Voids II

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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.

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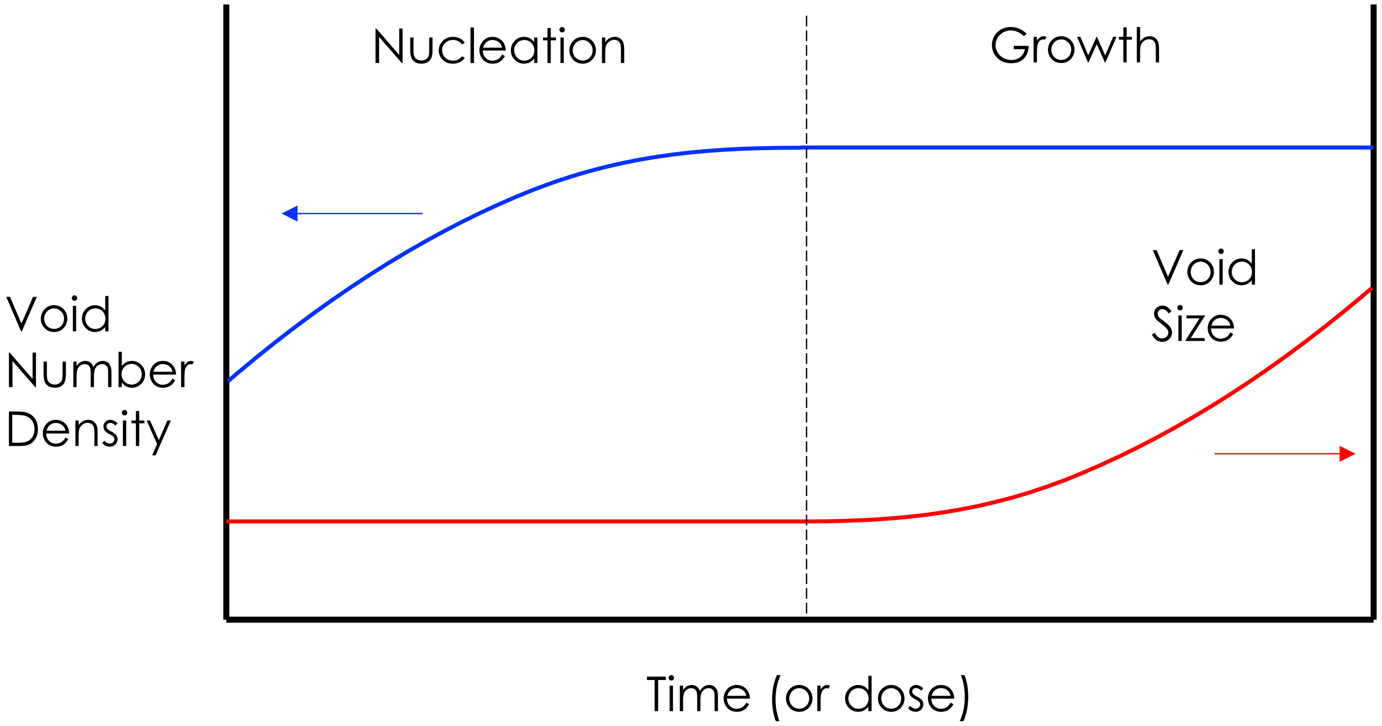
Nucleation vs. Growth



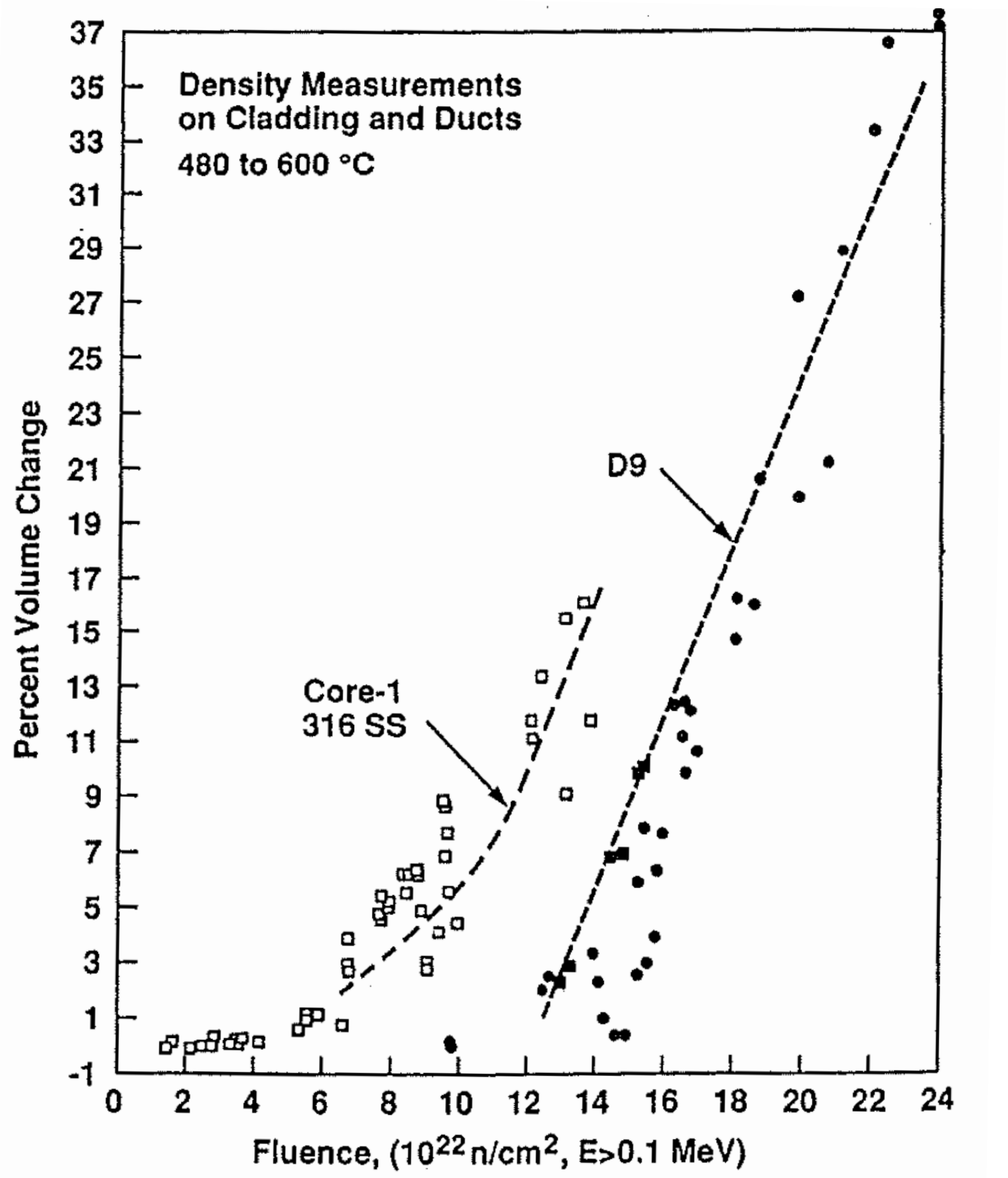


Fig. 3. Swelling observed in two cold-worked austenitic alloys after serving as fuel cladding in the open core of FFTF [23].

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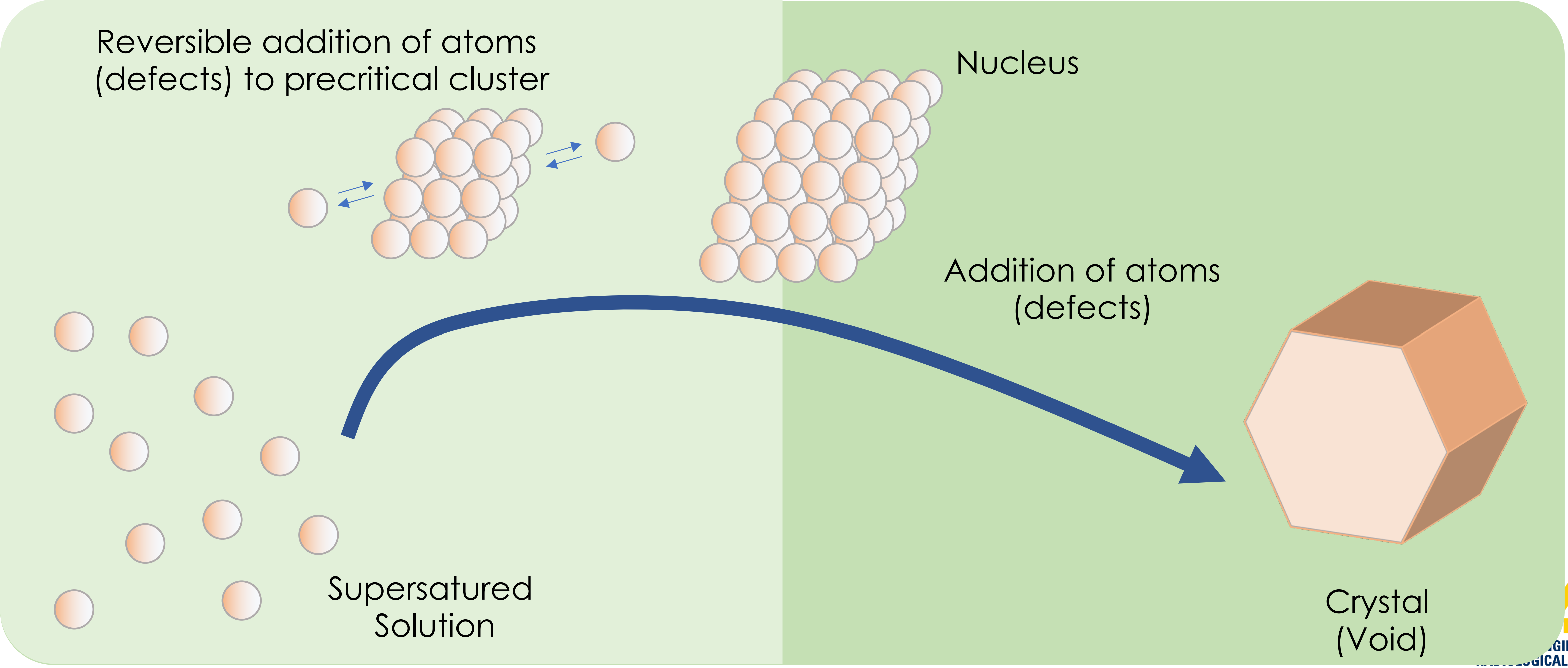
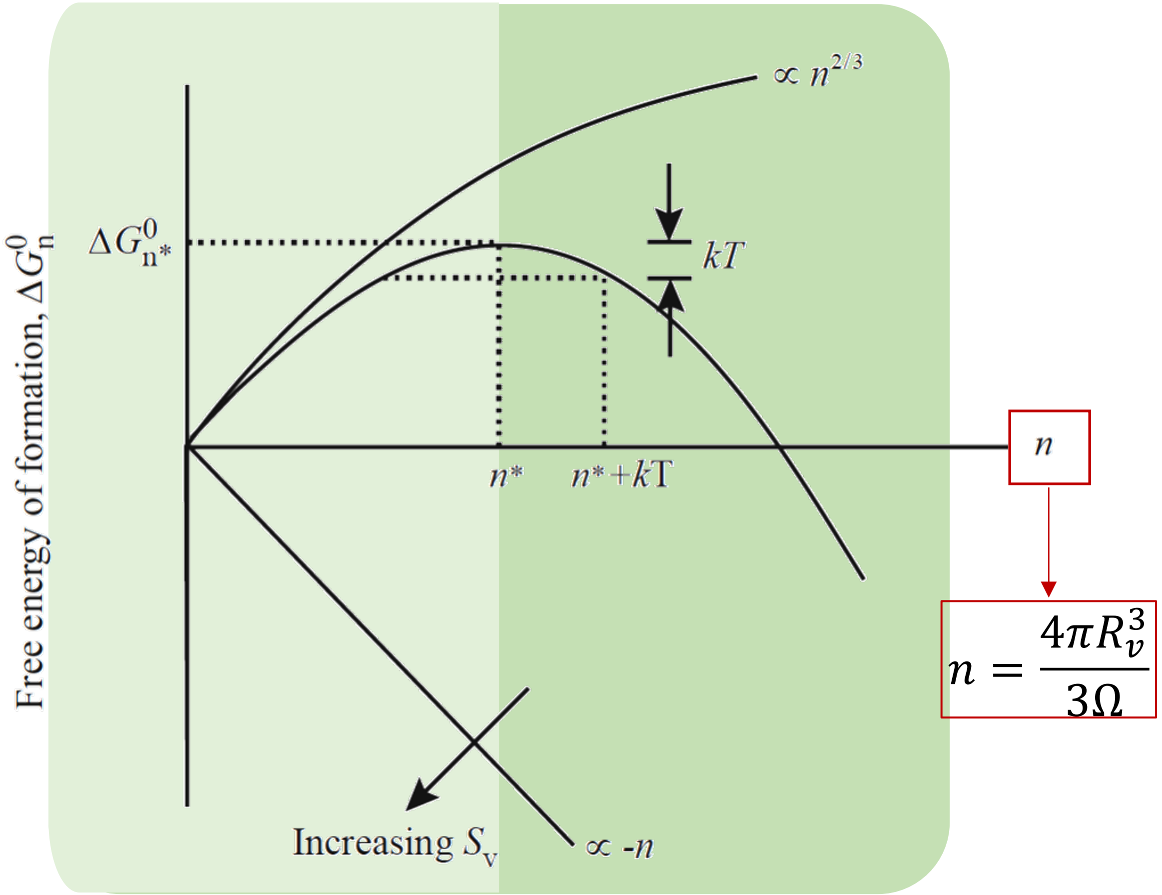
Nucleation

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



Void Nucleation Theory: Graphical depiction

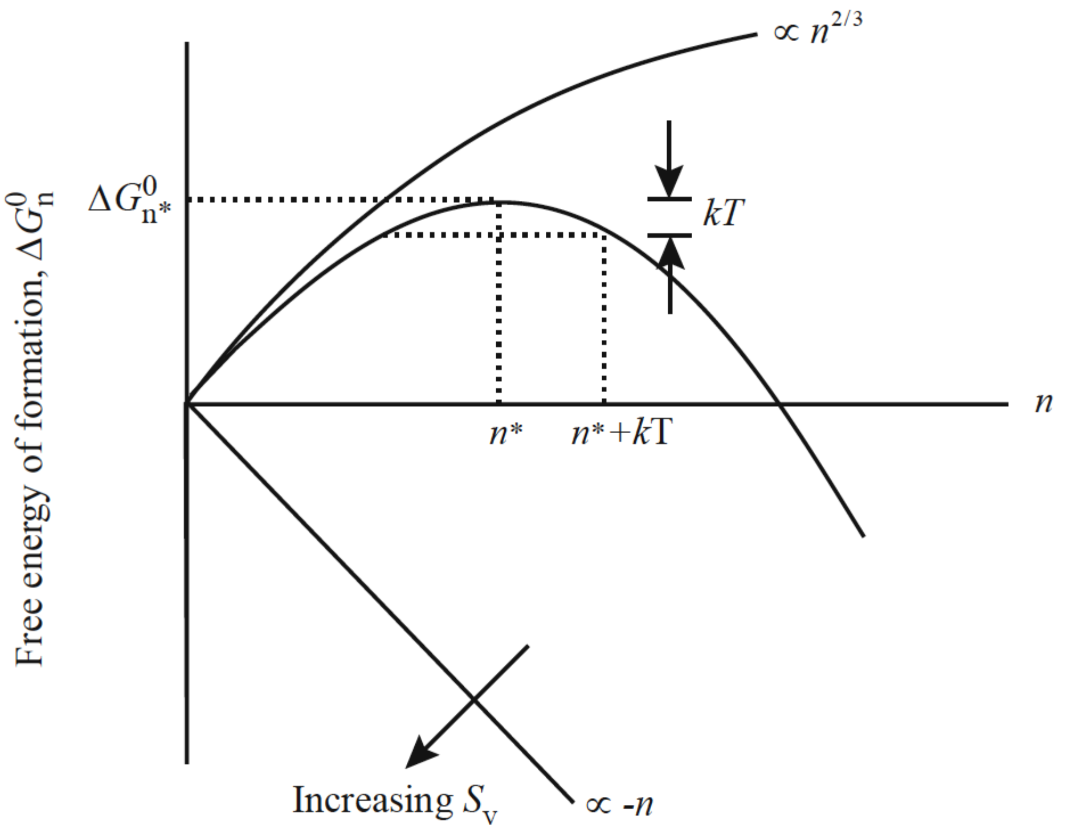
$$\Delta G_n^0 = -nkT \cdot \ln(S_v) + (36\pi\Omega^2)^{1/3}\gamma n^{2/3}$$



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

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

Convert to r

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

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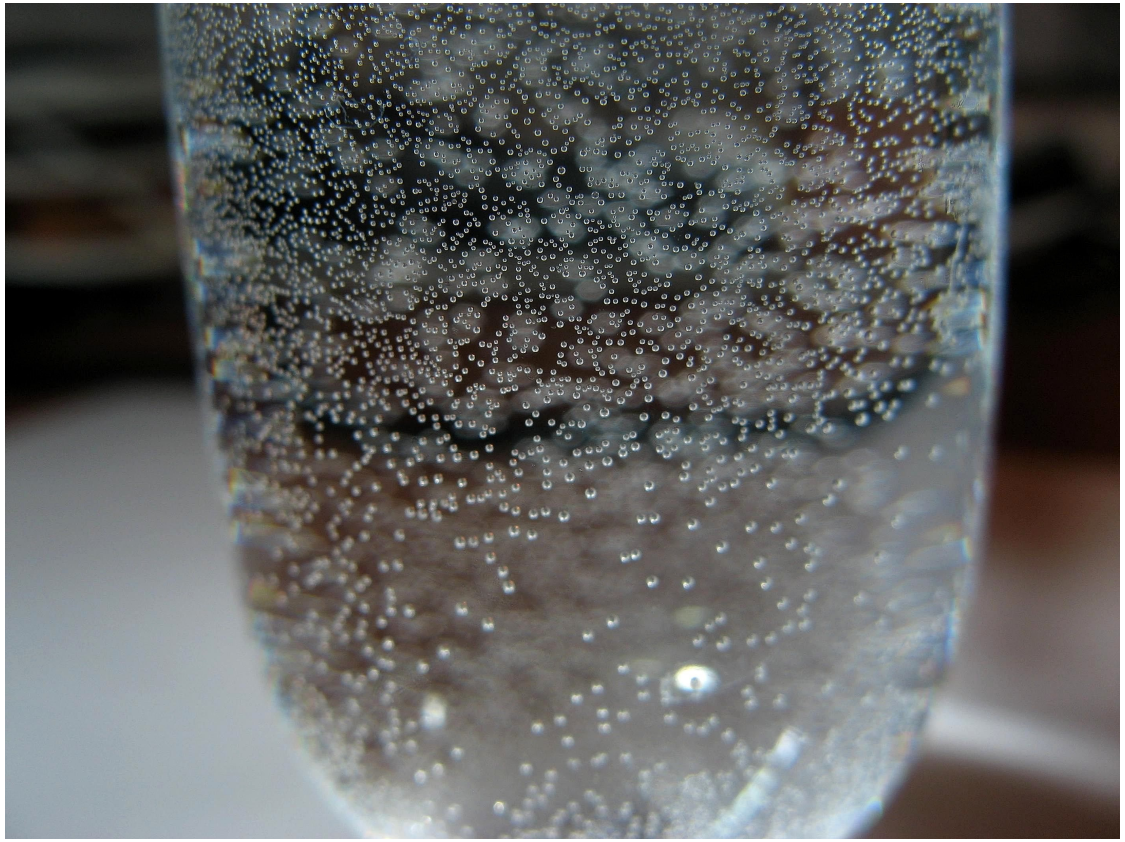
Void Nucleation Theory: Graphical depiction



- Homogeneous nucleation:

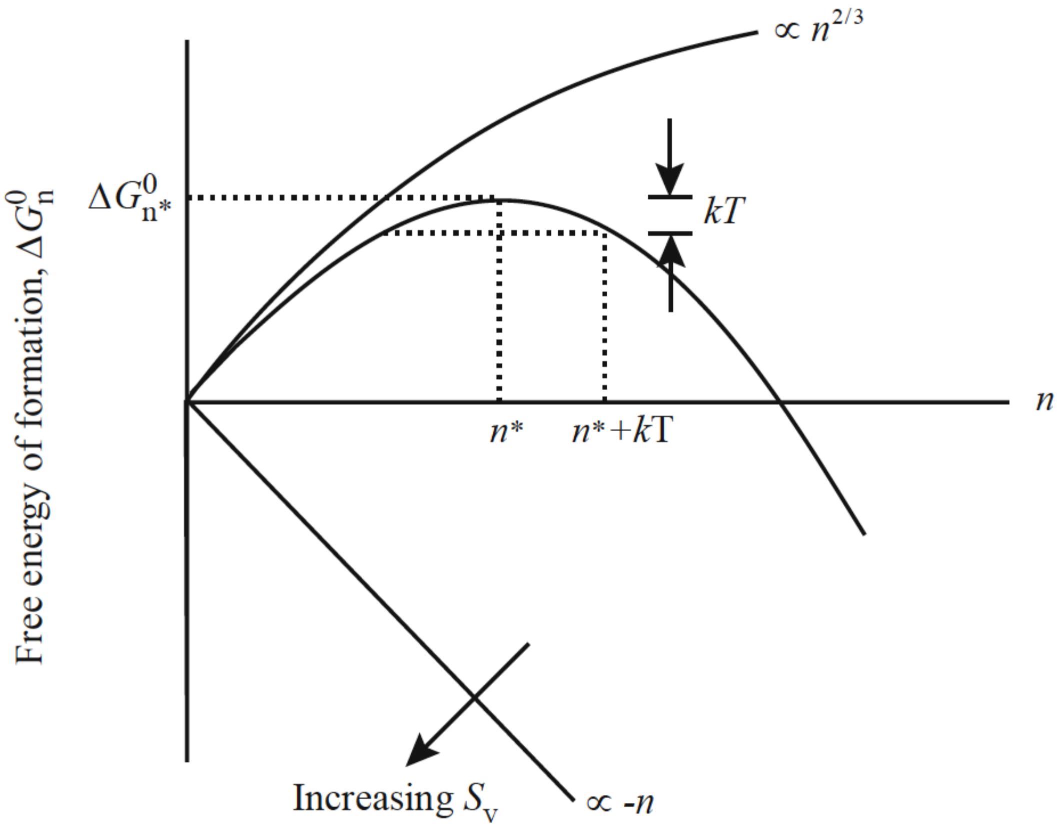
When supercritical particles are formed due to thermal fluctuations

- Heterogeneous nucleation:

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

Derivations and discussion in Was 8.1

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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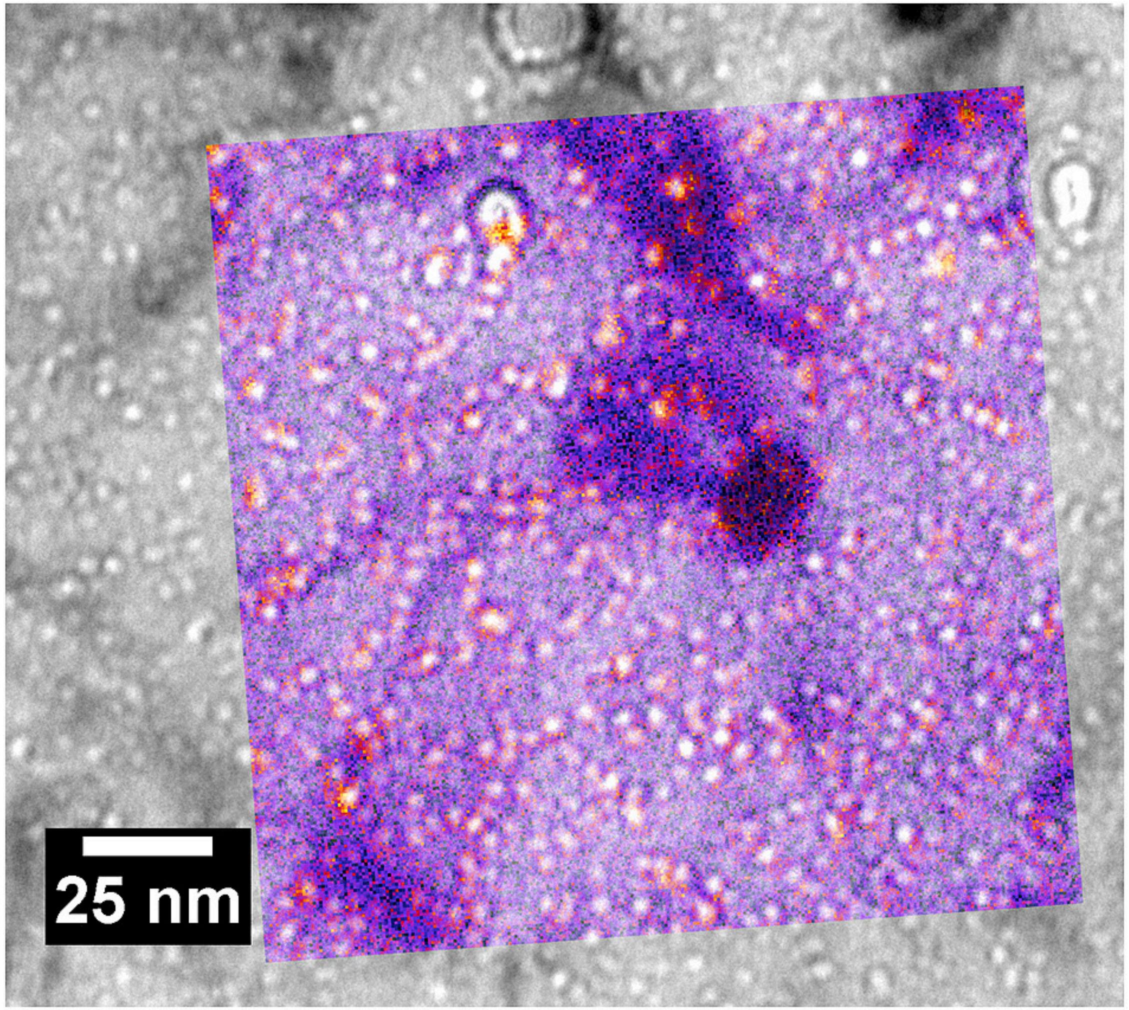
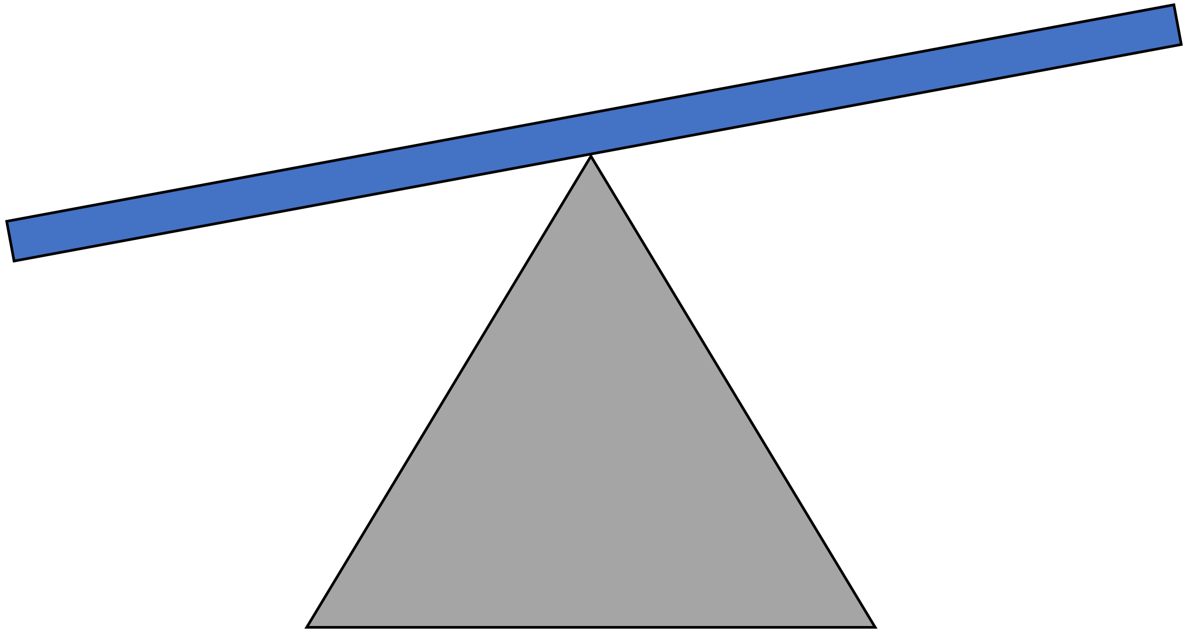
Void Nucleation Theory: Balance





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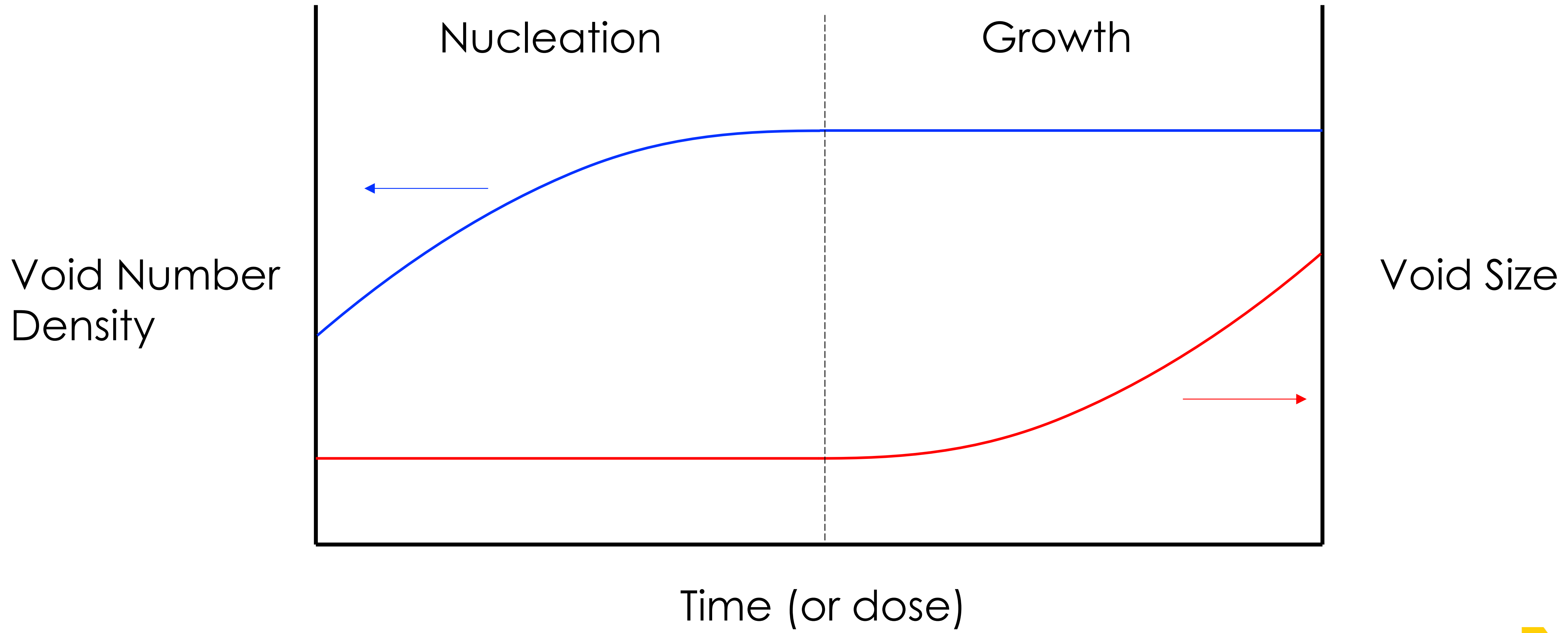
Nucleation vs. Growth



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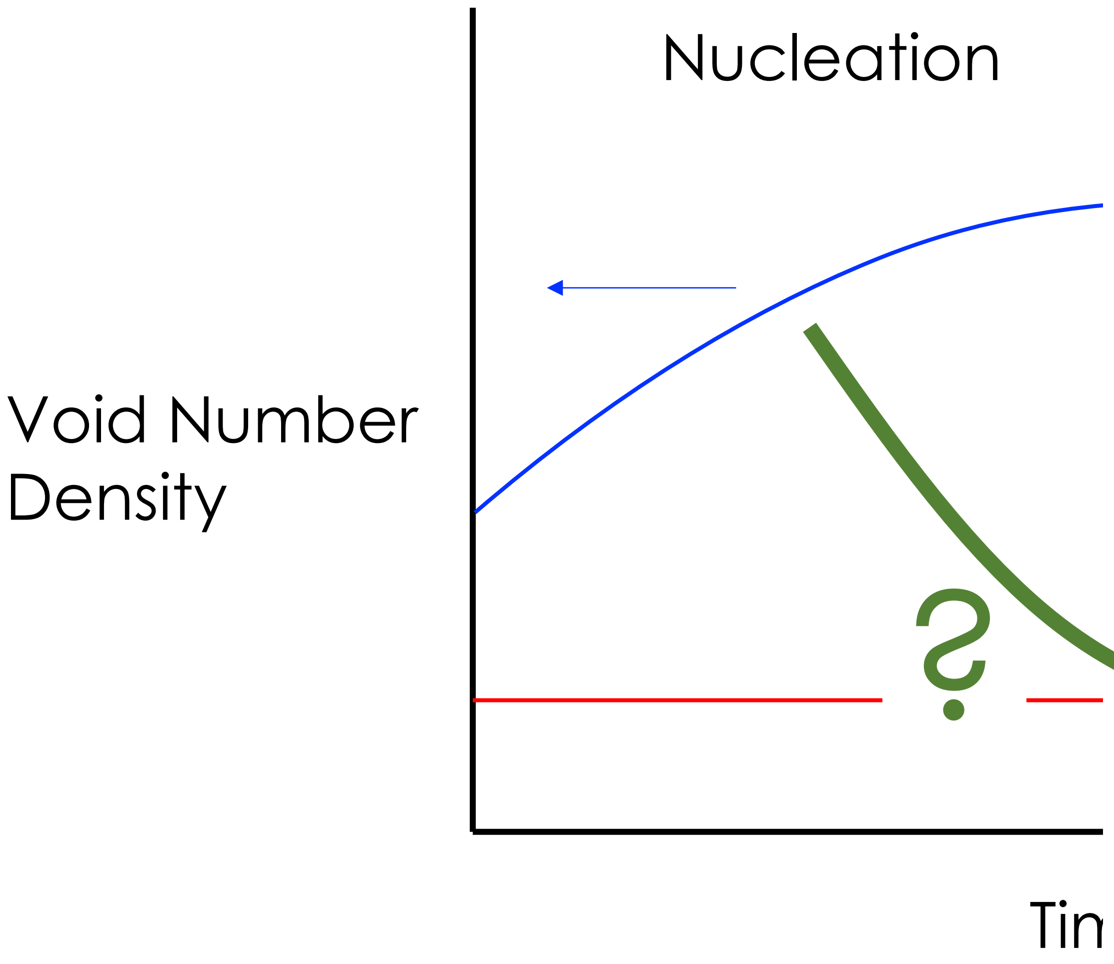
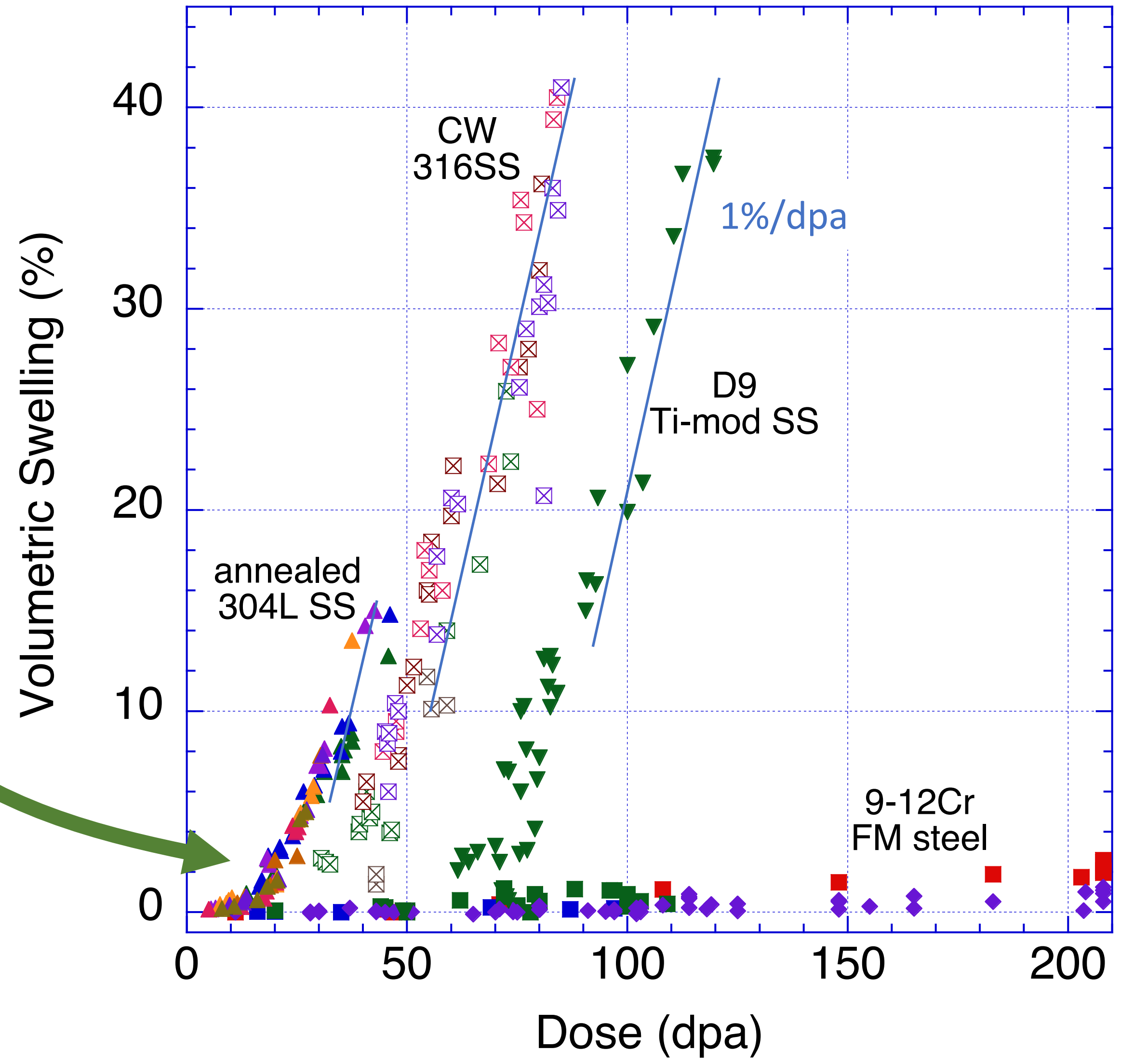
Nucleation vs. Growth





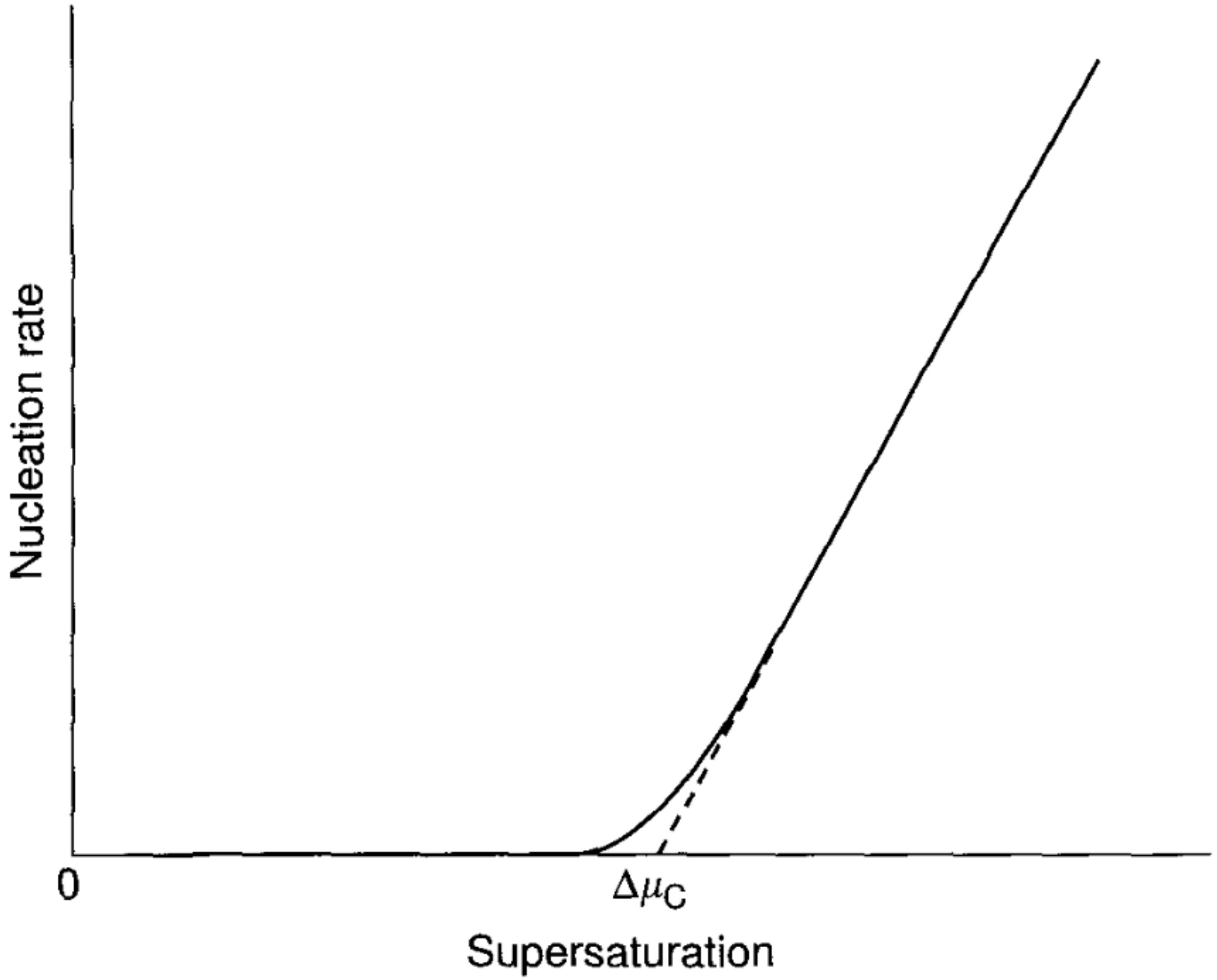
Void Nucleation Rate

Nucleation rate can be generalized as:

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

But it depends on:

- Dose rate
- Temperature
- Sink density, etc.



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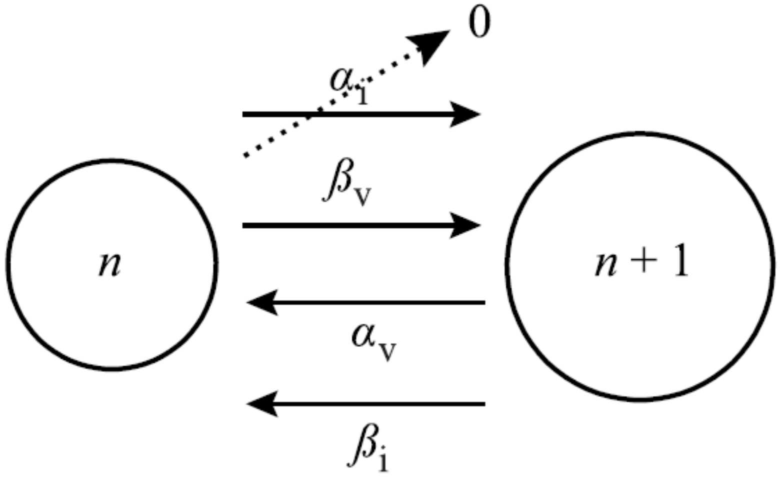
Void Nucleation Rate, J_0

- 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. $C_i^0 \sim 0$

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 $n+1$

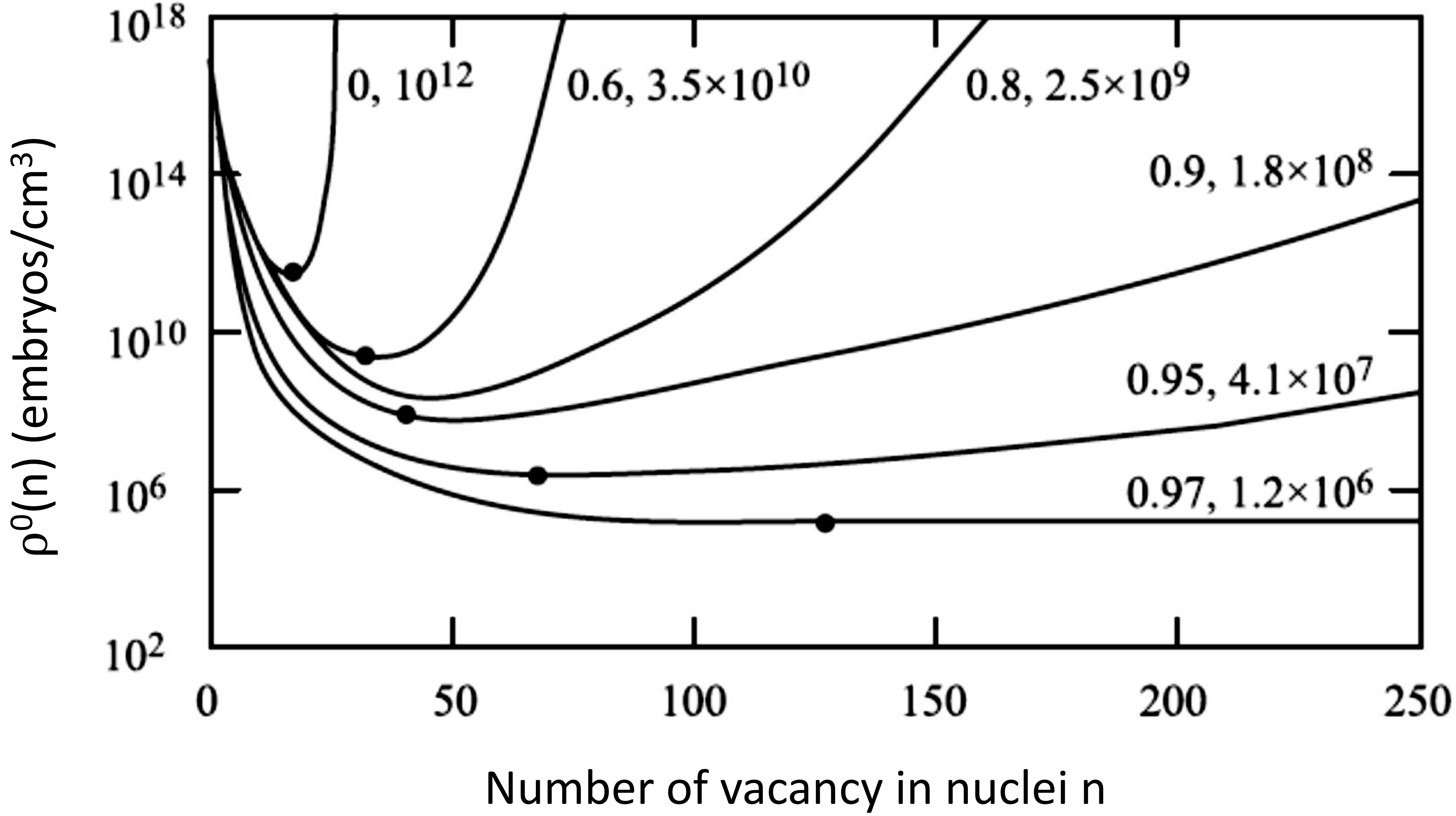
Void Nucleation Rate

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

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

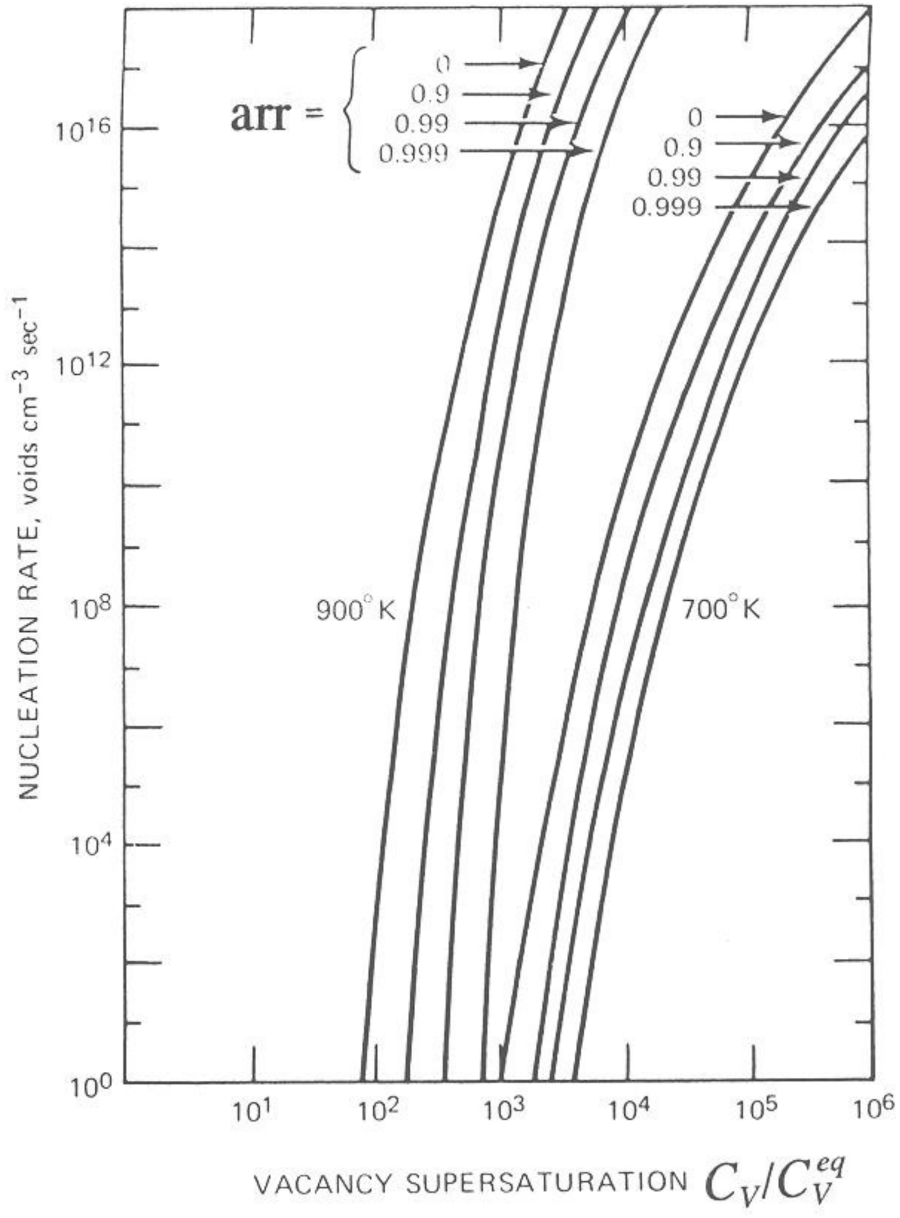
- C_v^{eq}/C_v is the inverse of vacancy supersaturation S_v^{-1}
- $(D_i C_i)/(D_v C_v)$ is the arrival rate ratio between v and *i*
- γ is the surface energy of the cavity
- *p* is the gas pressure in the cavity (p=0 for voids!)

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

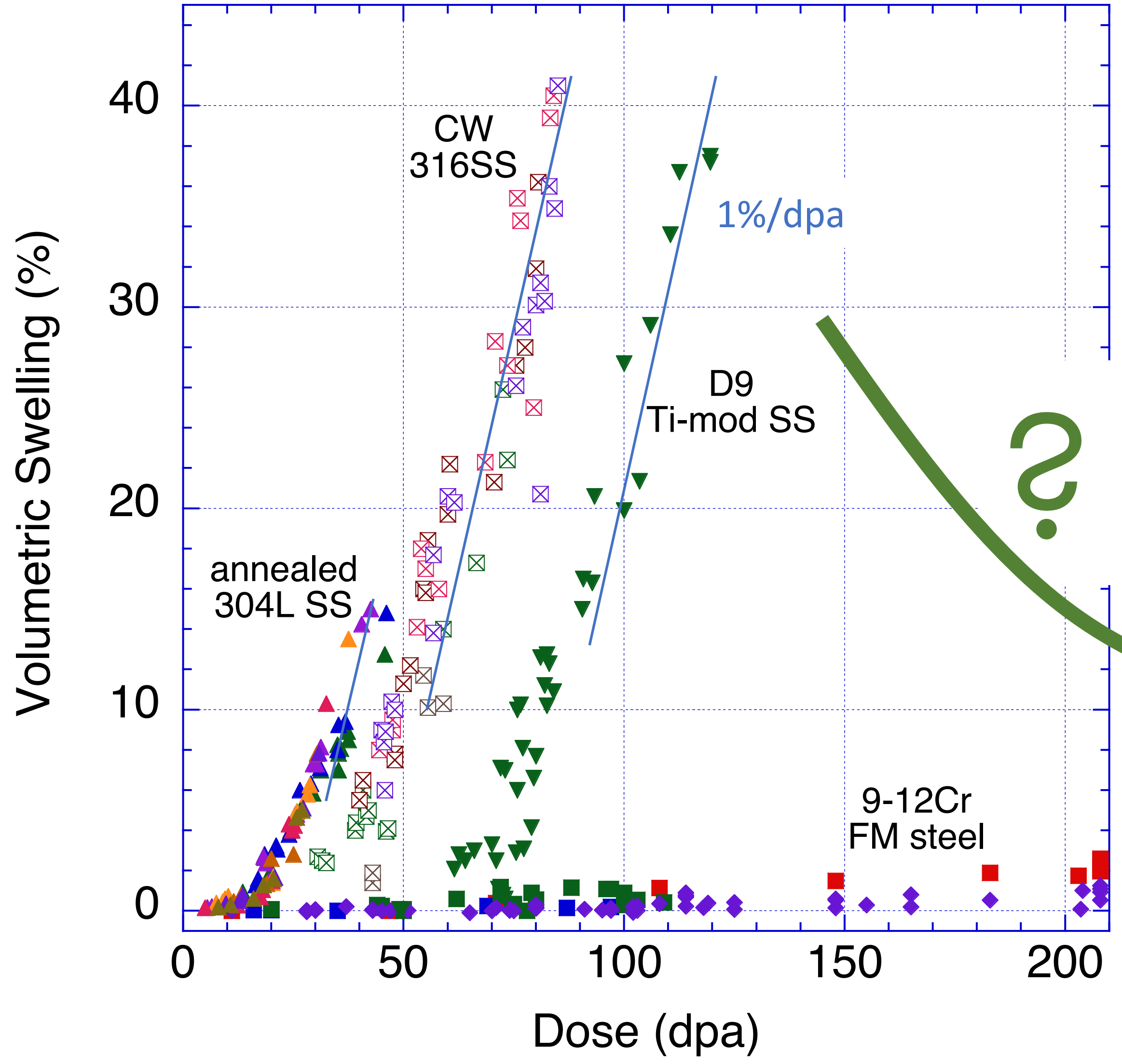
$J \sim 10^8$ voids nucleated/cm^3/s

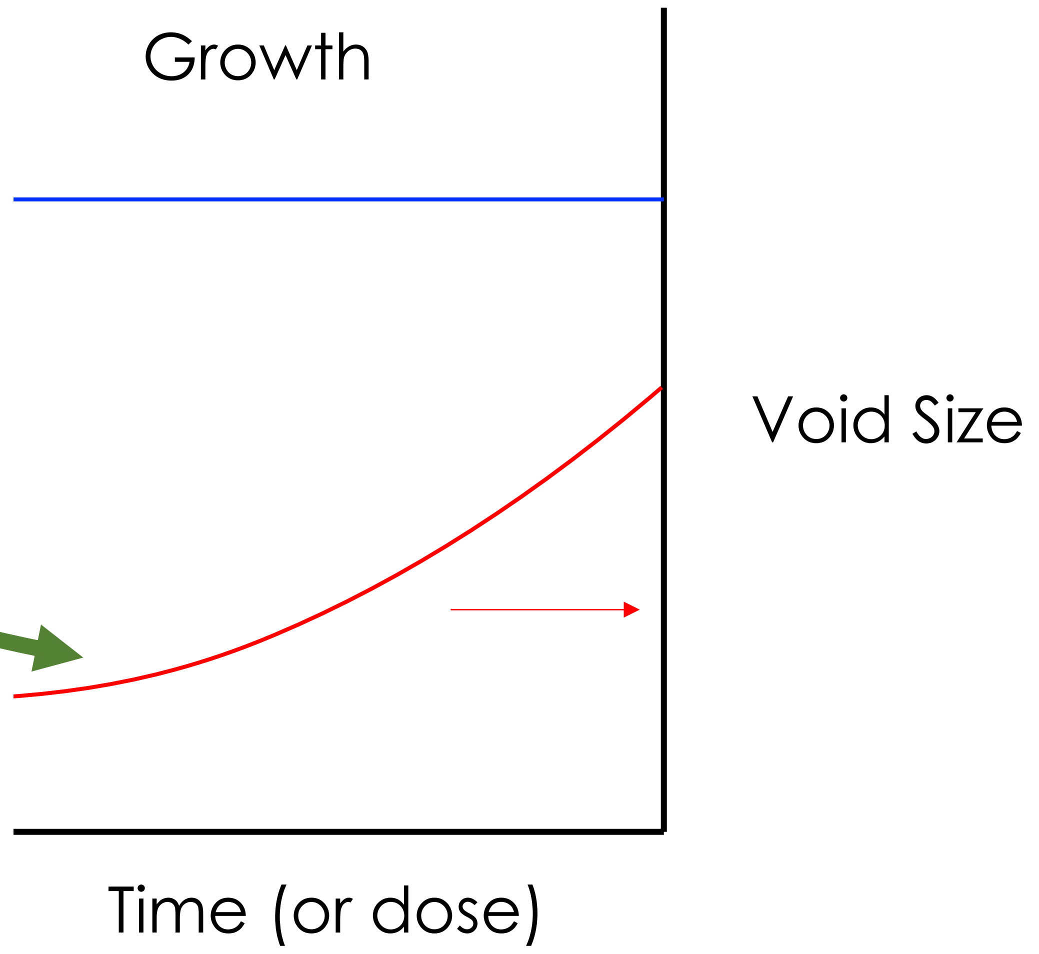
- After 1 year, $3\text{x}10^{15}$ voids/cm^3
- The voids are small, about the critical size

Lecture Break

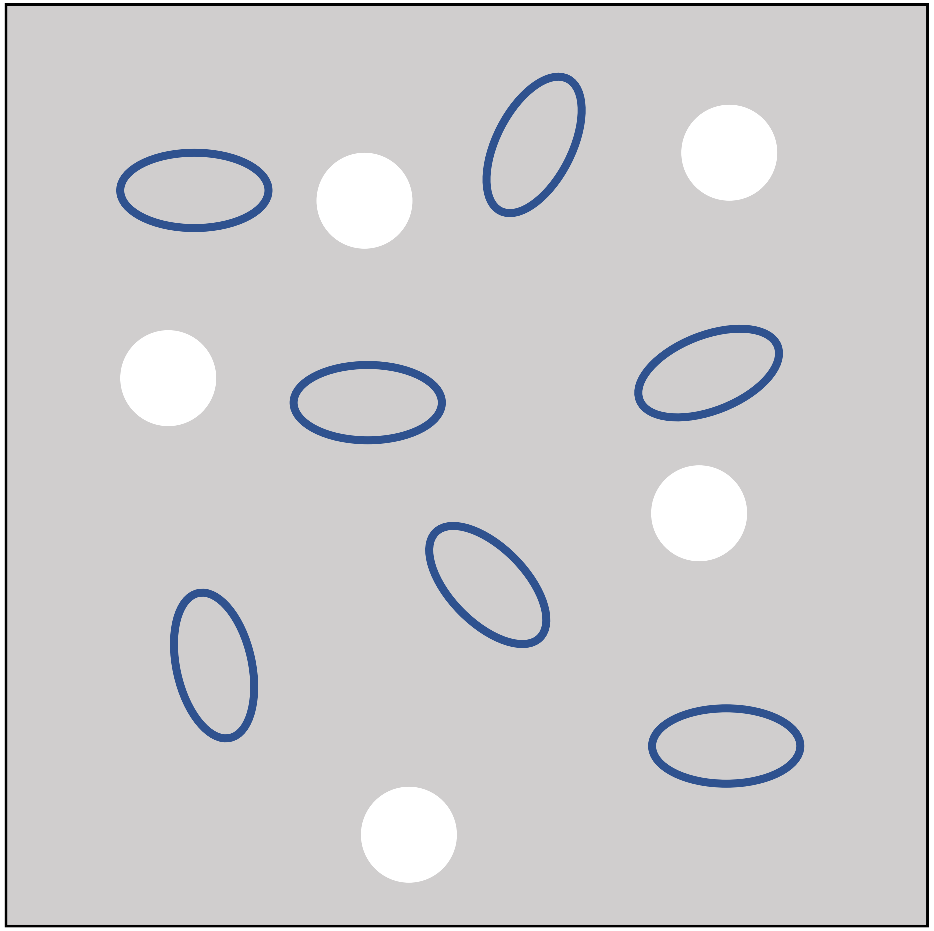
In the early 1800s Girolamo Luxardo moved to Croatia and founded a distillery that has now become the de facto maker of craft cocktail maraschino cherries. He originally traveled to Croatia as consul to what country?

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:

$$J_{net}^{V} = J_{v}^{V} - J_{i}^{V} = 4\pi R\Omega D_{v}(C_{v} - C_{v}^{V}) - 4\pi R\Omega D_{i}\left(C_{i} - C_{i}^{V}\right)$$

$$J_{net}^{V} = {}^{dV}\!/_{dt} = 4\pi R\Omega(D_{v}C_{v} - D_{i}C_{i})$$

$${}^{dR}\!/_{dt} = \dot{R} = \frac{\Omega}{R}(D_{v}C_{v} - D_{i}C_{i})$$

$$C_{v}^{V} = C_{v}^{0}exp\left(\frac{2\gamma\Omega}{Rk_{b}T}\right)$$

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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

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

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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:

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

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:

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

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Void Growth

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

- 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*
- *T*he 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:

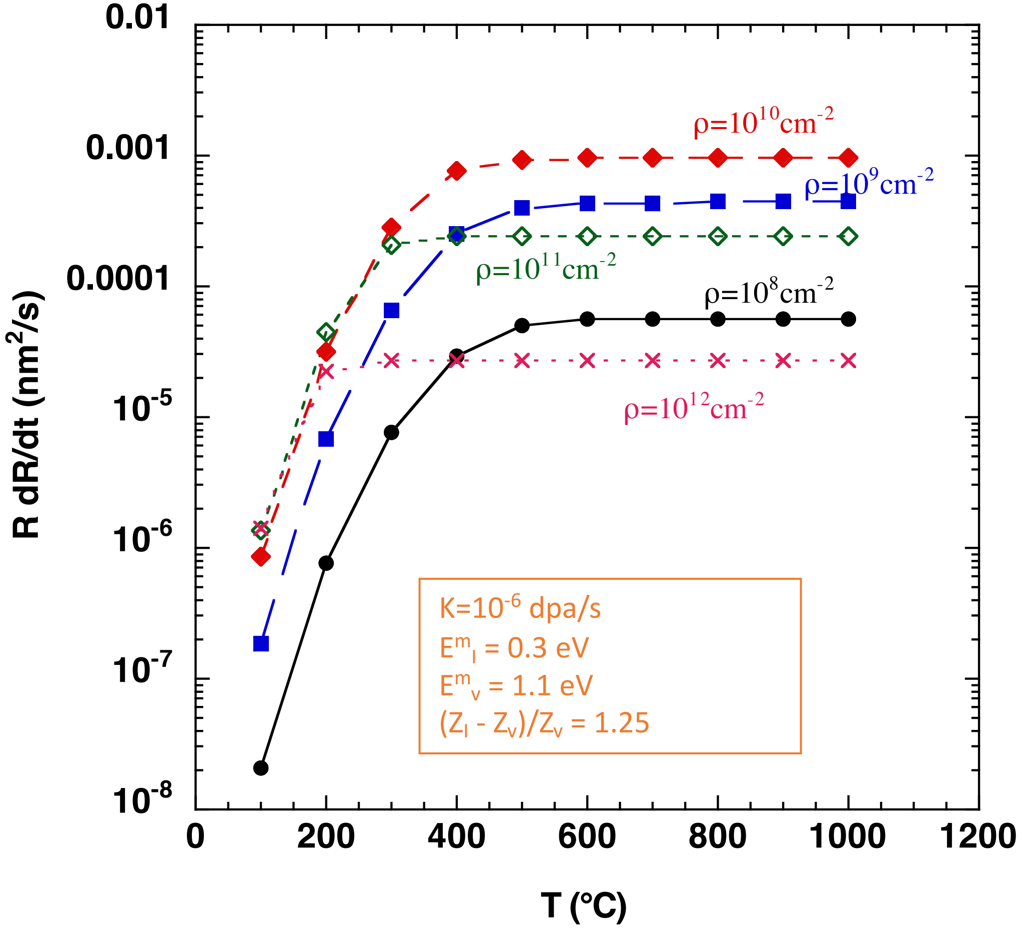
$$F(\eta) = 2\left(\sqrt{1+\eta} - 1\right)/\eta$$

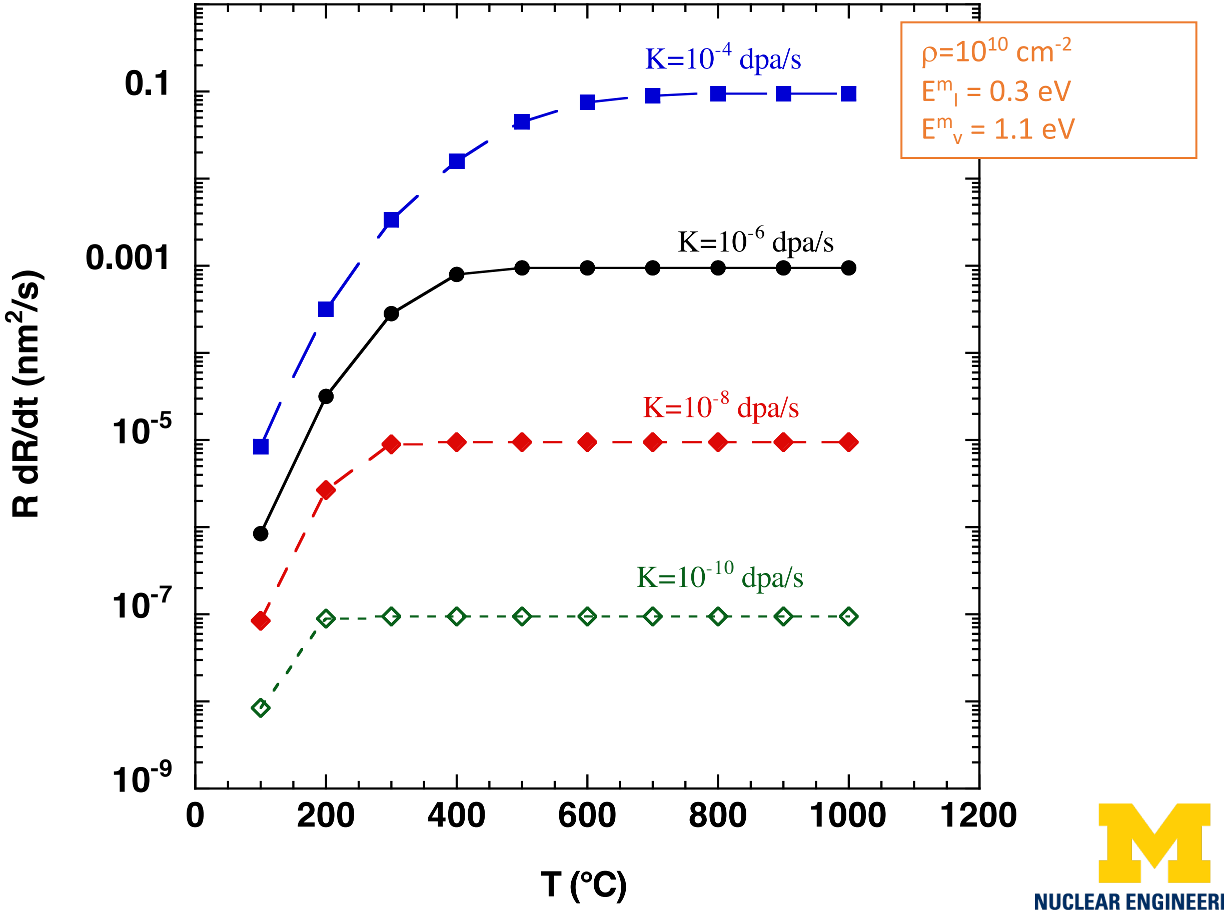
Since h decreases with increasing temperature and F decreases with increasing η:

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

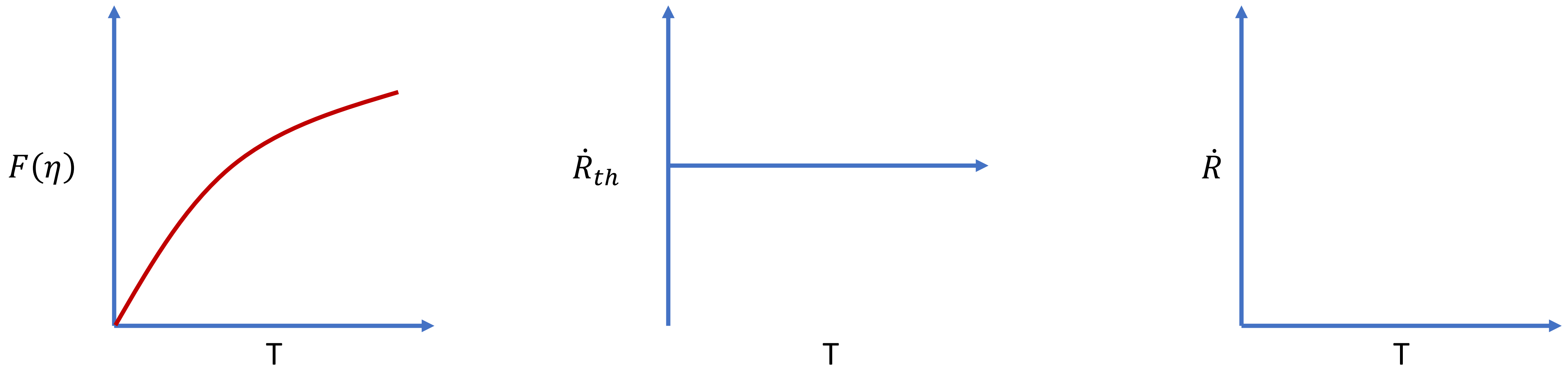
Void Growth

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





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:

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

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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:

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

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

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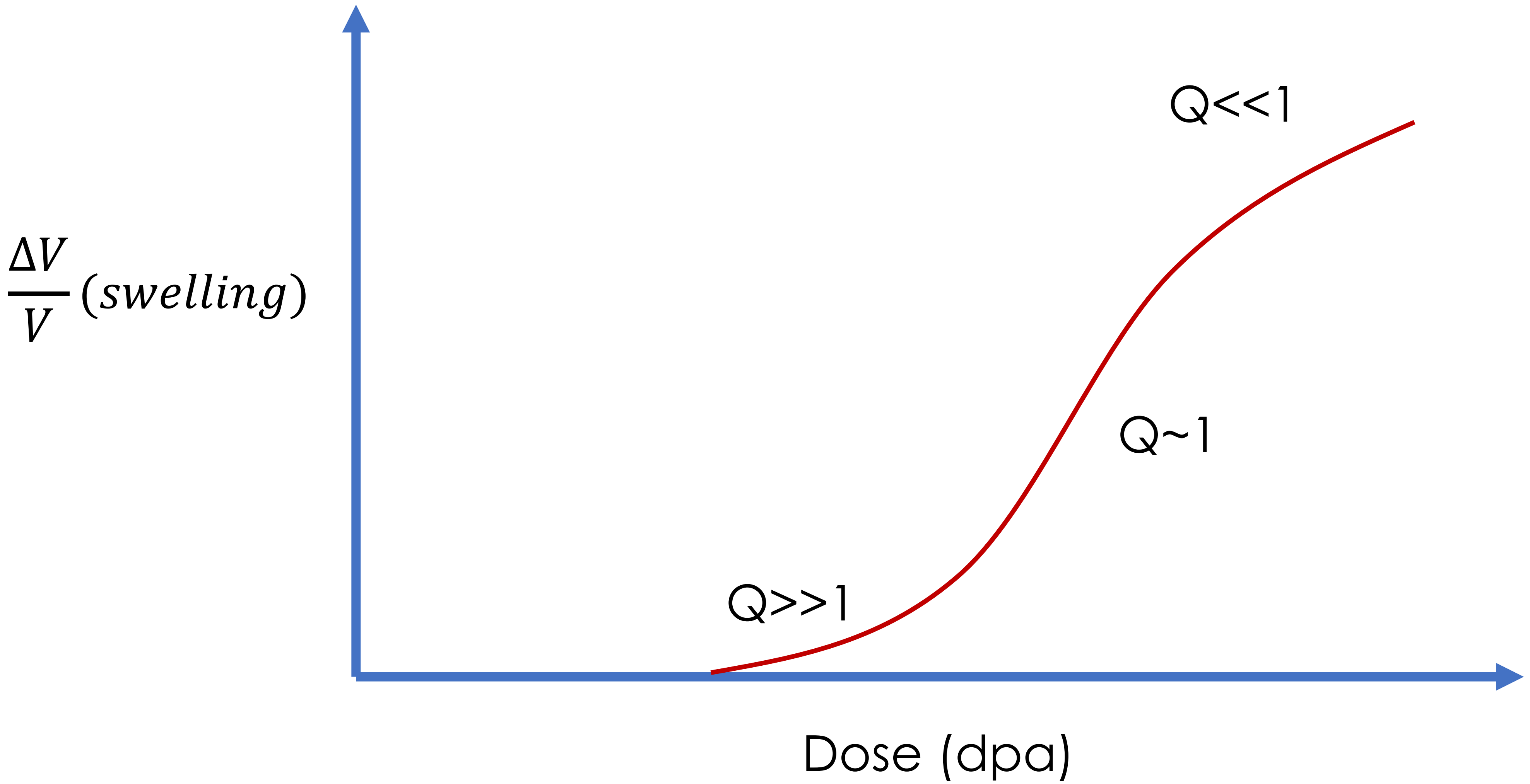
The Q-factor for structure dependence on dose



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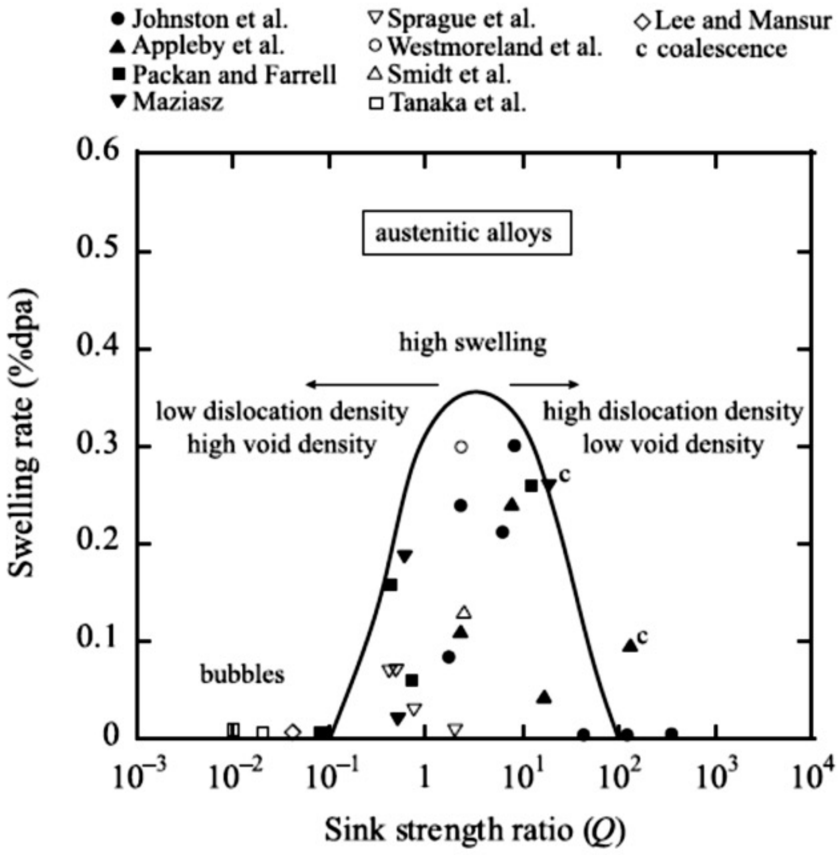
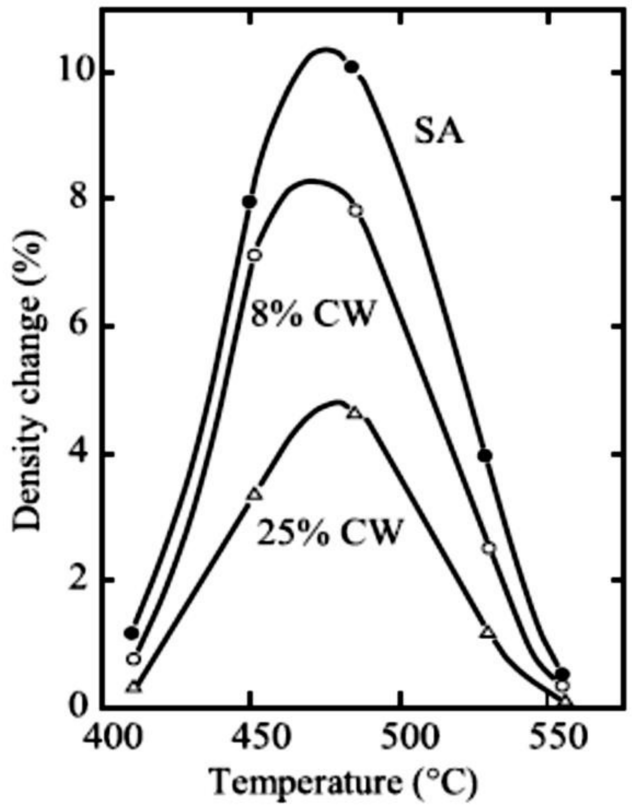
Effect of Structure on Void Swelling



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

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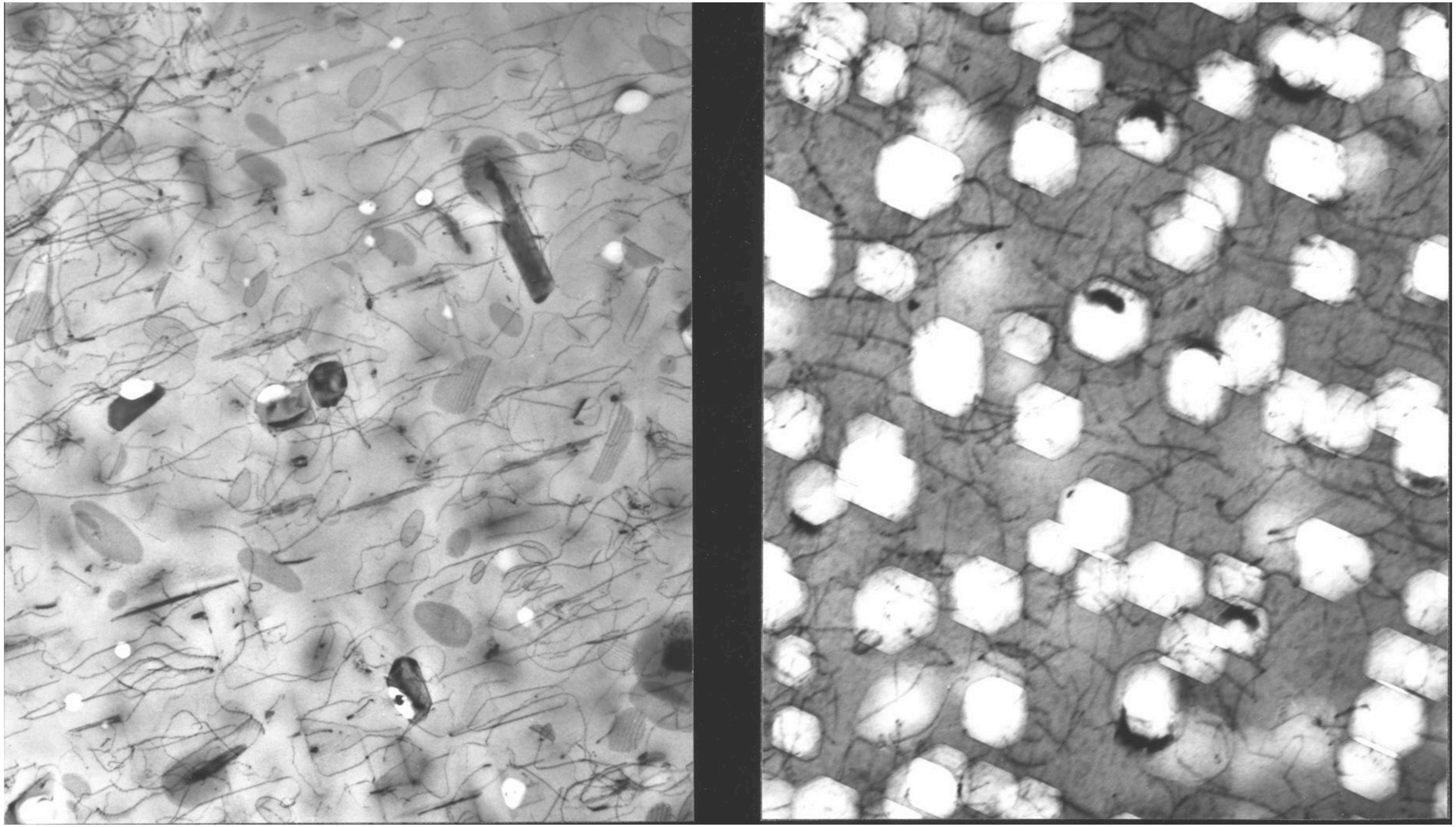
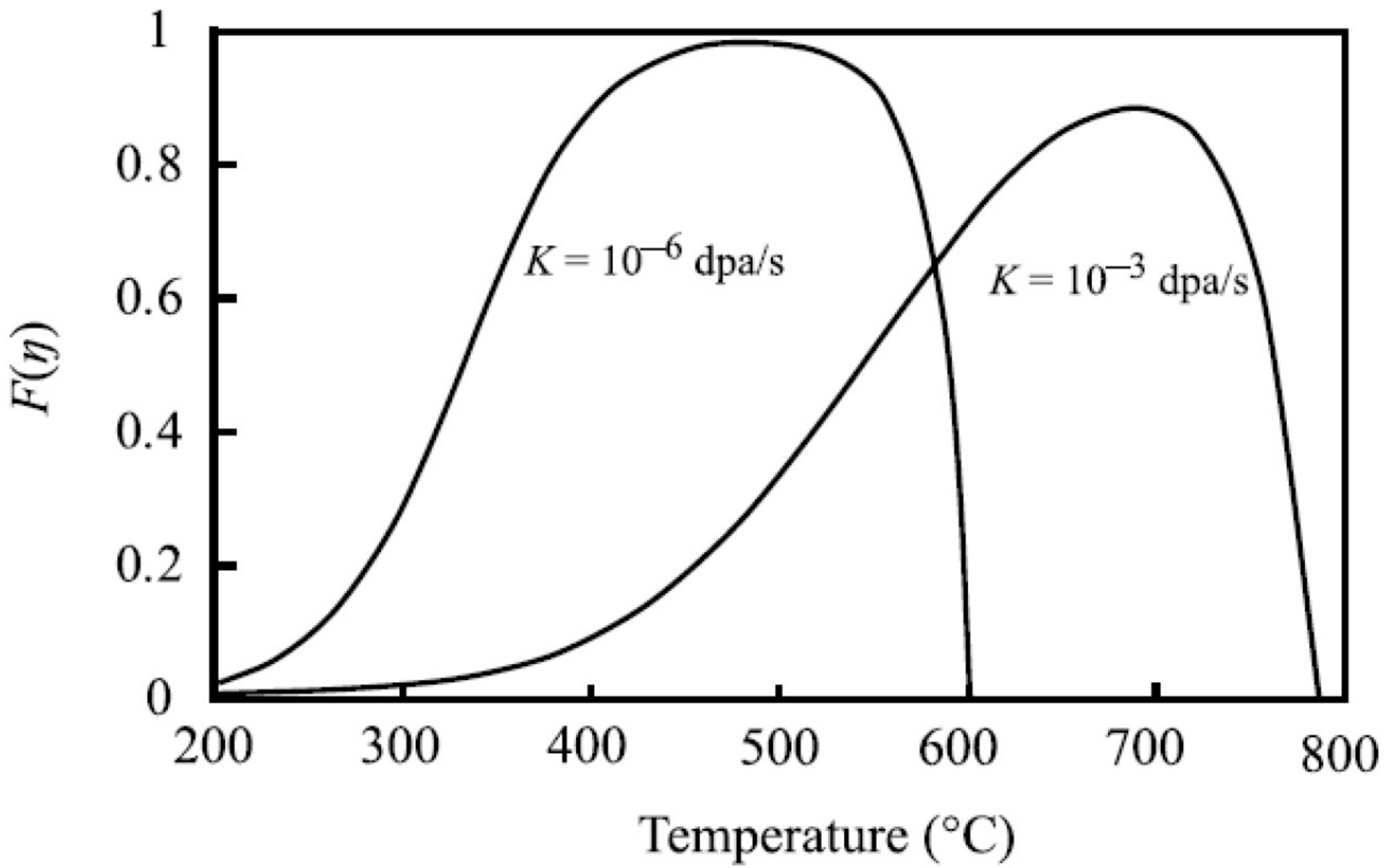
Image of voids + effect of sink strength

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:

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

Effect of Dose Rate

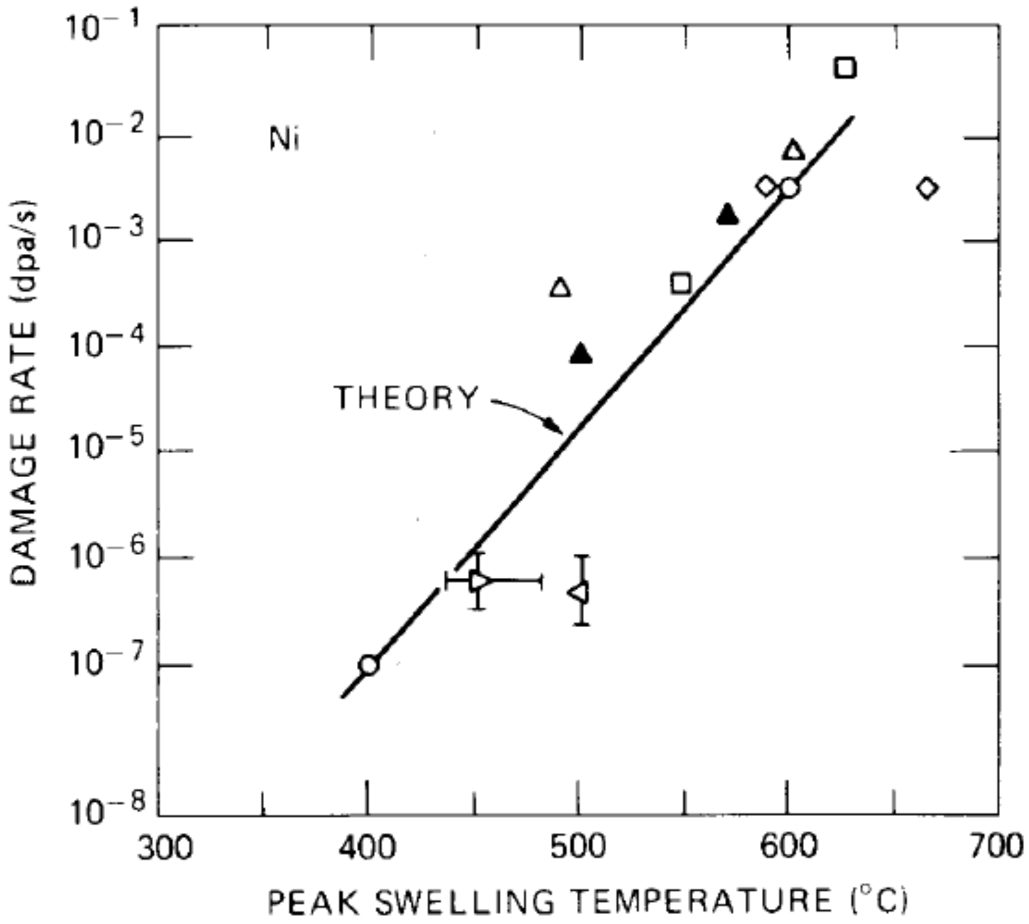


Figure 8.29. Compilation of experimental results for peak swelling temperature as a function of dose rate. Theoretically predicted trend is shown as the line. After Refs. 140 and 141.

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

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

And:

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

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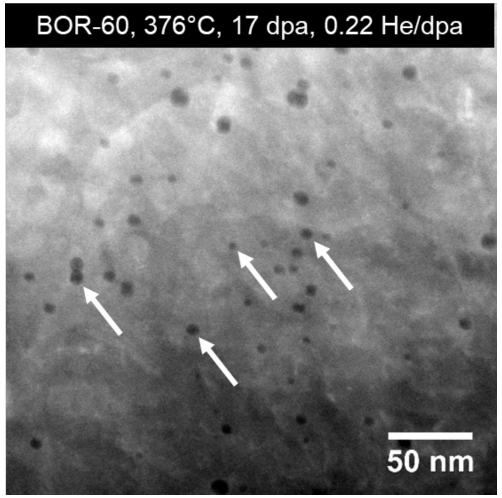
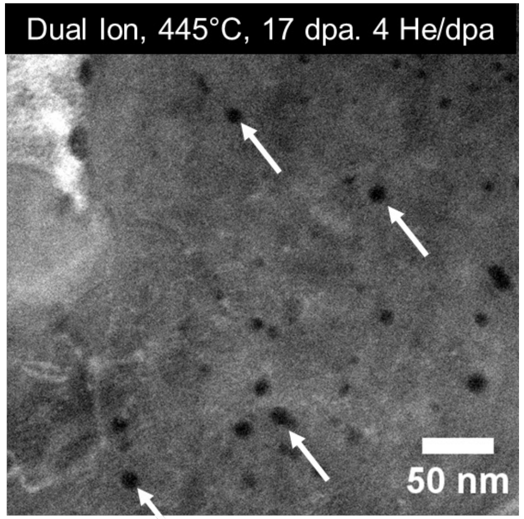
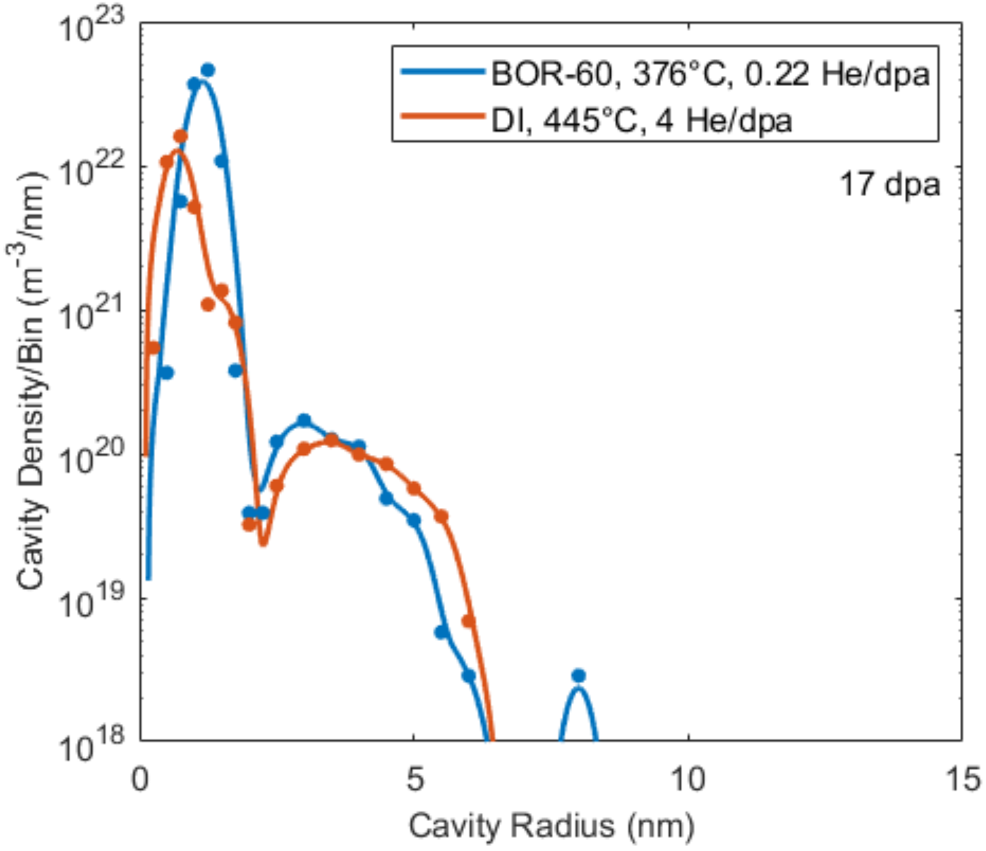
Effect of Dose Rate – Real World Example

STEM HAADF

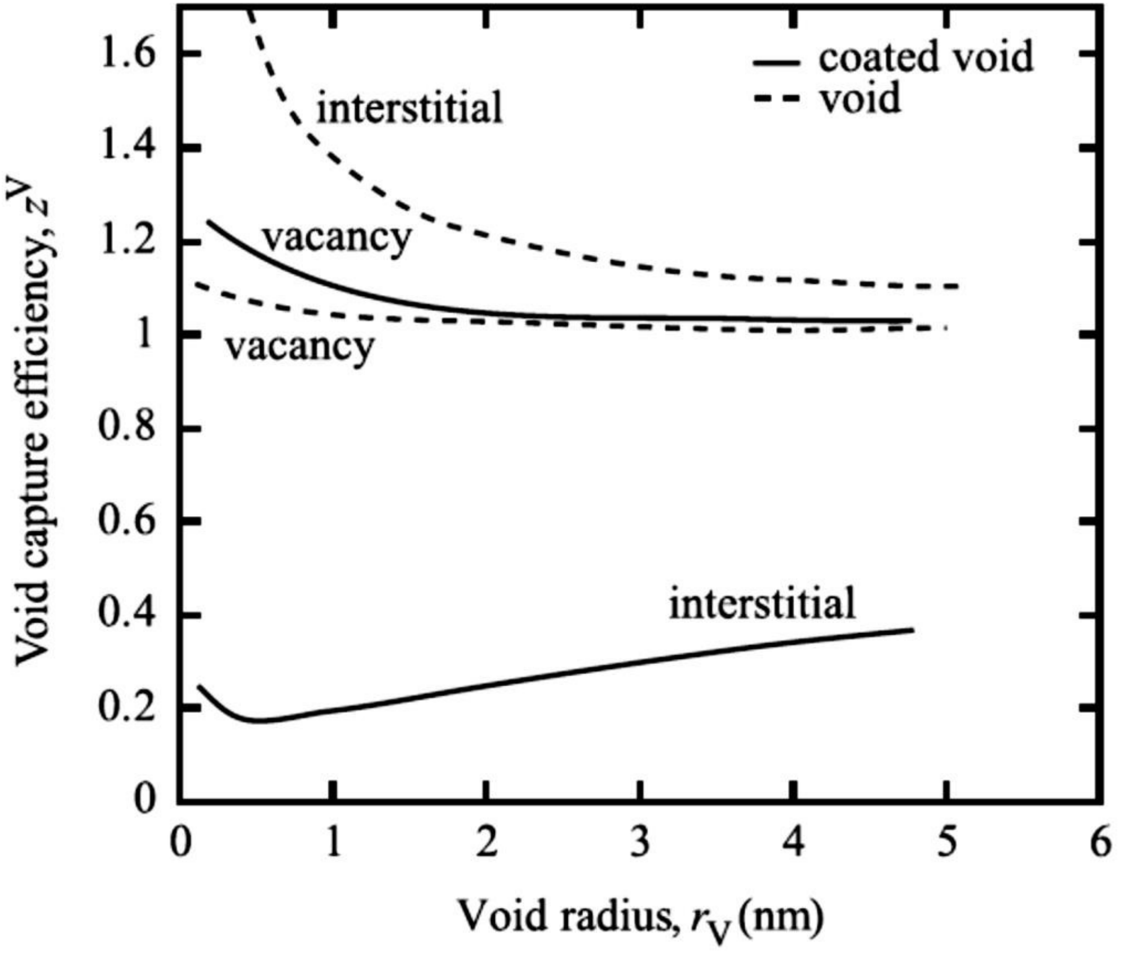






$$T_2 - T_1 = \frac{\dfrac{kT_1^2}{E_v^m + 2E_v^f}\ln\left(\dfrac{G_2}{G_1}\right)}{1 - \dfrac{kT_1}{E_v^m + 2E_v^f}\ln\left(\dfrac{G_2}{G_1}\right)}$$

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

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Questions?