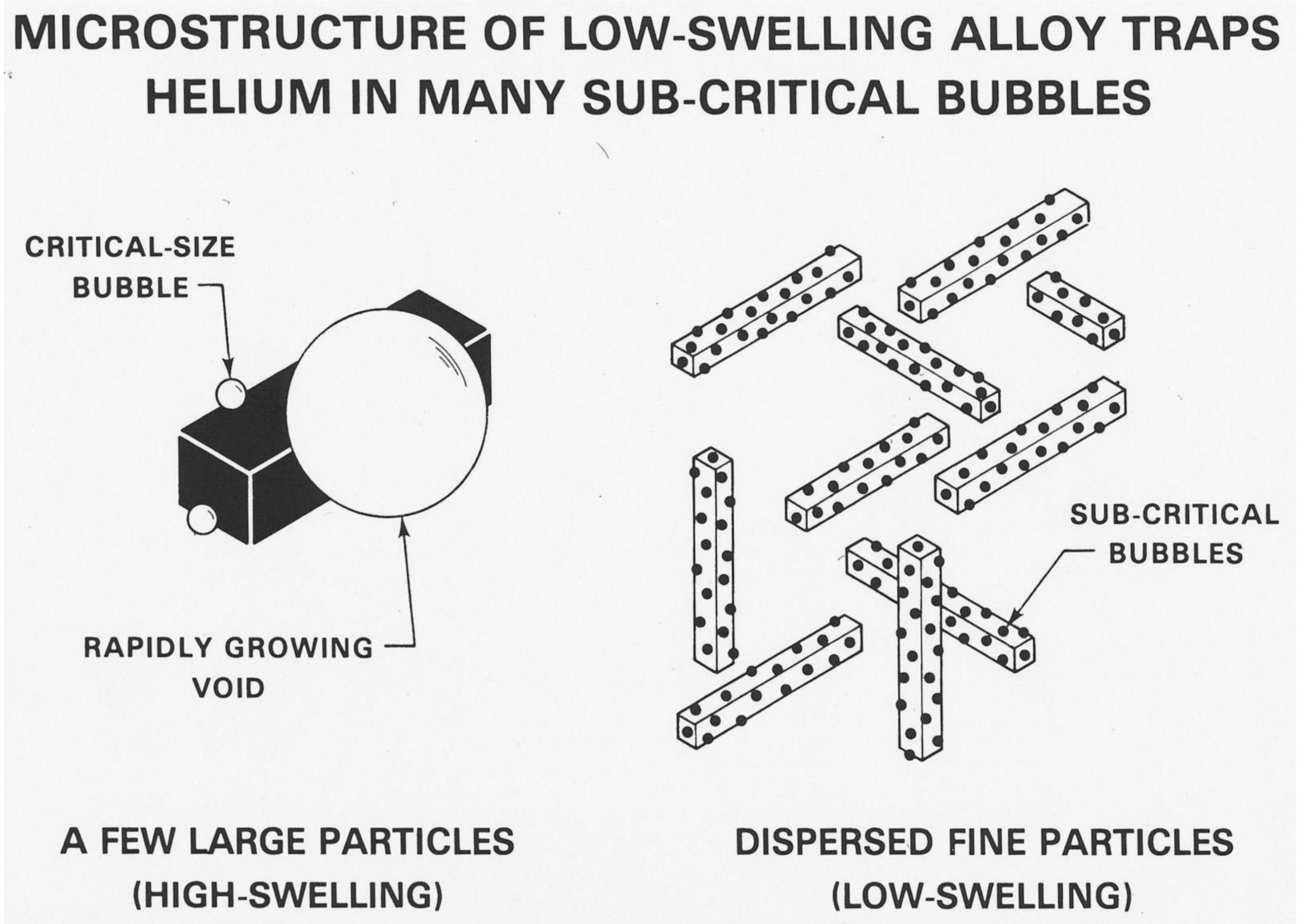
Design for Radiation Resistance III: High Sink Strength



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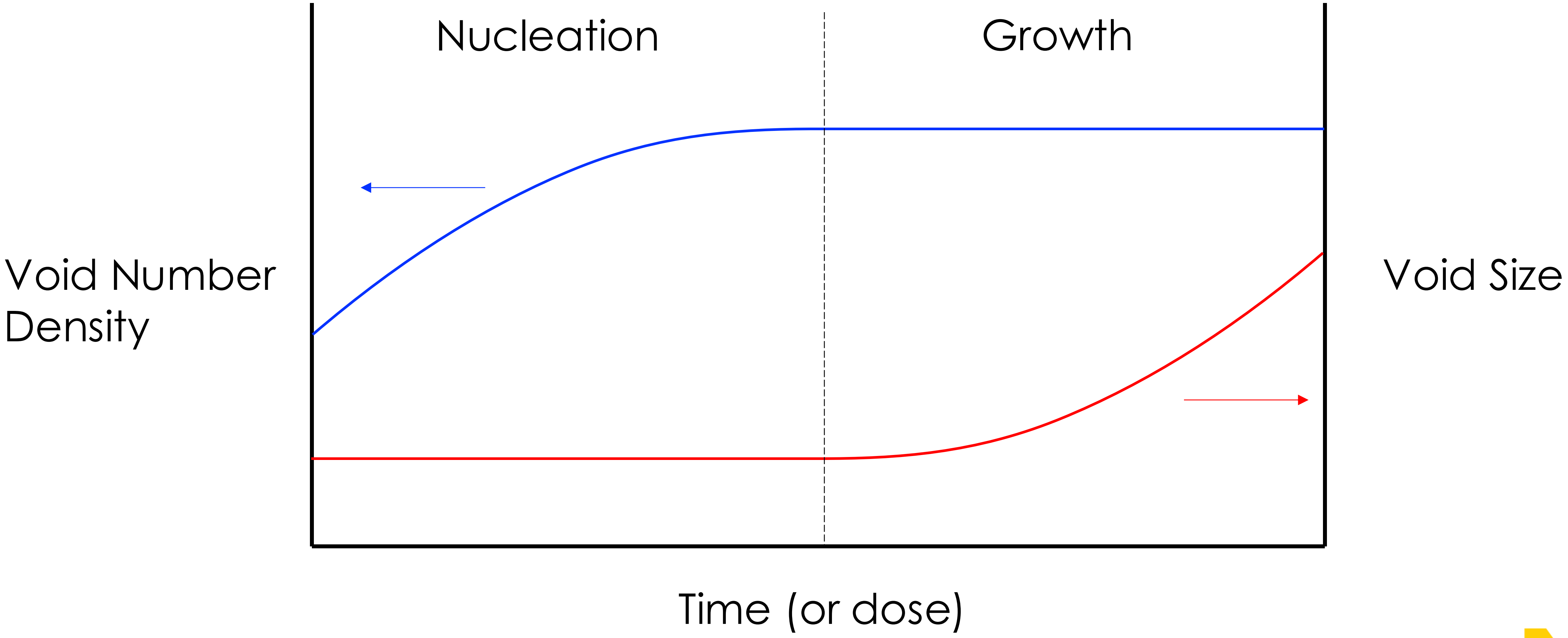
Nucleation vs. Growth



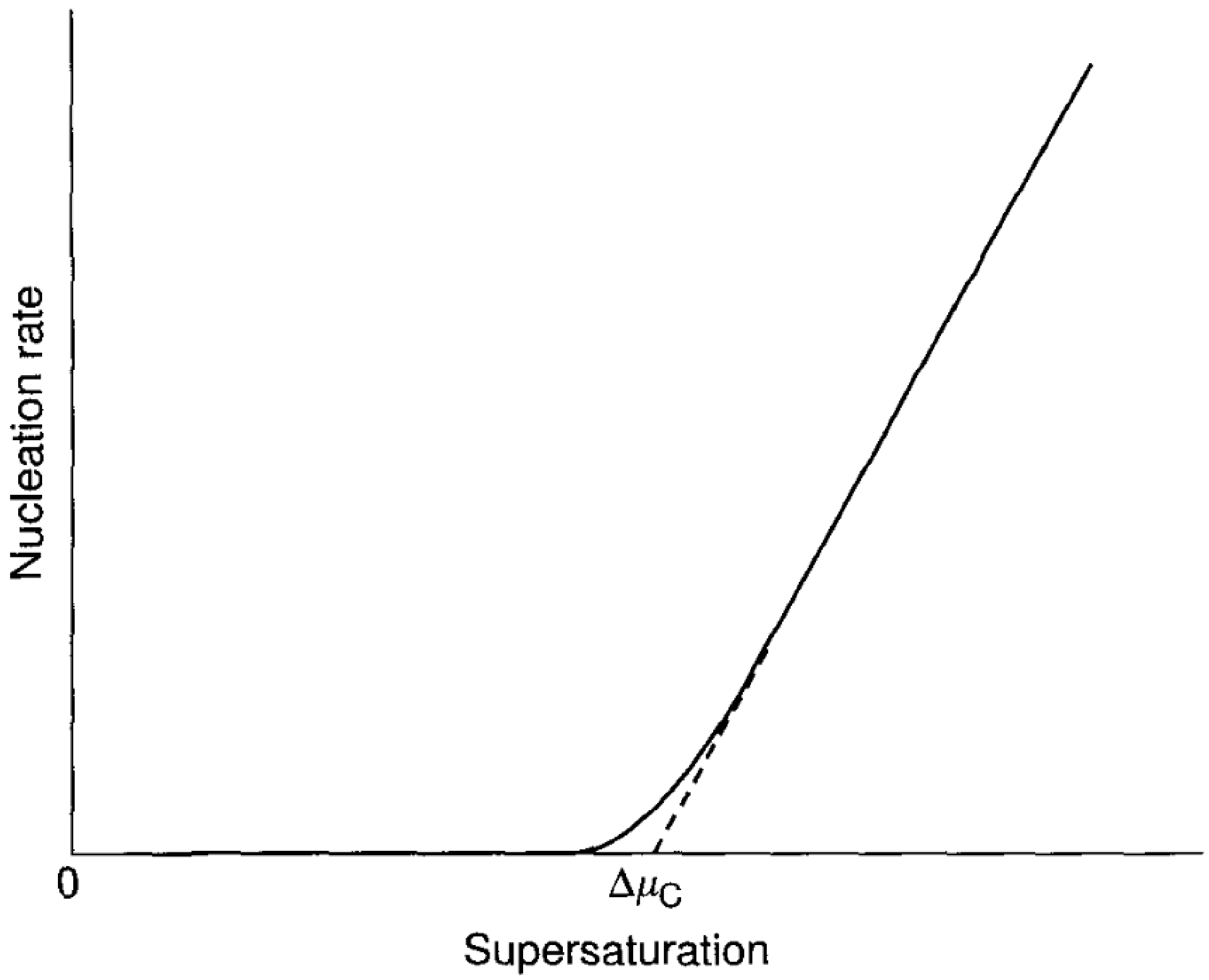
Void Nucleation Rate

Nucleation rate can be generalized as:

$$J_0 = exp\left(-\frac{\boldsymbol{\Delta G}}{kT}\right)$$

But it depends on:

- Dose rate
- Temperature
- Sink density, etc.



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Void Nucleation Rate

- Nucleation of v_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 v absorption: $v + v_j \rightarrow v_{j+1}$
  2. More generally, we consider **small cluster mobility**: $v_j + v_k \rightarrow v_{j+k}$
  3. **Cluster shrinkage** by v emission: $v_j \rightarrow v_{j-1} + v$
     - Depends on equilibrium v concentration at void surface - C_v^0 from the rate of absorption of v by cavities and also depends on the binding energy between the v and the cluster
  4. **Cluster shrinkage** by *i* absorption: $v_j + i_k \rightarrow v_{j-k}$
     - Depends on *i* and i_k concentrations
  5. Growth by *i* emission is neglected, e.g. $C_i^0 \sim 0$

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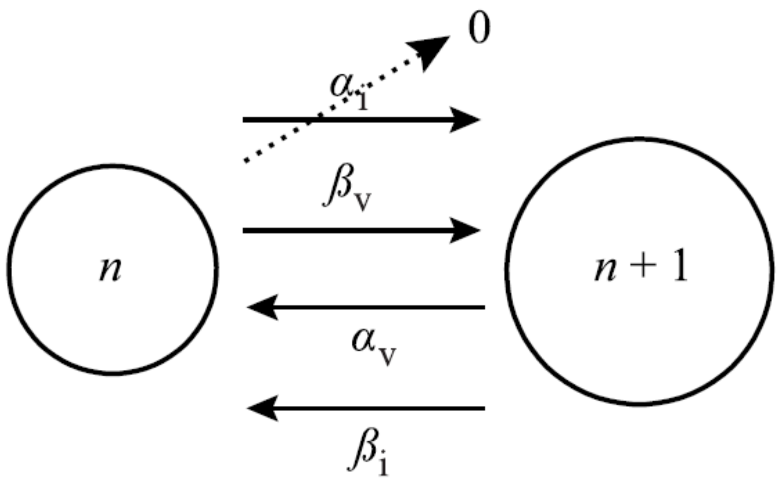
Void Nucleation Rate

- 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 $n+1$

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Void Nucleation Rate

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

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

- 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!)

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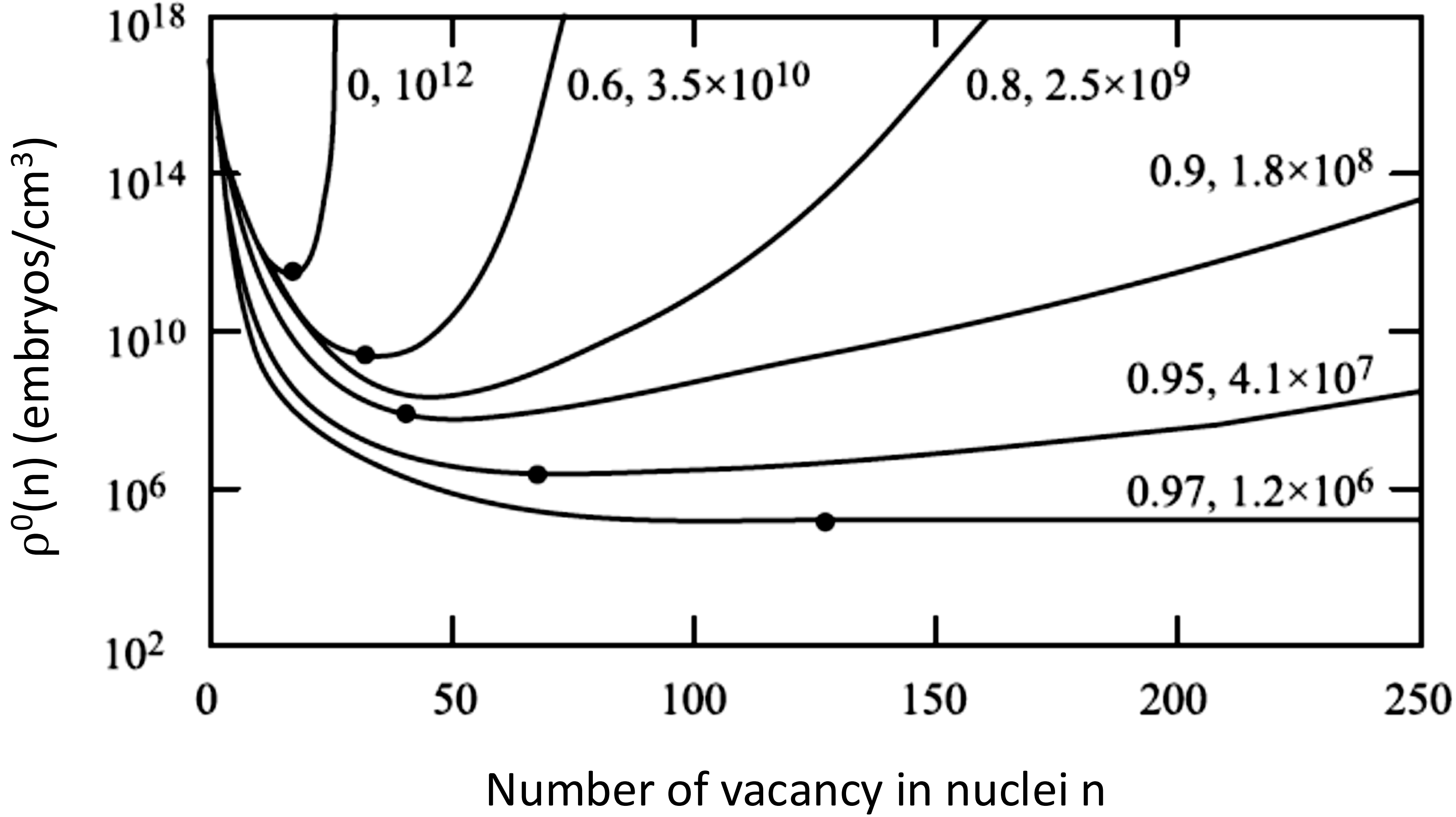

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Void Nucleation Rate

- To obtain void nucleation as $(D_iC_i)/(D_vC_v)$ approaches 1 requires higher vacancy supersaturation
- Strong dependence of nucleation on vacancy supersaturation

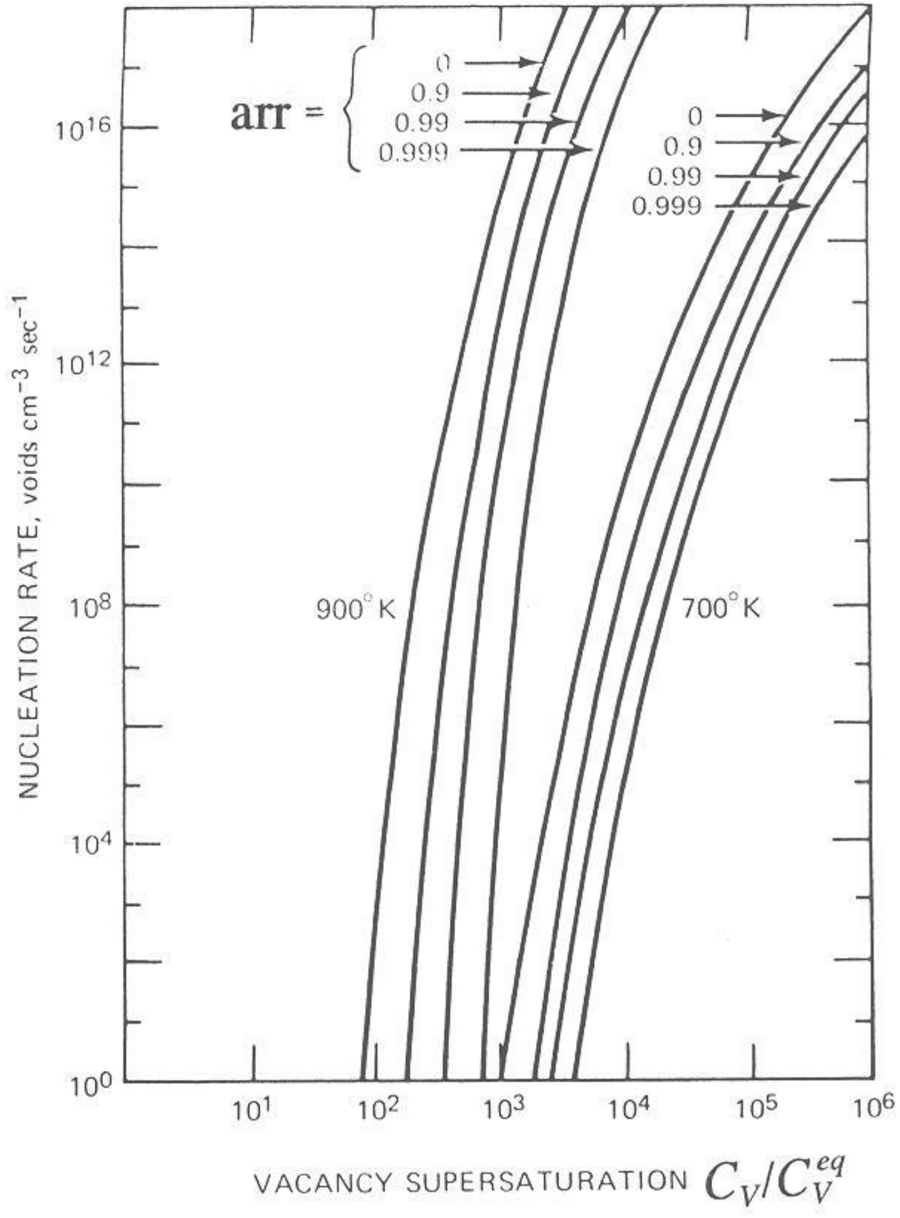
<u>Typical results:</u>

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

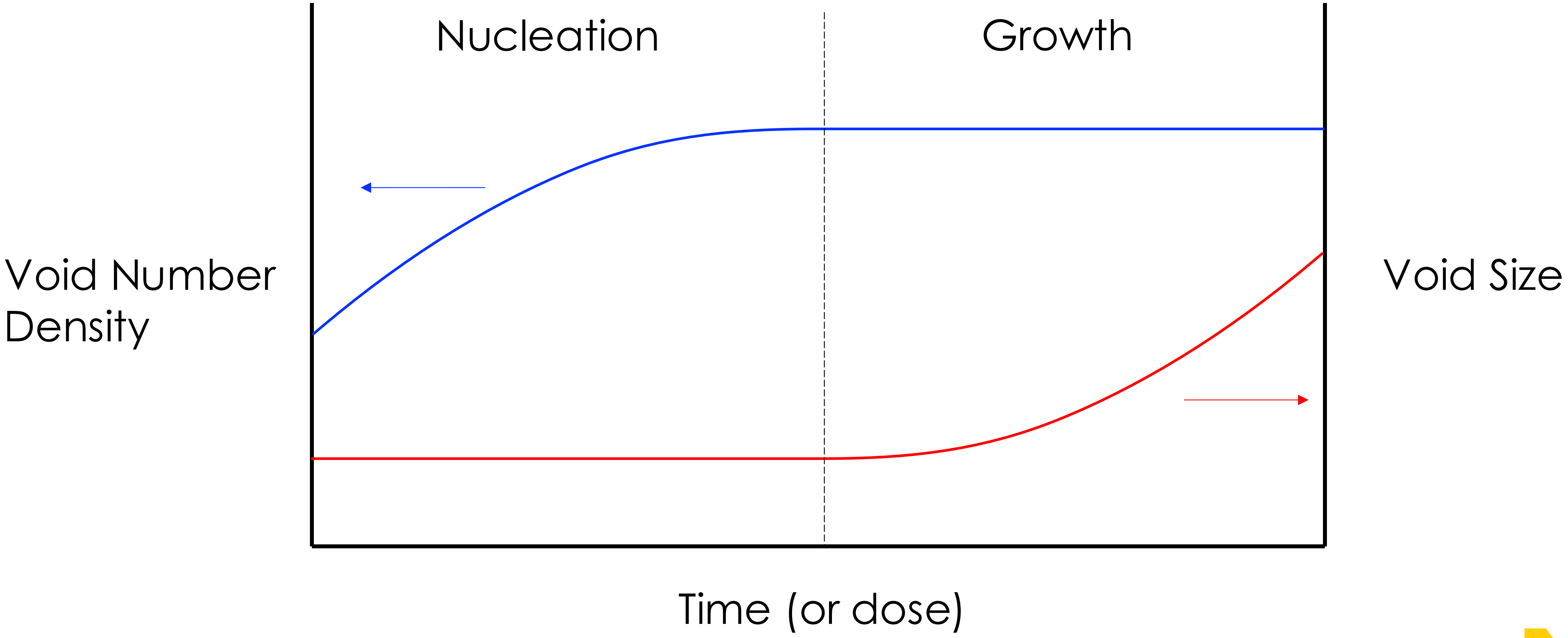
arr = $(D_IC_I)/(D_vC_v) = 0.99$

J ~ 10^8 voids nucleated/cm^3/s

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

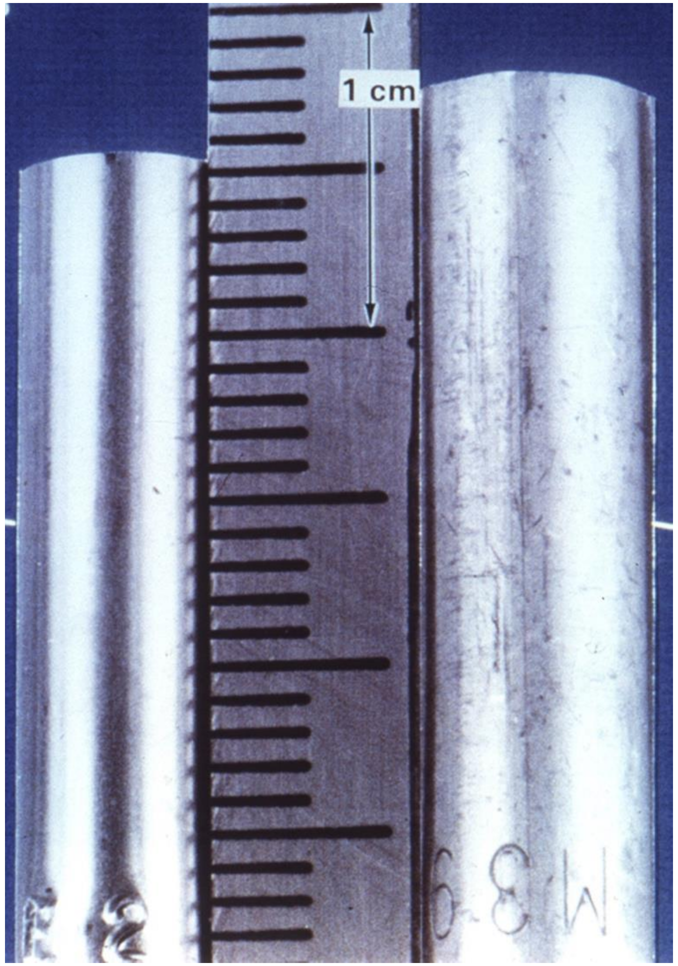


Nucleation vs. Growth



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 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:



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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

$$ {}^{dV}\!/_{dt} = 4\pi R\Omega(D_v C_v - D_i C_i) $$

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

Void Growth

Remember:

$$C_v = \frac{-K_{is}C_s}{2K_{iv}} + \left[\frac{K_0 K_{is}}{K_{iv}K_{vs}} + \frac{K_{is}^2 C_s^2}{4K_{iv}}\right]^{1/2}$$

$$C_i = \frac{-K_{vs}C_s}{2K_{iv}} + \left[\frac{K_0 K_{vs}}{K_{iv}K_{is}} + \frac{K_{vs}^2 C_s^2}{4K_{iv}}\right]^{1/2}$$

and

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

Void Growth

- With everything defined,

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

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

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

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

- 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:

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

Since h 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.

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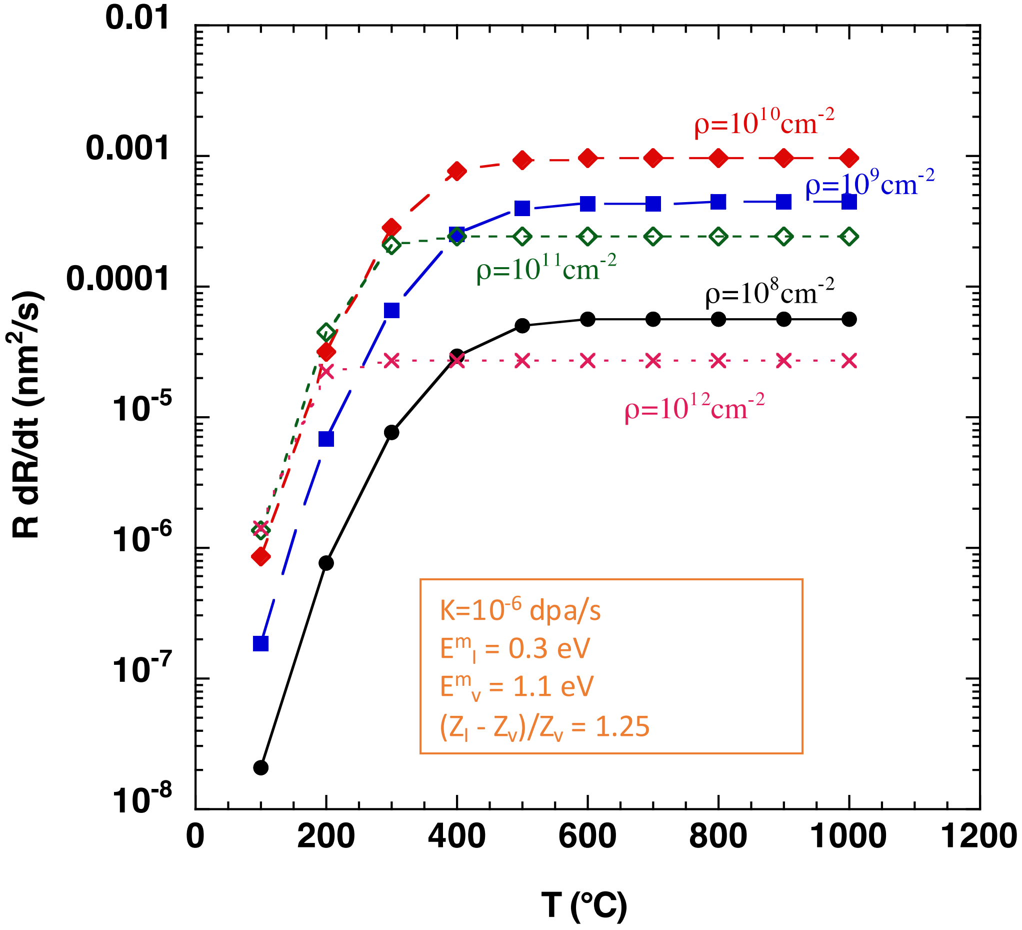
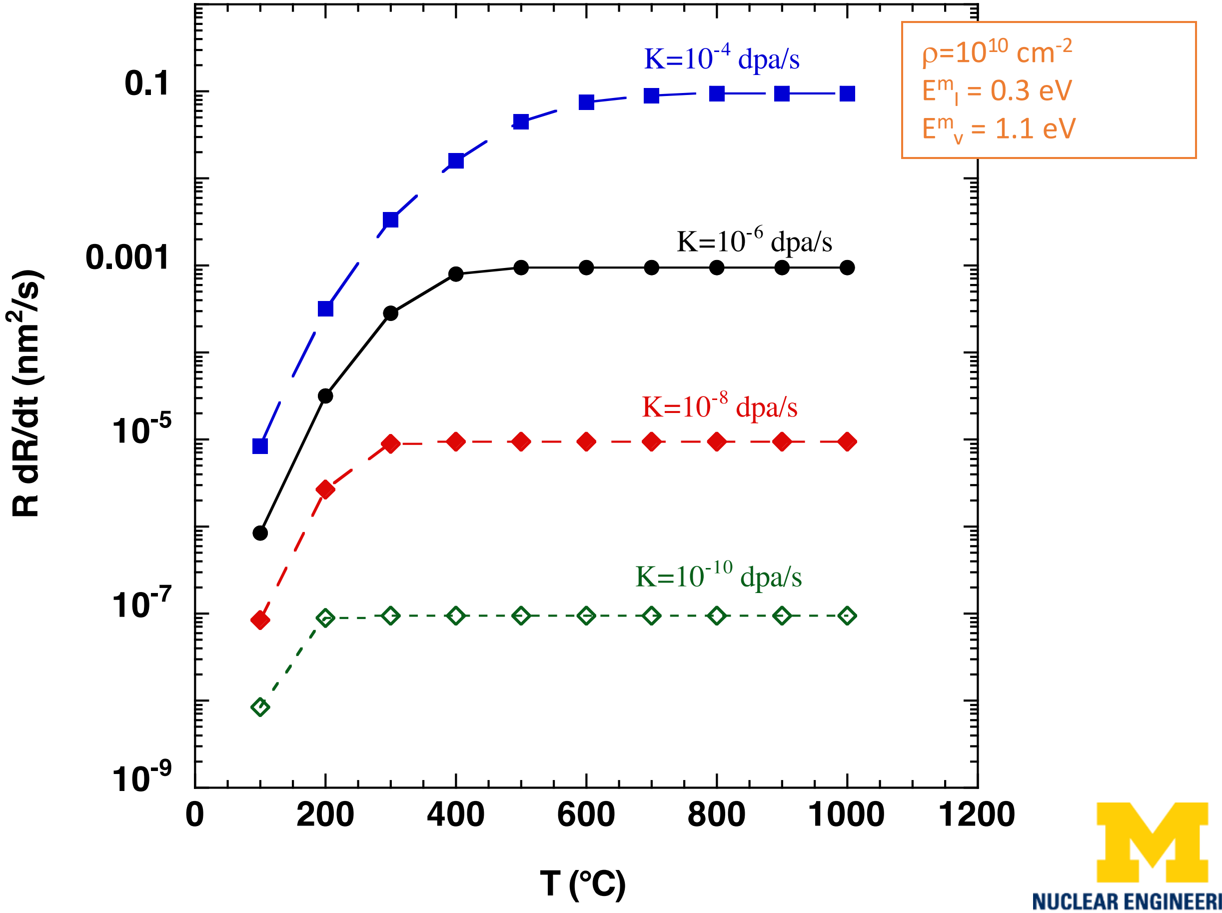
Void Growth

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





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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 ~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

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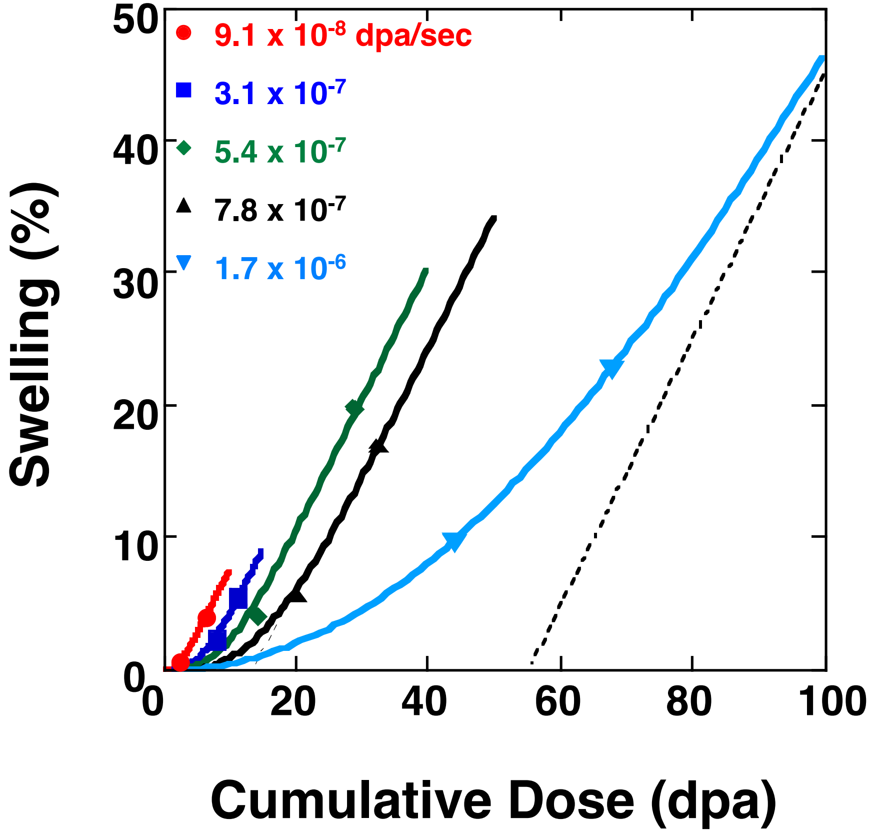
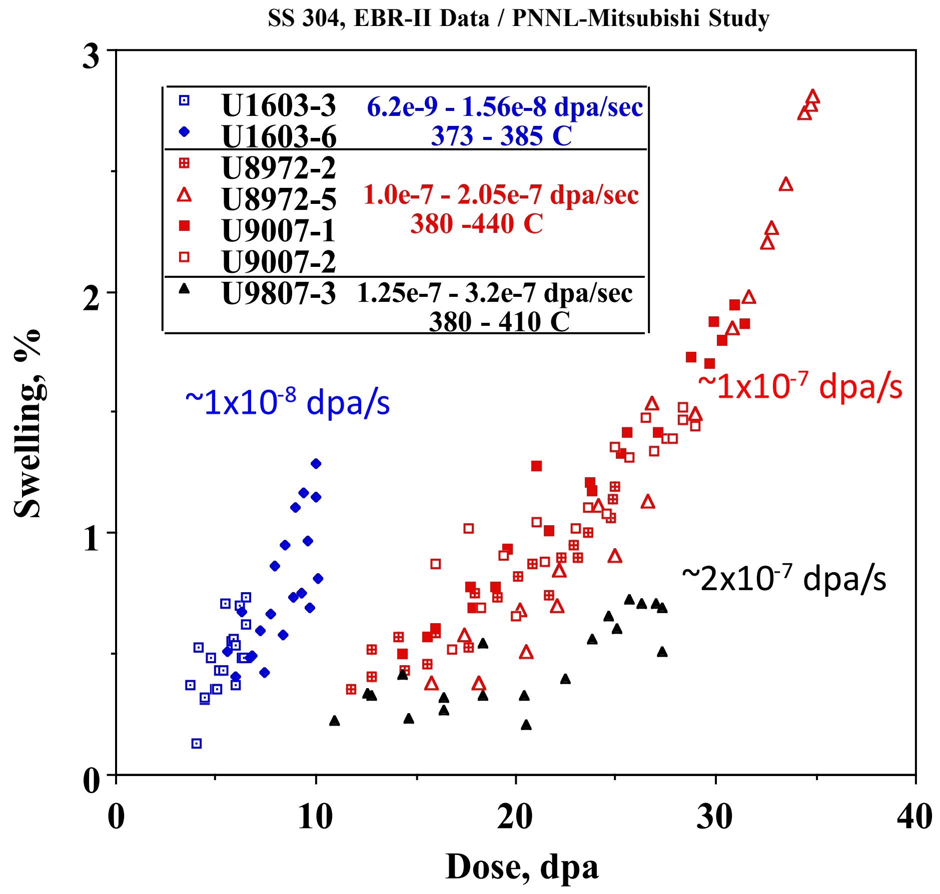
The onset of void swelling can be a strong function of the dose rate

Okita et al.

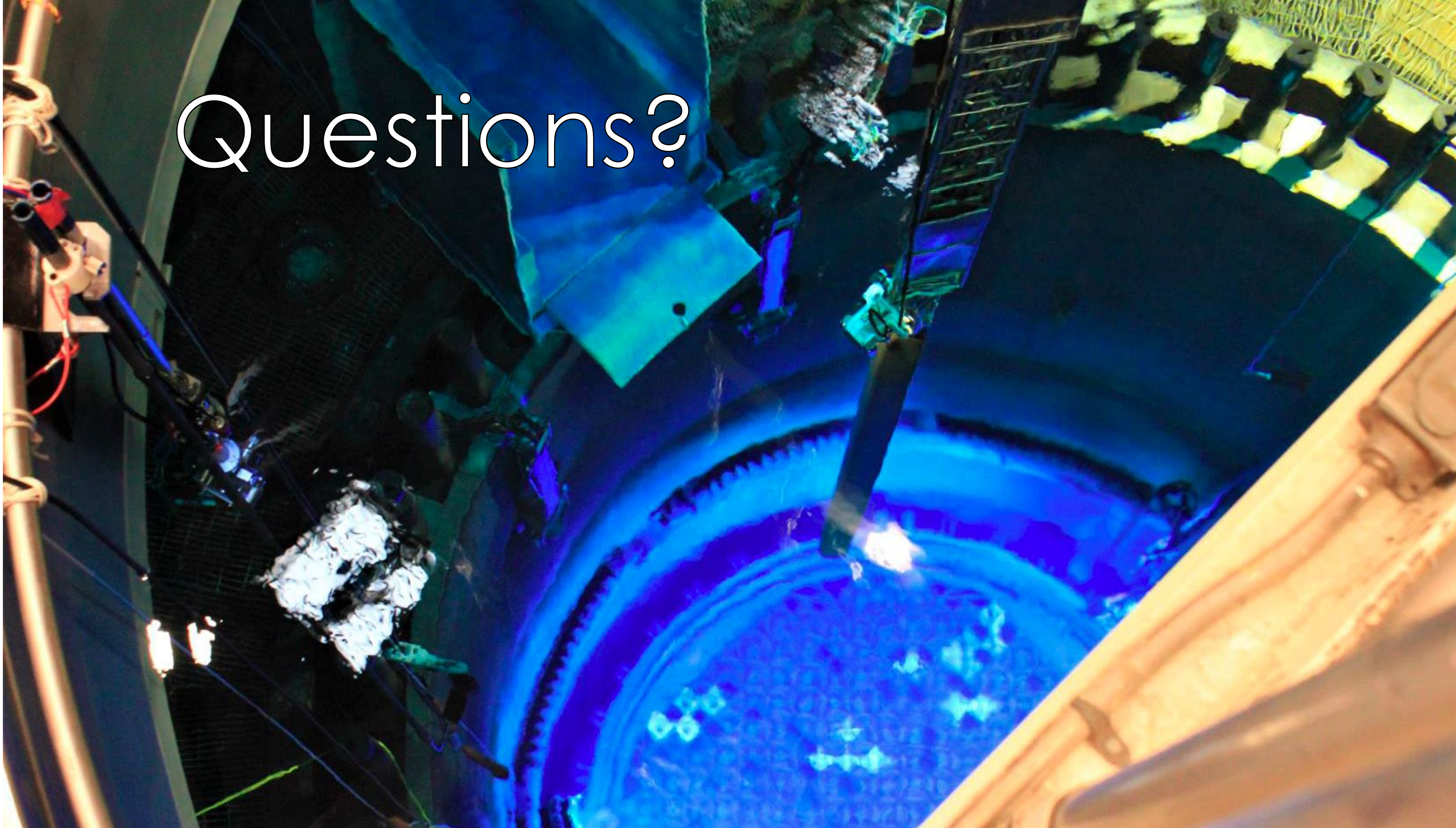
Pure 69% Fe, 15% Cr, 16% Ni
FFTF MOTA, 387-444 C



Garner et al., PNNL



W.G. Wolfer, LLNL


Questions?