

Voids II

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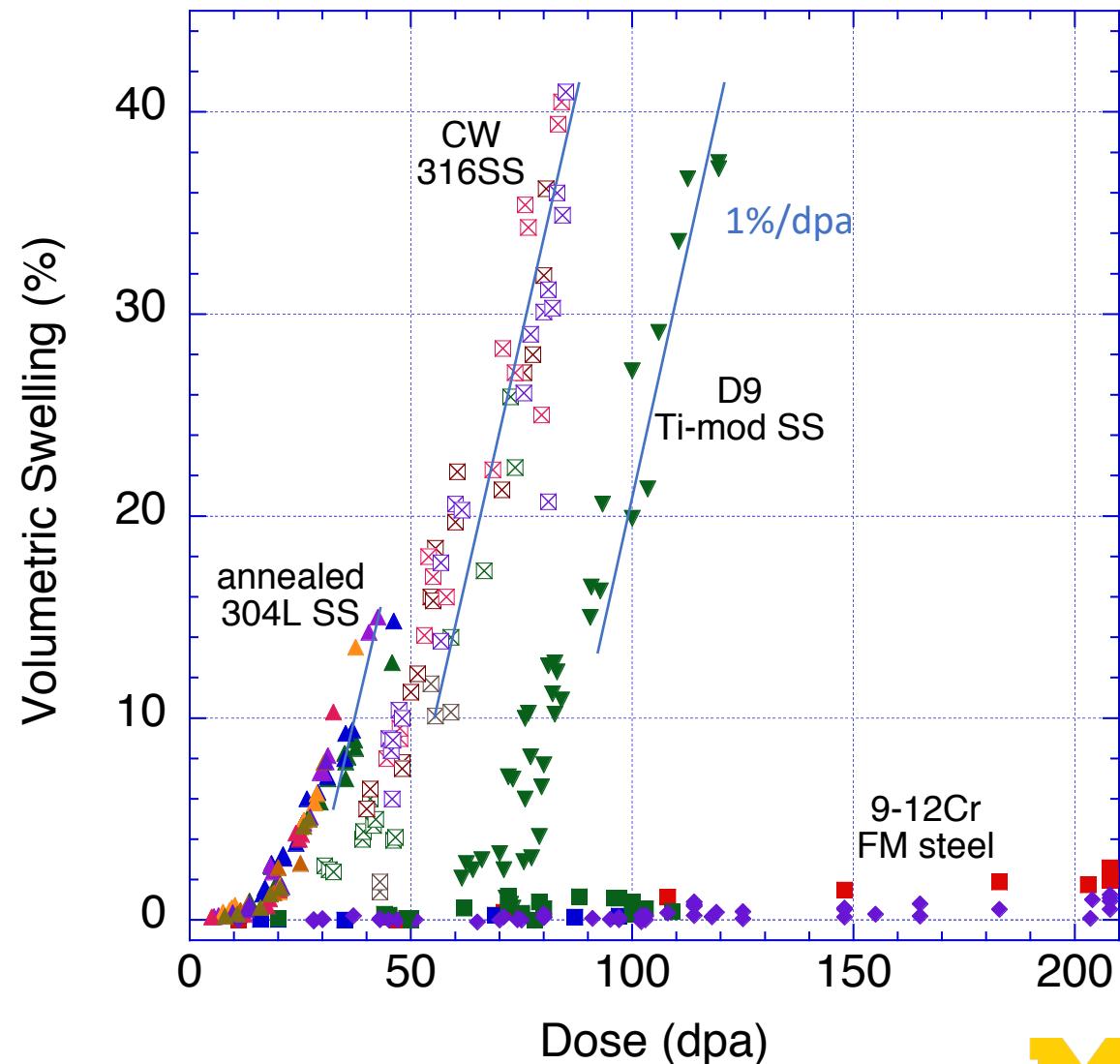
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Physical effect of void formation in a material

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:

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



Nucleation vs. Growth

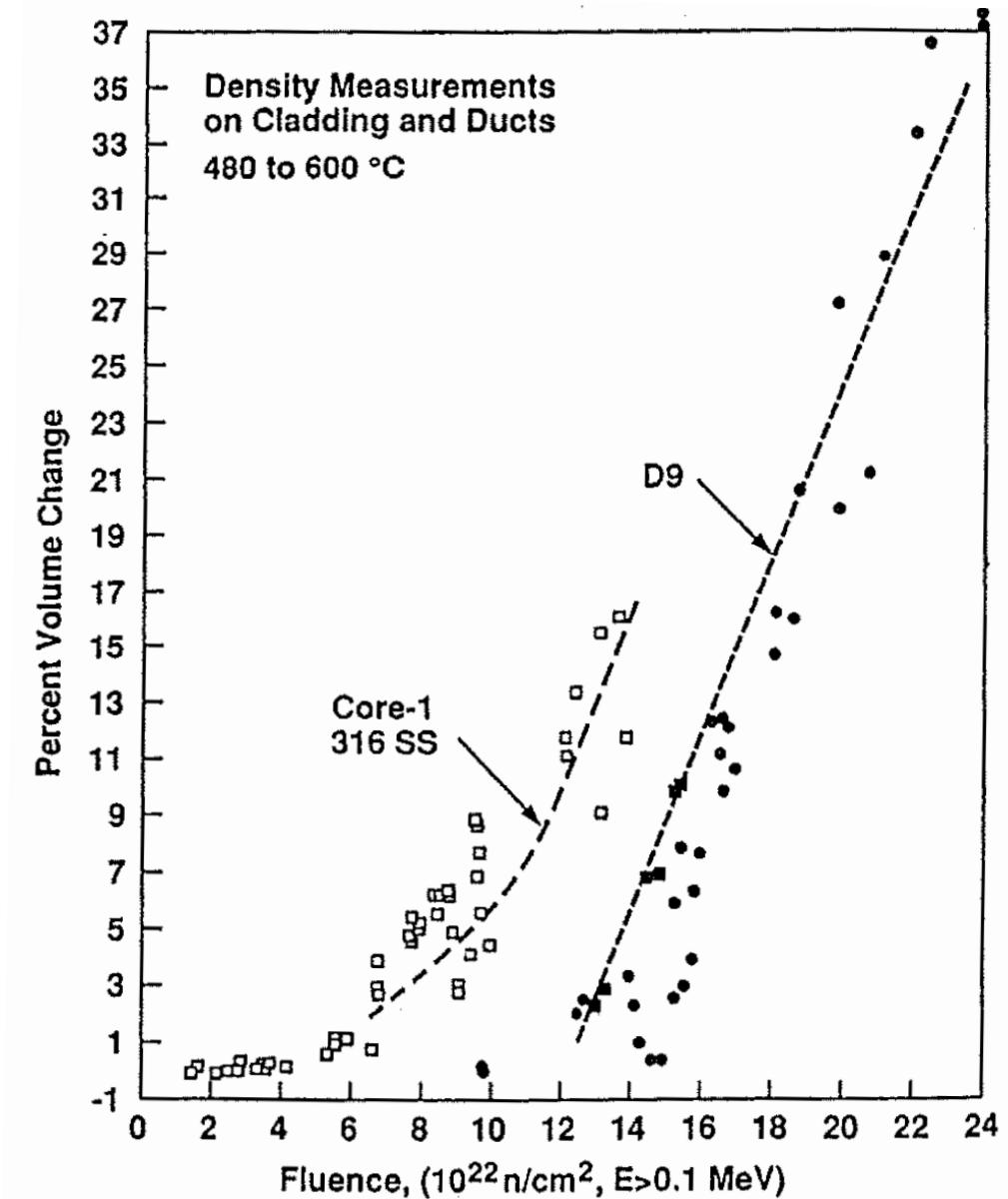
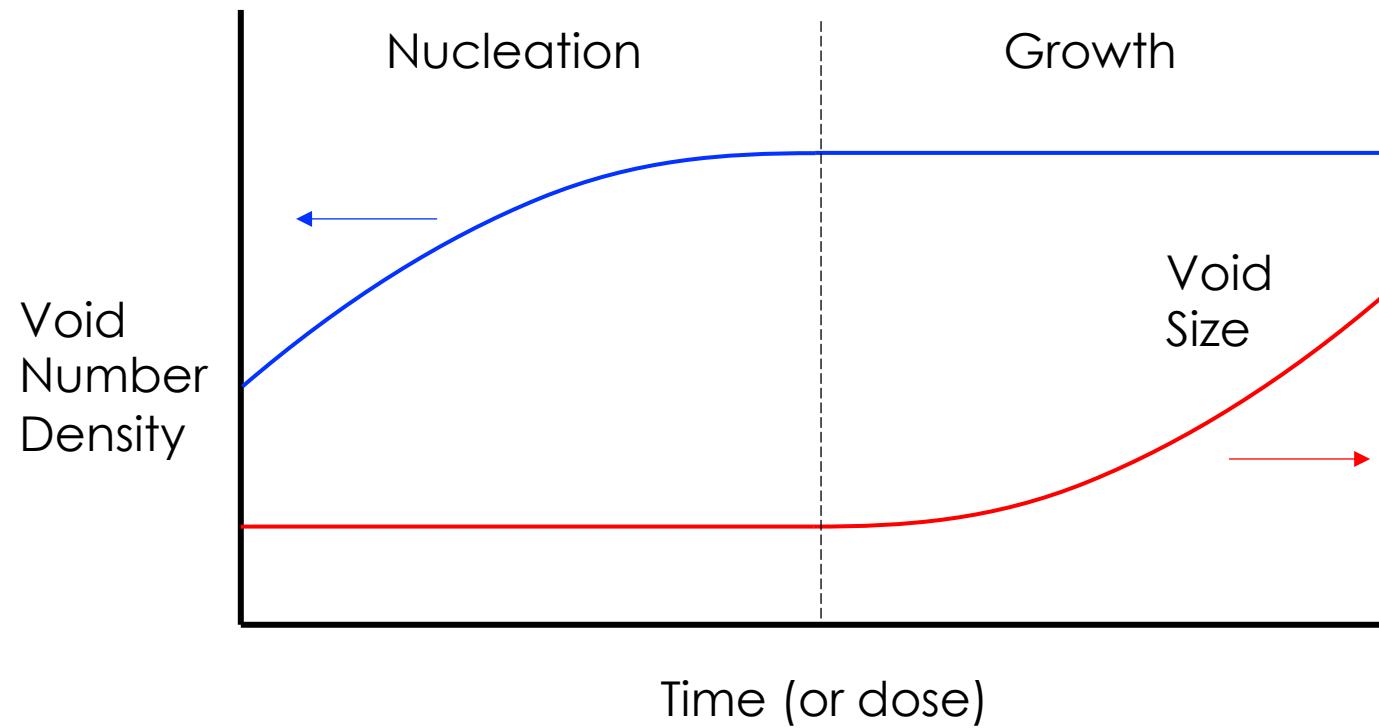
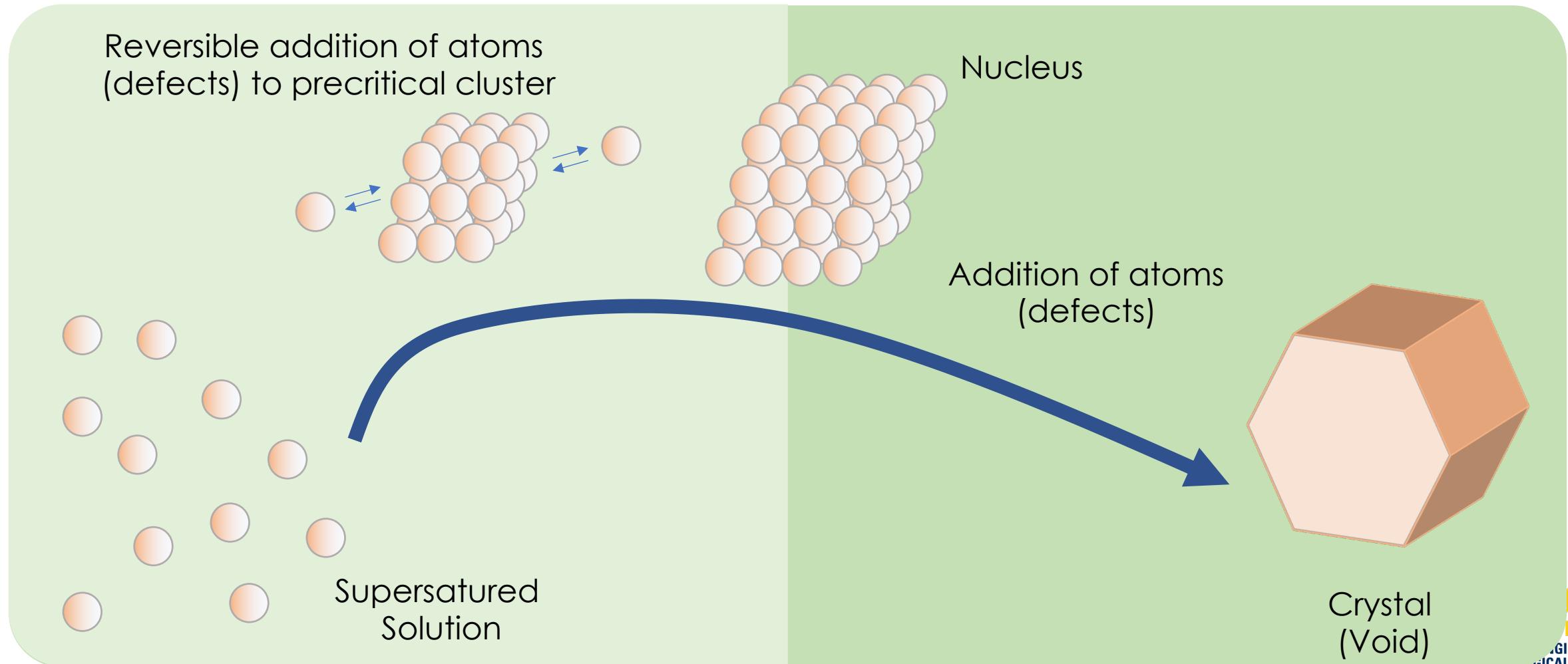


Fig. 3. Swelling observed in two cold-worked austenitic alloys after serving as fuel cladding in the open core of FFTF [23].

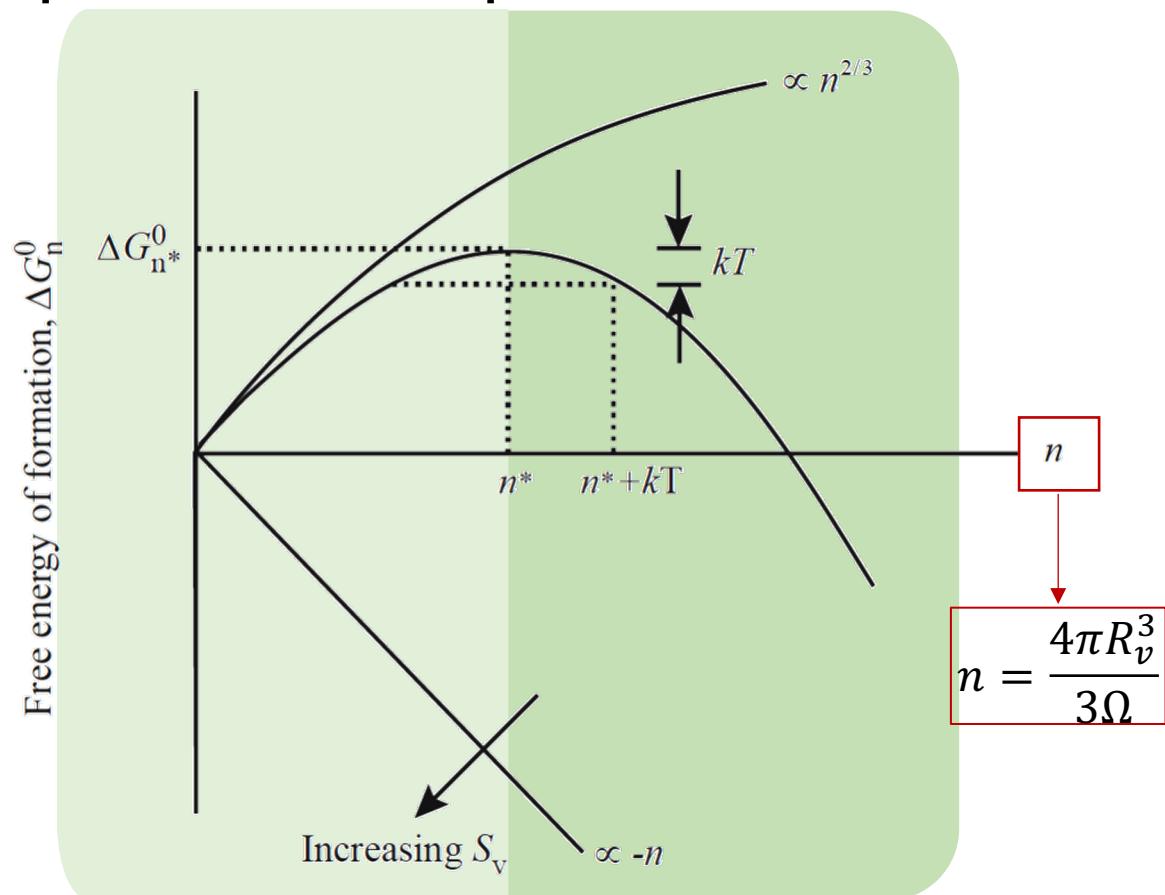
Nucleation

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



Void Nucleation Theory: Graphical depiction

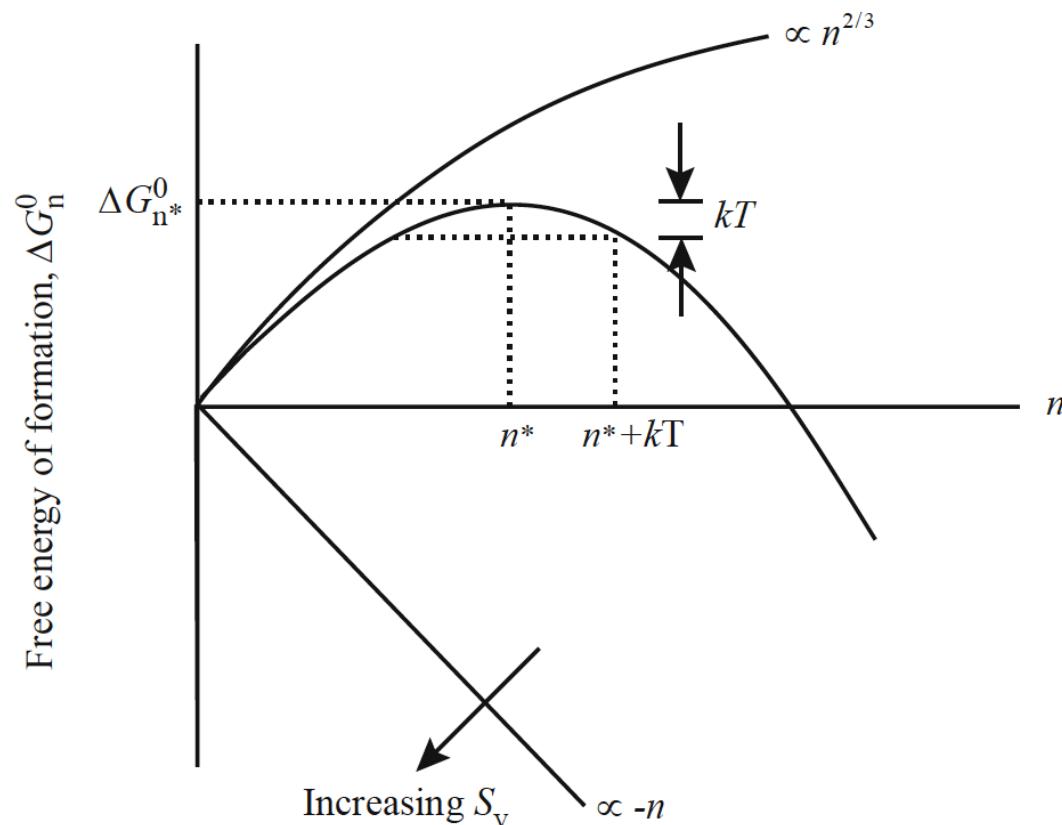
$$\Delta G_n^0 = -nkT \cdot \ln(S_v) + (36\pi\Omega^2)^{1/3} \gamma n^{2/3}$$



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



Derivations and
discussion in Was 8.1

We can solve for the critical embryo size, n^* or r^* , by:

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

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

Solve for n

$$n^* = \frac{32\pi\gamma^3\Omega^2}{3(k_b T \ln S_v)^3}$$

Convert to r

$$r^* = \frac{2\gamma\Omega}{(k_b T \ln S_v)}$$

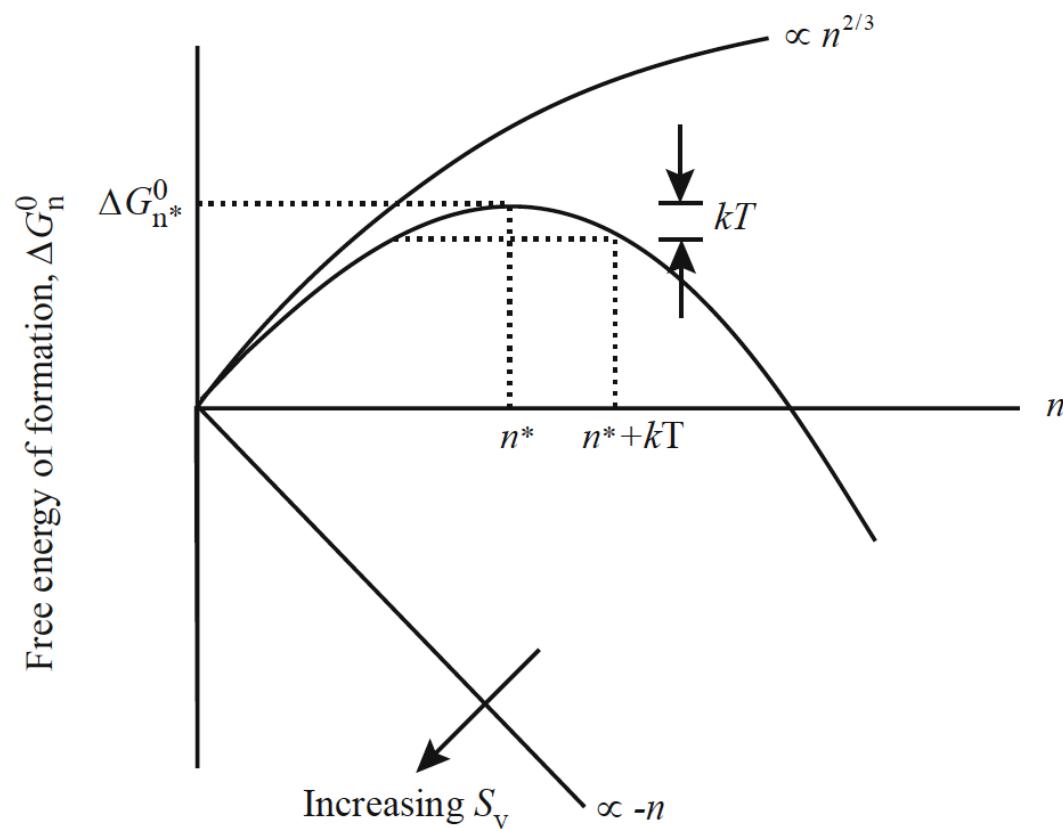
Void Nucleation Theory: Graphical depiction



- 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

Void Nucleation Theory: Graphical depiction



Derivations and discussion in Was 8.1

- Homogeneous nucleation:

When supercritical particles are formed due to thermal fluctuations

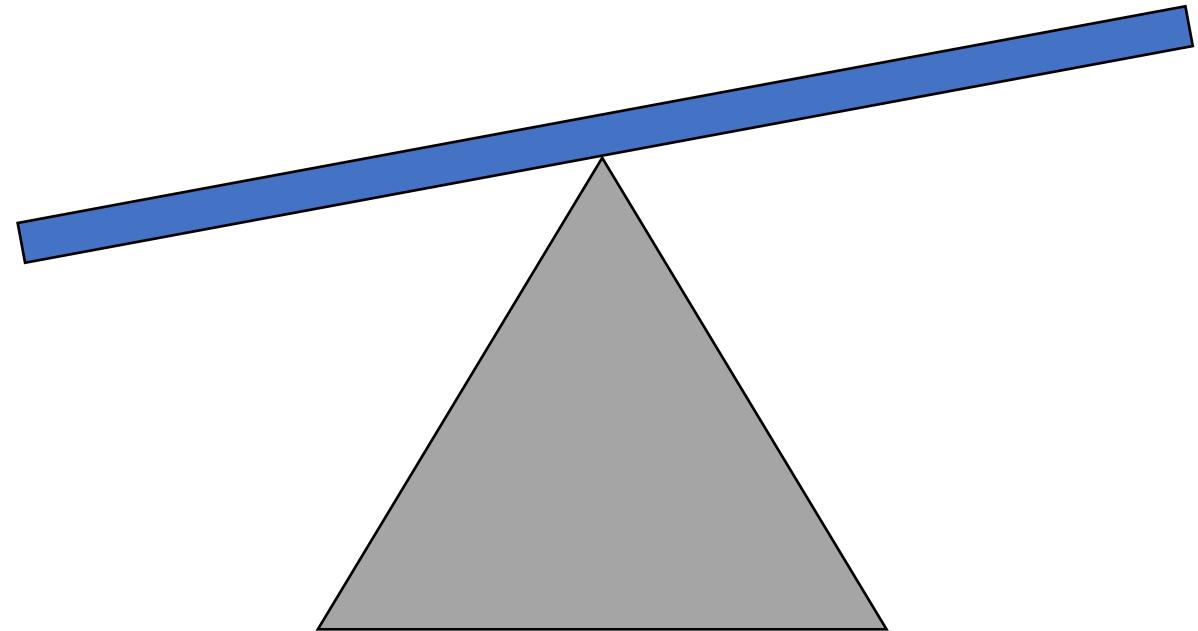
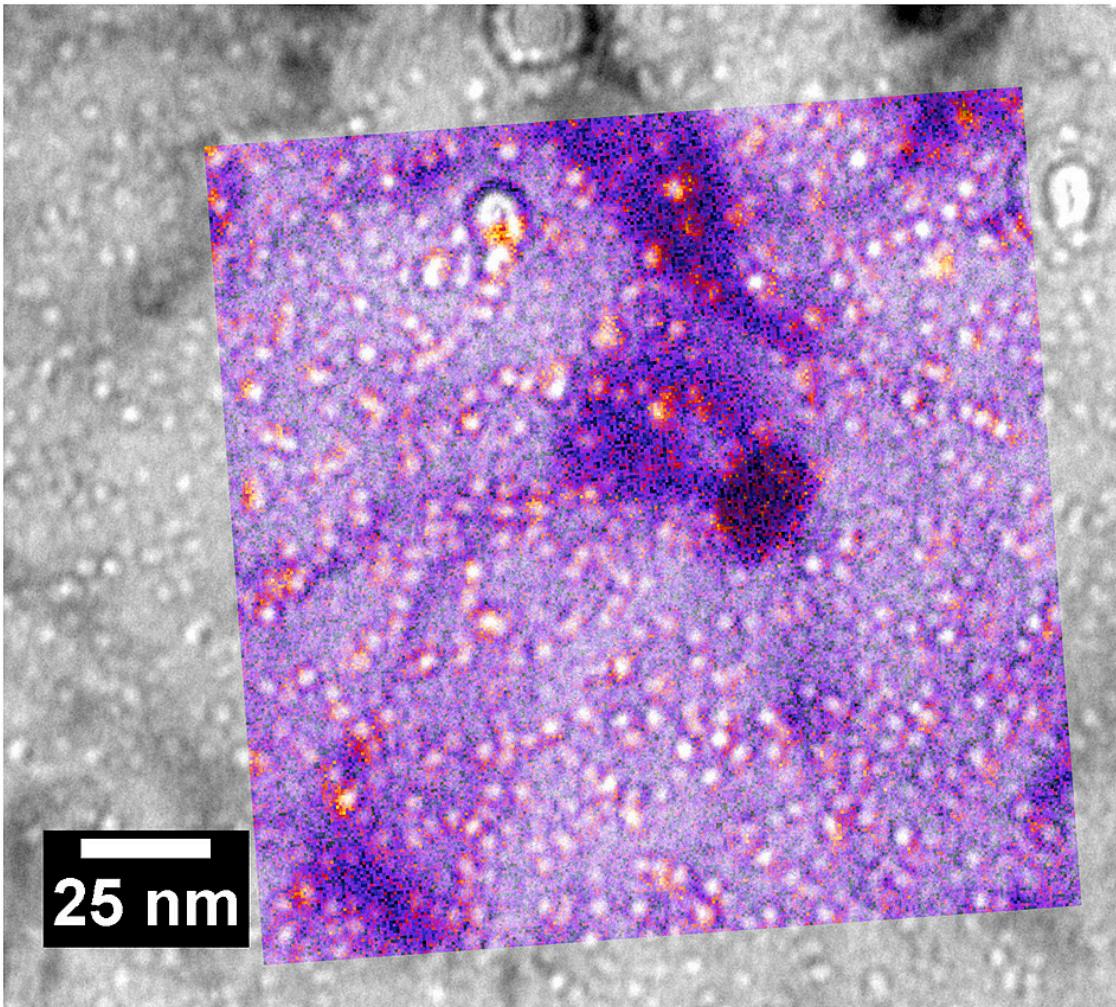
- Heterogeneous nucleation:

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

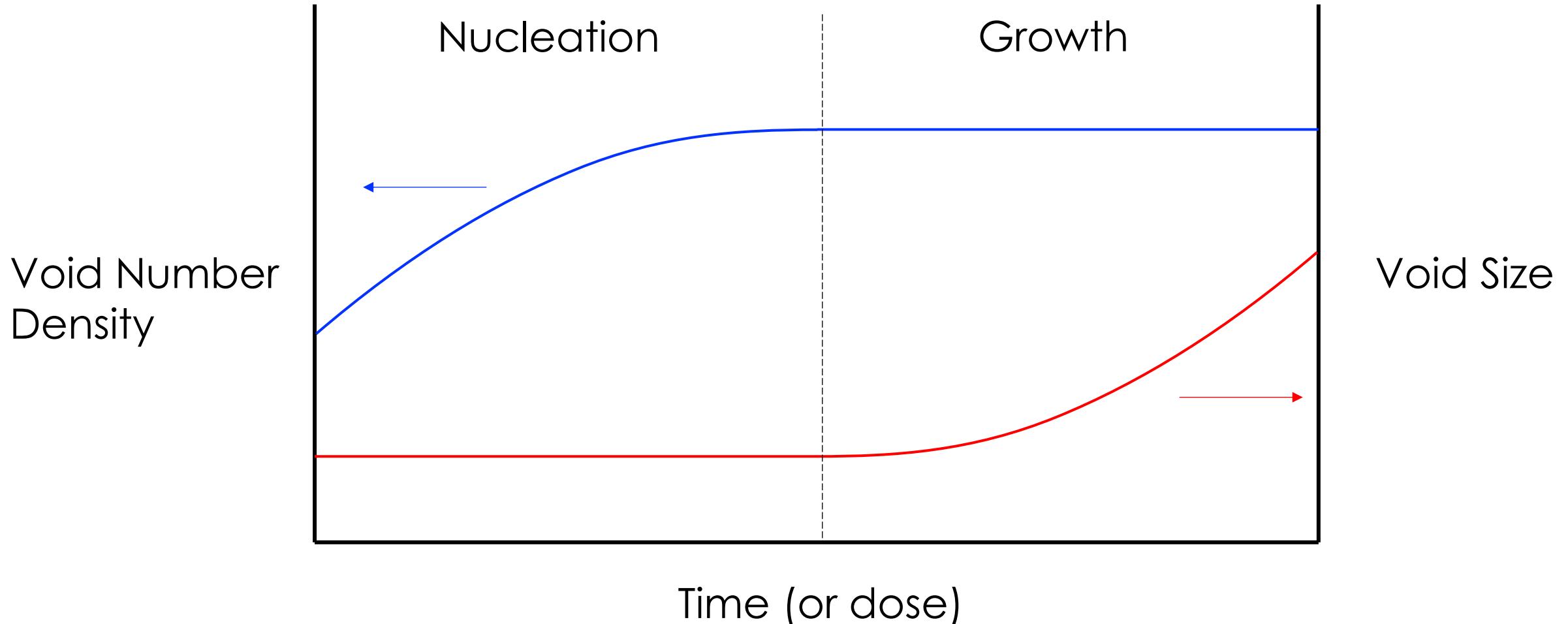
What happens to the graph with heterogeneous nucleation?



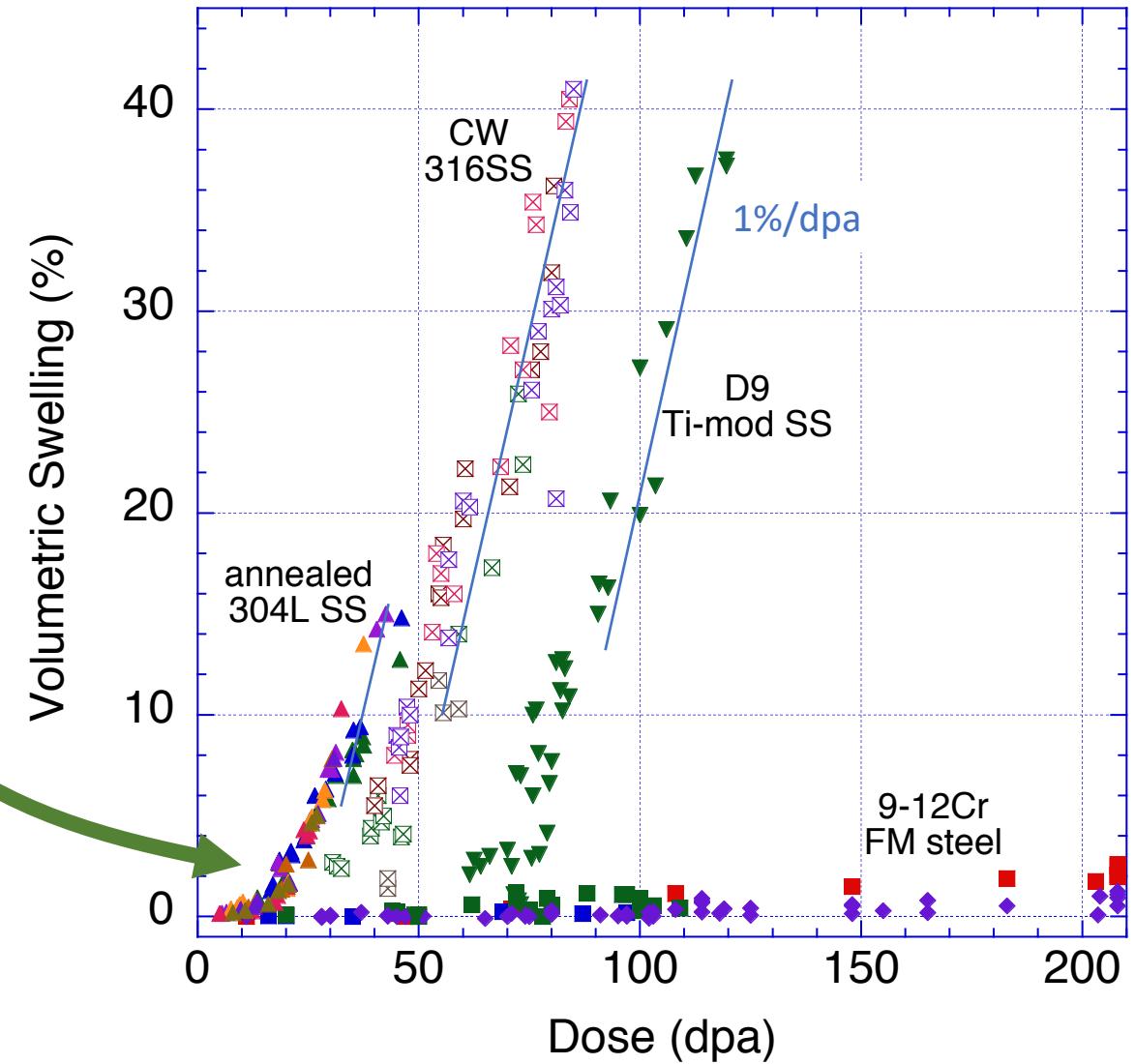
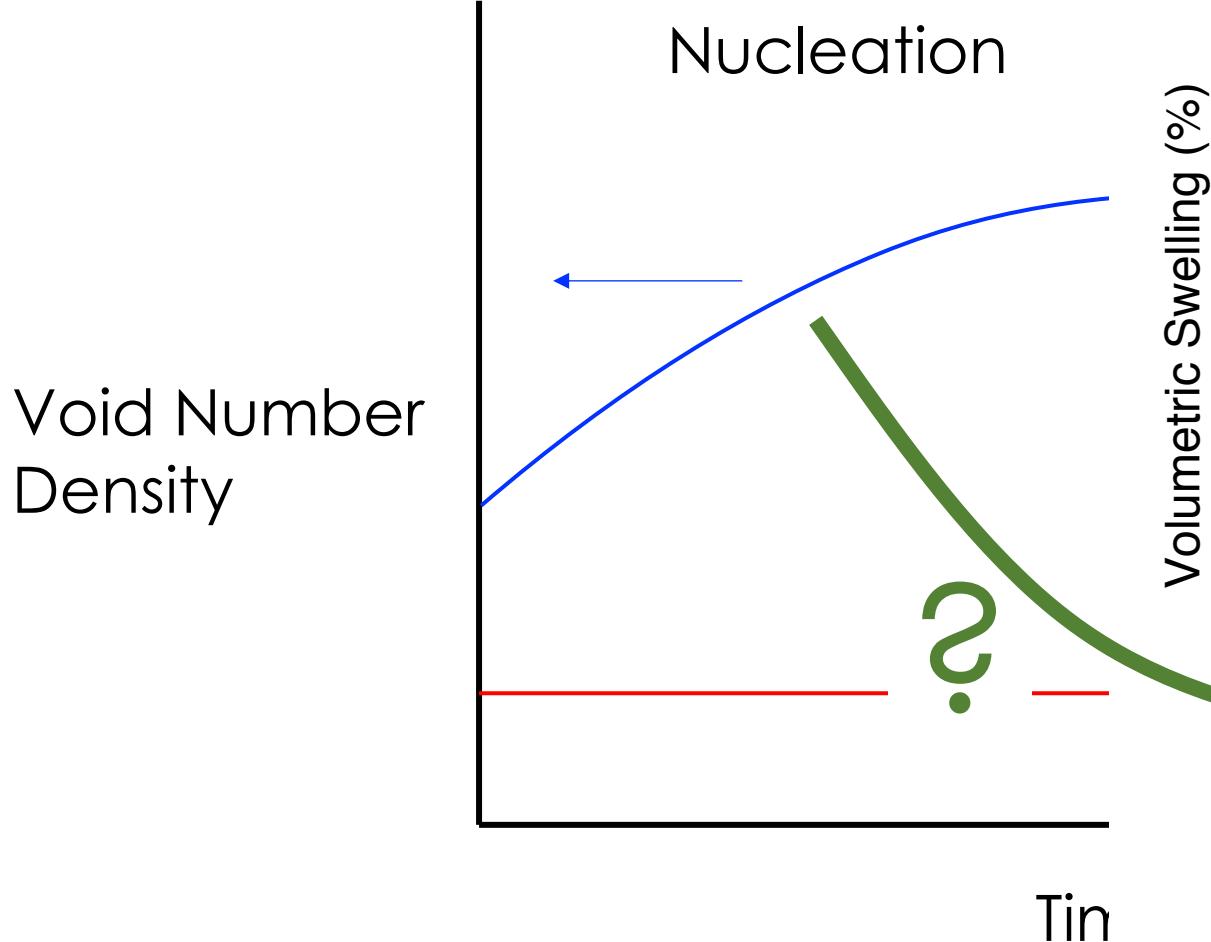
Void Nucleation Theory: Balance



Nucleation vs. Growth



Nucleation vs. Growth



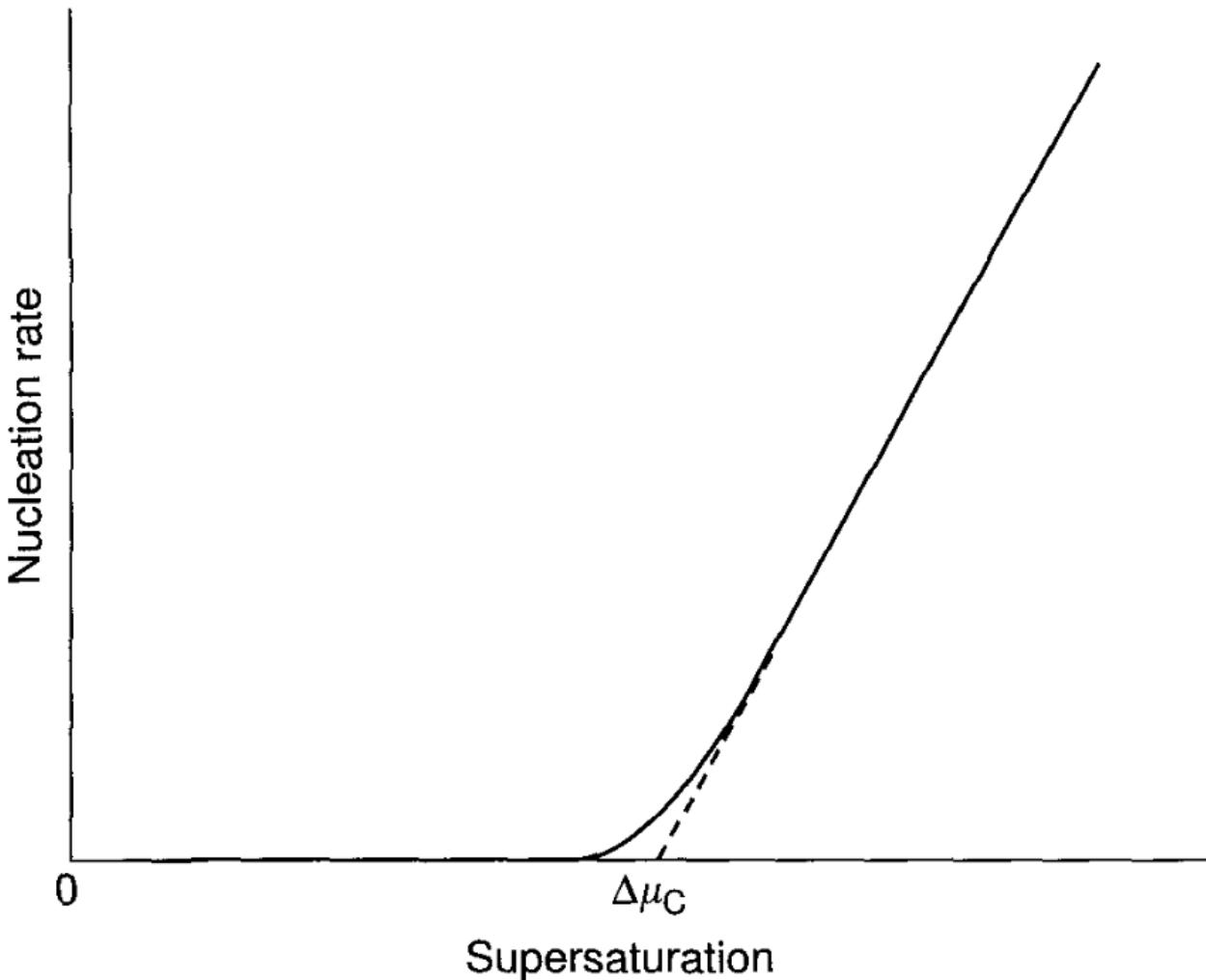
Void Nucleation Rate

Nucleation rate can be generalized as:

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

But it depends on:

- Dose rate
- Temperature
- Sink density, etc.



Void Nucleation Rate, J_0

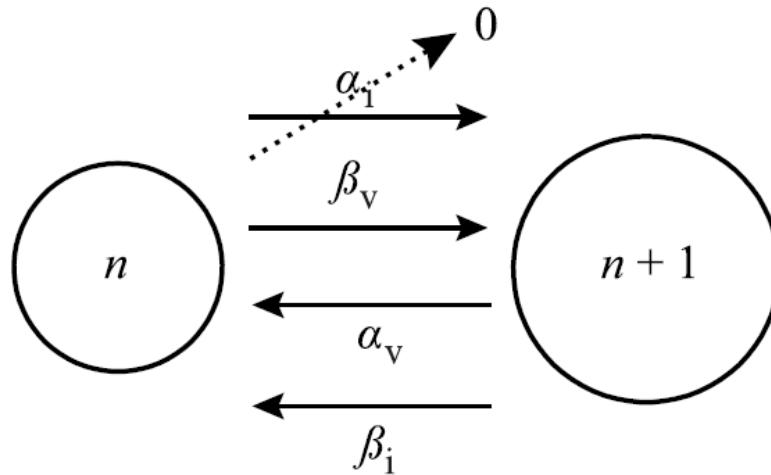
- Voids are three-dimensional clusters of vacancies formed by the following reactions
 1. **Cluster growth** by ν absorption: $\nu + \nu_j \rightarrow \nu_{j+1}$
 2. More generally, we consider **small cluster mobility**: $\nu_j + \nu_k \rightarrow \nu_{j+k}$
 3. **Cluster shrinkage** by ν emission: $\nu_j \rightarrow \nu_{j-1} + \nu$
 - 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

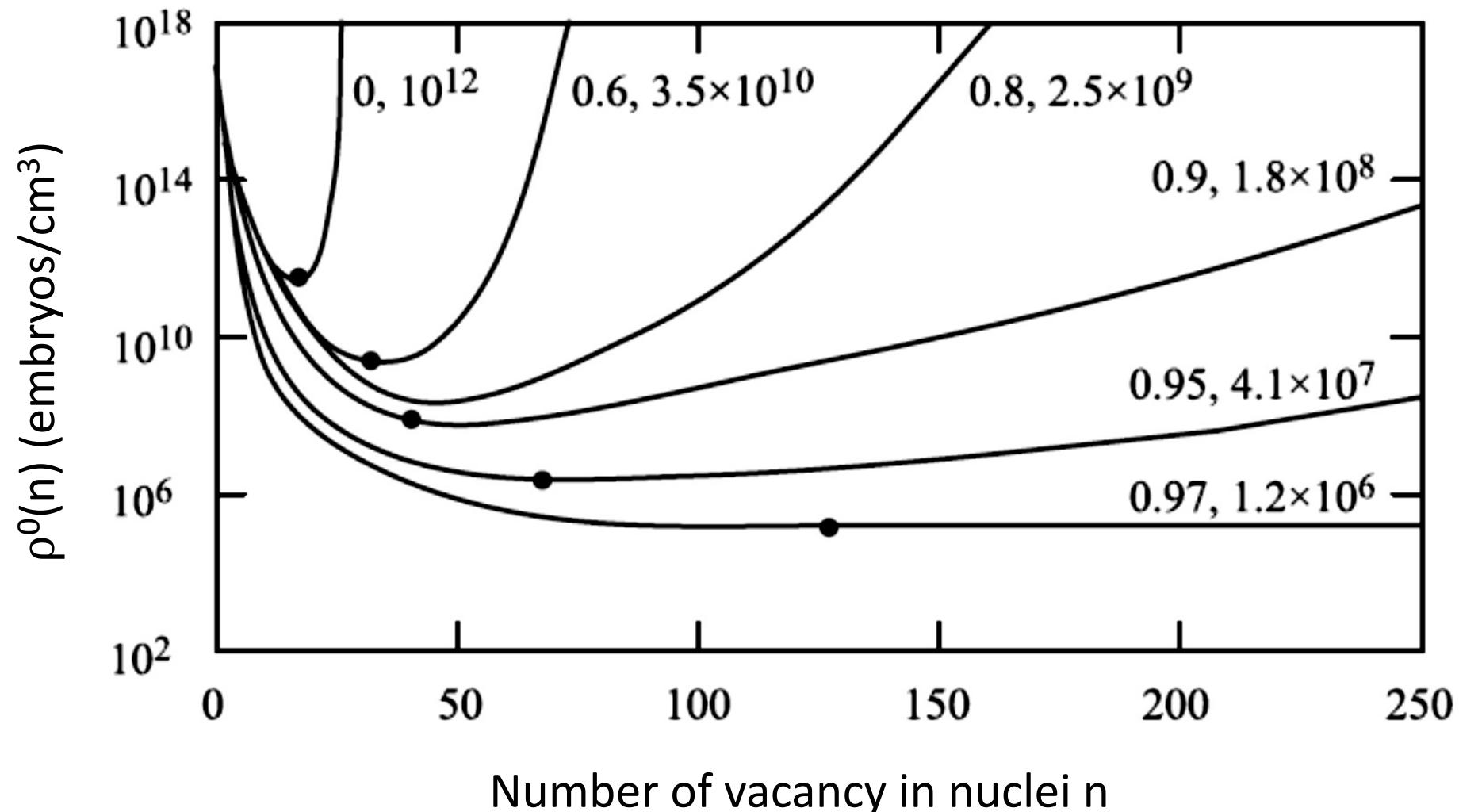
- Lengthy derivation covered in Was 8.1.2
- For sake of simplicity, the # of void embryos can be written as:

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

- 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!)



Concentration of void embryo sizes w/ nucleation rate



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

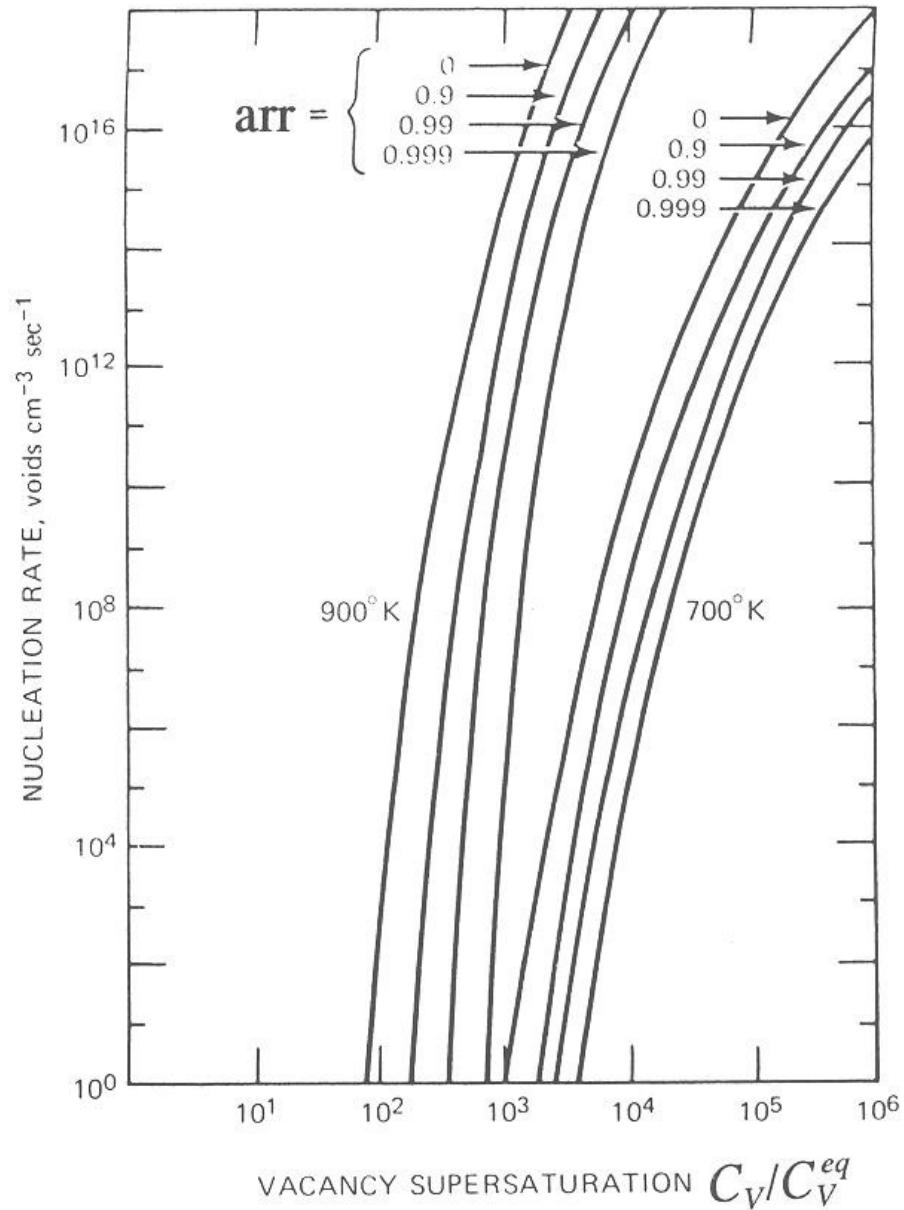
Typical results:

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

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

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

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

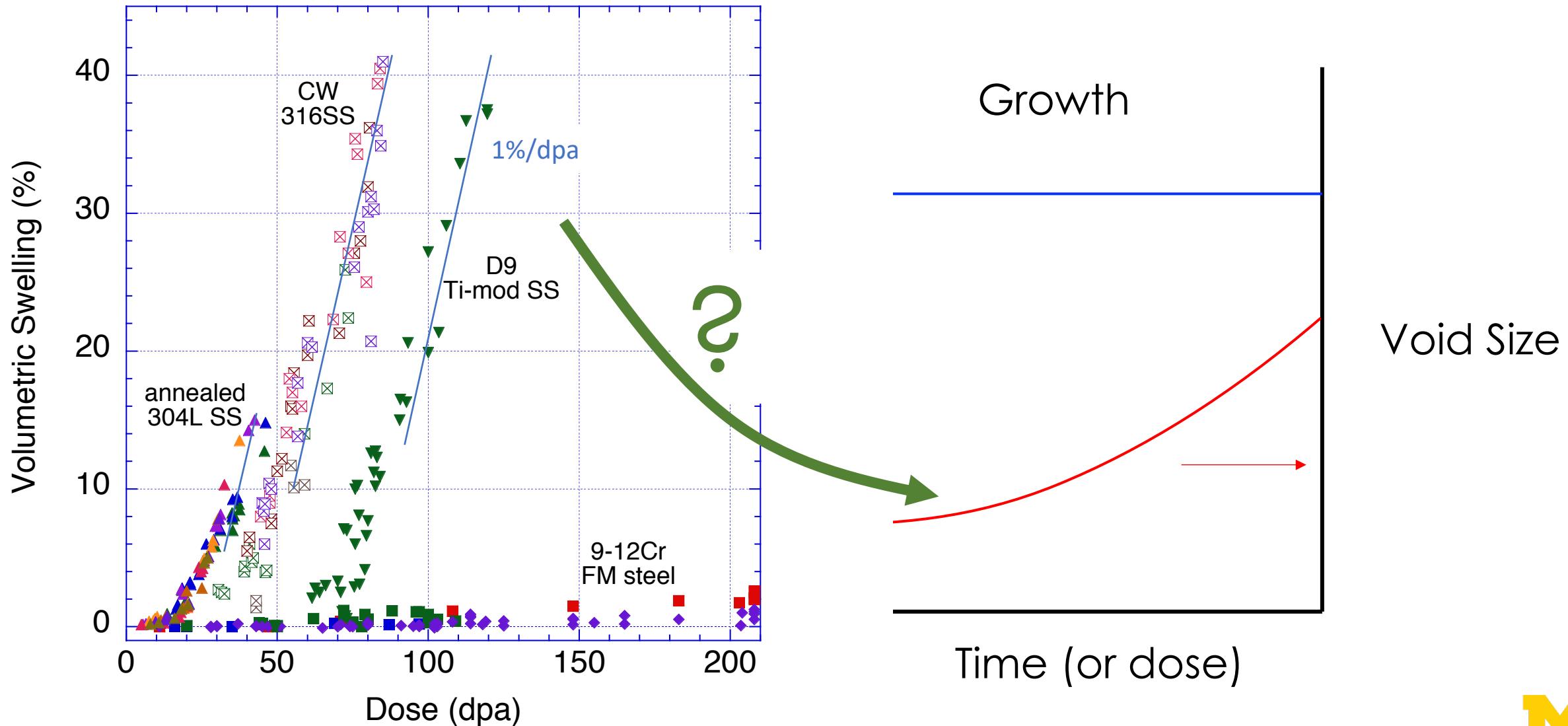


Lecture Break

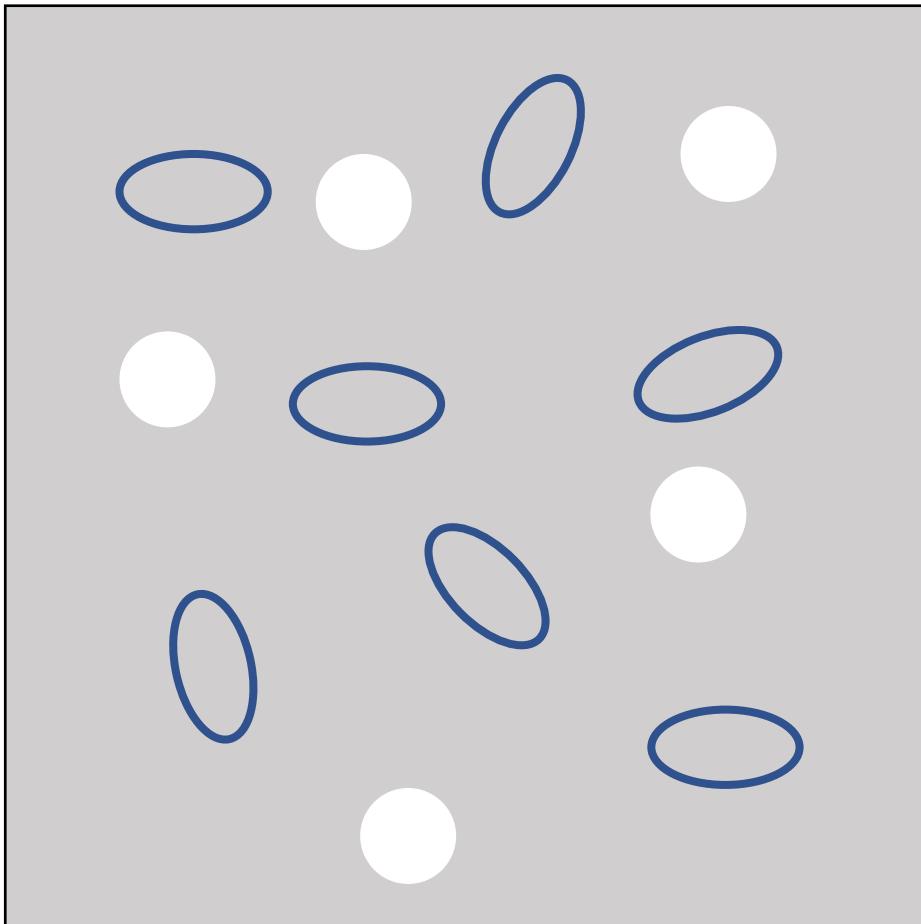
During the Abu Dhabi Grand Prix what percent of the time are the drivers on full power for a single lap?



Nucleation vs. Growth



Void Growth – Simple Model



Let's assume a material with nucleated voids and dislocation loops only, then the total sink strength can be defined as (from Table 5.2 Was):

$$k_v^2 = z_v \rho_d + 4\pi R \rho_v$$

$$k_i^2 = z_i \rho_d + 4\pi R \rho_v$$

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 nucleated void, where:

$$J_{net}^V = J_v^V - J_i^V = 4\pi R\Omega D_v(C_v - C_v^V) - 4\pi R\Omega D_i(C_i - C_i^V)$$

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

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

$$C_v^V = C_v^0 \exp\left(\frac{2\gamma\Omega}{Rk_bT}\right)$$



Void Growth

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - K_{vs}C_vC_s = 0$$

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

Next slide

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

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

Next slide

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - K_{vs}C_iC_s = 0$$



Void Growth

Remember:

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

and

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

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

and

$$k_v^2 = z_v\rho_d + 4\pi R\rho_V$$

$$k_i^2 = z_i\rho_d + 4\pi R\rho_V$$

You can now pull all three equations above together to get:

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

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

Where:

$$\eta = \frac{4K_0K_{iv}}{D_iD_v(4\pi R\rho_v + z_vp_d)^2}$$



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:

$$\dot{R}R = \frac{\Omega}{2K_{iv}} D_i D_v (z_i \rho_d - z_v \rho_d)(\sqrt{1+\eta} - 1)$$



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:

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

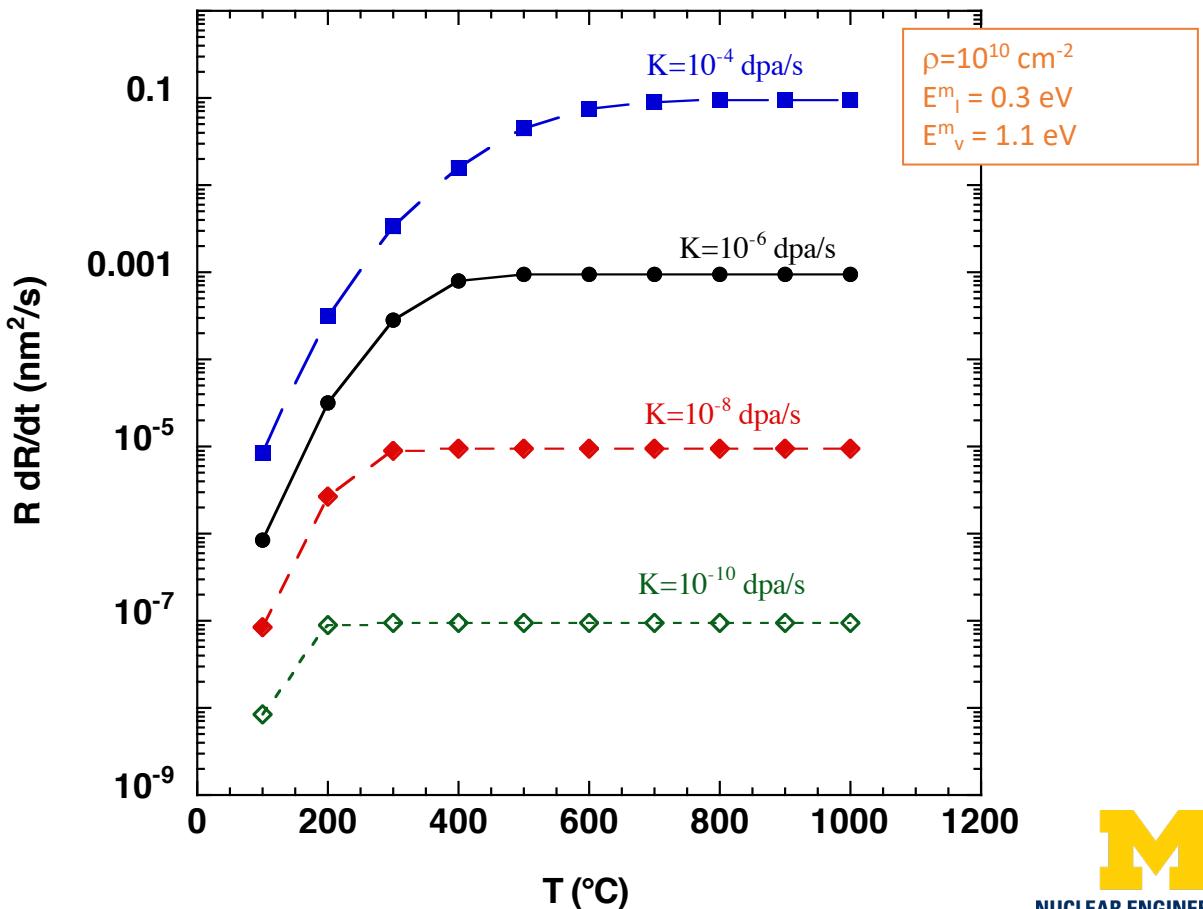
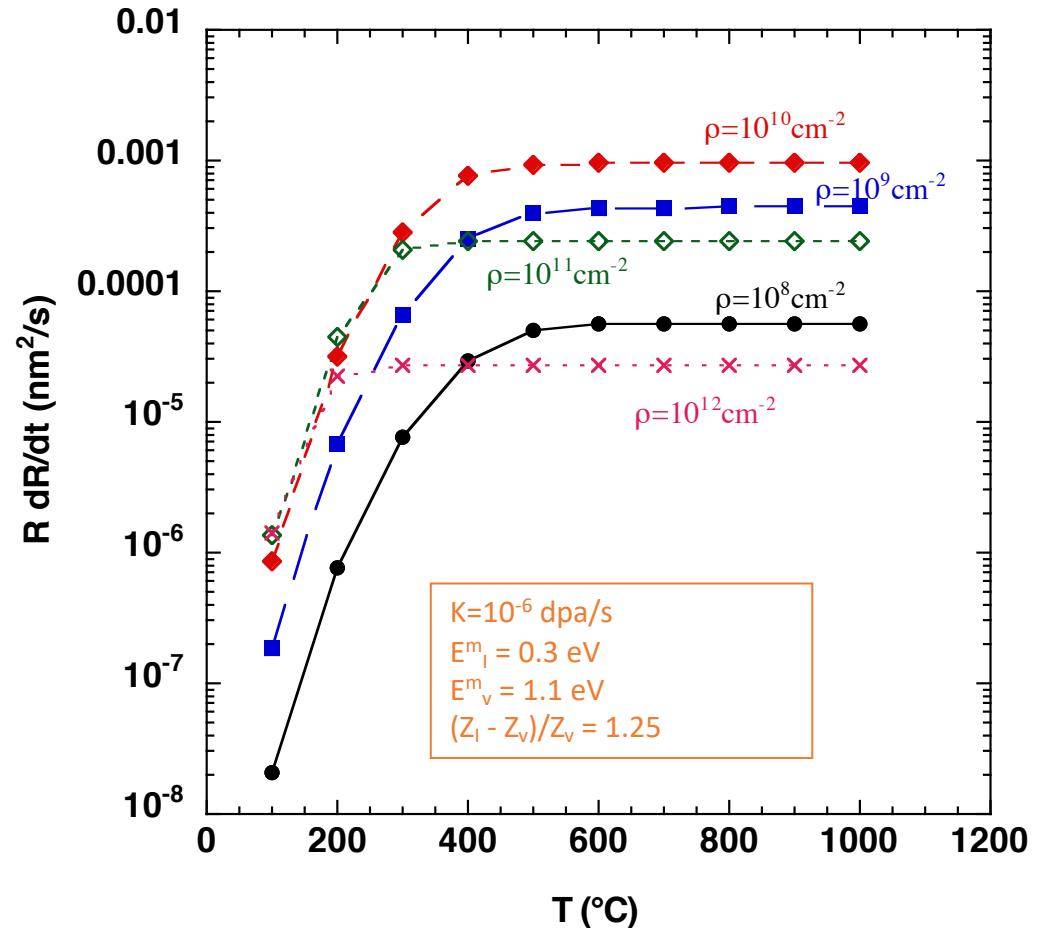
Since η decreases with increasing temperature and F decreases with increasing η :

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

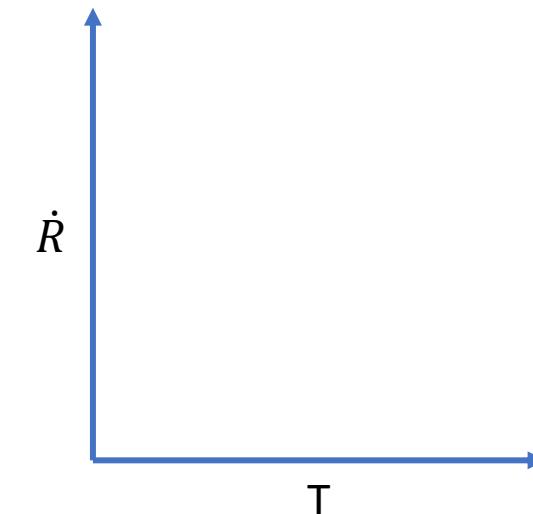
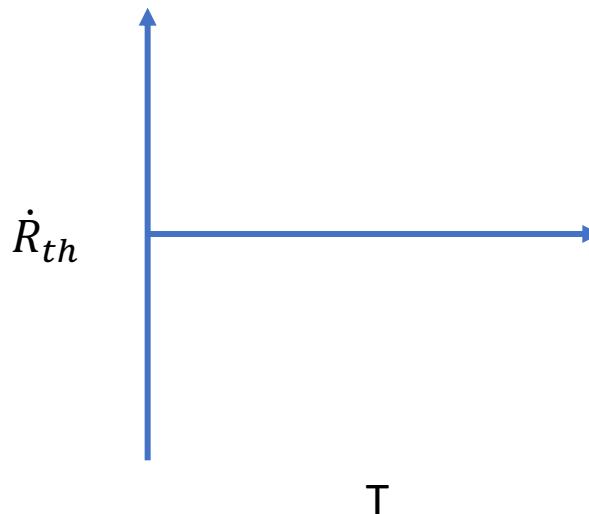
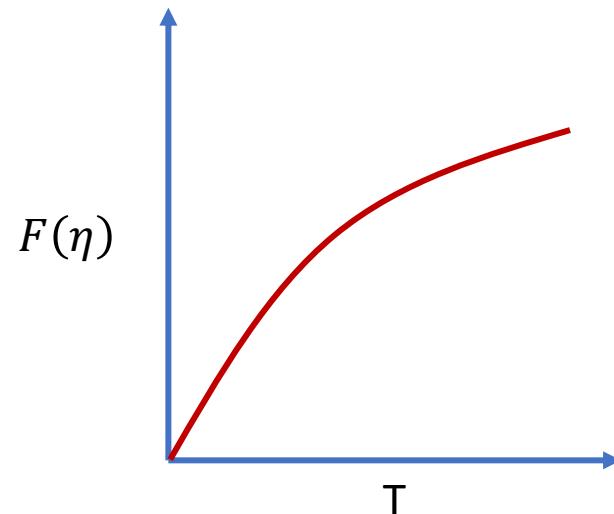


Void Growth

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



Void Swelling Temperature Dependence



At very high temperatures, void growth ceases because the vacancies “boil off” the voids. Repeating the previous derivation without neglecting C_v^0 gives the following shrinkage rate that competes with the growth rate:

$$R\dot{R}_{th} = -\frac{D_v C_v^0 \Omega^2 z_v \rho_d}{kT(4\pi RN + z_v \rho_d)} (e^y - 1)$$



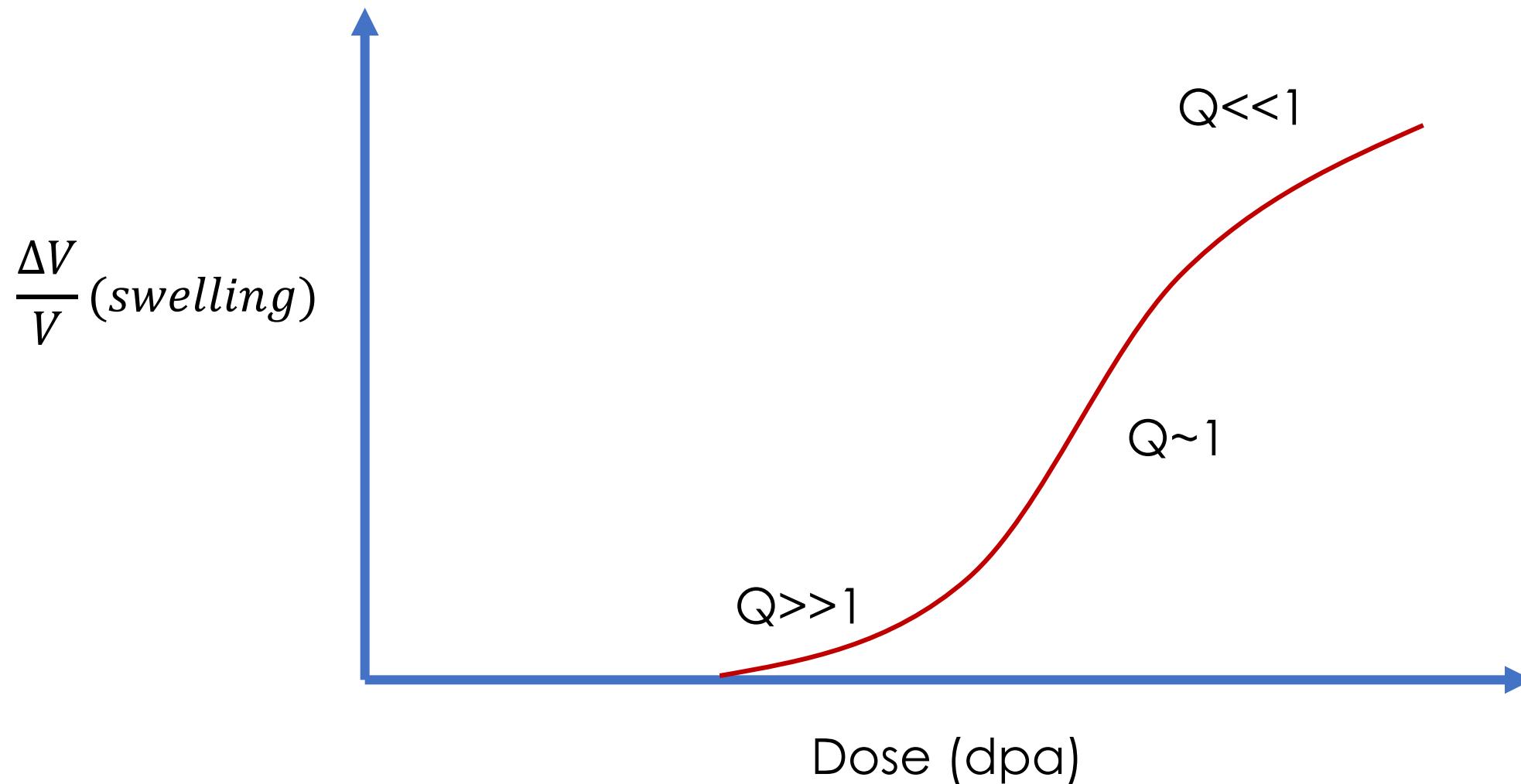
Effect of Structure on Void Swelling

- Ferritic steels swell at rates ~0.2%/dpa
- Structure alone is not sufficient to explain the difference between α -Fe (BCC) and γ -Fe (FCC)
- BCC vanadium alloys can swell at rates more like austenitic steels
- Difference is likely in the relative bias for point defects at sinks
- If the bias is removed: $z_i = z_v$, void growth is impossible
- Recall the 3rd term, put simply:

$$\left\{ \frac{z_v \rho_d}{(4\pi R \rho_v + z_v \rho_d)(4\pi R \rho_v + z_i \rho_d)} \right\} \frac{Q}{(1+Q)^2} \quad \text{Where: } Q = \frac{\rho_d z_d}{z_v 4\pi R \rho_d}$$

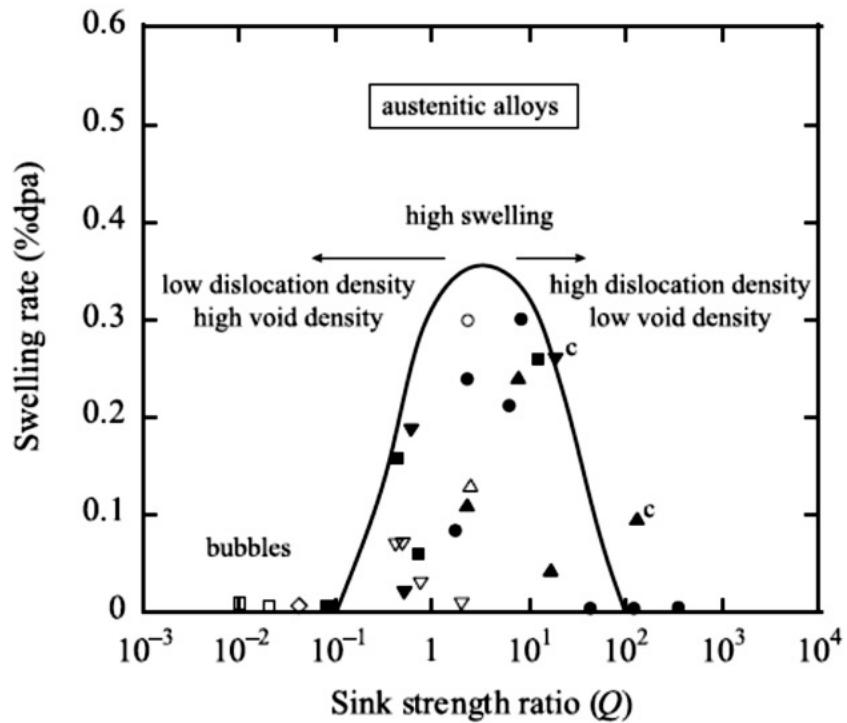


The Q-factor for structure dependence on dose



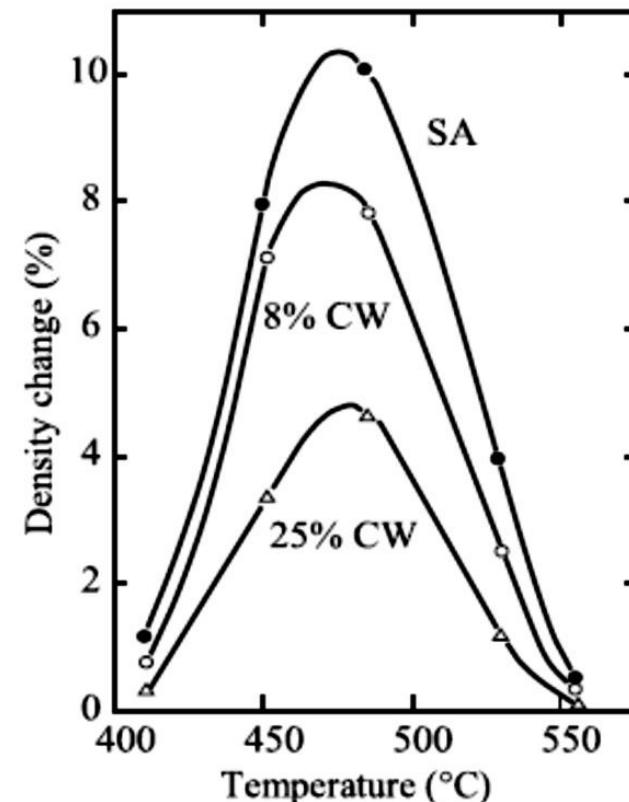
Effect of Structure on Void Swelling

● Johnston et al.
▲ Appleby et al.
■ Packan and Farrell
▼ Maziasz
▽ Sprague et al.
○ Westmoreland et al.
□ Tanaka et al.
△ Smidt et al.
◊ Lee and Mansur
c coalescence



Experimentally observed swelling rates as a function of Q for austenitic stainless steels (Mansur LK (1994) J Nucl Mater 216:97–123)

- Growth rate is maximum when $Q \sim 1$
- Growth decreases for $Q \neq 1$
- Observed experimentally
- CW reduces swelling because $Q \gg 1$

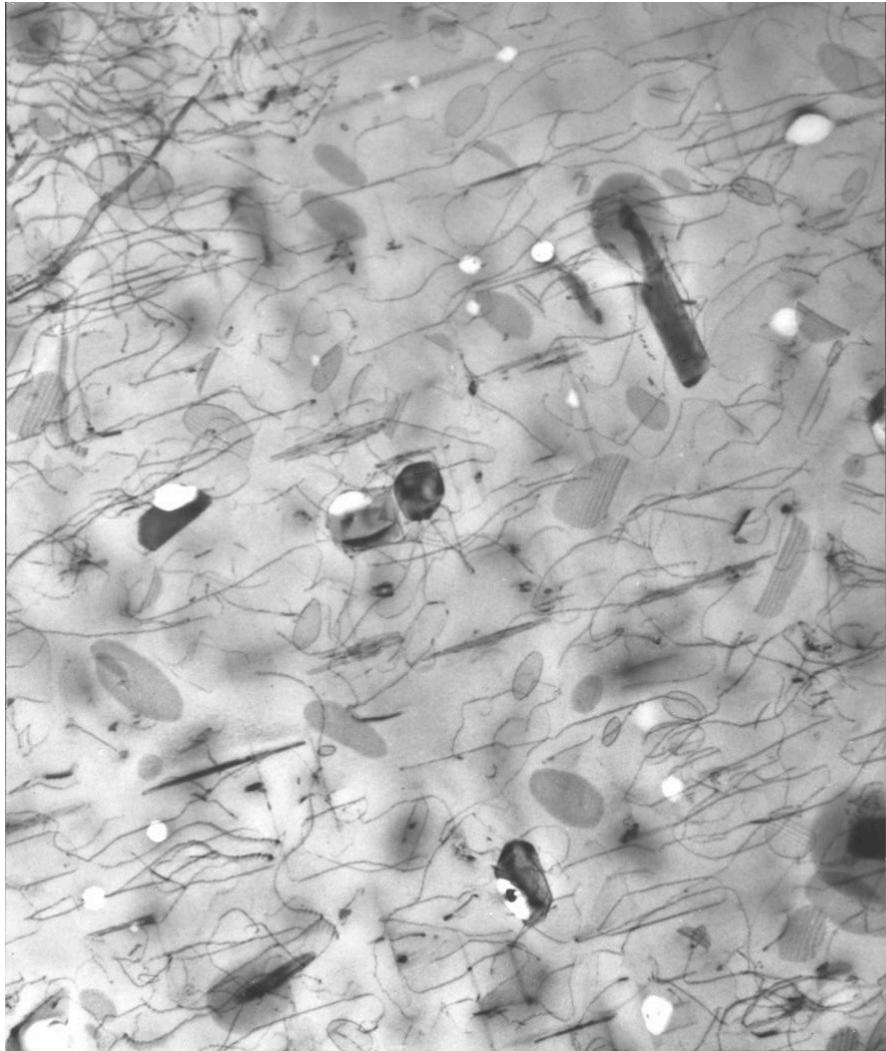


Dependence of swelling on cold-work for various temperatures for 316 stainless steel irradiated in the RAPSODIE reactor to doses of 20–71dpa (Dupouy JM, Lehmann J, Boutard JL (1978) In: Proceedings of the Conference on Reactor Materials Science, vol. 5, Alushta, USSR. Moscow, USSR Government, pp 280–296)

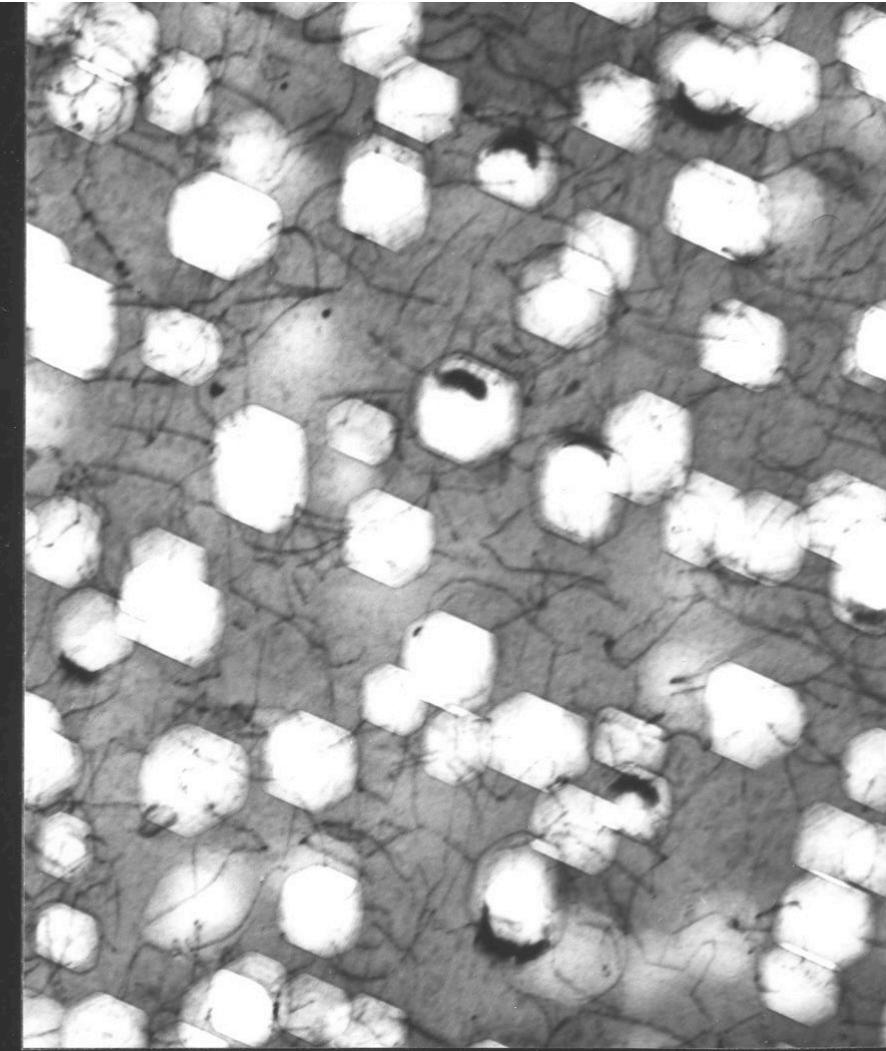


Image of voids + effect of sink strength

Commercial 316 SS (high sink strength)

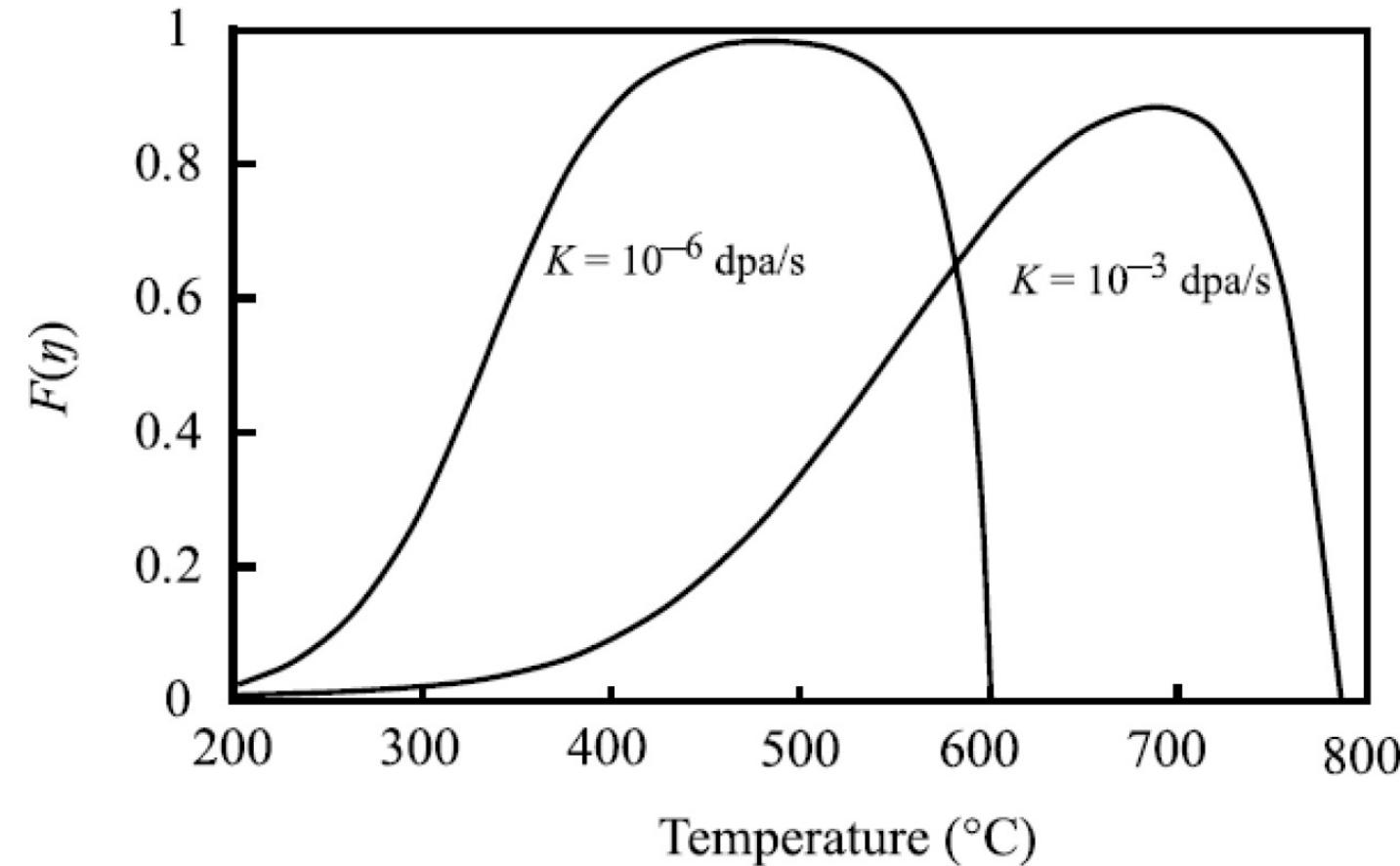


High-purity (low sink strength)



100 nm

Effect of Dose Rate



Dose rate is captured in the **fourth term** where:

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

And:

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



Effect of Dose Rate

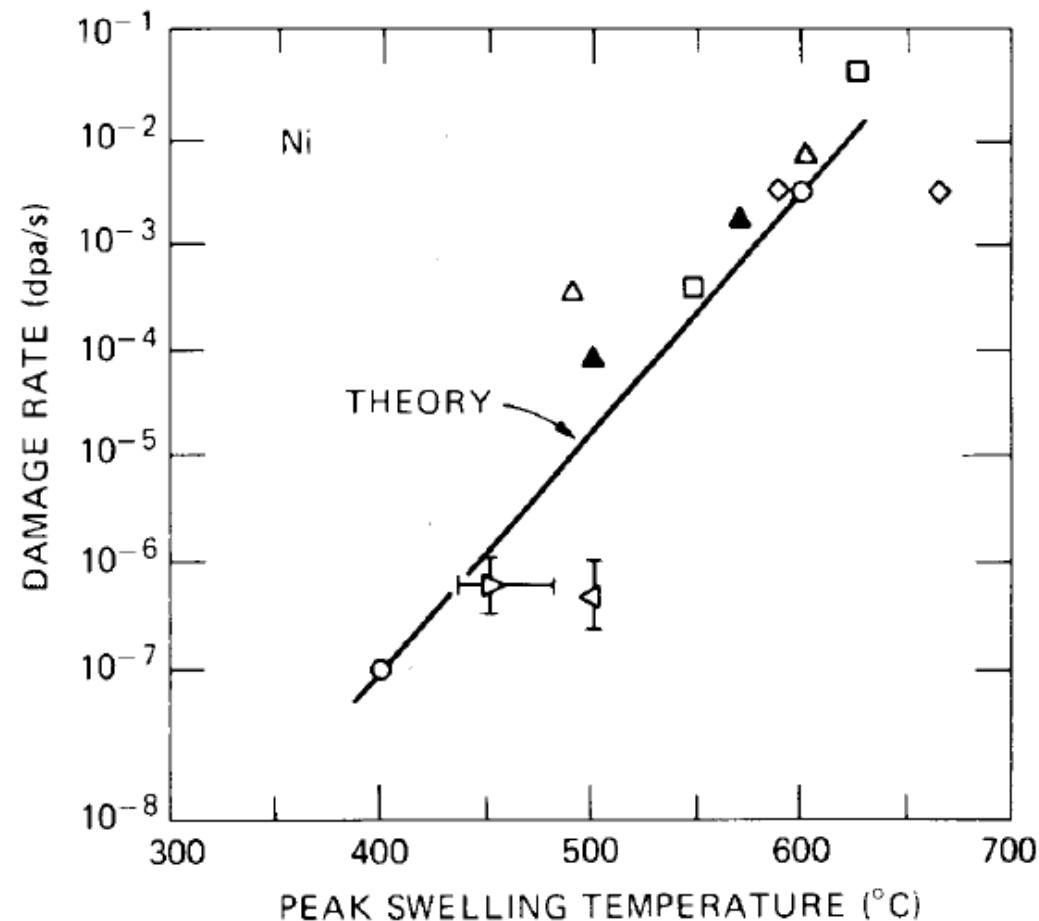


Figure 8.29. Compilation of experimental results for peak swelling temperature as a function of dose rate. Theoretically predicted trend is shown as the line. After Refs. 140 and 141.

Dose rate is captured in the **fourth term** where:

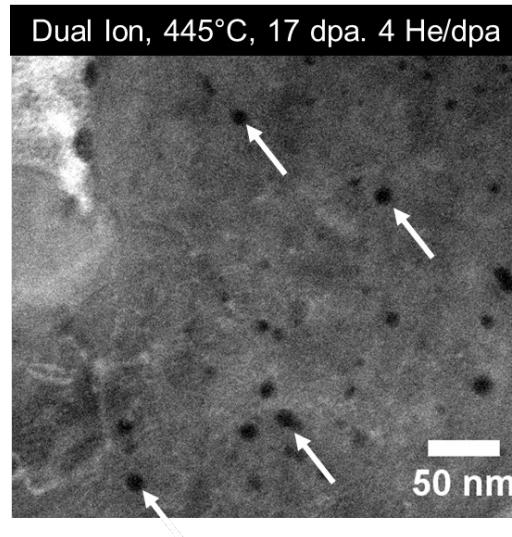
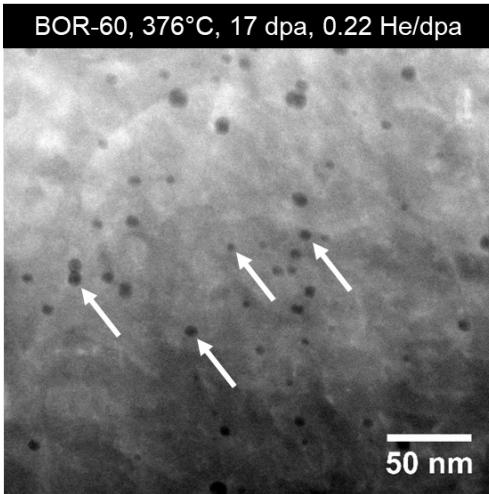
$$F(\eta) = 2\left(\sqrt{1 + \eta} - 1\right)/\eta$$

And:

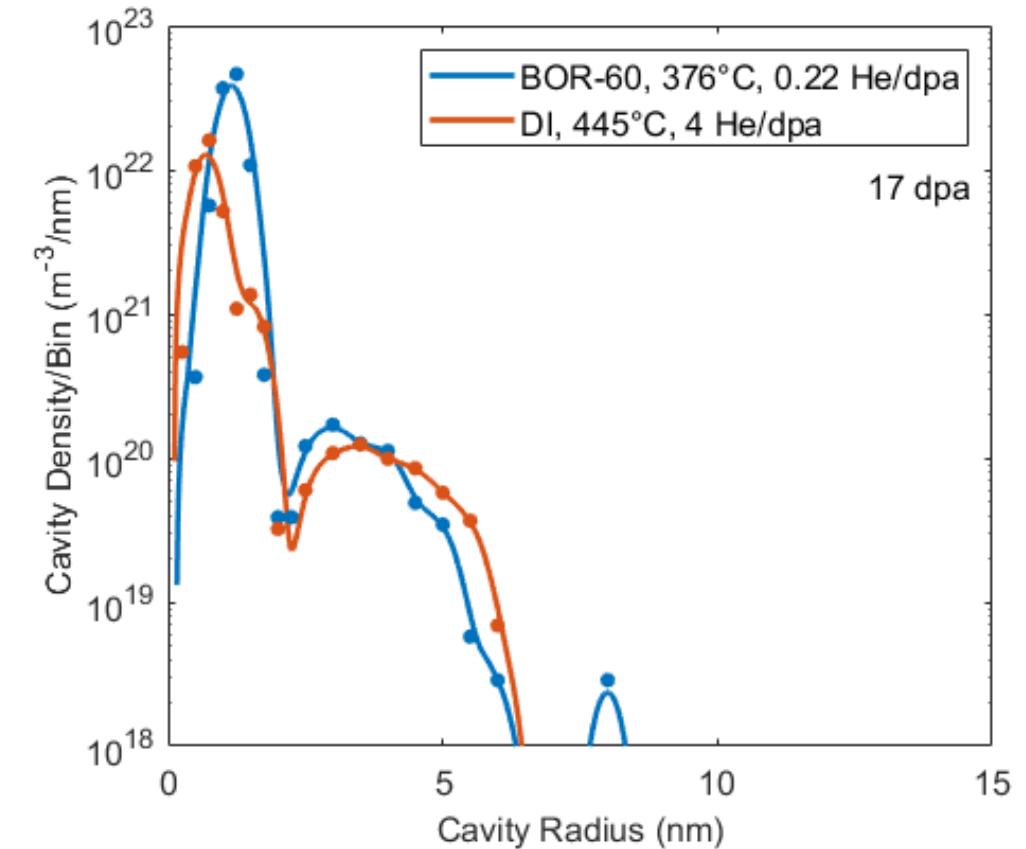
$$\eta = \frac{4K_0 K_{iv}}{D_i D_v (4\pi R \rho_v + z_v p_d)^2}$$

Effect of Dose Rate – Real World Example

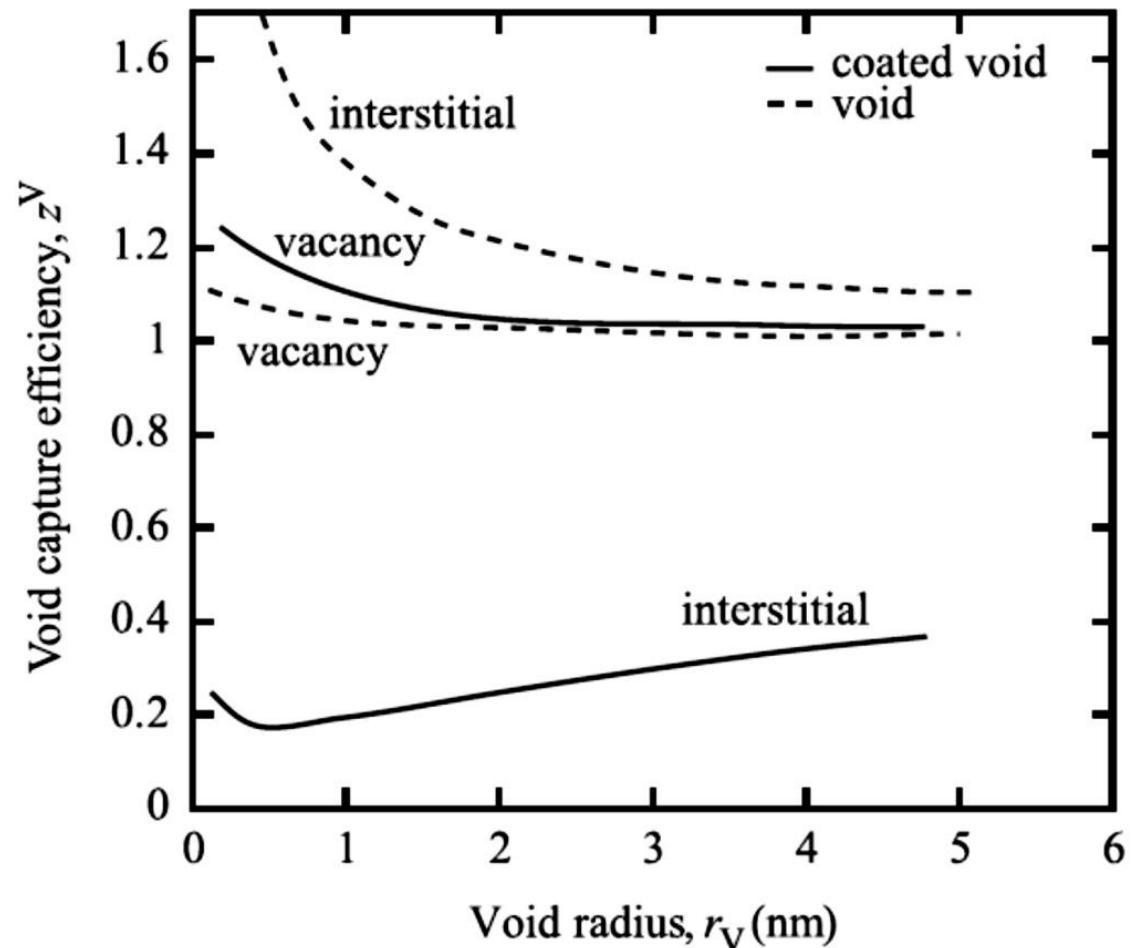
STEM HAADF



$$T_2 - T_1 = \frac{\frac{kT_1^2}{E_v^m + 2E_v^f} \ln \left(\frac{G_2}{G_1} \right)}{1 - \frac{kT_1}{E_v^m + 2E_v^f} \ln \left(\frac{G_2}{G_1} \right)}$$

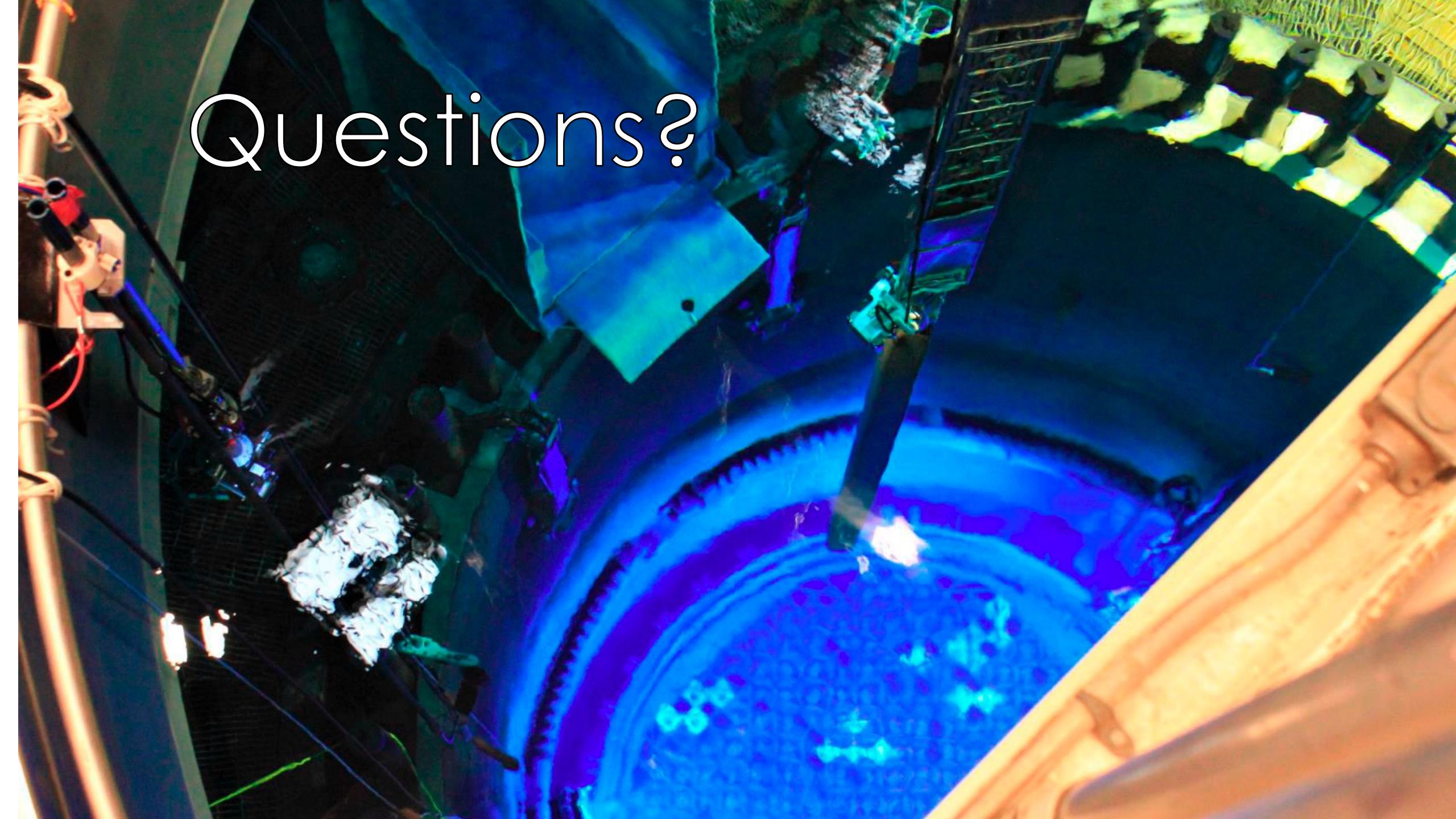


Effect of void surface segregation on defect bias



- For a bare unpressurized void, **interstitial bias is greater than vacancy bias**. Voids will shrink
- If “shell” shear modulus or lattice parameter is greater than matrix shear modulus, **vacancy bias becomes greater than interstitial bias**
 - This effect can occur because of **radiation induced segregation**
- Thicker shells have a greater effect

Capture efficiency for point defects diffusion to a void and a coated void as a function of void radius RV . (W.G. Wolfer, L.K. Mansur, The capture efficiency of coated voids, Journal of Nuclear Materials, Volume 91, Issue 2, 1980, Pages 265-276)



Questions?