Voids II

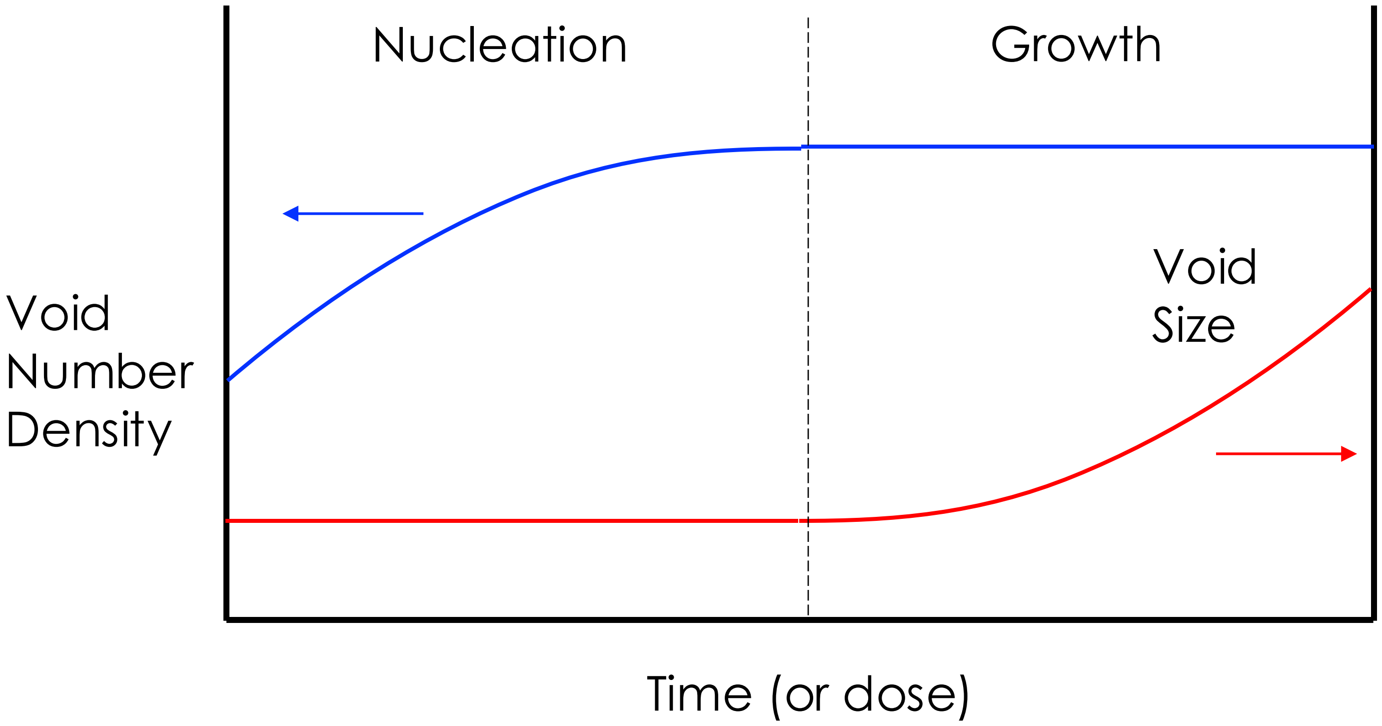
K.G. Field[1,a],

[a] kgfield@umich.edu

[1]University of Michigan

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Nucleation vs. Growth



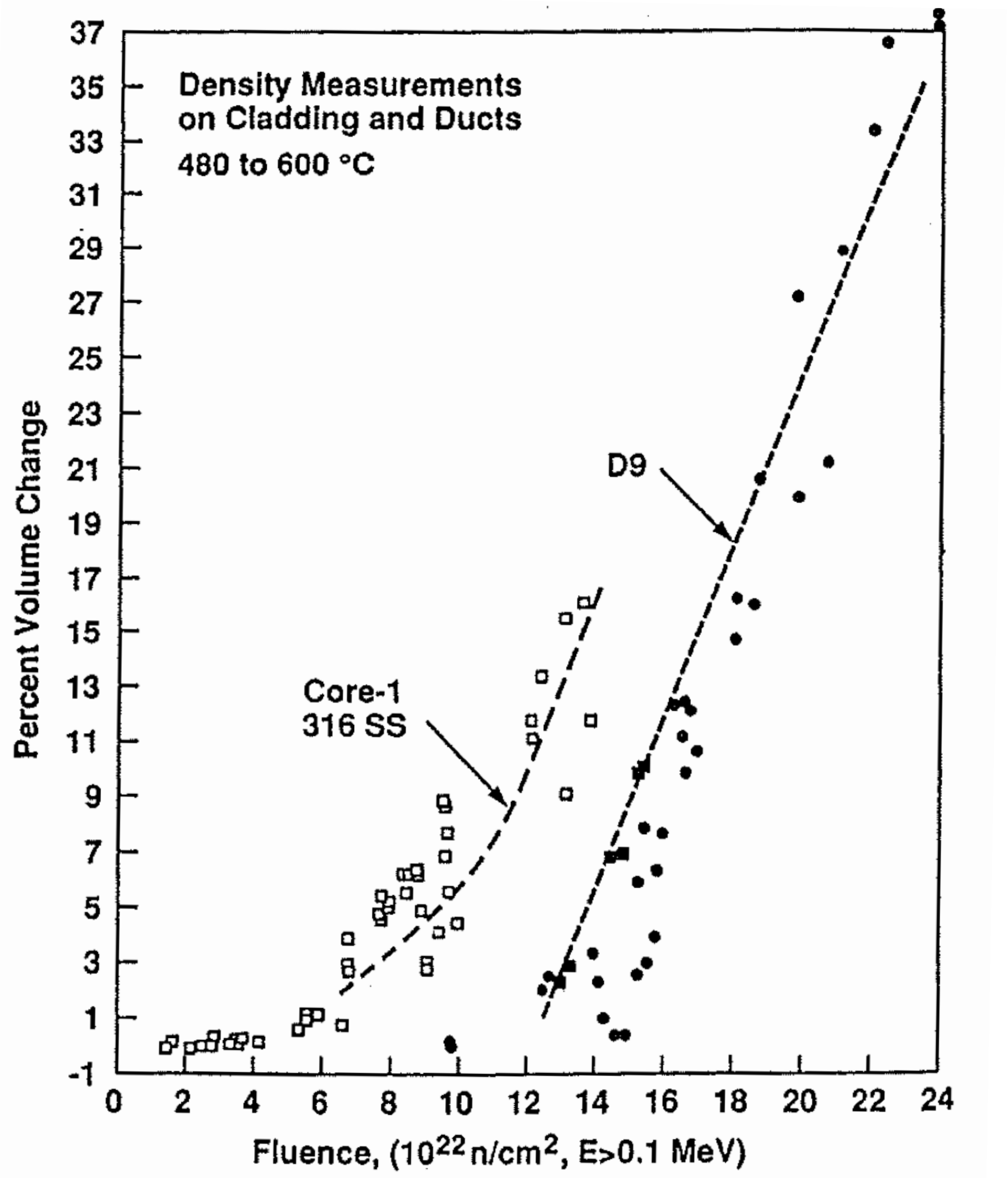
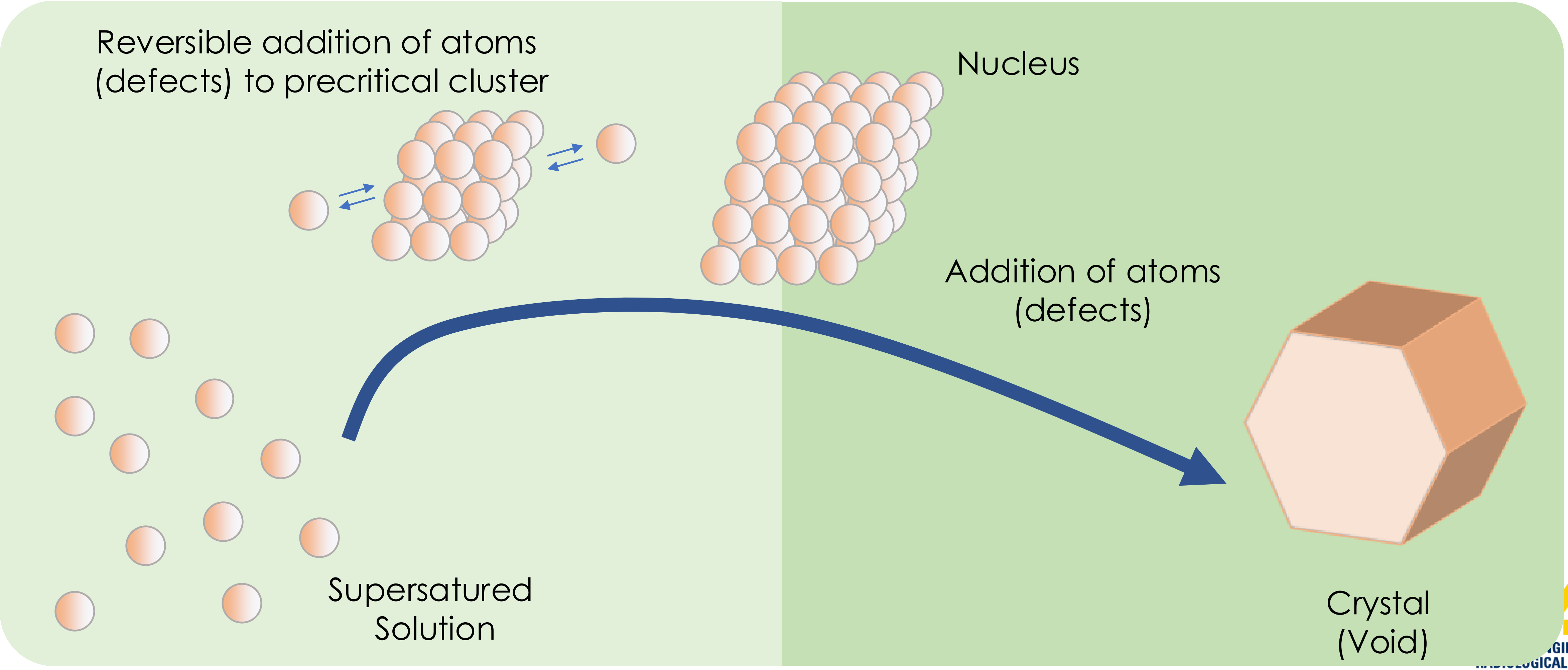


Fig. 3. Swelling observed in two cold-worked austenitic alloys after serving as fuel cladding in the open core of FFTF [23].

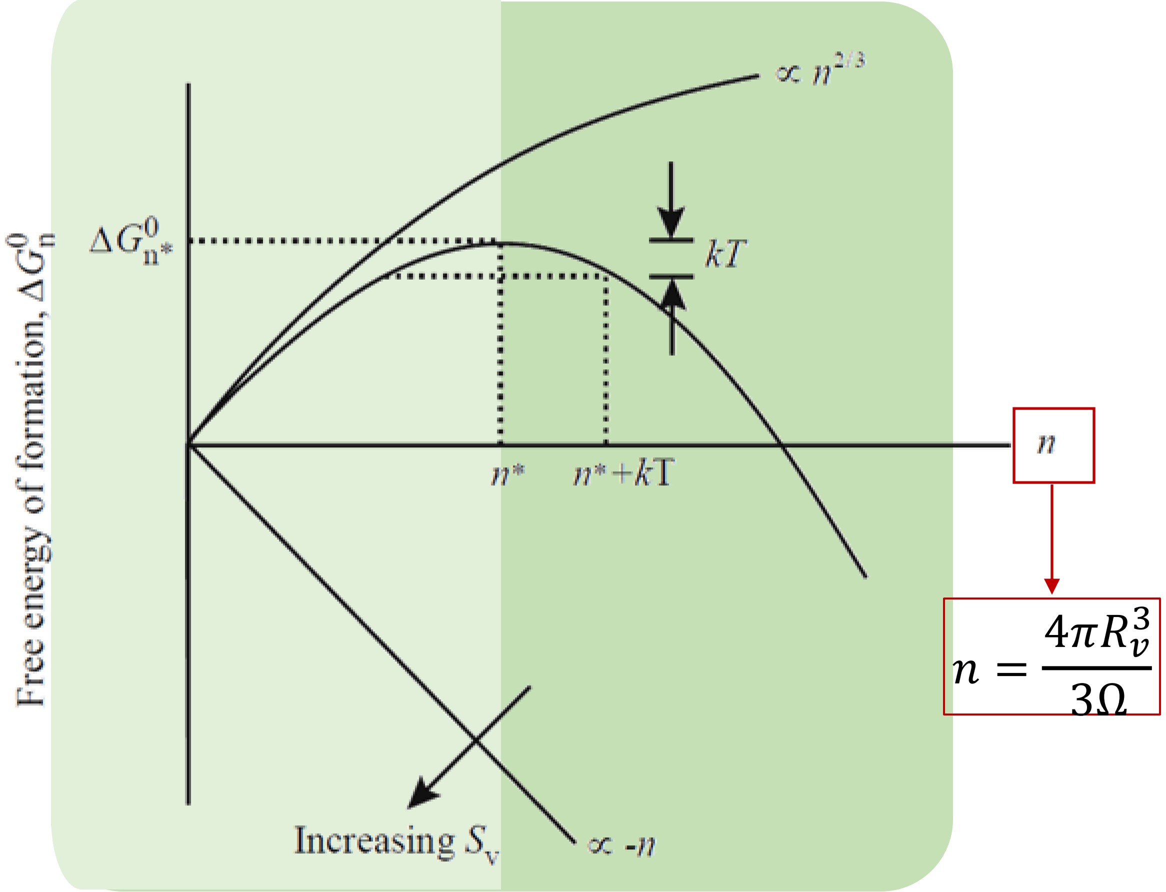
Nucleation

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



Void Nucleation Theory: Graphical depiction

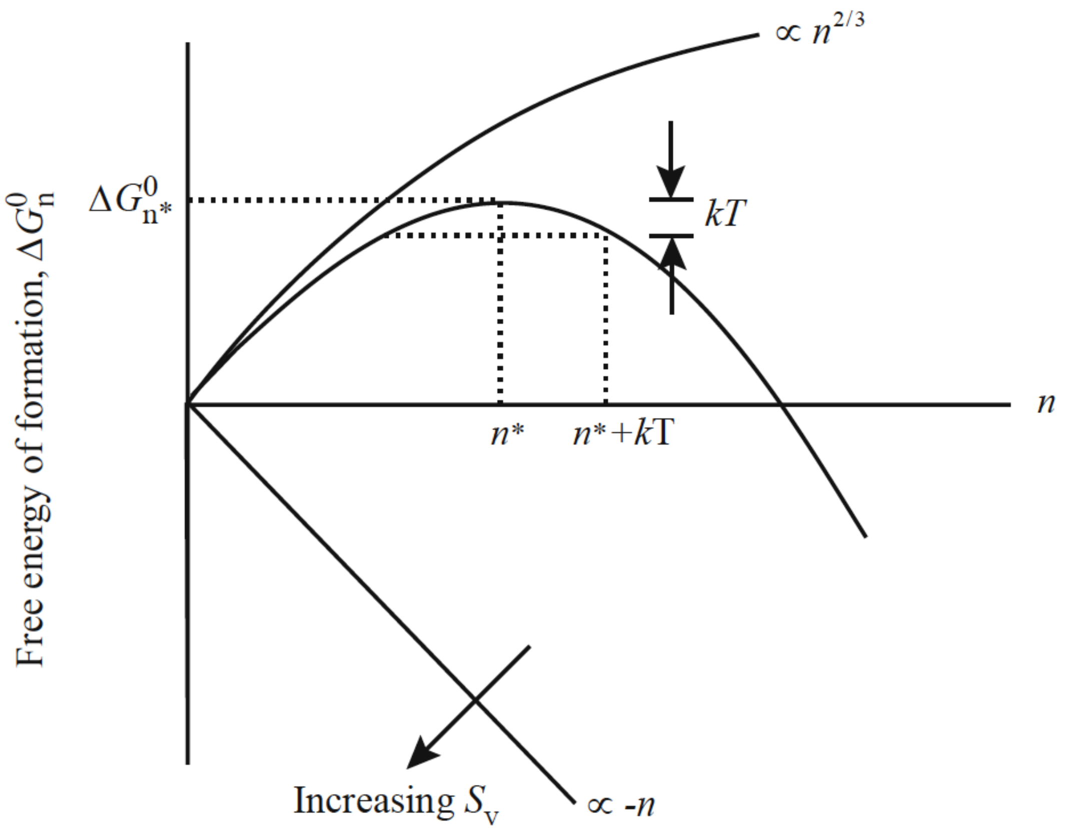
$$\Delta G_n^0 = -nkT \cdot \ln(S_v) + (36\pi\Omega^2)^{1/3}\gamma n^{2/3}$$



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:

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

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

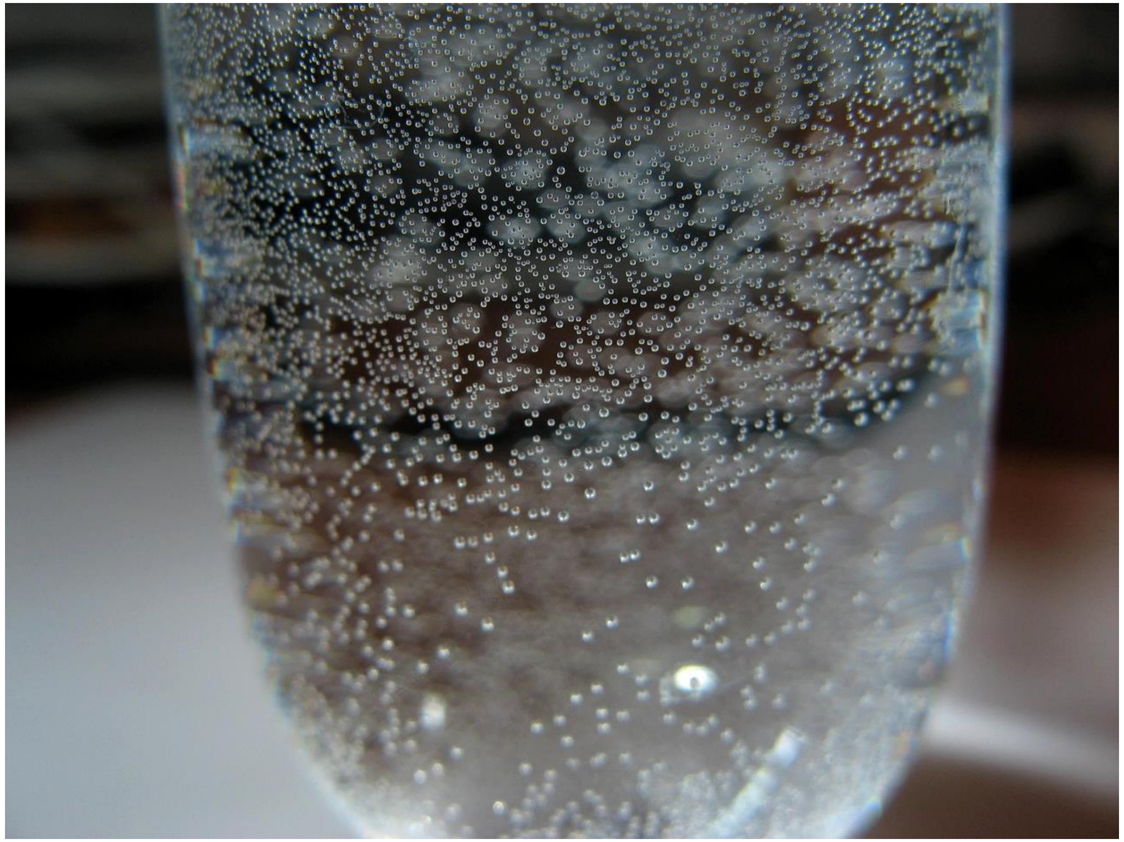
Solve for n

$$\boldsymbol{n}^* = \frac{32\pi\gamma^3\Omega^2}{3(k_bT\,\boldsymbol{lnS_v})^3}$$

Convert to r

$$\boldsymbol{r}^* = \frac{2\gamma\Omega}{(k_bT\,\boldsymbol{lnS_v})}$$

Void Nucleation Theory: Graphical depiction



- Homogeneous nucleation:

When supercritical particles are formed due to thermal fluctuations

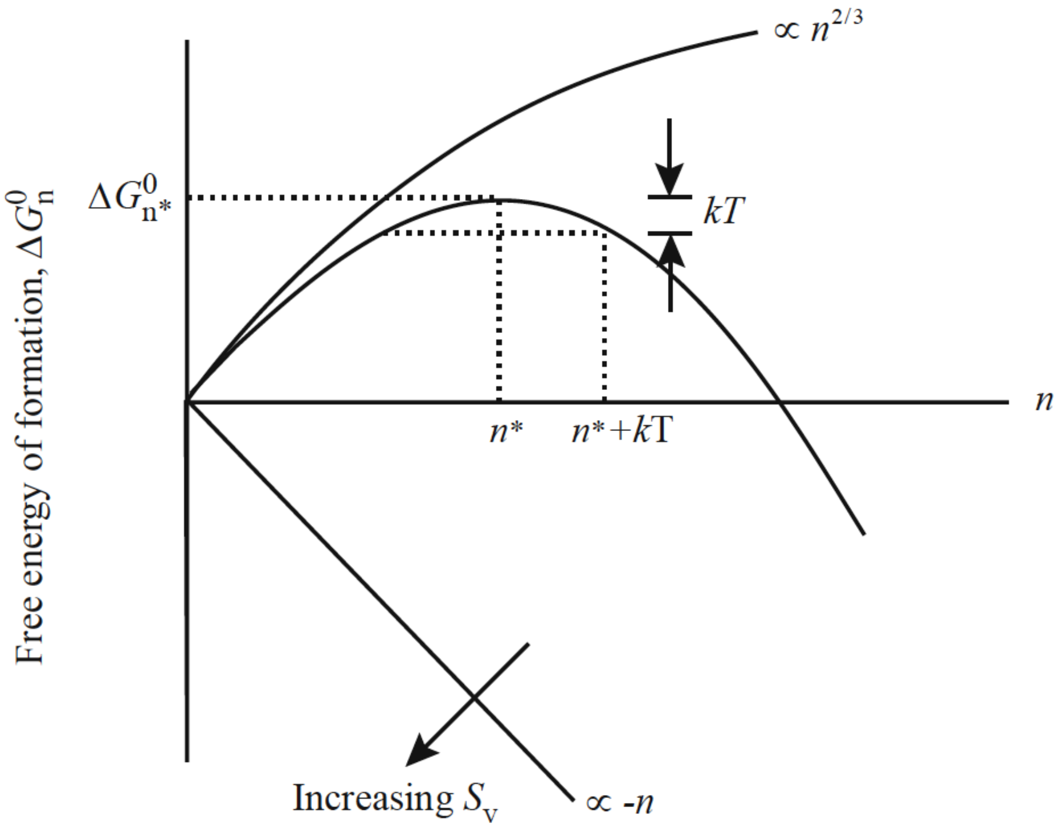
- Heterogeneous nucleation:

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

Derivations and discussion in Was 8.1

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Void Nucleation Theory: Graphical depiction



Derivations and discussion in Was 8.1

- Homogeneous nucleation:

When supercritical particles are formed due to thermal fluctuations

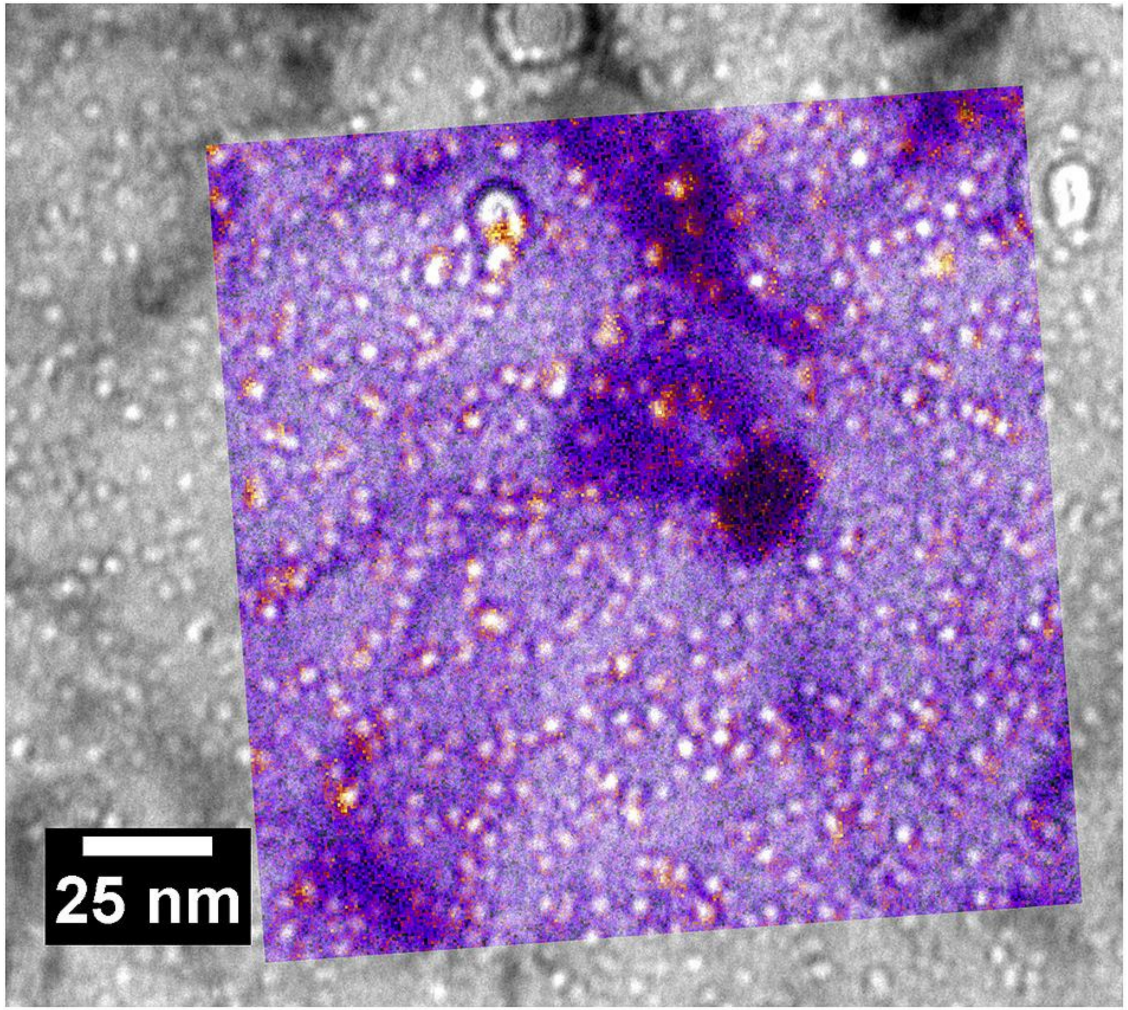
- Heterogeneous nucleation:

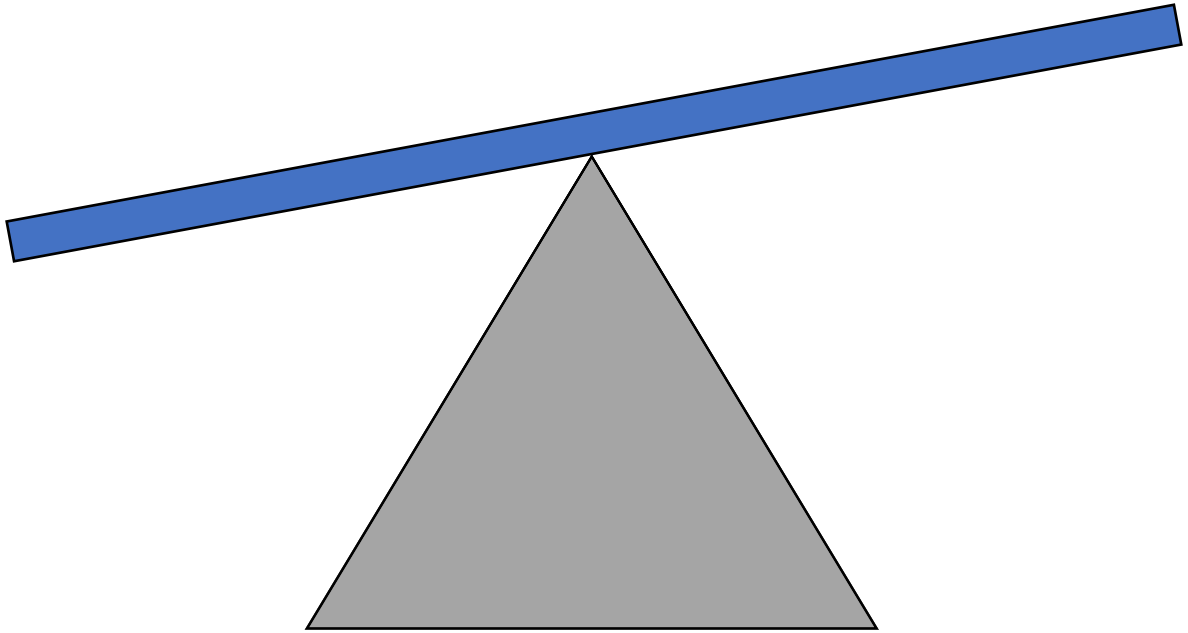
When external objects (surfaces, interfaces, impurities, defects, seeds) lower the barrier for nucleation

What happens to the graph with heterogeneous nucleation?

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

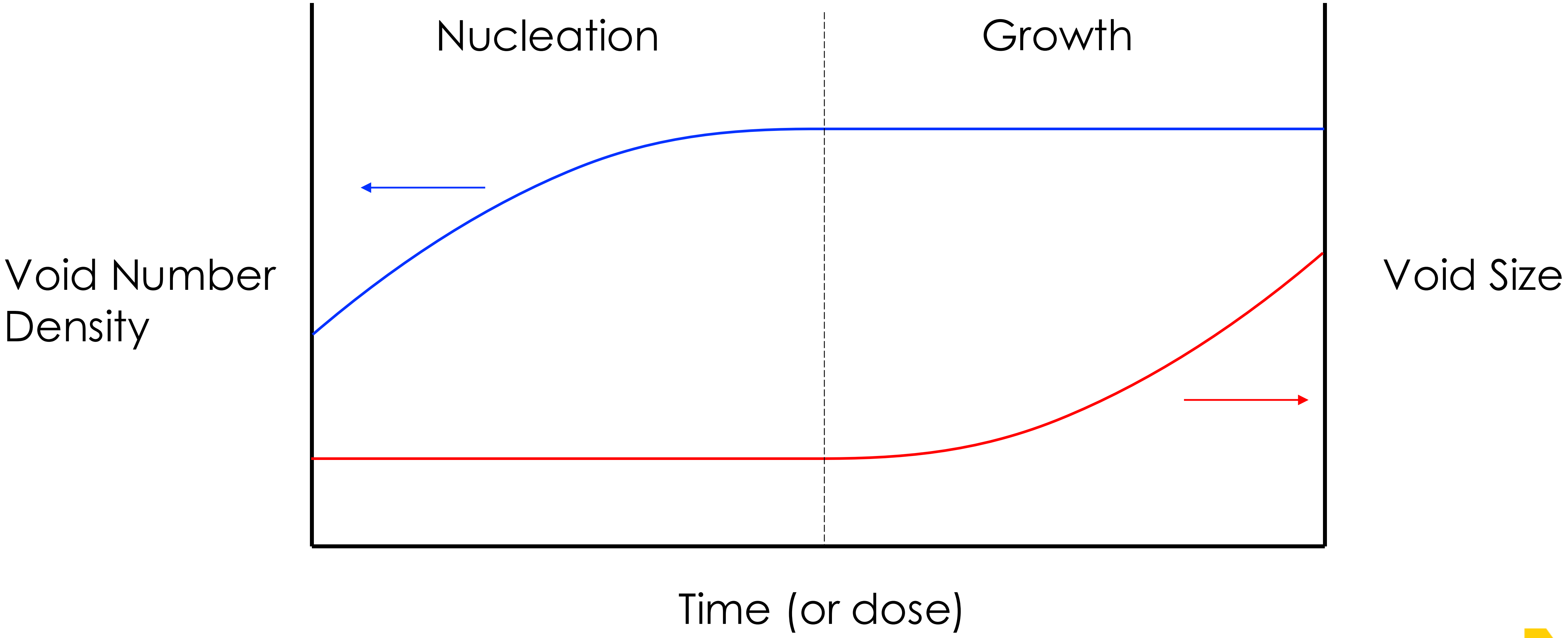
Void Nucleation Theory: Balance





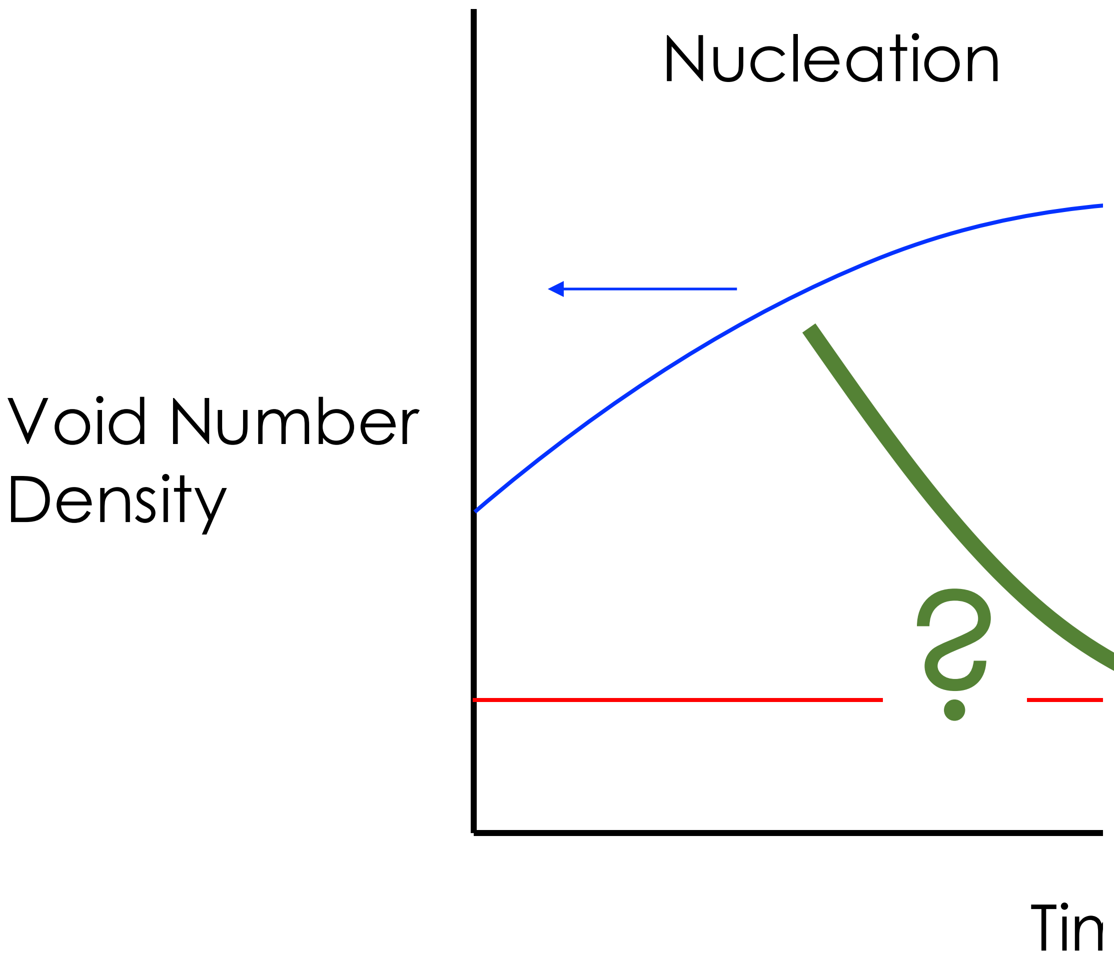
NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

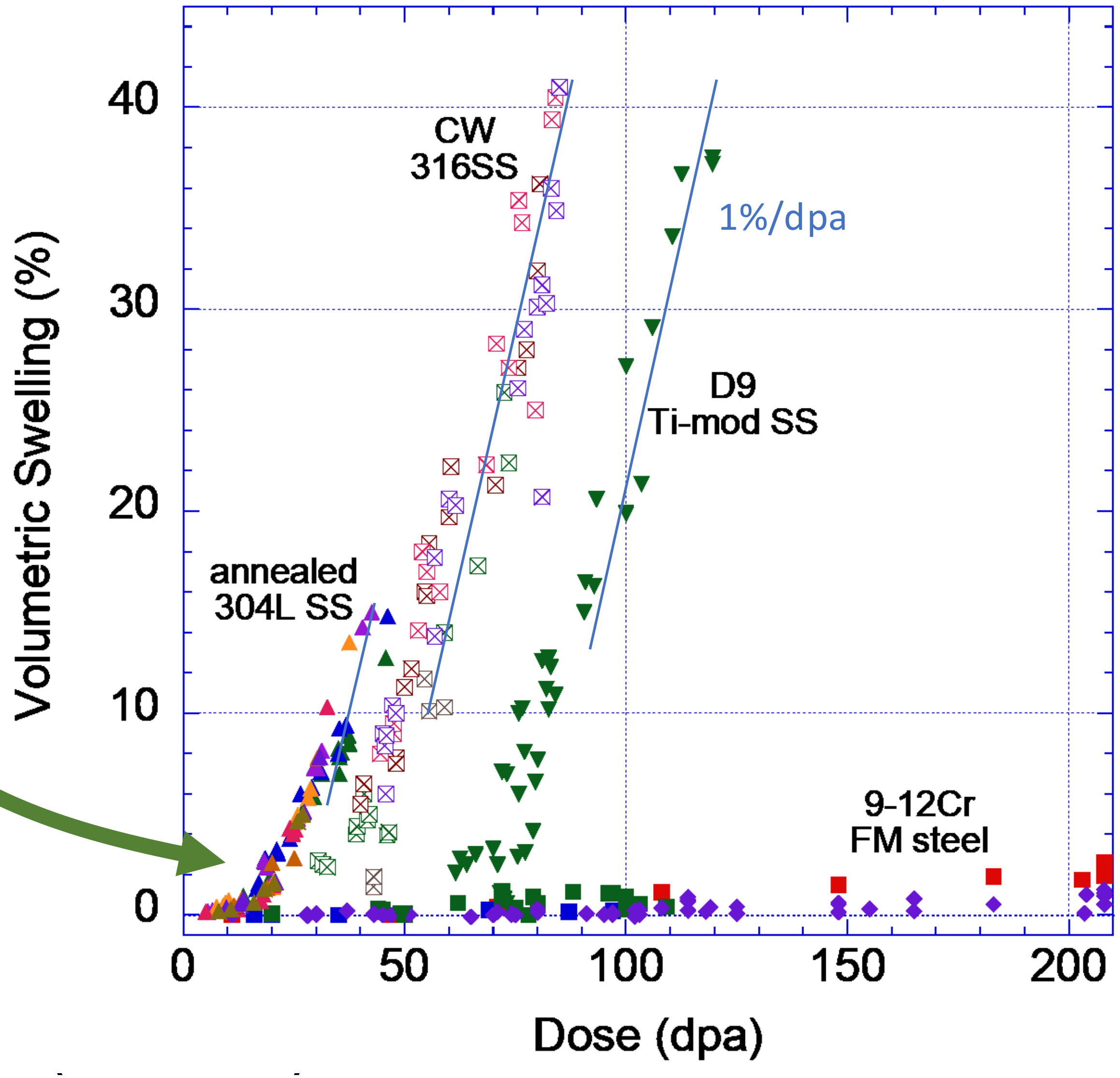
Nucleation vs. Growth



NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Nucleation vs. Growth





NUCLEAR ENGINEERING &
RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

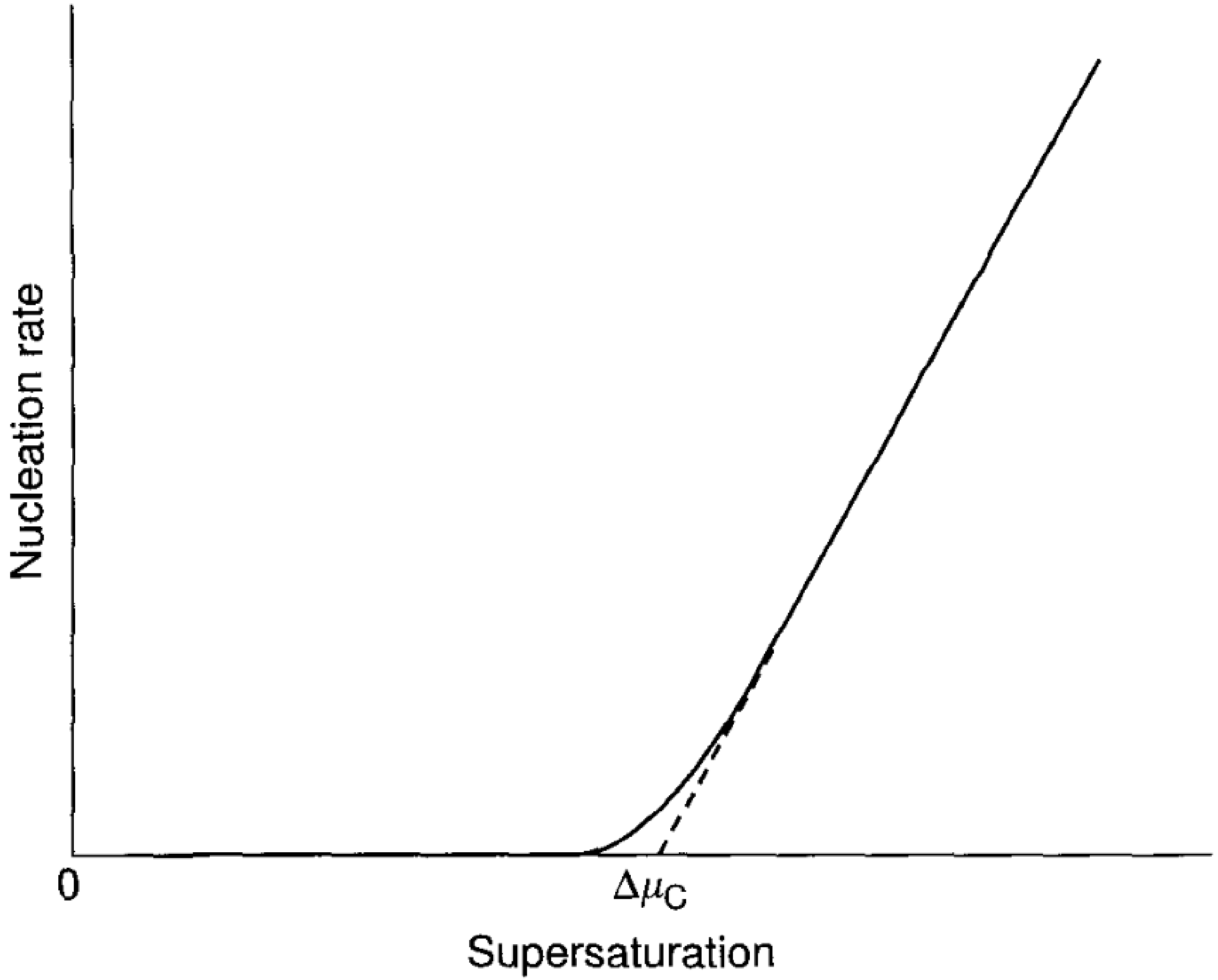
Void Nucleation Rate

Nucleation rate can be generalized as:

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

But it depends on:

- Dose rate
- Temperature
- Sink density, etc.



NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Void Nucleation Rate, J_0

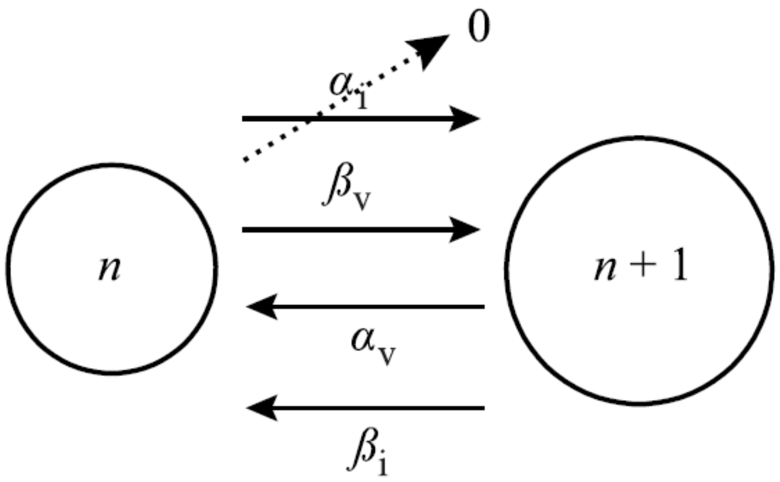
- Voids are three-dimensional clusters of vacancies formed by the following reactions
  1. **Cluster growth** by v absorption: $v + v_j \rightarrow v_{j+1}$
  2. More generally, we consider **small cluster mobility**: $v_j + v_k \rightarrow v_{j+k}$
  3. **Cluster shrinkage** by v emission: $v_j \rightarrow v_{j-1} + v$
     - 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. $C_i^0 \sim 0$

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

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 $n+1$

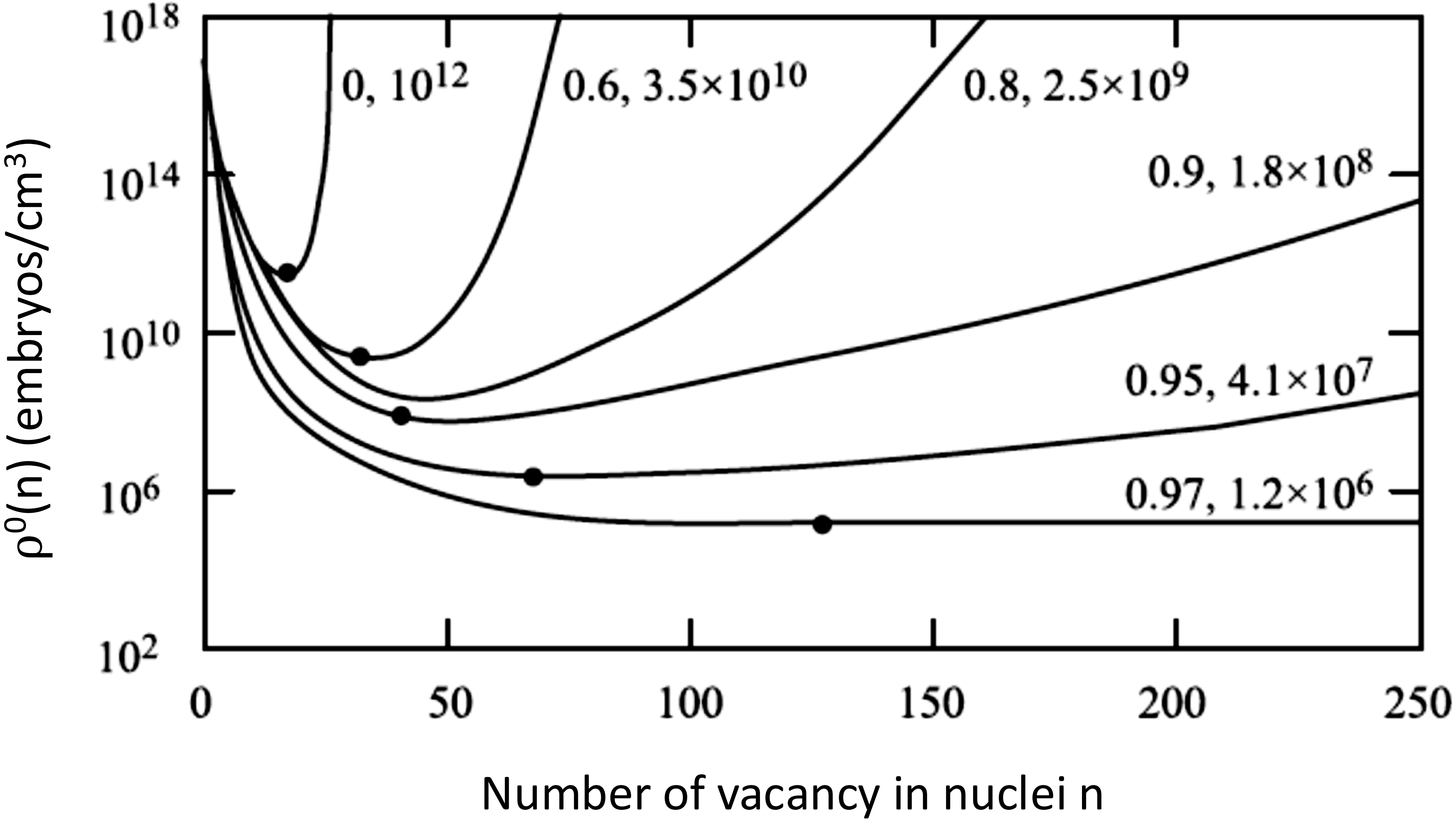
Void Nucleation Rate

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

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

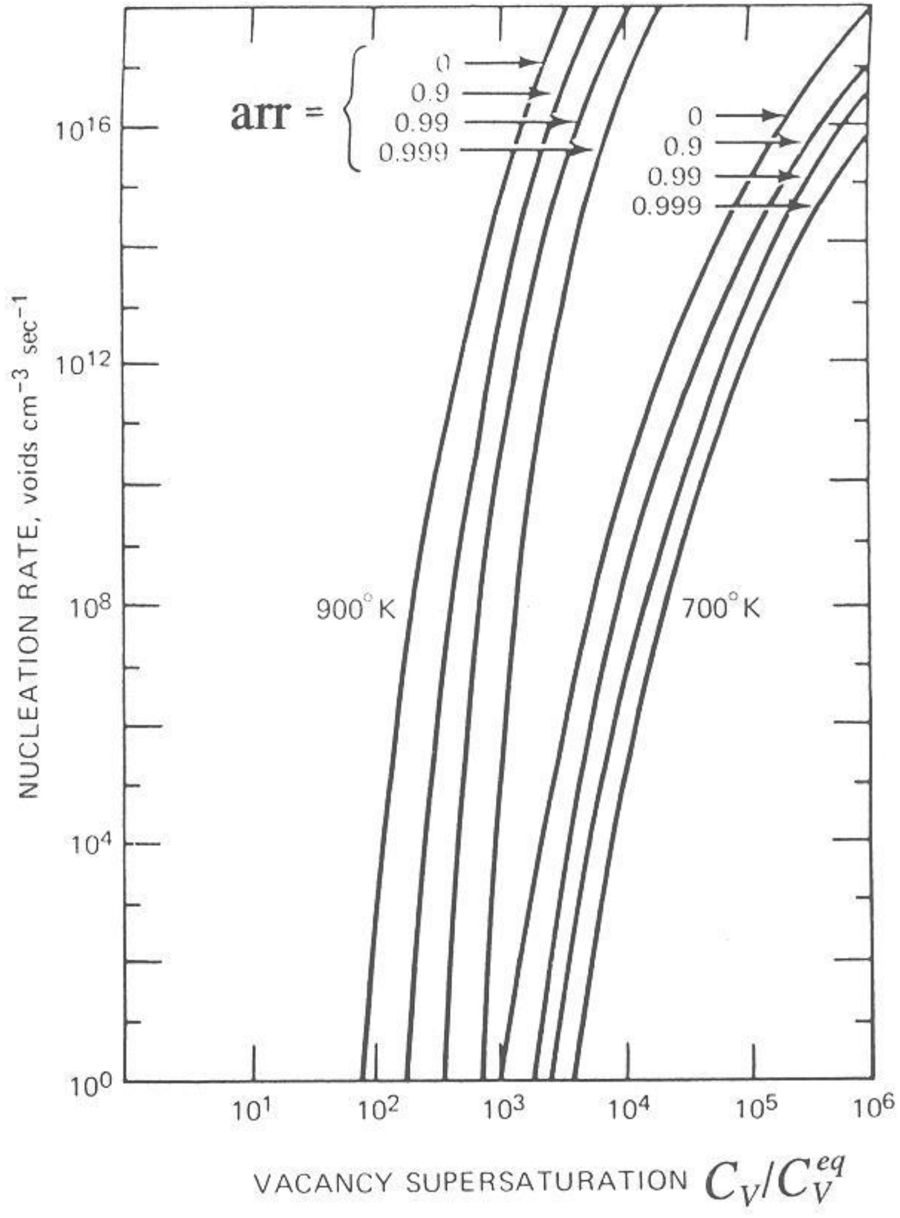
- C_v^{eq}/C_v is the inverse of vacancy supersaturation S_v^{-1}
- $(D_i C_i)/(D_v C_v)$ is the arrival rate ratio between v and *i*
- γ is the surface energy of the cavity
- *p* is the gas pressure in the cavity (p=0 for voids!)

Concentration of void embryo sizes w/ nucleation rate



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

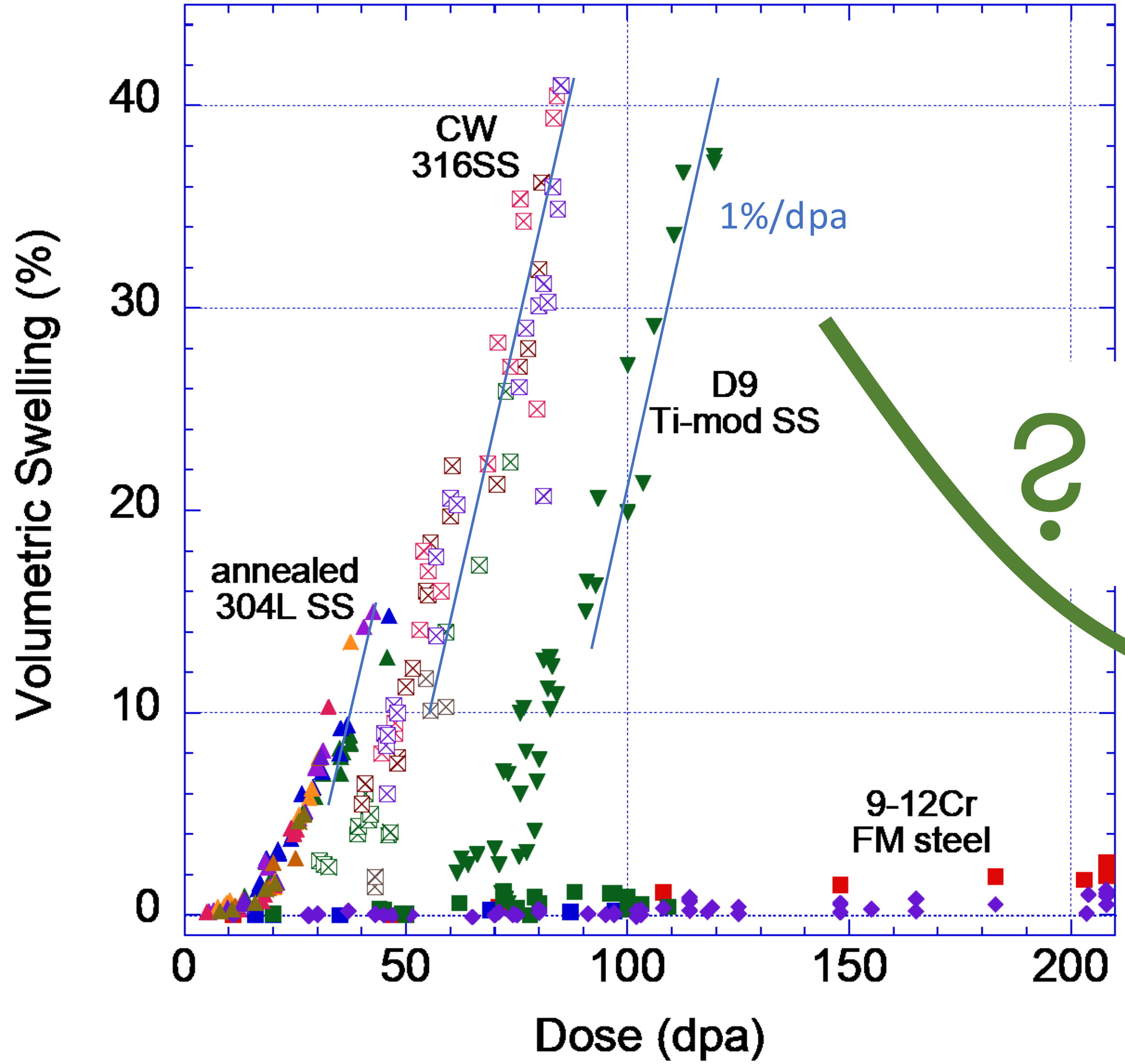
Lecture Break

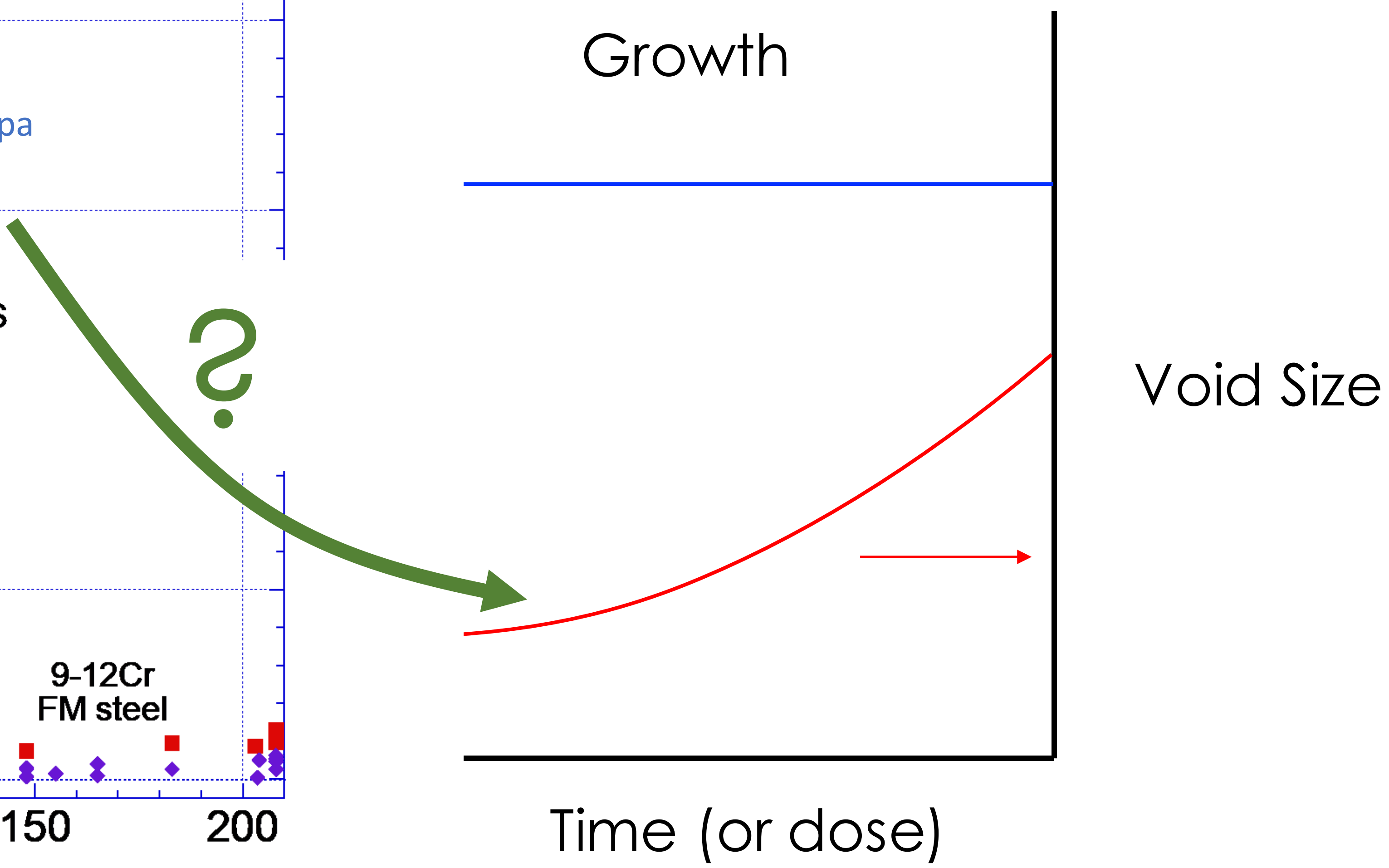
While the Stormy Kromer company is famous for its iconic, warm hats now handcrafted in **Ironwood, Michigan**, its namesake had another passion.

George "Stormy" Kromer, a former semi-pro baseball player himself, was also a *notorious* minor league manager. In 1951, while managing the Vincennes Velvets, he led the team to an embarrassing, nationally recognized losing streak.

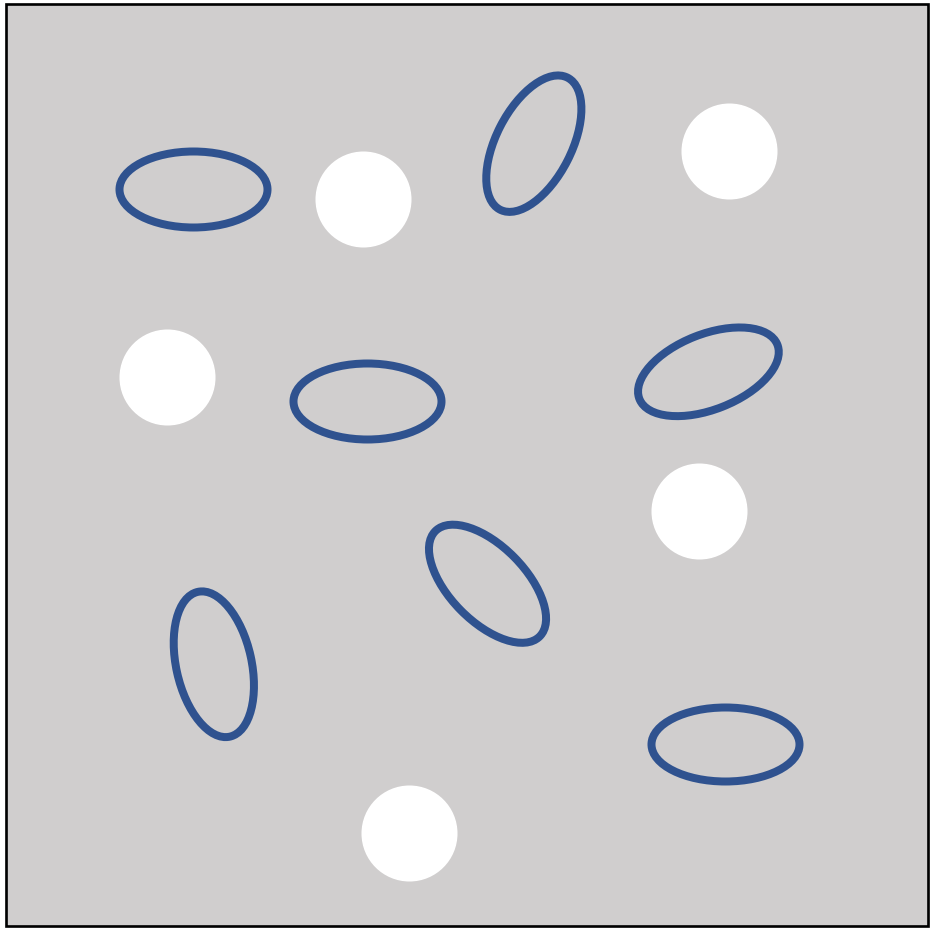
How many consecutive games did Stormy Kromer's team lose during that infamous streak?

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:

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

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

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

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

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

$$dR/_{dt} = \dot{R} = \frac{\Omega}{R}(D_vC_v - D_iC_i)$$

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

Next slide

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

Void Growth

Remember:

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

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

and

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

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:

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

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

Where:

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

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

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:

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

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

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:

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

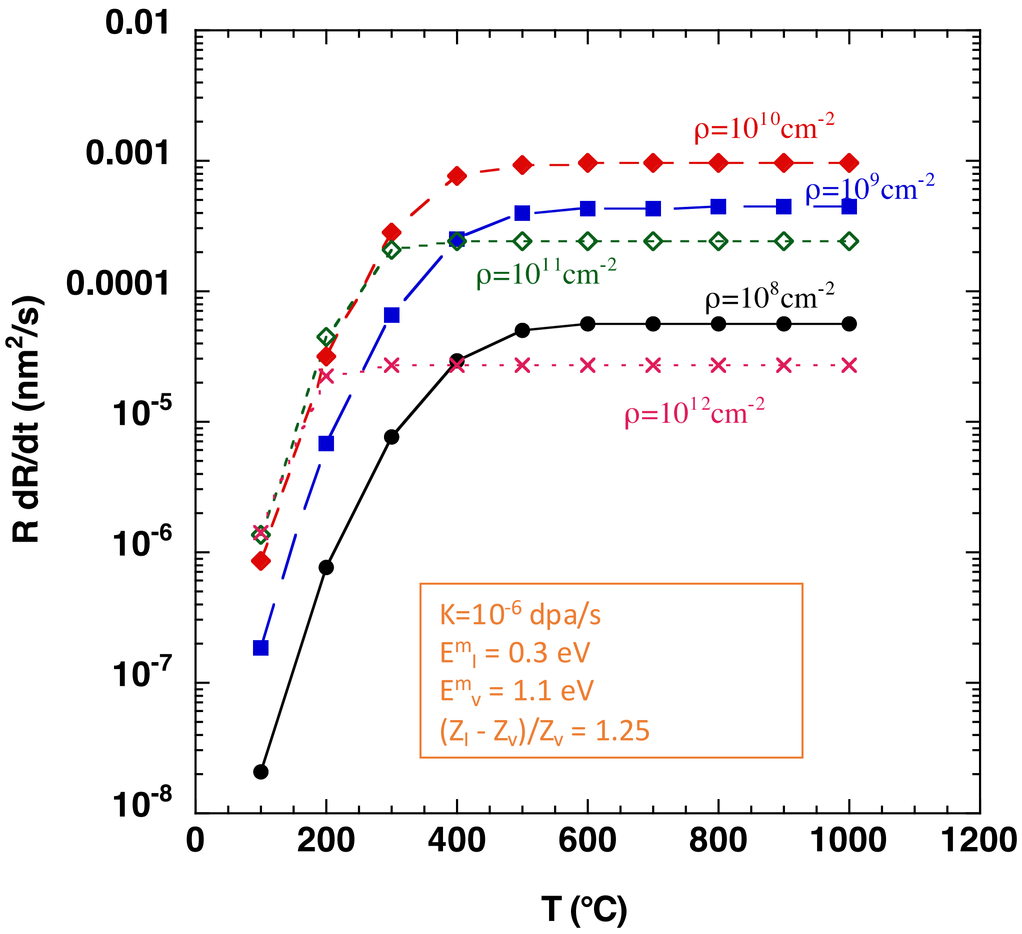
Since h decreases with increasing temperature and F decreases with increasing η:

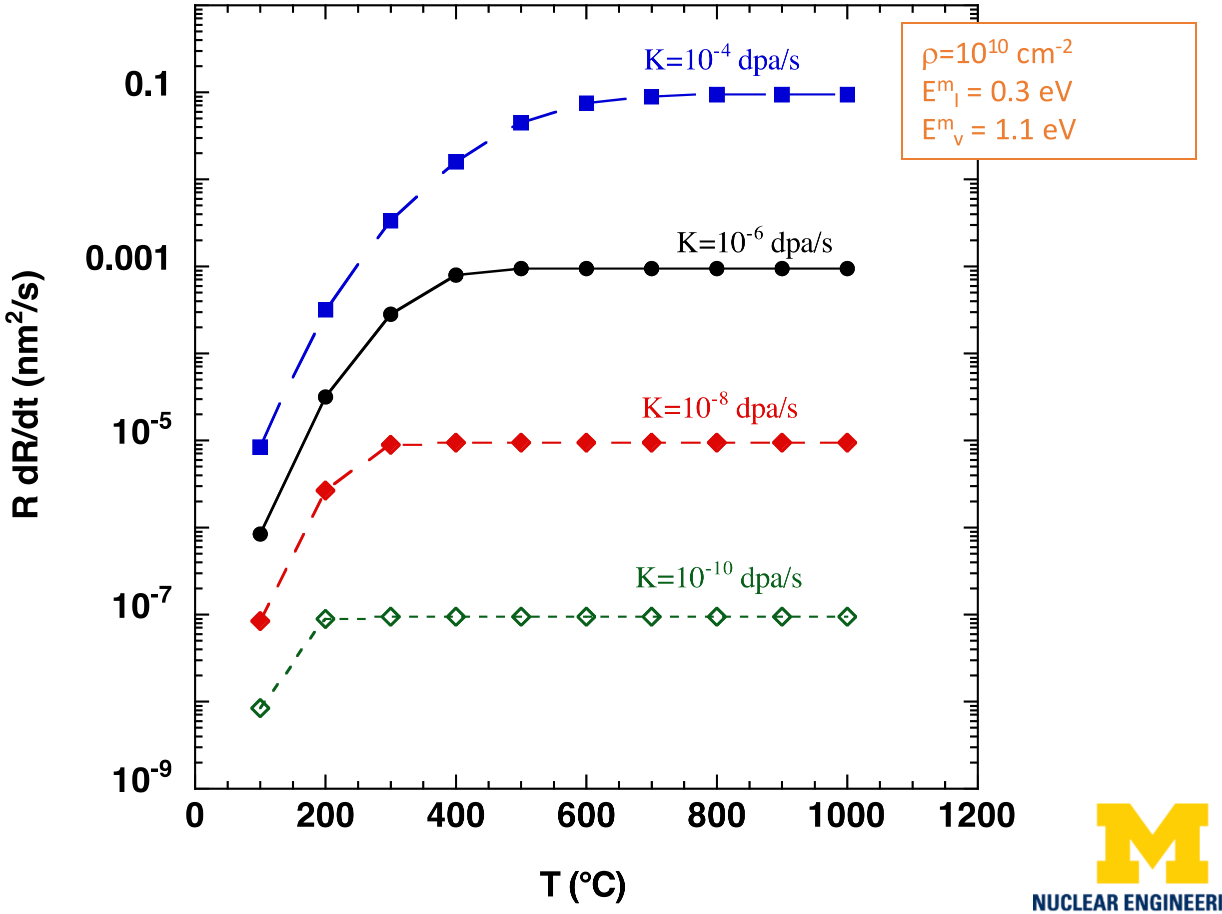
- At high temperature, F $\rightarrow$ 1 and recombination does not effect void growth
- At low temperature, F $\rightarrow$ 0 and recombination prevents void growth.

NUCLEAR ENGINEERING &
RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Void Growth

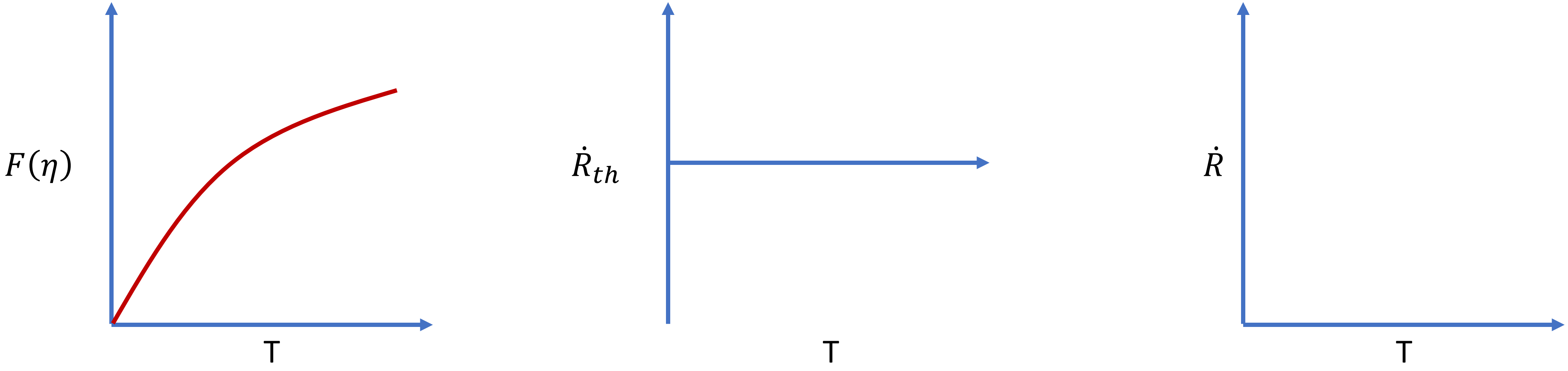
$$R\dot{R} = K_o\Omega\left(\frac{z_i - z_v}{z_v}\right)\frac{z_v\rho_d}{(4\pi R\rho_v + z_v\rho_d)(4\pi R\rho_v + z_i\rho_d)}F(\eta)$$





NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

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:

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

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

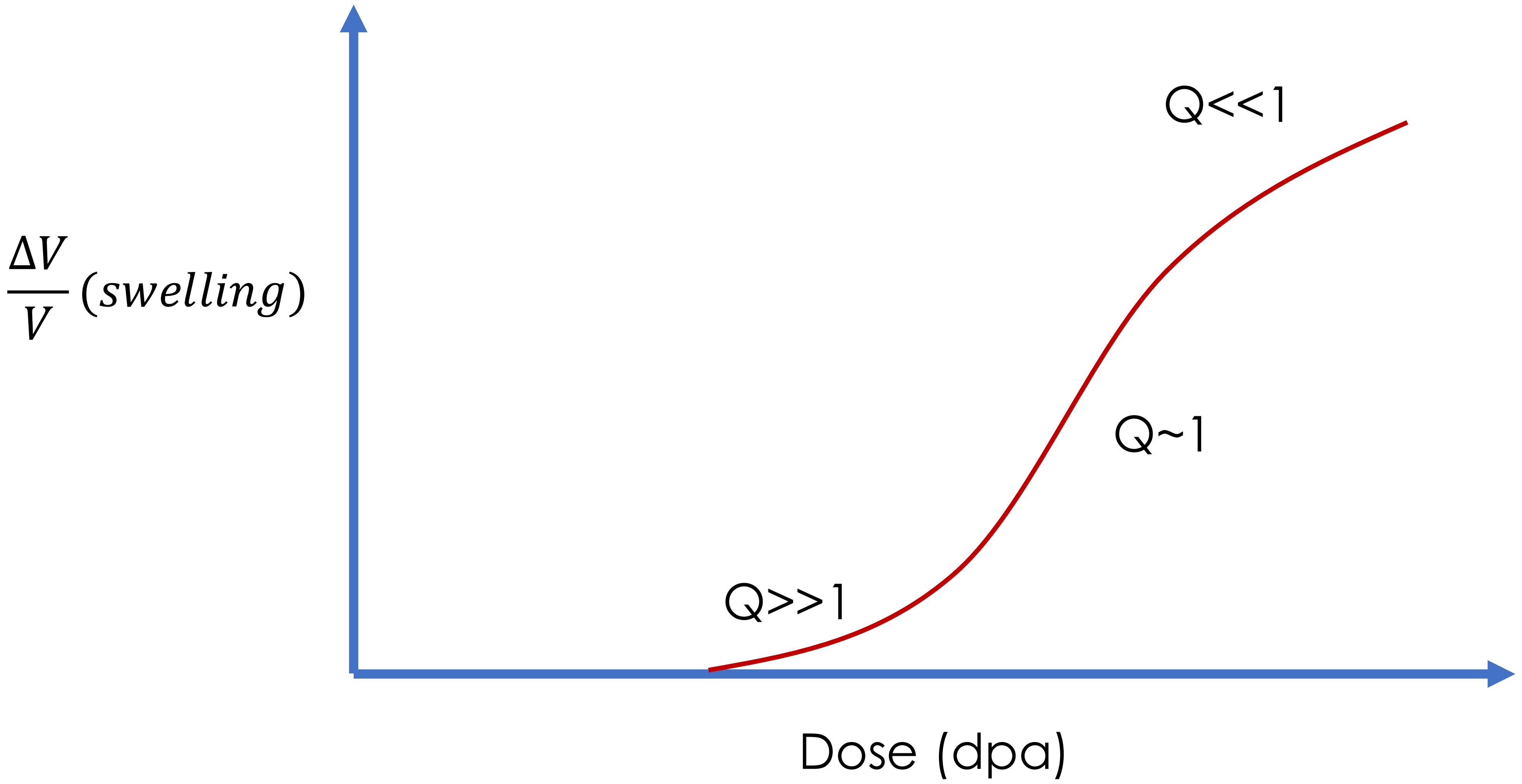
Effect of Structure on Void Swelling

- 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:

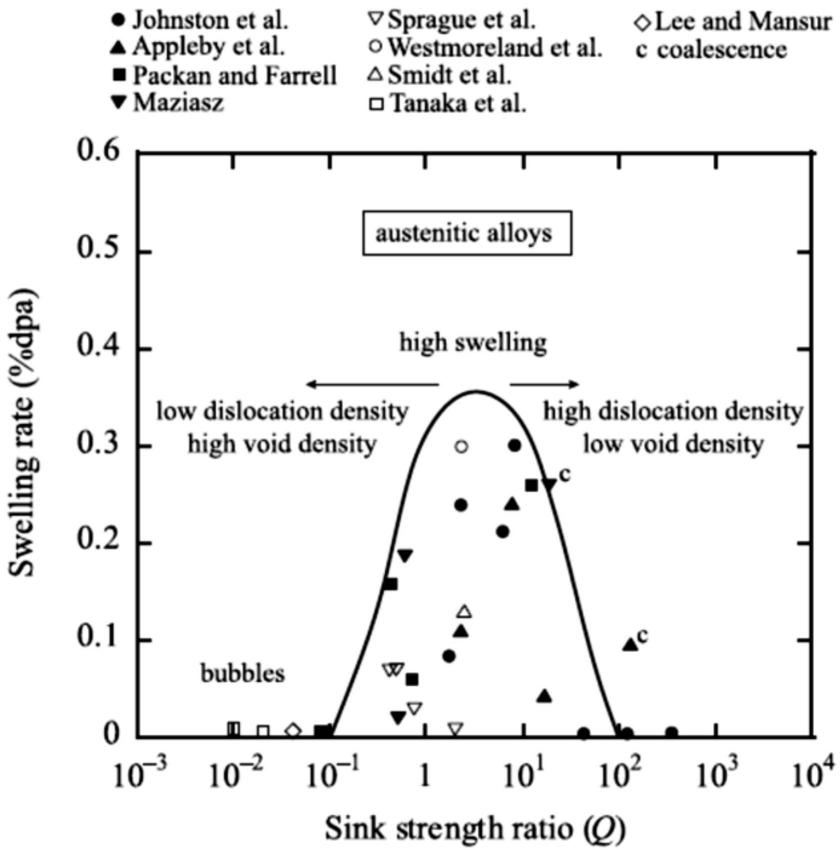
$$\left.\frac{z_v \rho_d}{(4\pi R \rho_v + z_v \rho_v)(4\pi R \rho_v + z_i \rho_d)}\right\} \frac{Q}{(1+Q)^2}$$

Where: $Q = \dfrac{\rho_d z_i}{z_v 4\pi R \rho_v}$

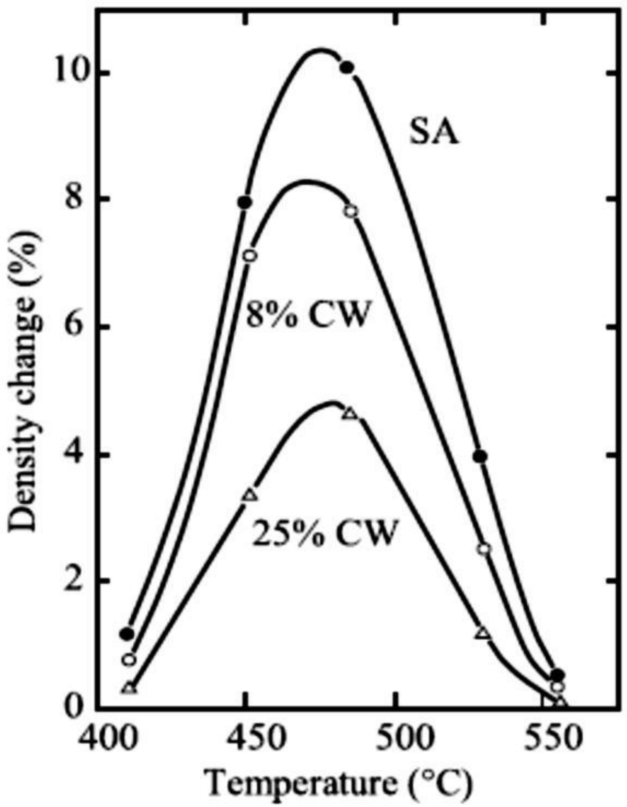
The Q-factor for structure dependence on dose



Effect of Structure on Void Swelling



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

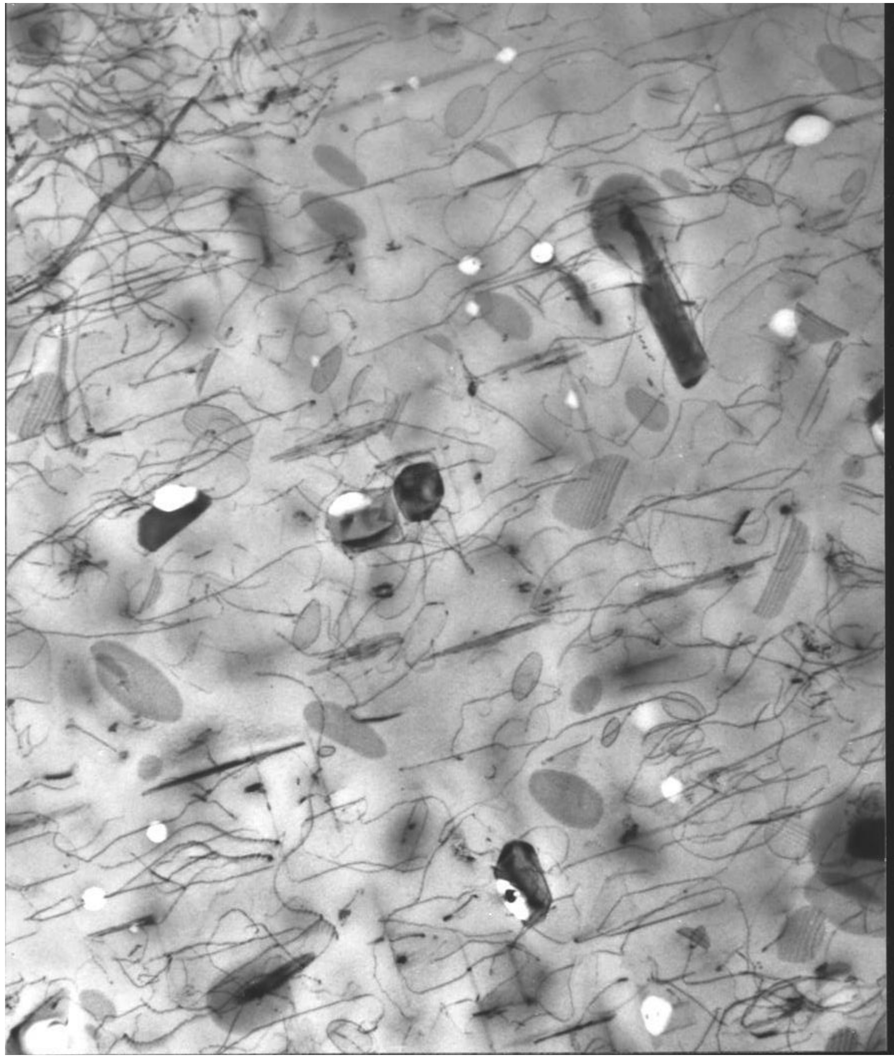


Dependence of swelling on cold-work for various temperatures for 316 stainless steel irradiated in the RAPSODIE reactor to doses of 20–71dpa (DupouyJM, Lehmann J, BoutardJL (1978) In: Proceedings of the Conference on Reactor Materials Science, vol. 5, Alushta, USSR. Moscow, USSR Government, pp 280–296)

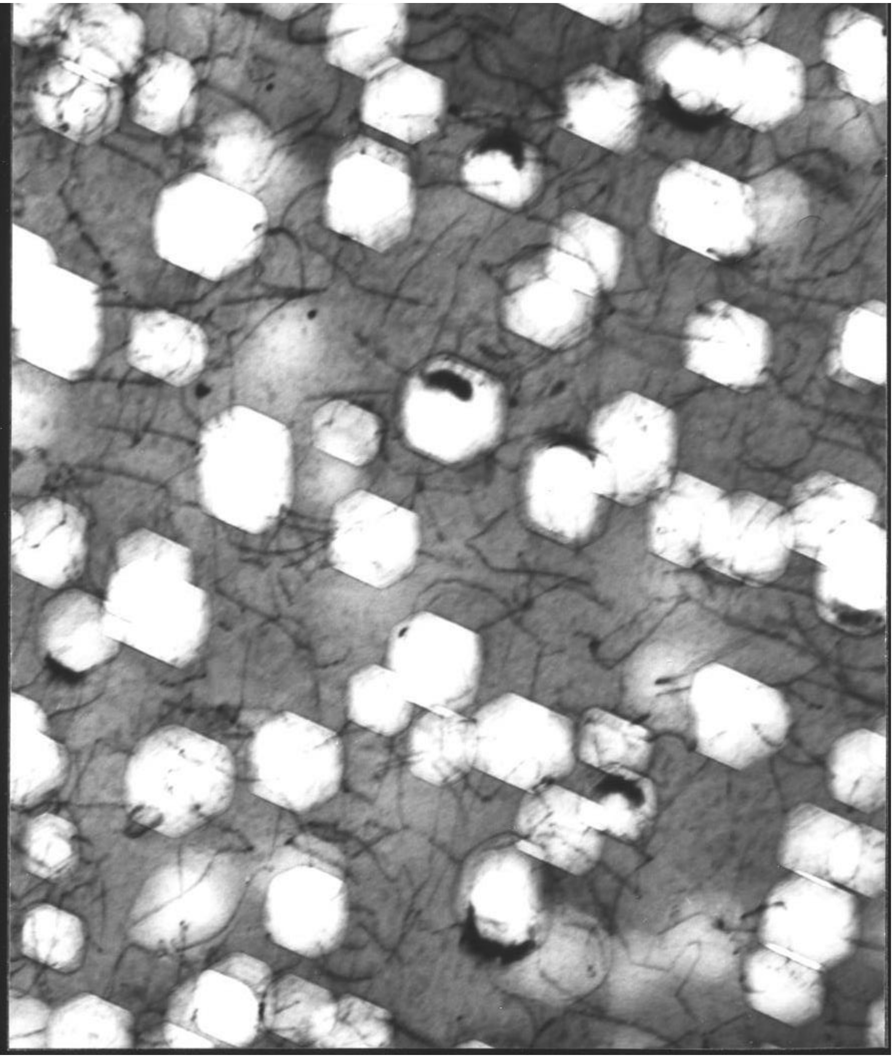
- Growth rate is maximum when Q~1
- Growth decreases for Q != 1
- Observed experimentally
- CW reduces swelling because Q>>1

Image of voids + effect of sink strength

Commercial 316 SS (high sink strength)



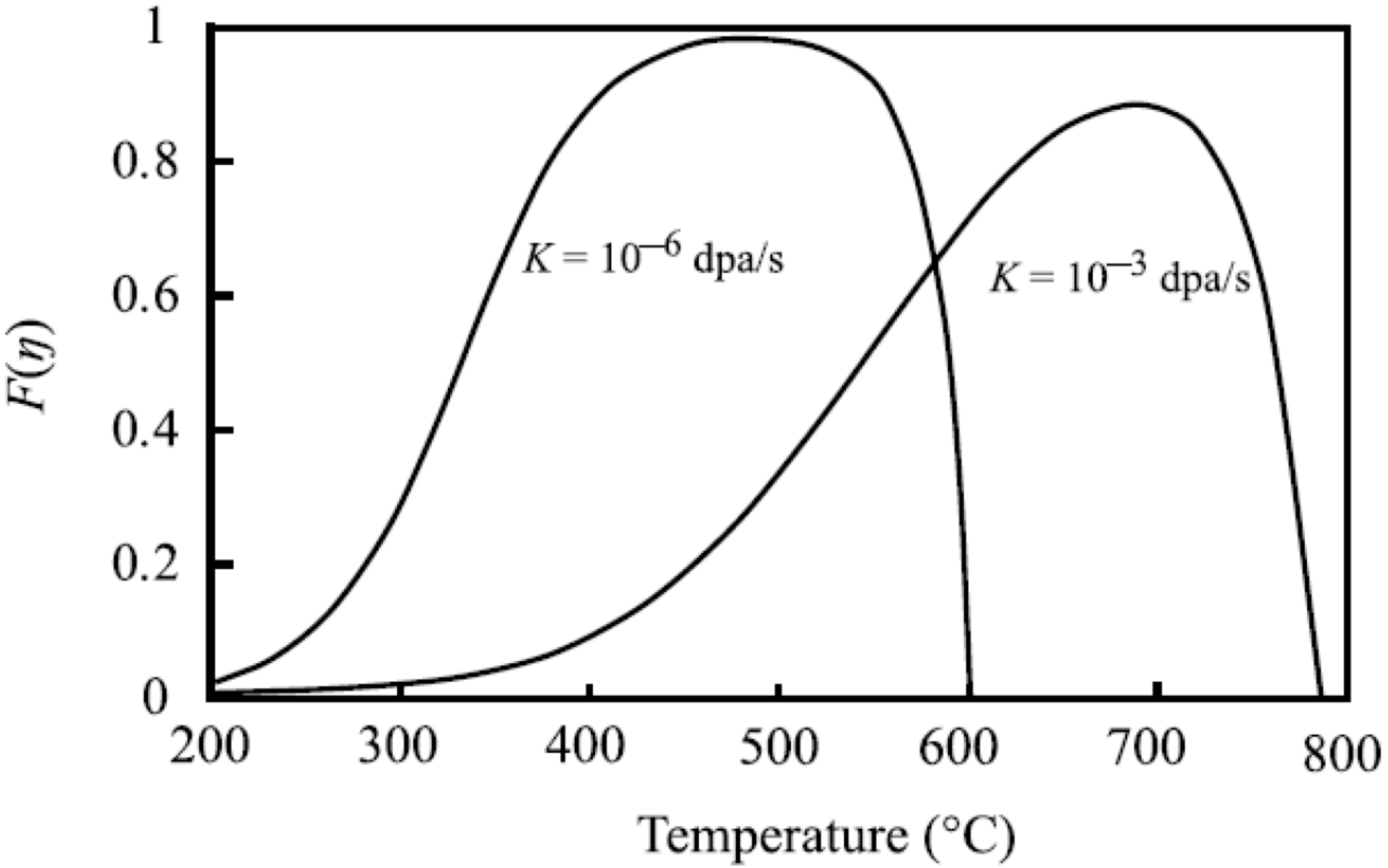
High-purity (low sink strength)



100 nm

NUCLEAR ENGINEERING &
RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Effect of Dose Rate



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

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

And:

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

Effect of Dose Rate

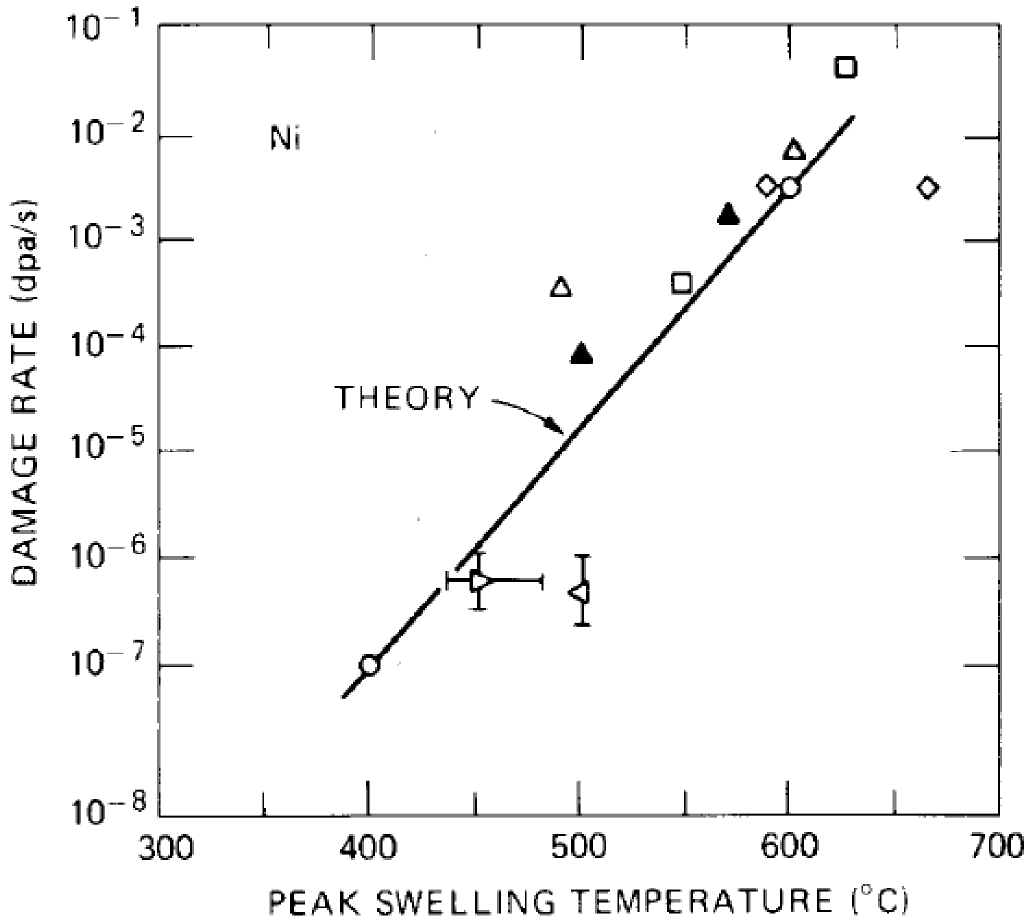


Figure 8.29. Compilation of experimental results for peak swelling temperature as a function of dose rate. Theoretically predicted trend is shown as the line. After Refs. 140 and 141.

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

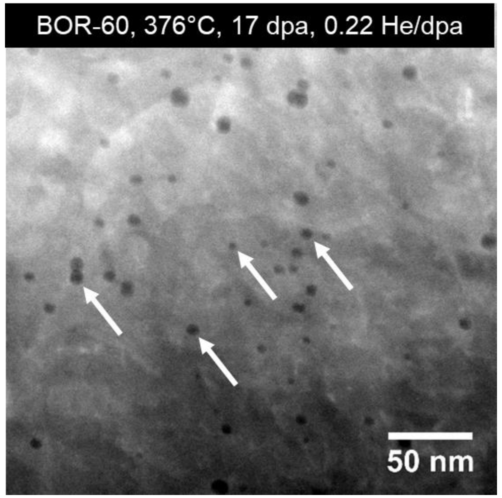
$$F(\eta) = 2\left(\sqrt{1+\eta} - 1\right)/\eta$$

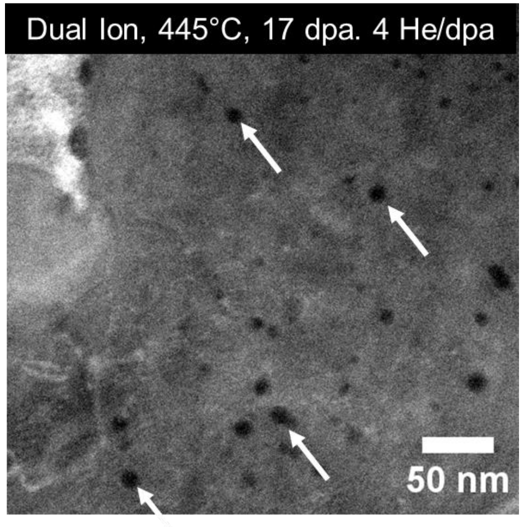
And:

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

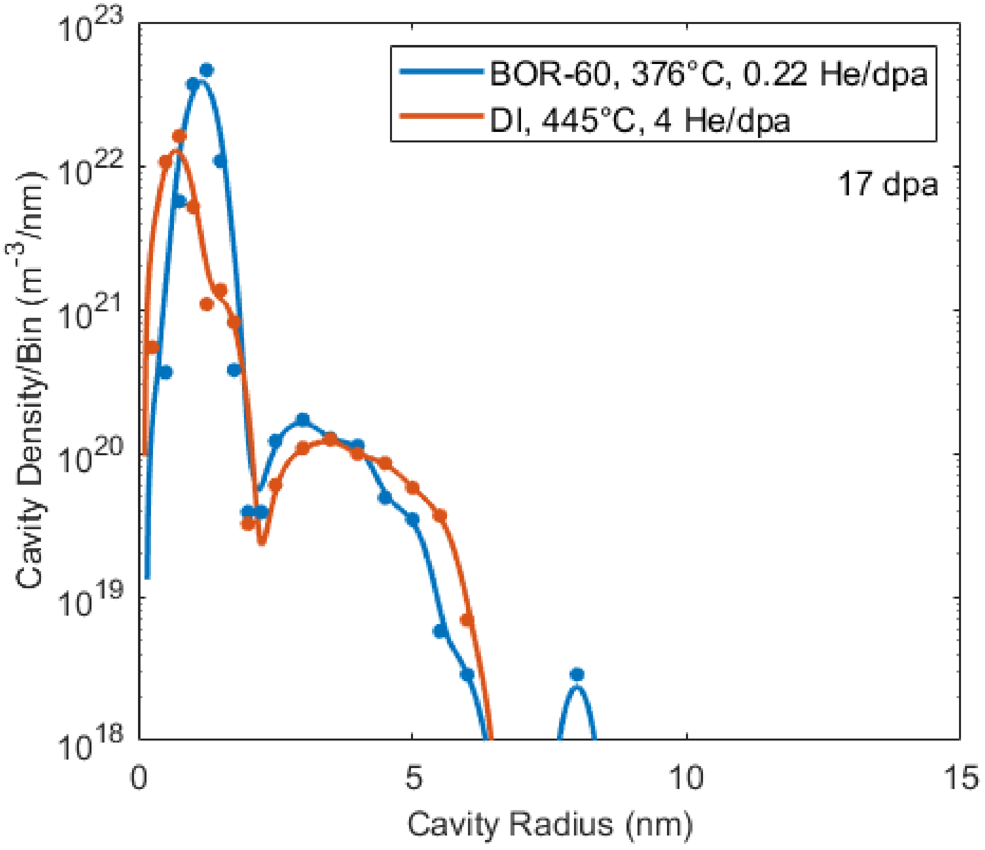
Effect of Dose Rate – Real World Example

STEM HAADF

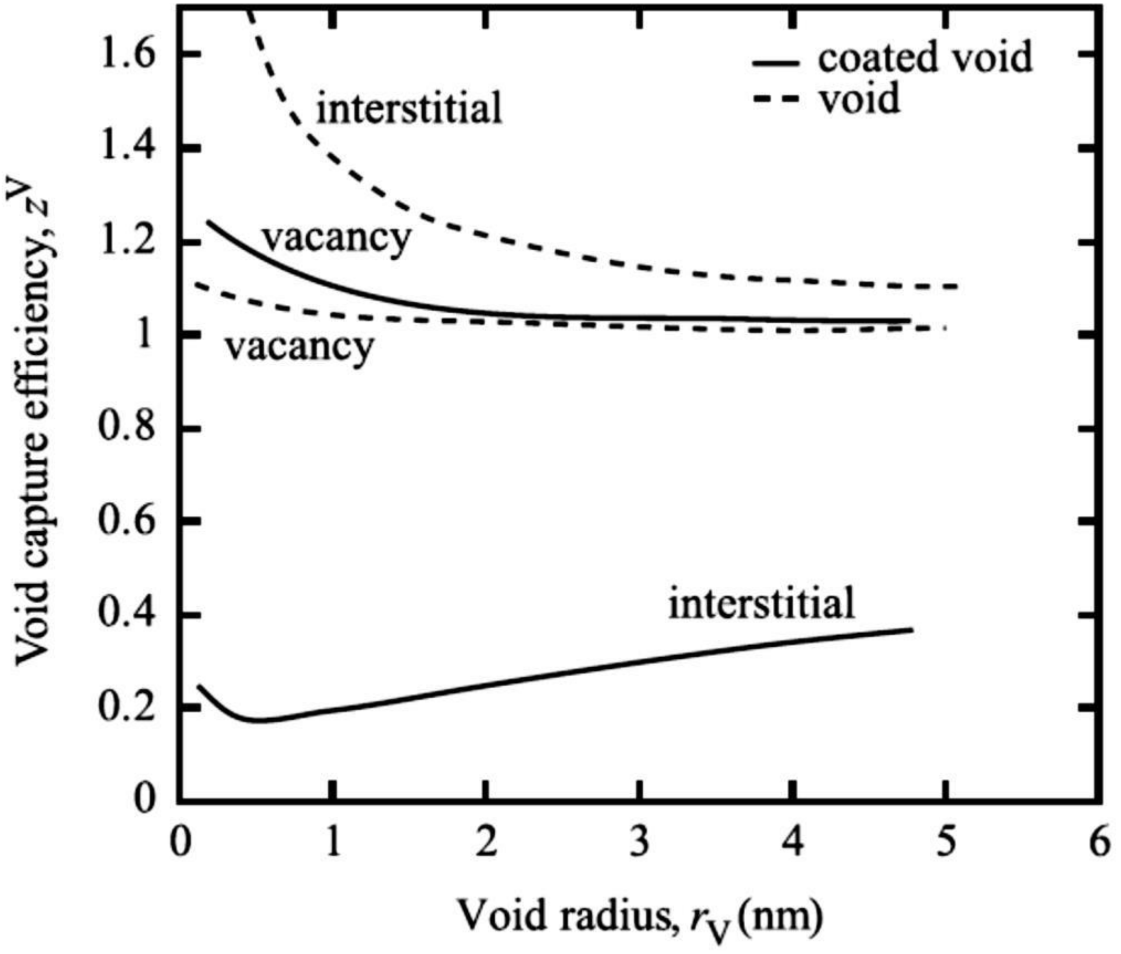




$$T_2 - T_1 = \frac{\dfrac{kT_1^2}{E_v^m + 2E_v^f} \ln\left(\dfrac{G_2}{G_1}\right)}{1 - \dfrac{kT_1}{E_v^m + 2E_v^f} \ln\left(\dfrac{G_2}{G_1}\right)}$$



Effect of void surface segregation on defect bias

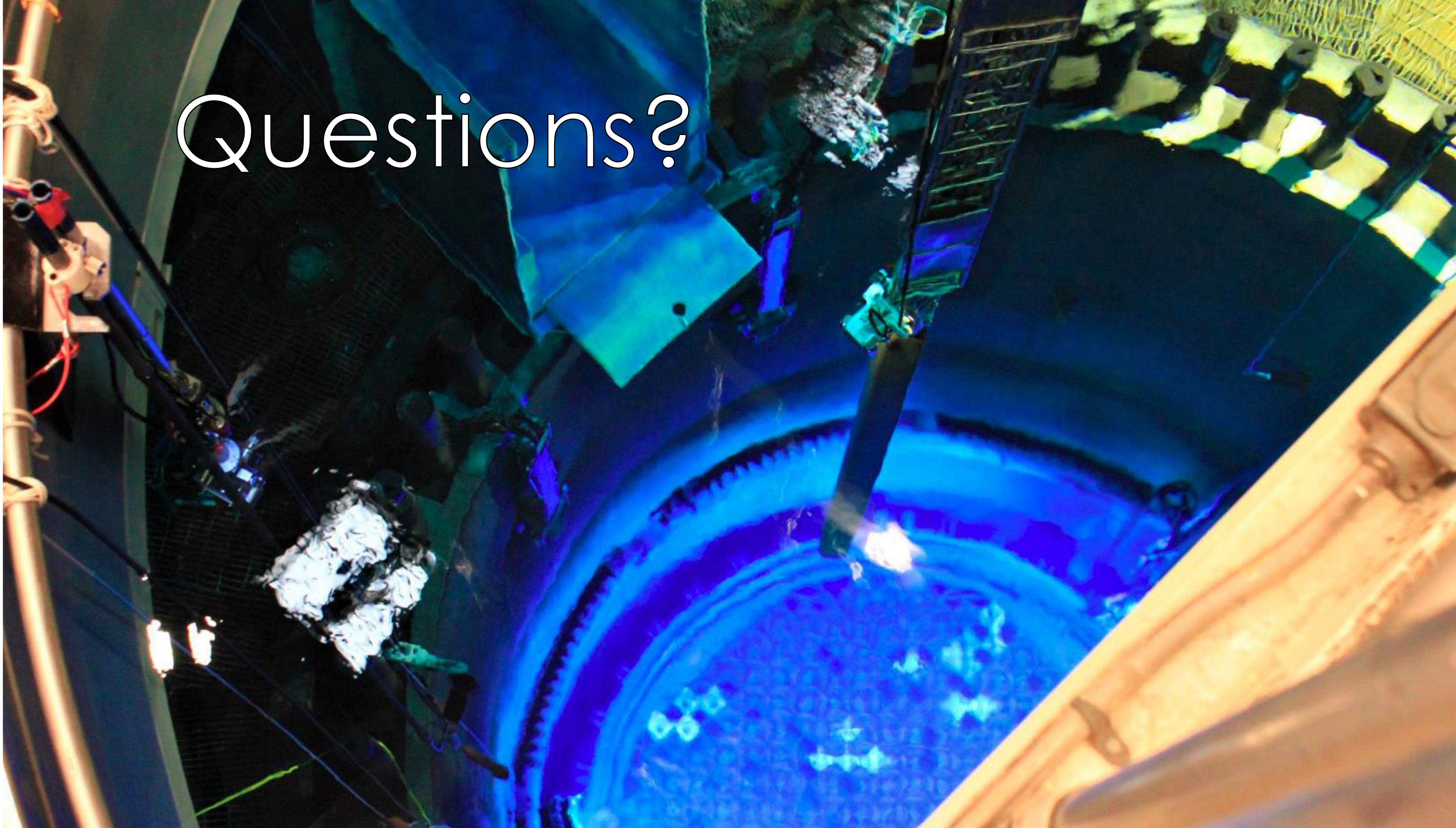


Capture efficiency for point defects diffusion to a void and a coated void as a function of void radius RV. (W.G. Wolfer, L.K. Mansur, The capture efficiency of coated voids, Journal of Nuclear Materials, Volume 91, Issue 2, 1980, Pages 265-276)

- 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

NUCLEAR ENGINEERING & RADIOLOGICAL SCIENCES
UNIVERSITY OF MICHIGAN

Questions?



HW4

- Q#3 can be treated separate (e.g. enrich/deplete concepts will be different) from Q#2
- In Q#4 should should assume that loops will form, and thus the question is asking if you expect to see these loops as faulted or perfect loops
- In Q#5, keep the final expression in terms of constants (Ω, $\gamma_{SFE}, \sigma, G, b$).
  - Unity of a_o means a_o=1 (simply, it can be ignored)
  - The equation for a cavity should be disc. This has been updated in Canvas.