Defect Sinks and Their Reactions

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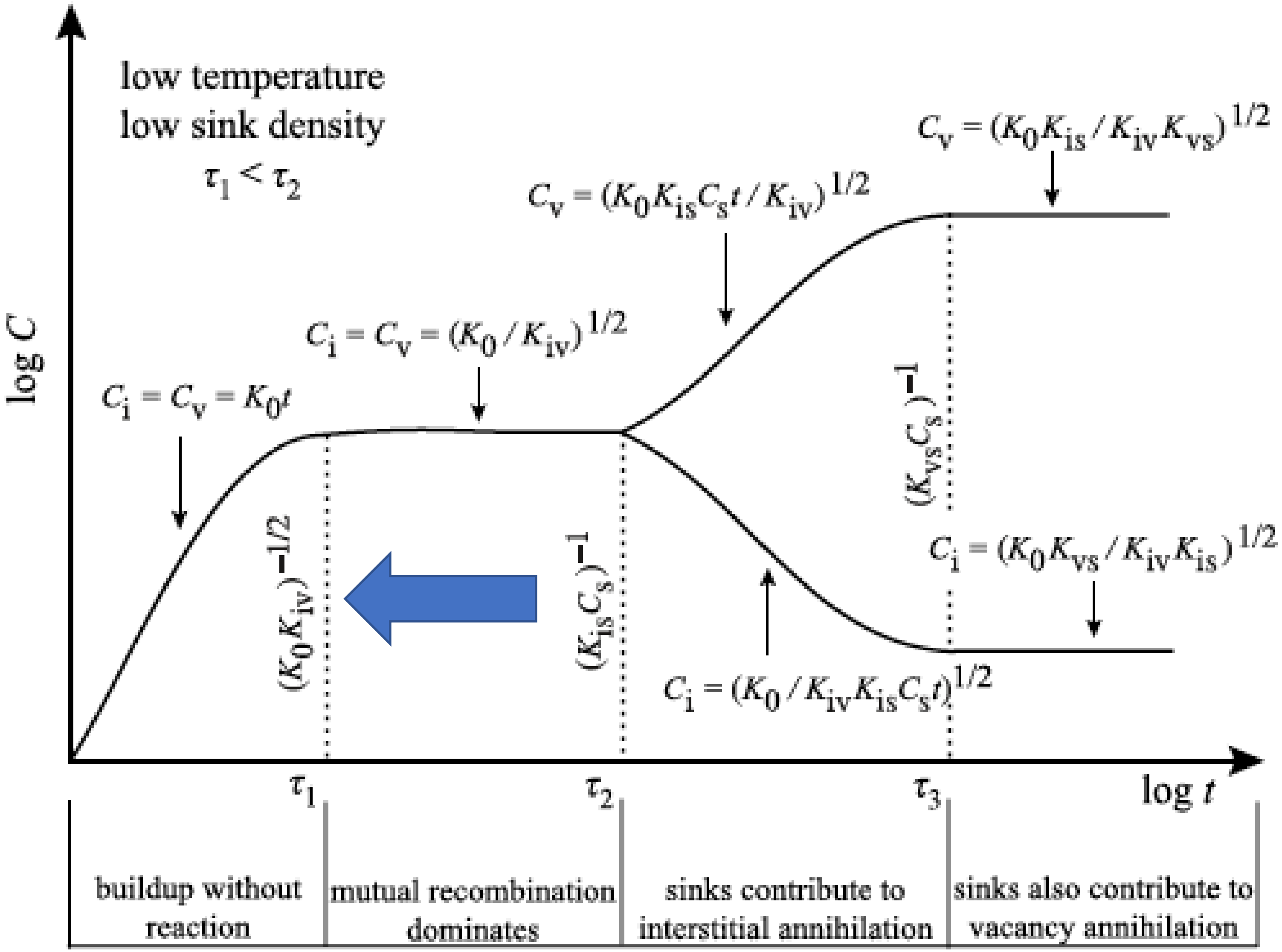
Low Temperature, Increasing Sink Density



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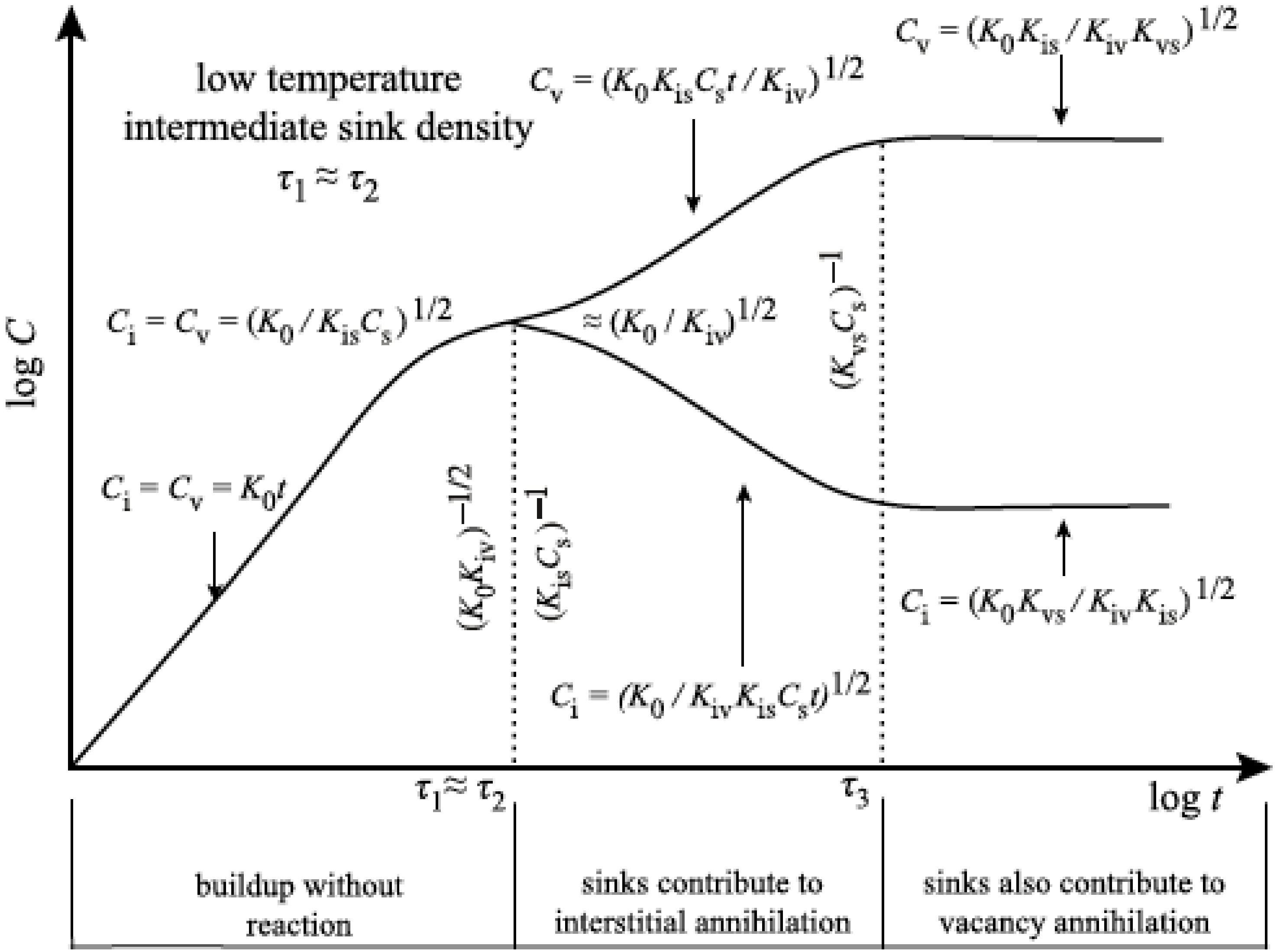
Low Temperature, Increasing Sink Density



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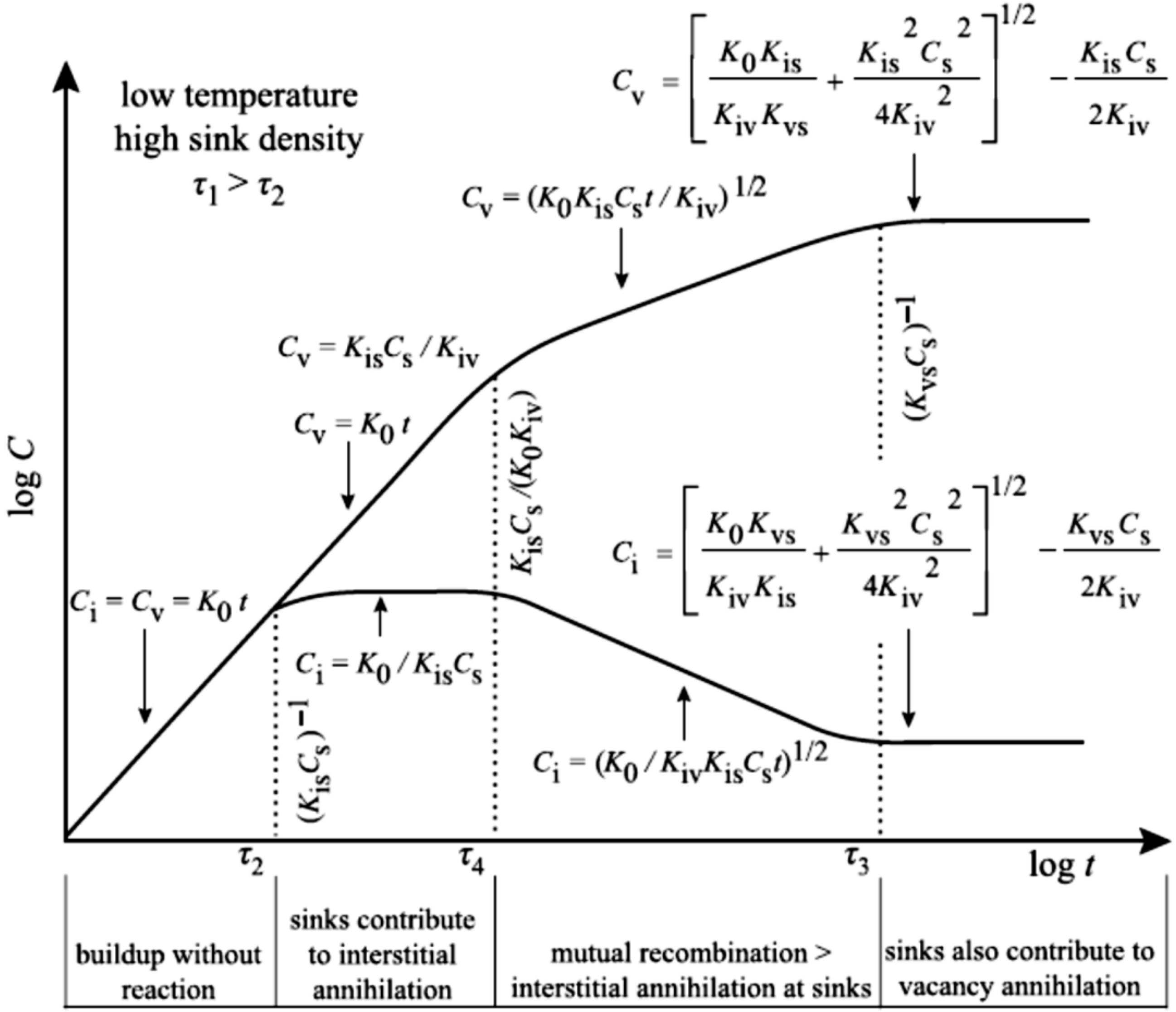
Low T, High C_s



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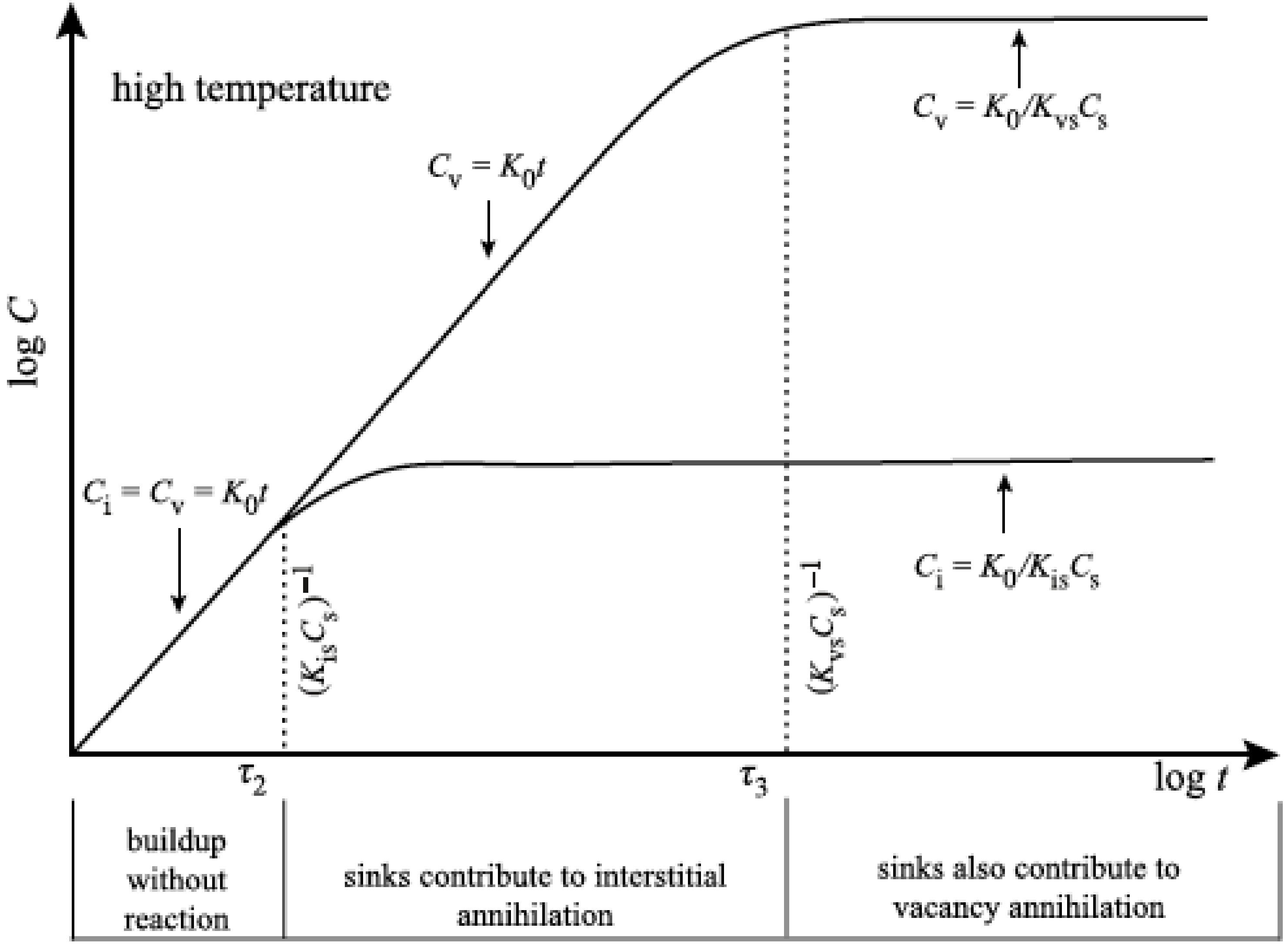
High Temperature



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Note on vacancy concentration

- C_v must be accounted for thermal vacancies:

- Why are we ignoring this for interstitials?!

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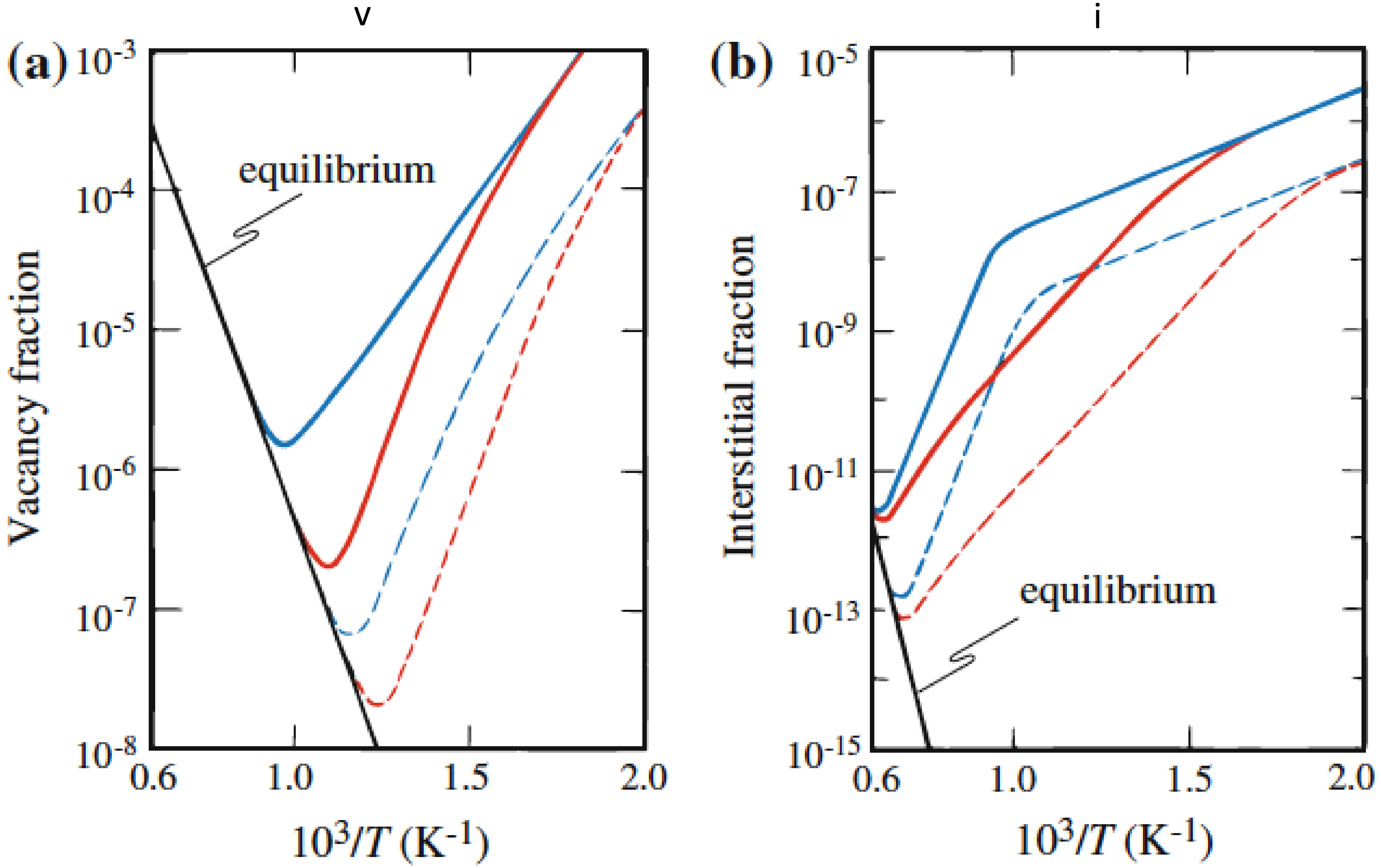
Pulling this now together:

upper solid line	K_0 high ρ low
lower solid line	K_0 high ρ high
upper dashed line	K_0 low ρ low
lower dashed line	K_0 low ρ high



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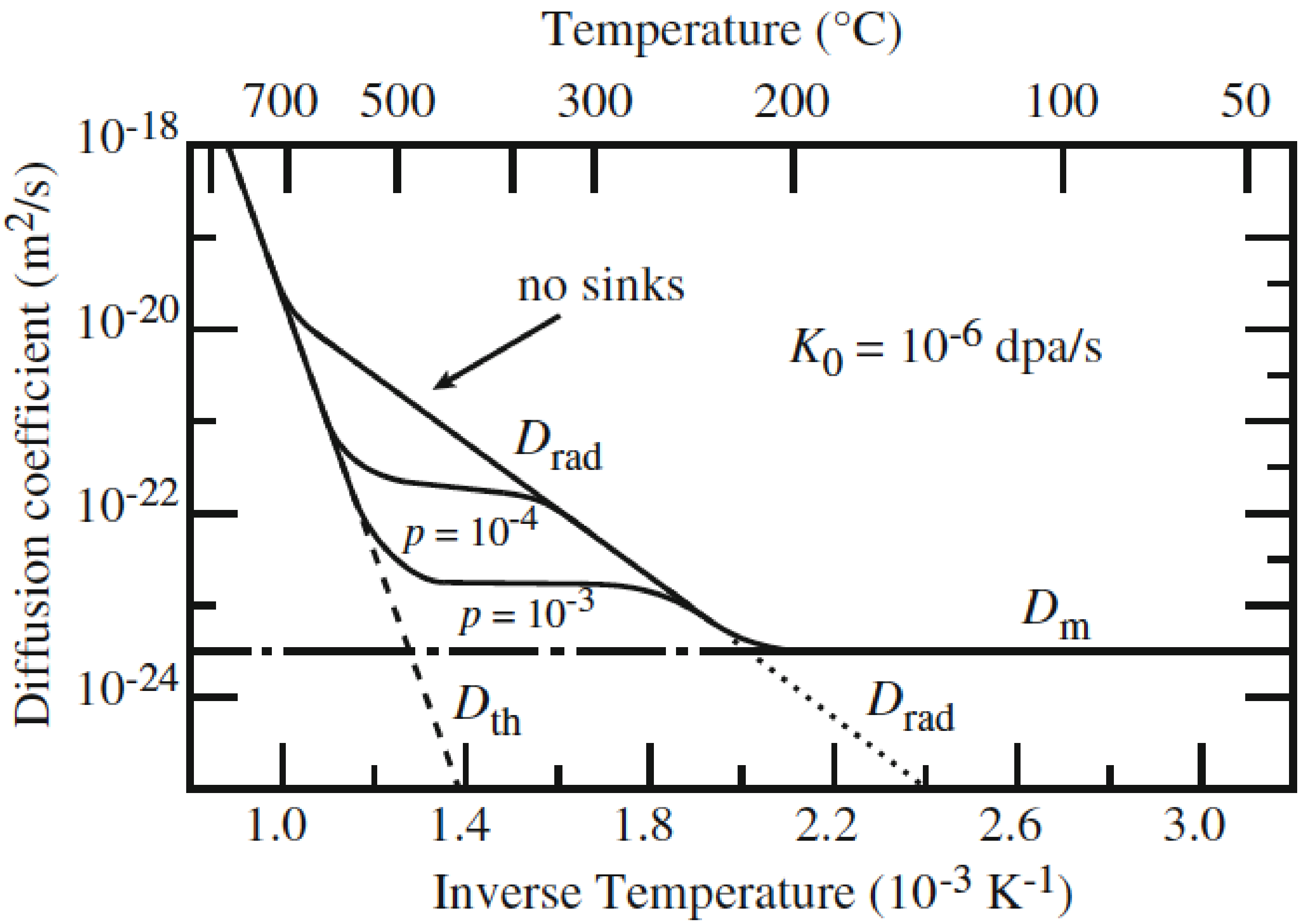

For systems where atoms can migrate both via interstitials and vacancies:

$$D_{rad} = D_v C_v + D_i C_i$$

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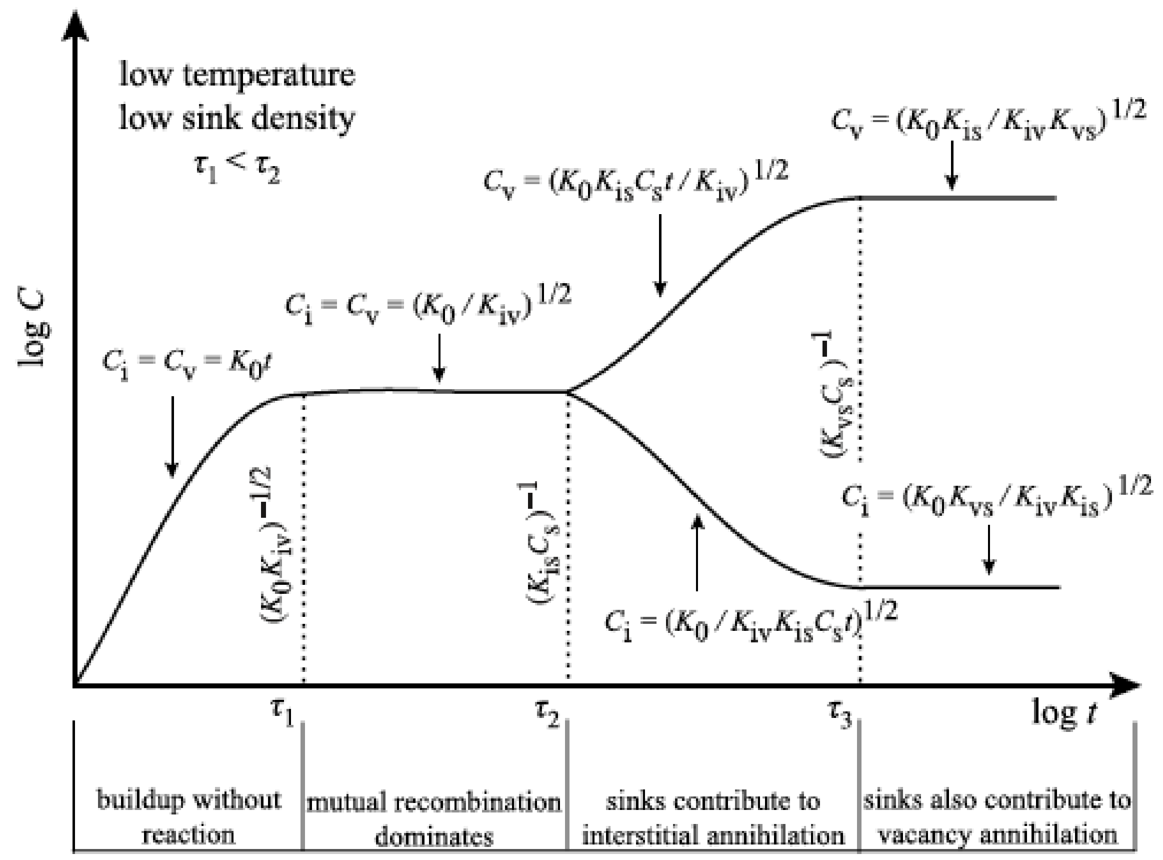
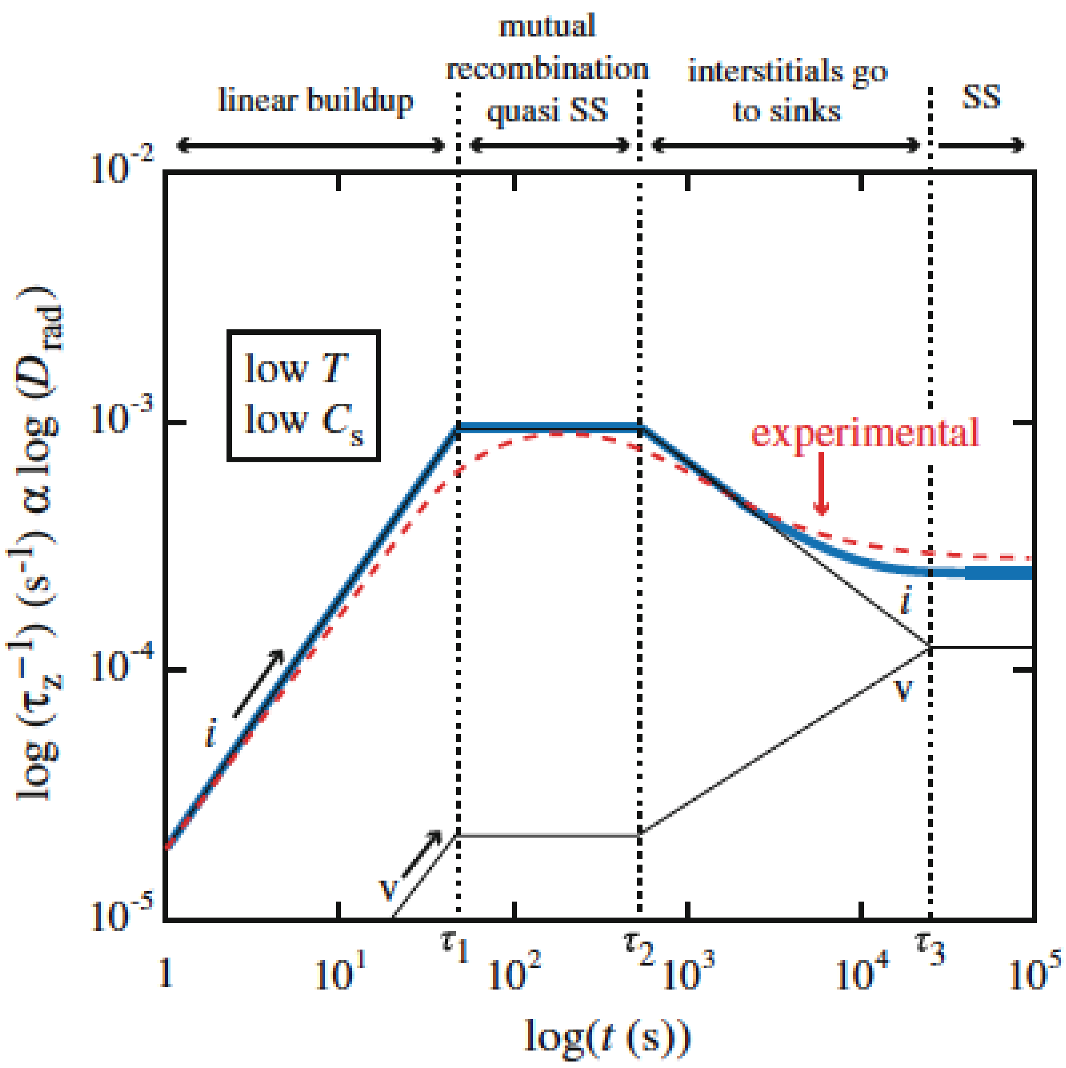
Pulling this now together:





Log(D_{rad}) vs. log(t)

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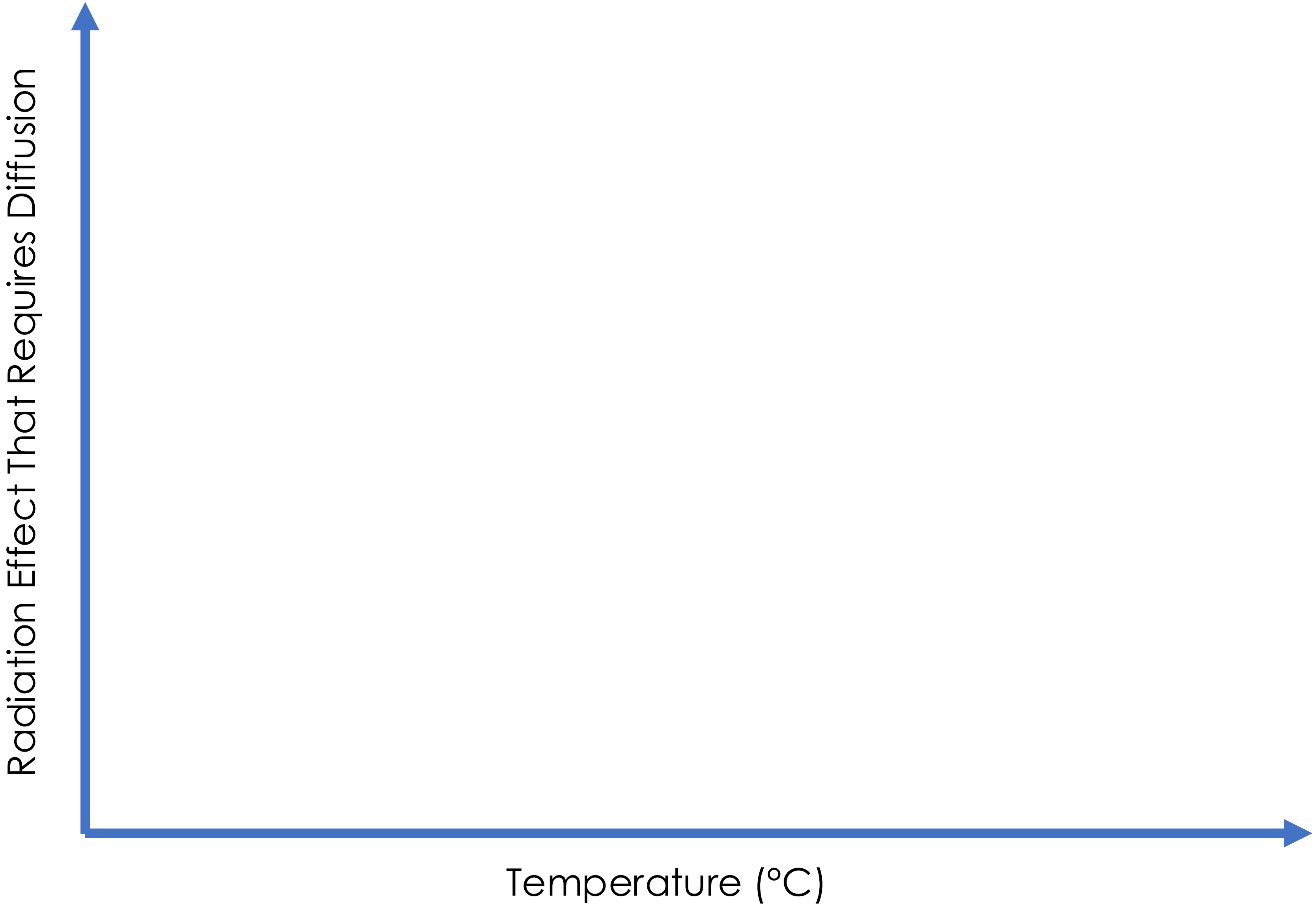
Thought Experiment: What should the shape of the magnitude of a radiation diffusion dependent response be?



This historic landmark, the oldest continuously operating cider mill in Michigan, first opened its doors the same year the Statue of Liberty was dedicated in New York Harbor. In what year did the Dexter Cider Mill begin pressing apples?

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Rate of Reaction

- We have now determined the relative change of C_i and C_v, but the ***rates are dependent on the reaction rate constant*** K_{AB} (s^{-1}), where the rate of reaction between A & B is:

$$K_{AB} C_A C_B \; reactions/cm^3 s$$

- Analogous to first order chemical reactions
- We will consider two types of reactions:
  - Defect-defect reactions
  - Defect-extended sinks reactions

Reaction Rate vs. Sink Strength

- Reaction Rate (K_{jX}, s^{-1}): Describe the reaction between a point defect and sink
  - j: mobile point defect
  - X: the sink
  - Includes the diffusion coefficient, thus dependent on temperature, defect geometry, migration path, etc.
- Sink Strength (k_j^2, cm^{-2}): The affinity (or "strength") of a sink to accept defects
  - Independent of defect properties (e.g. diffusion)
  - Square indicates that the rate constant for absorption to sinks is always positive

Point-defect reactions with extended sinks

- To a *first approximation*, sinks at as "perfect" sinks
- In a perfect sink, all defects "stick" completely to the sink and never leak the sink -> think of these as black holes!
  - Result is the point-defect concentration at the surface of the sink is zero
- The rate of defect absorption at a sink, S, is then:

- The sink strength describes the strength or affinity of a sink for defects and is measured in [length^{-2}]. Physically, k_j^{-1} is the mean distance a free defect of type j travels in the solid before becoming trapped.
- For discussion, we will assume unsaturable sinks

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Sink types

- Sinks can behave differently:
  - Neutral (unbiased) sinks:
  - Biased sinks:
  - Variable (traps) sinks

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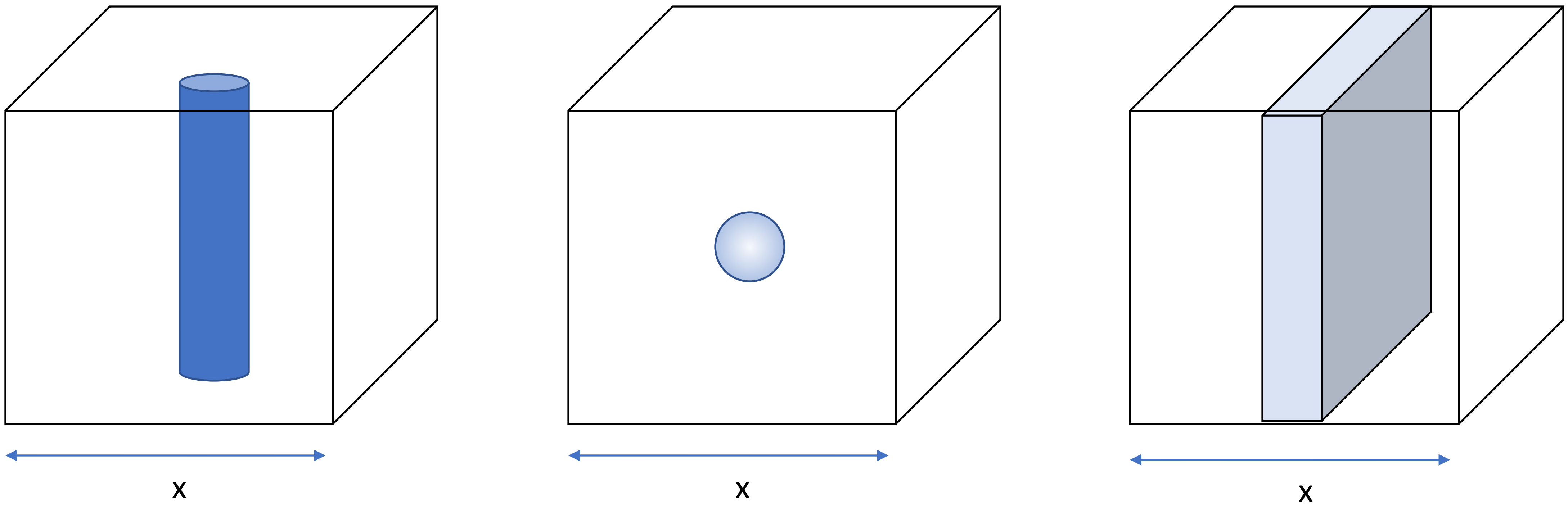
A simple thought experiment for K_{vs}/K_{is}

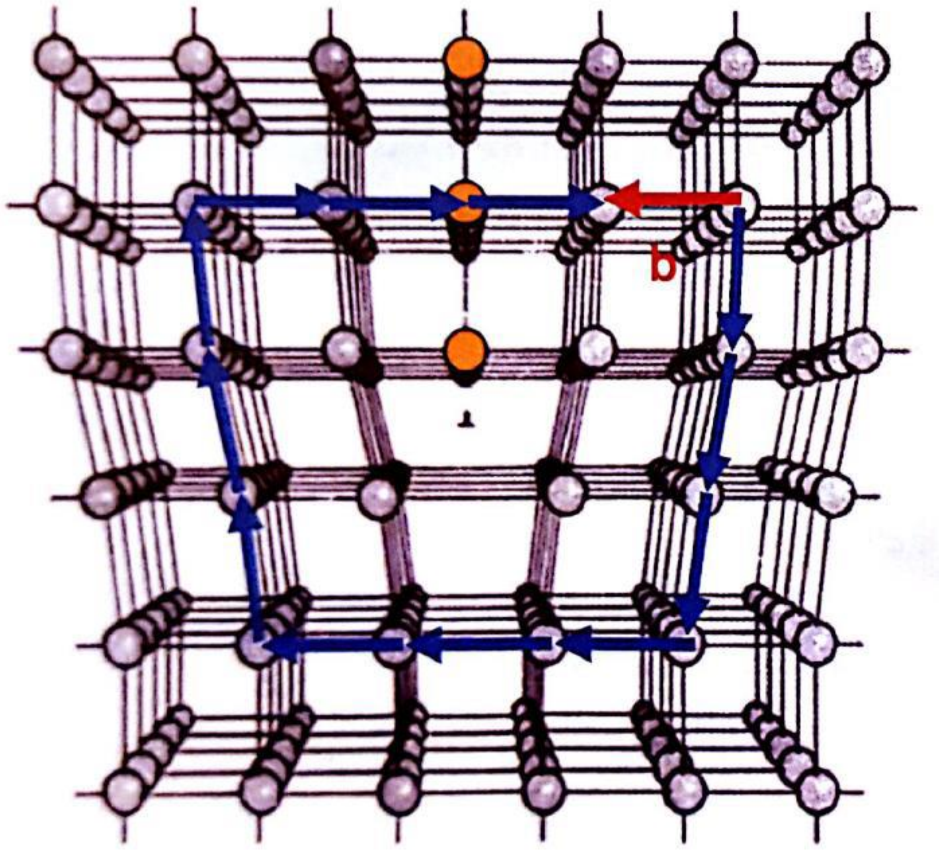
- Assume unbiased defect sink, radius/length of interaction is $10a_0$

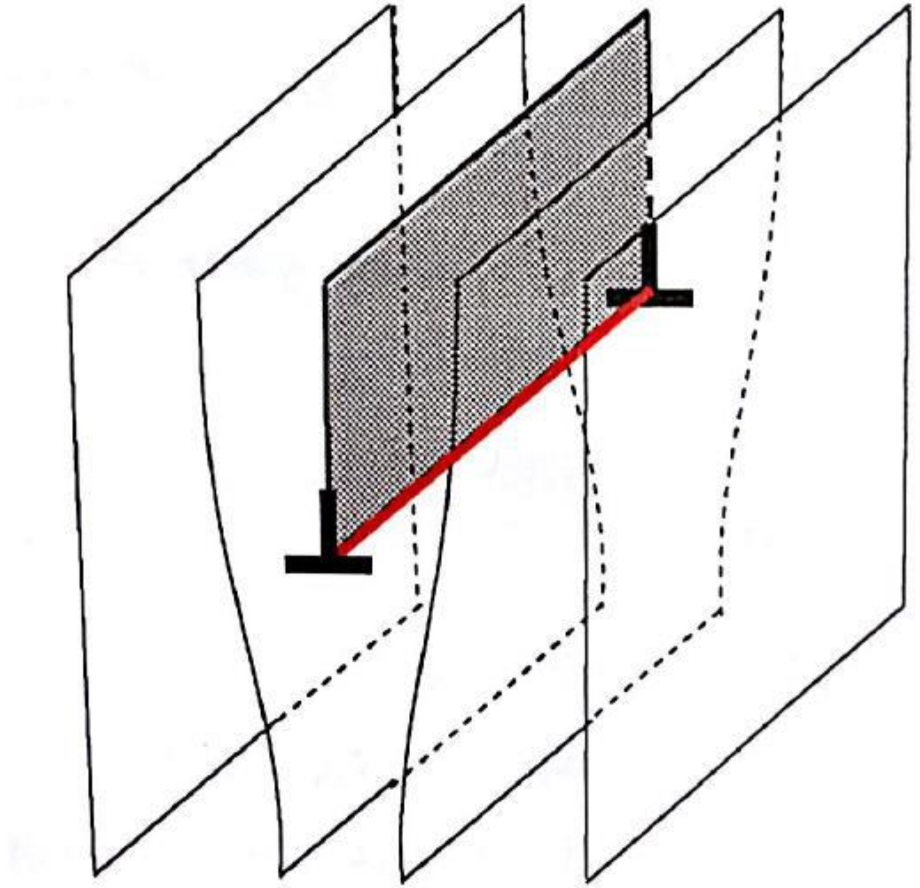


What sink will have the highest reaction rate (e.g. sink strength)?

Sink Type I - Dislocations

- Linear defect
- Edge dislocation is an additional half plane of atoms
- Burgers vector and slip plane defines dislocation





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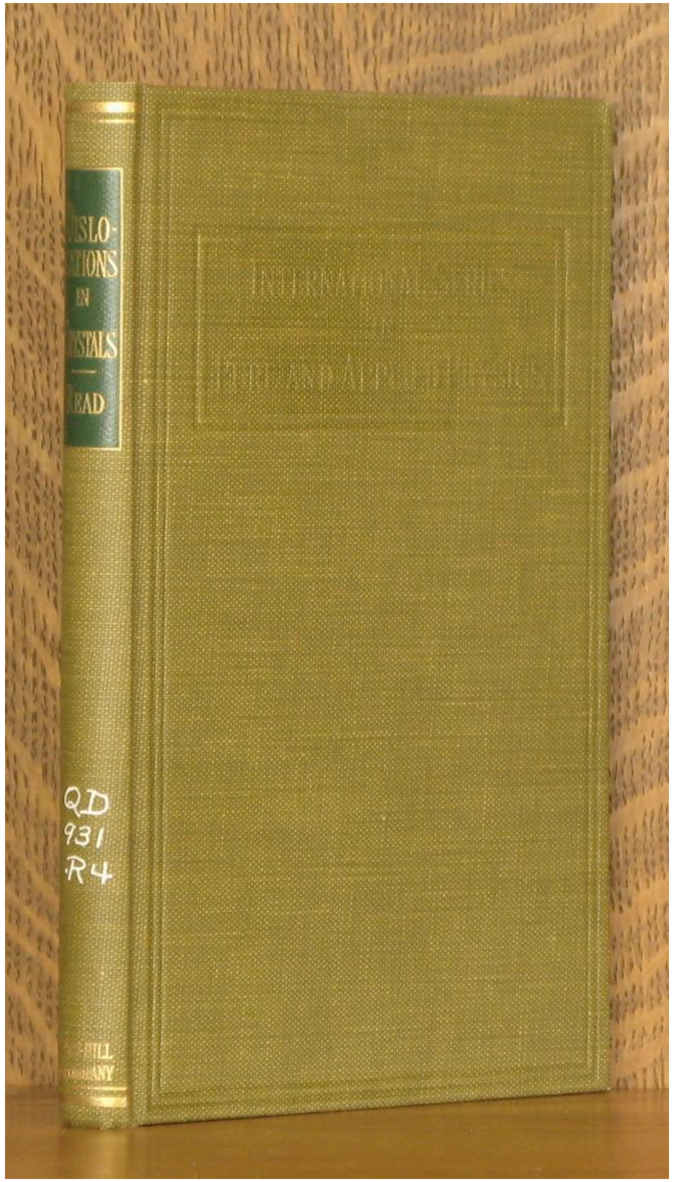
This section on dislocations could be a whole book and class…

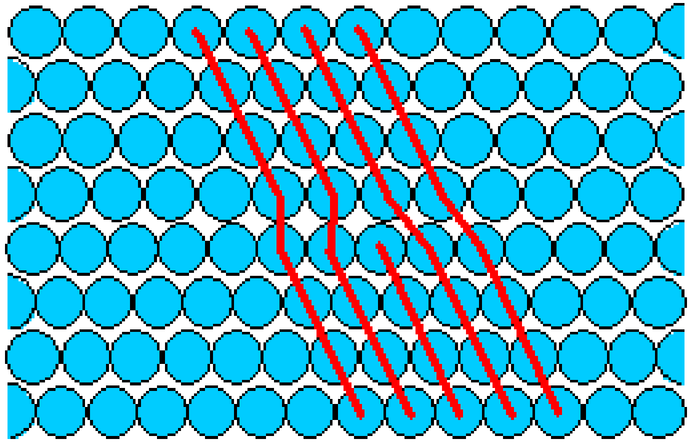


What is a dislocation – a simple 2D picture

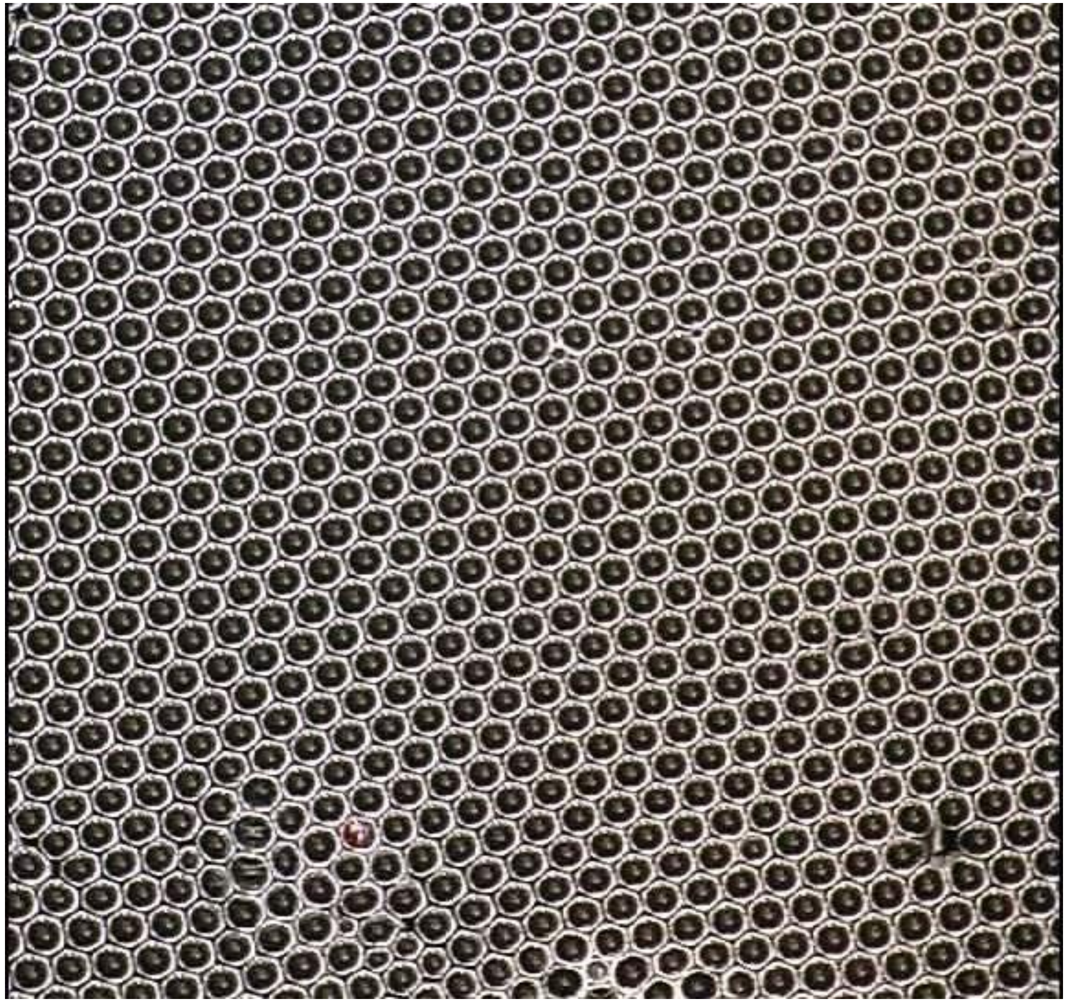
- "Old school" method to visualize dislocations:

→ **Bubble rafts**

What is a dislocation – a simple 2D picture



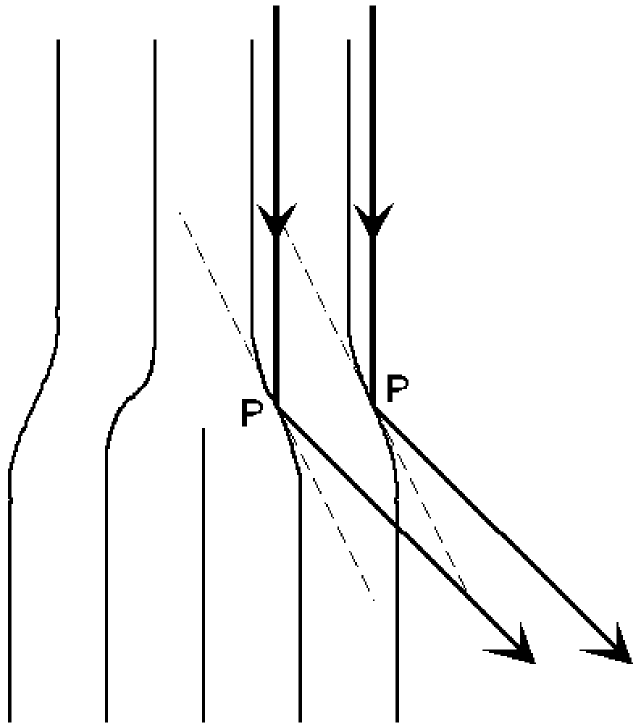
A dislocation in a 2D close-packed plane can be described as an extra 'half-row' of atoms in the structure. Dislocations can be characterized by the Burgers vector which gives information about the orientation and magnitude of the dislocation



Bubble raft that contains defects

Quick view of calculating Burgers vector → https://www.doitpoms.ac.uk/tlplib/dislocations/burgers.php

Dislocations are commonly observed using transmission electron microscopy (TEM)



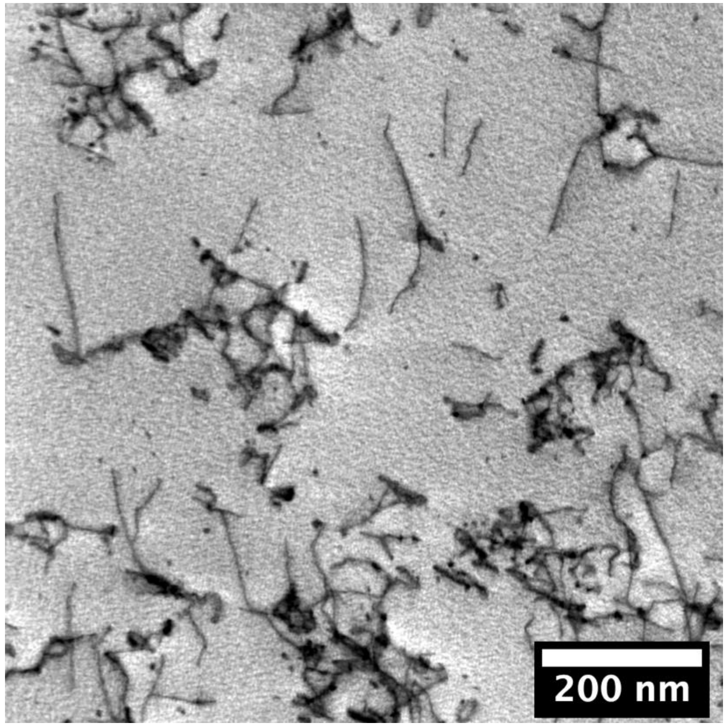


Image showing line dislocations (black contrast) in an accident tolerant FeCrAl alloy after cold working but before irradiation. Image take using on-zone [100] Scanning Transmission Electron Microscopy (STEM) technique.

From: Your professor :0)

Dislocations can be observed in TEM due to the lattice distortion around the dislocation core resulting in Bragg diffraction of the electron beam

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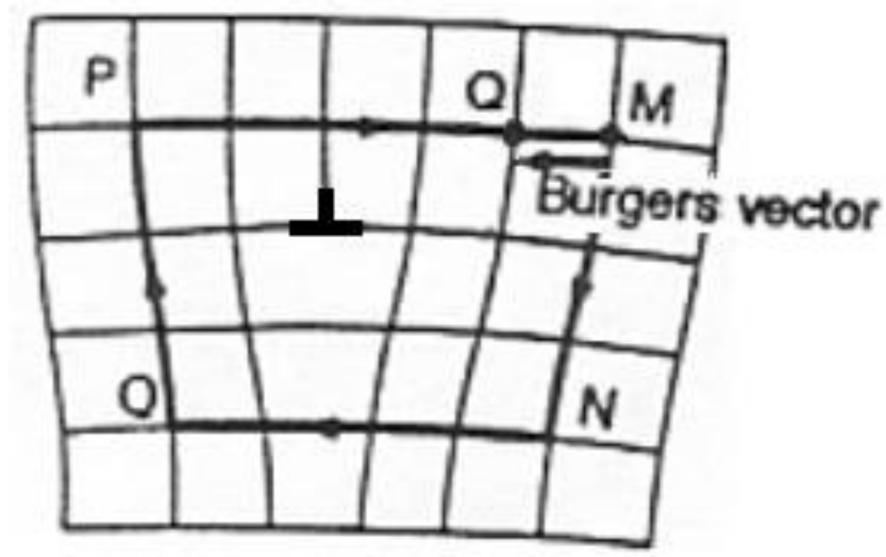
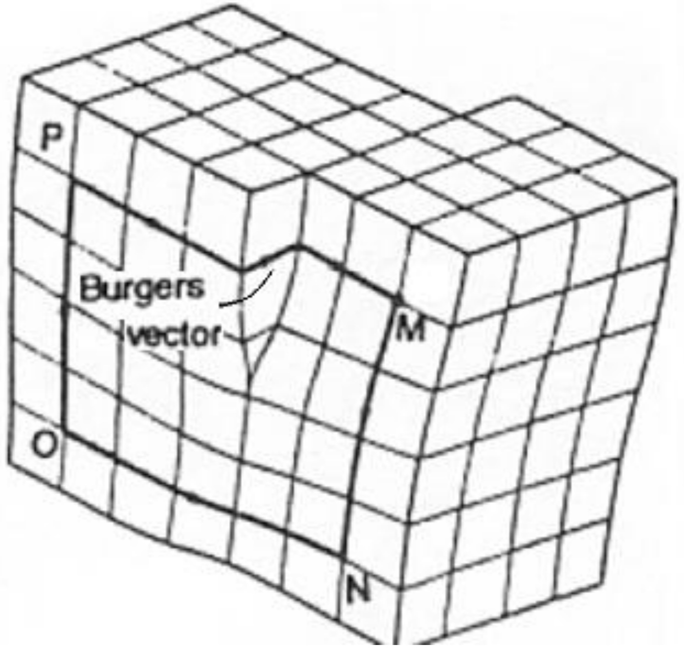
Sink Type I - Dislocations



Edge Dislocation

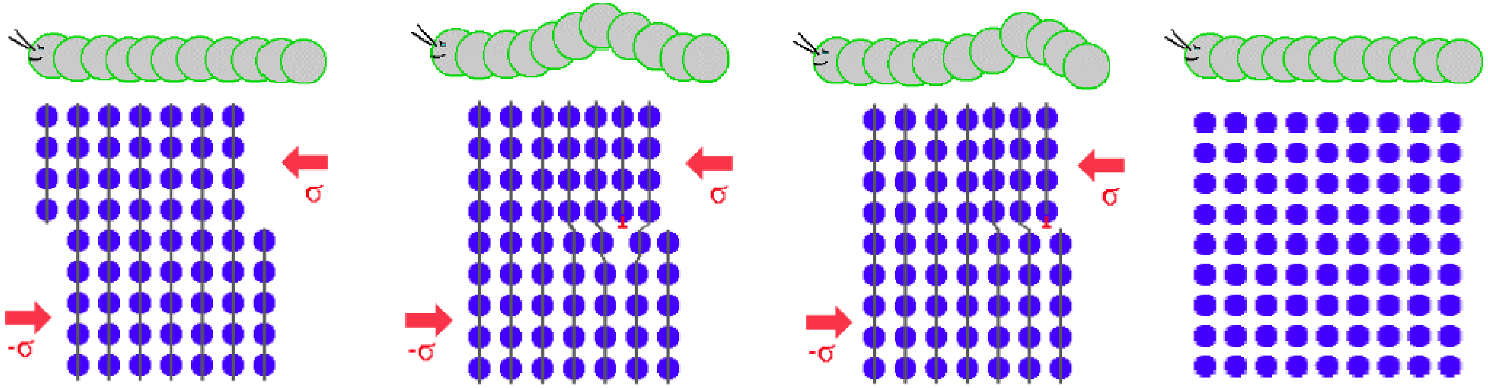


Screw Dislocation

- Three types: Edge, Screw, and Mixed
  - Edge dislocation: line is perpendicular to the Burgers vector
  - Screw dislocation: line is parallel to Burgers vector
  - Mixed dislocations: a combination of edge and screw characterisitics

Sink Type I - Dislocations

- Dislocation motion is the primary form of deformation in a material



- Anything which impedes dislocation motion will strengthen the material, but may make it brittle
  - Defects which impede dislocation motion:
    - *Other dislocations*
    - *Interstitials*
    - *Impurities*
    - *Grain boundaries*
    - *Etc…*

www.people.virginia.edu/~lz2n/ mse201/mse201-defects.pdf

Dislocation motion is the primary form of deformation in a material

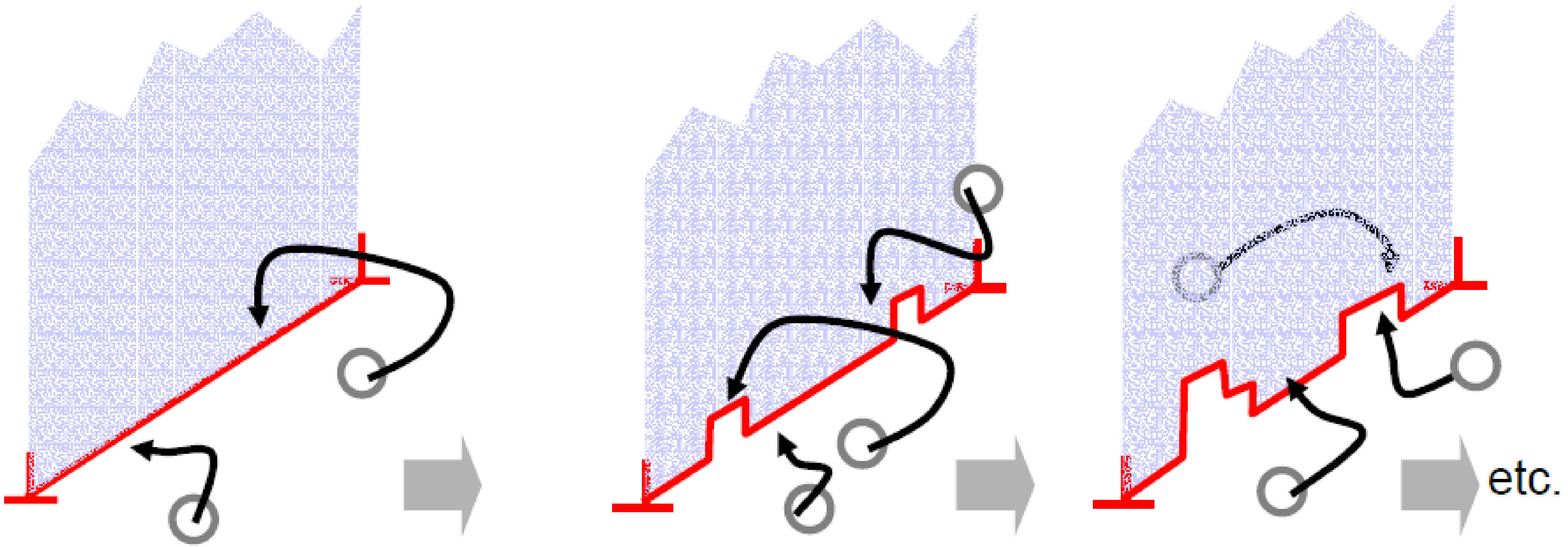
Stress

Video of bubble raft undergoing sheer stresses leading to dislocation motion and deformation
From: https://www.doitpoms.ac.uk/tlplib/dislocations/videos/shear-stresses.mp4

www.people.virginia.edu/~lz2n/ mse201/mse201-defects.pdf

Sink Type I - Dislocations

- Dislocation climb by vacancy absorption
- Leads to irradiation glide and creep



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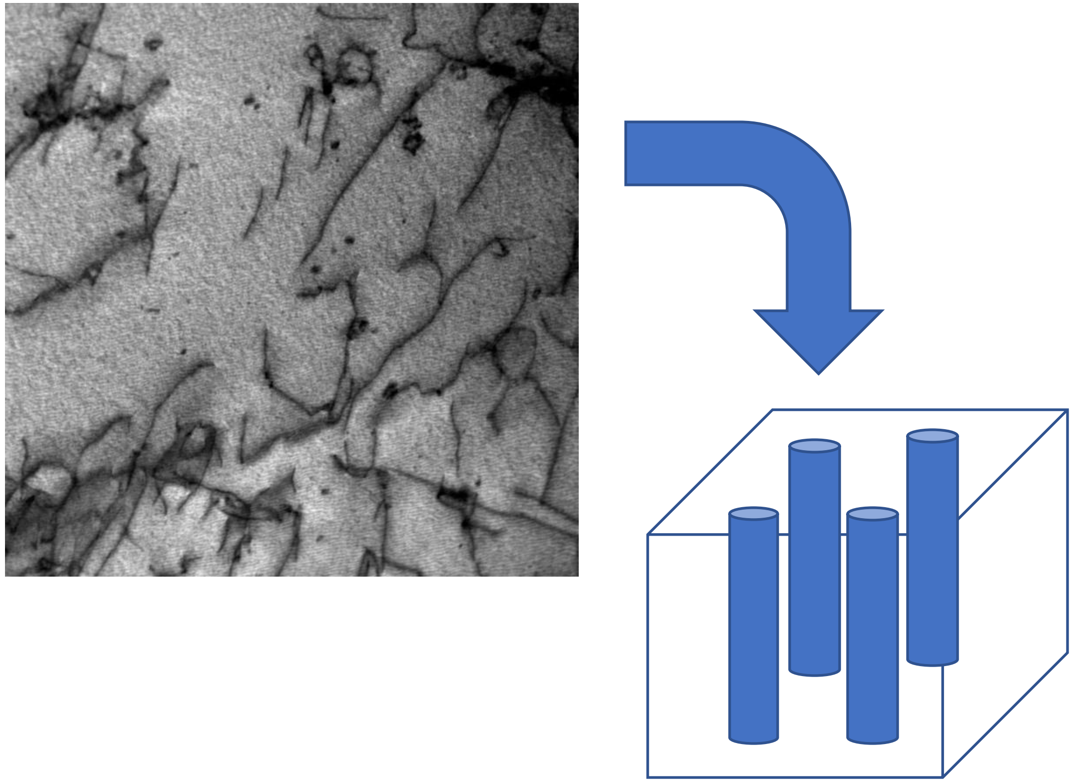
Point Defect Absorption by Dislocations

- Net reduction of strain energy
- Absorption leads to jog formation and climb



- Assumptions to determine rate of absorption
  - Even distribution of dislocation line density ($\mathbf{p_d}$ – cm^{-2})
  - Only one type of dislocation defect
  - Defects enter but do not exit the dislocation core r_0
  - At a distance R_d the concentration of defects is equal to $C_{i,v}^{bulk}$
  - No influence of the dislocation strain field

Point Defect Absorption by Dislocations

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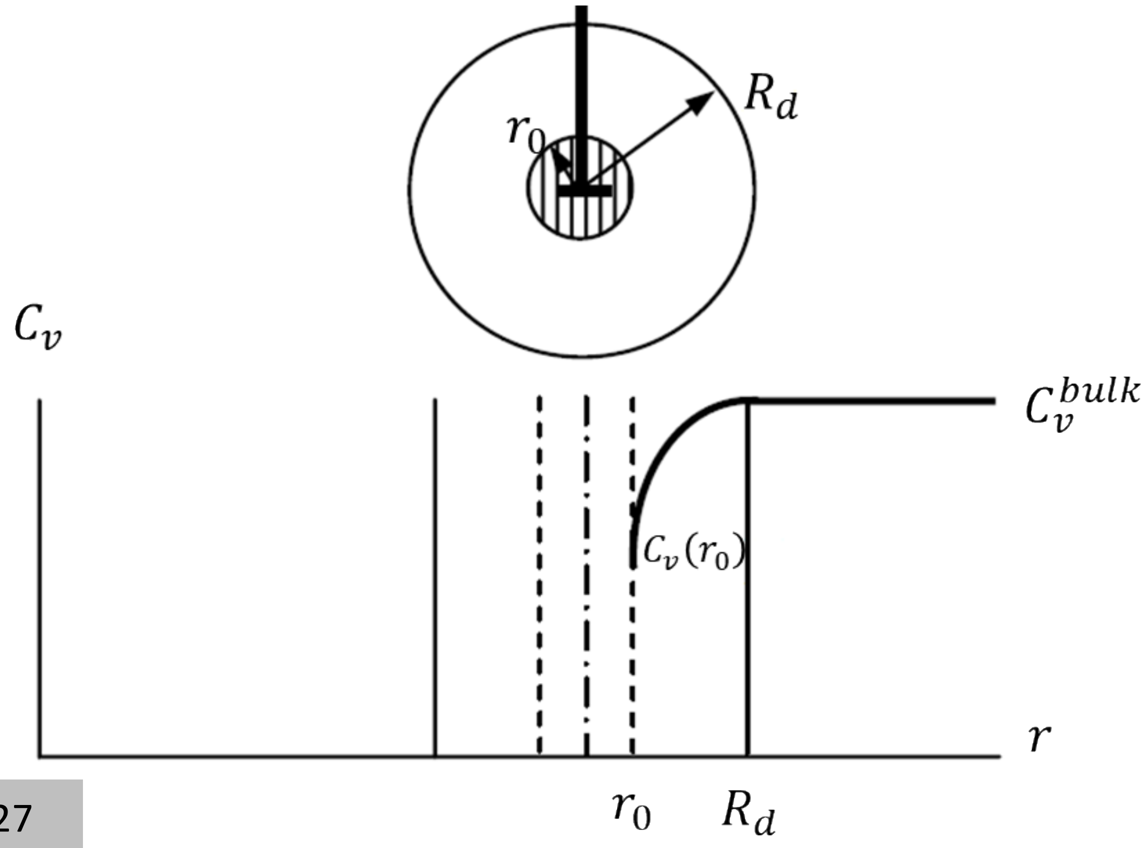

- Assumptions to determine rate of absorption
  - Even distribution of dislocation line density (**ρ_d** – cm^{-2})
  - Only one type of dislocation defect
  - Defects enter but do not exit the dislocation core r_0
  - At a distance R_d the concentration of defects is equal to $C_{i,v}^{bulk}$
  - No influence of the dislocation strain field

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Point Defect Absorption by Dislocations

- Our steady state assumption gives (in radial coordinates):

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{dC_{i,v}}{dr}\right) = 0$$

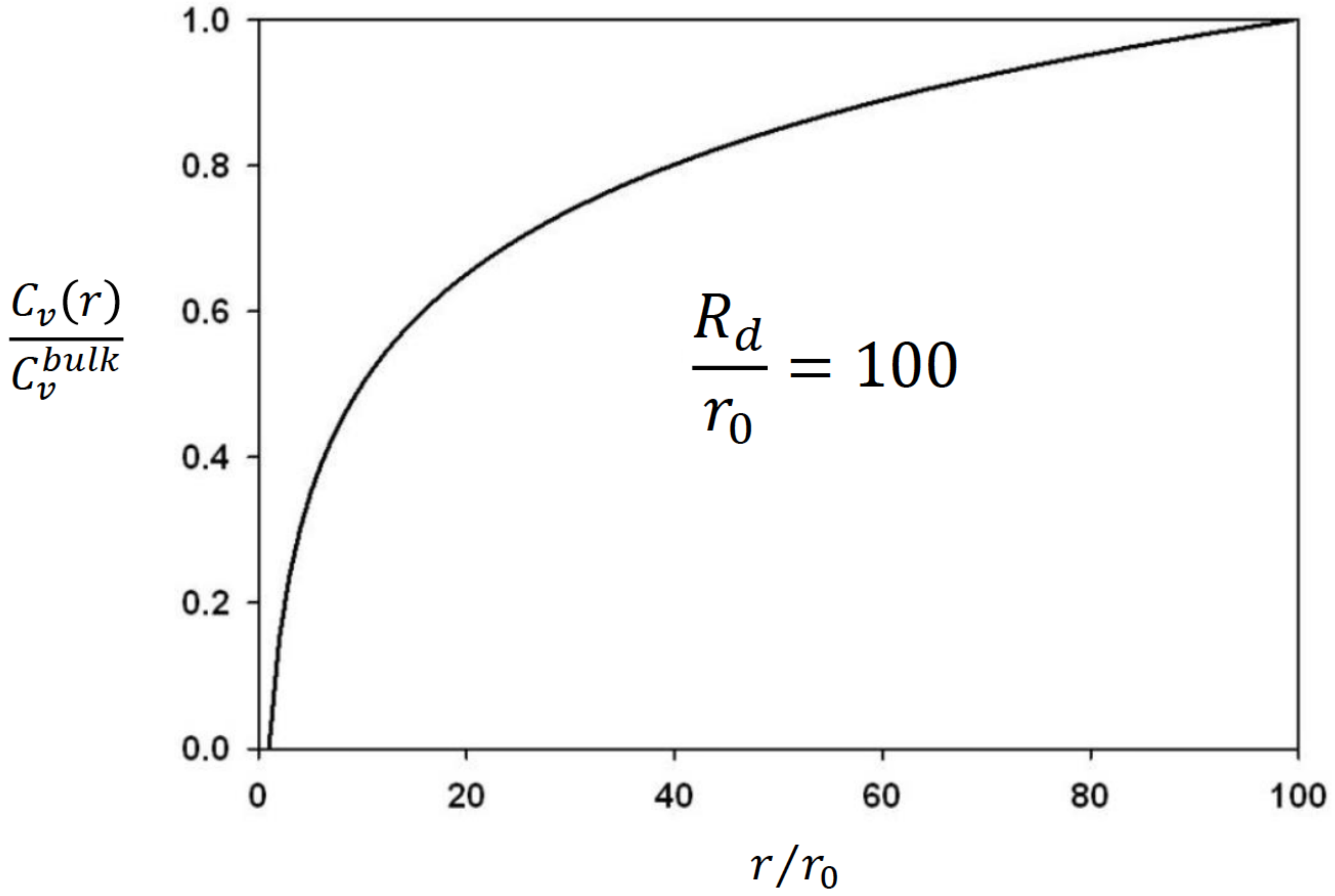
- The solution is then:

$$C_{i,v} = Aln(r) + B$$

- Using the boundary conditions established by our assumptions:

- Gives us:

Point Defect Absorption by Dislocations



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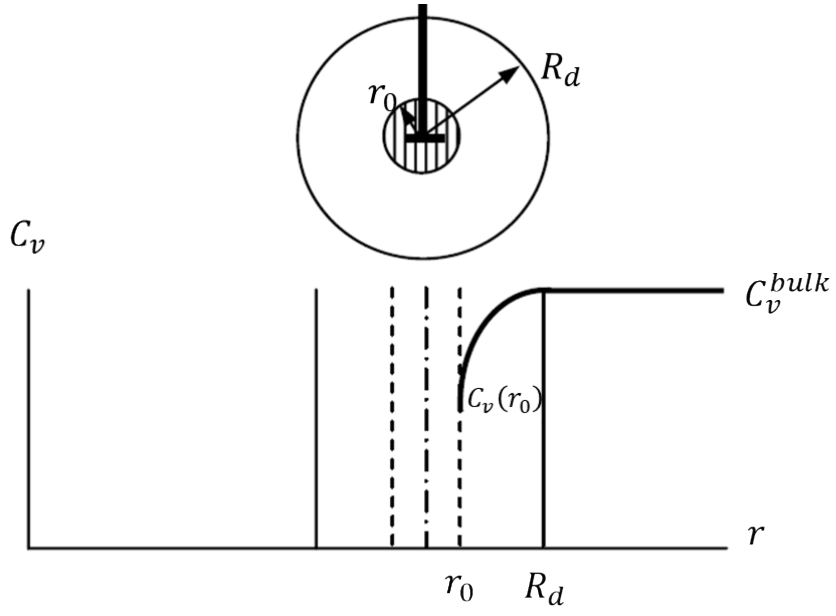
Point Defect Absorption by Dislocations

We now need the rate of absorption per unit length of the dislocation, e.g. the flux to the line dislocation:

$$j^{disl} = \frac{disl.\, surface\ area \times\ defect\ flux}{dislocation\ length}$$

$$j^{disl} = \frac{2\pi r_o L \times\ defect\ flux}{L} = 2\pi r_o \times\ defect\ flux$$



The defect flux is dependent on the diffusion of the defects and their concentration, giving:

$$j^{disl} = 2\pi r_o D_{i,v} \left(\frac{dC_{i,v}}{dr}\right)_{r_o}$$

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Point Defect Absorption by Dislocations

- Now that we have:

$$j^{disl} = 2\pi r_o D_{i,v} \left(\frac{dC_{i,v}}{dr}\right)_{r_o}$$

- We can substitute our previous equation:

$$C_{i,v}(r) = C_{i,v}^{bulk} \frac{ln\frac{r}{r_0}}{ln\frac{R_d}{r_0}}$$

- Into the above giving:

$$j^{disl} = 2\pi D_{i,v} \frac{C_{i,v}^{bulk}}{ln\frac{R_d}{r_0}}$$

- Since there is $\mathbf{p_d}$ cm of dislocation line per cm^3:

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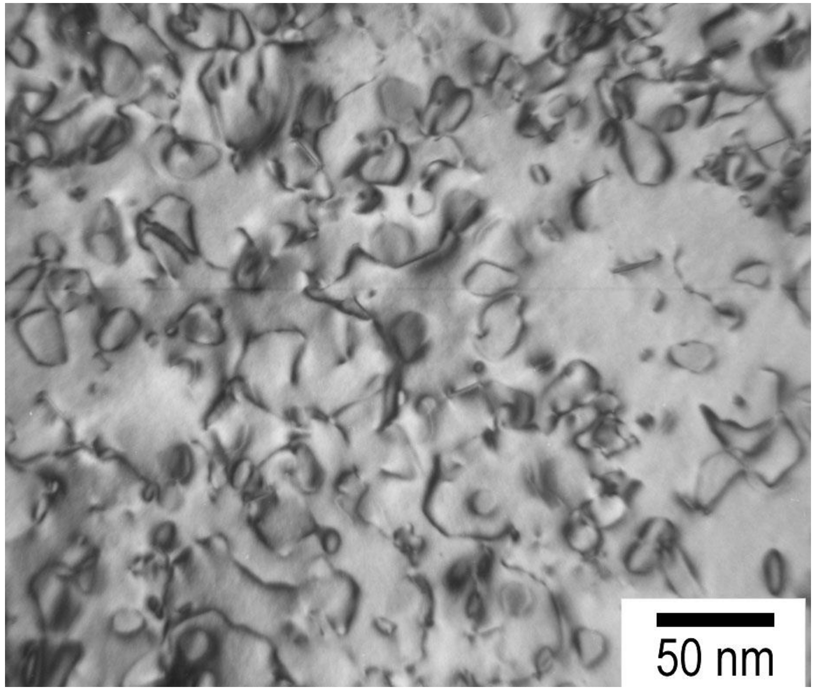
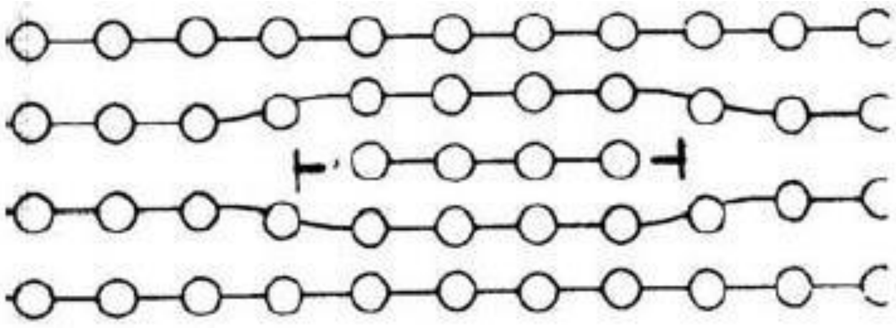
Accounting for dislocation loops

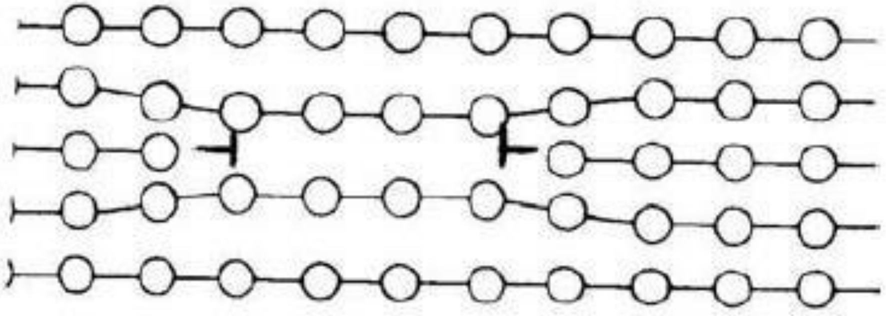
Dislocation Loops in Irradiated 316 SS (2 dpa)



Interstitial Loop

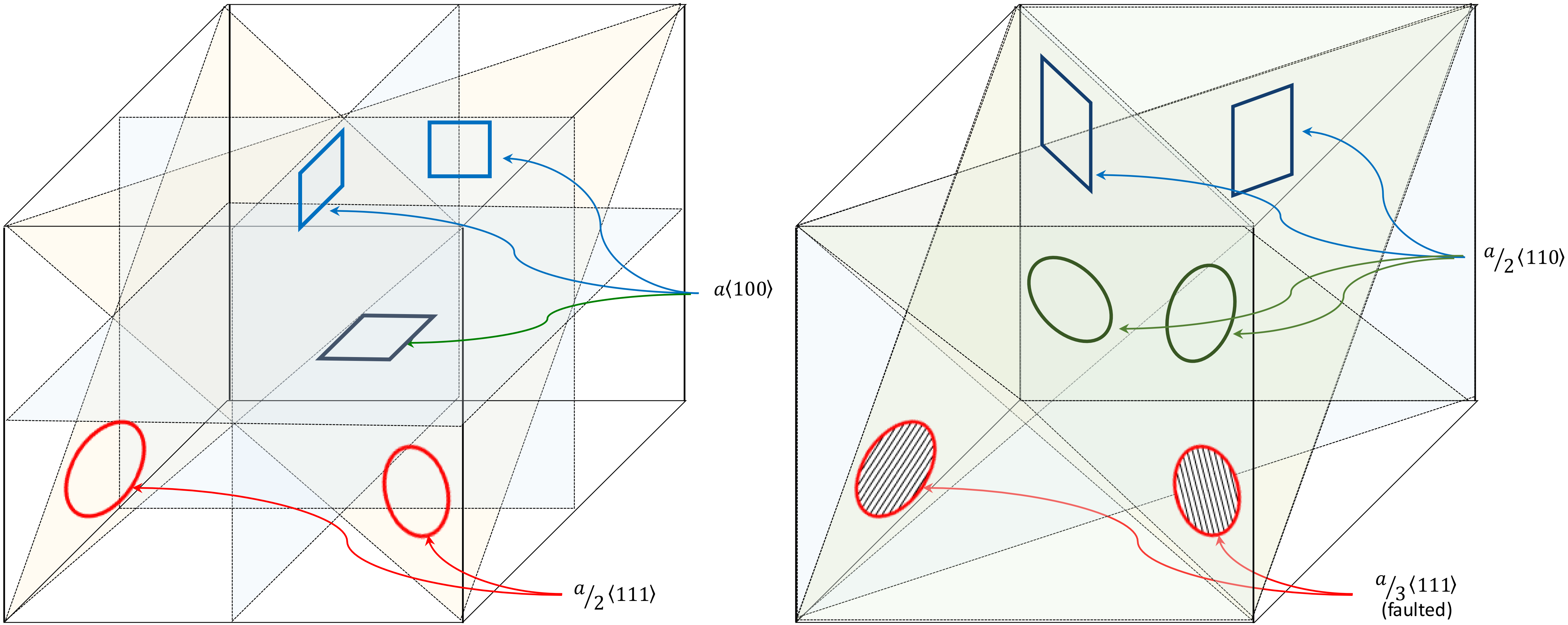


Vacancy Loop



- Dislocation Loop: when a dislocation line forms a closed loop instead of extending until it reaches an interface
    - Character of the dislocation (edge, screw, mixed) changes continuously along the line
    - Loops typically grow

For most BCC and FCC materials the Burgers vector and habit plane are well known



Body Centered Cubic (BCC)

Face Centered Cubic (FCC)

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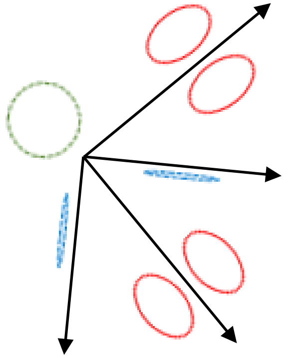
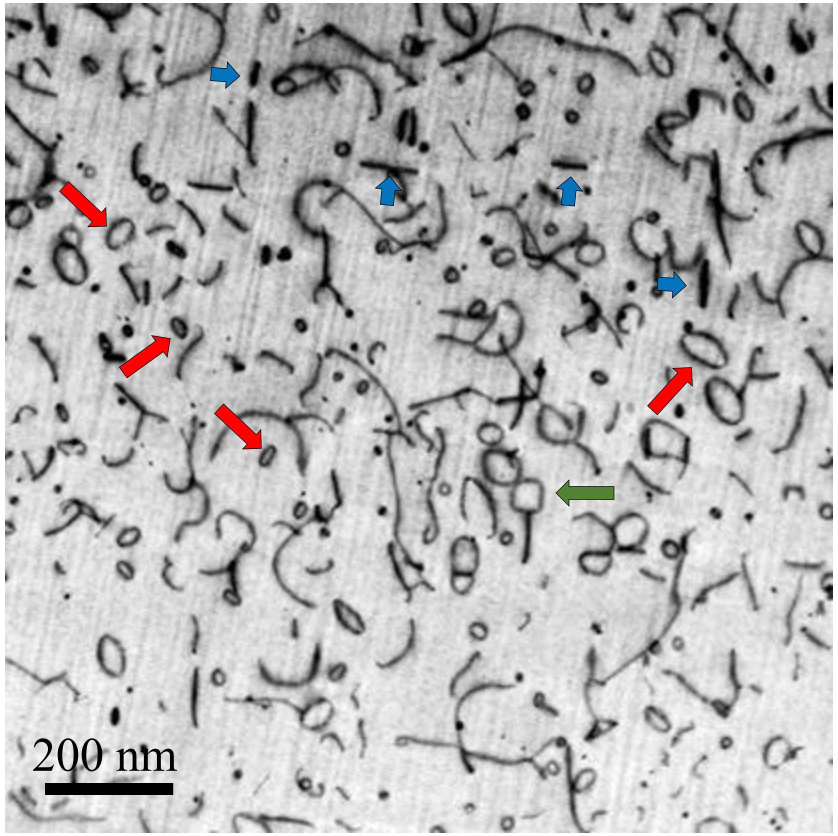
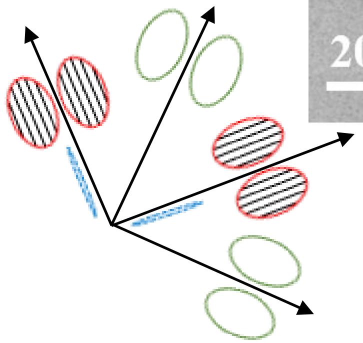
For most BCC and FCC materials the Burgers vector and habit plane are well known

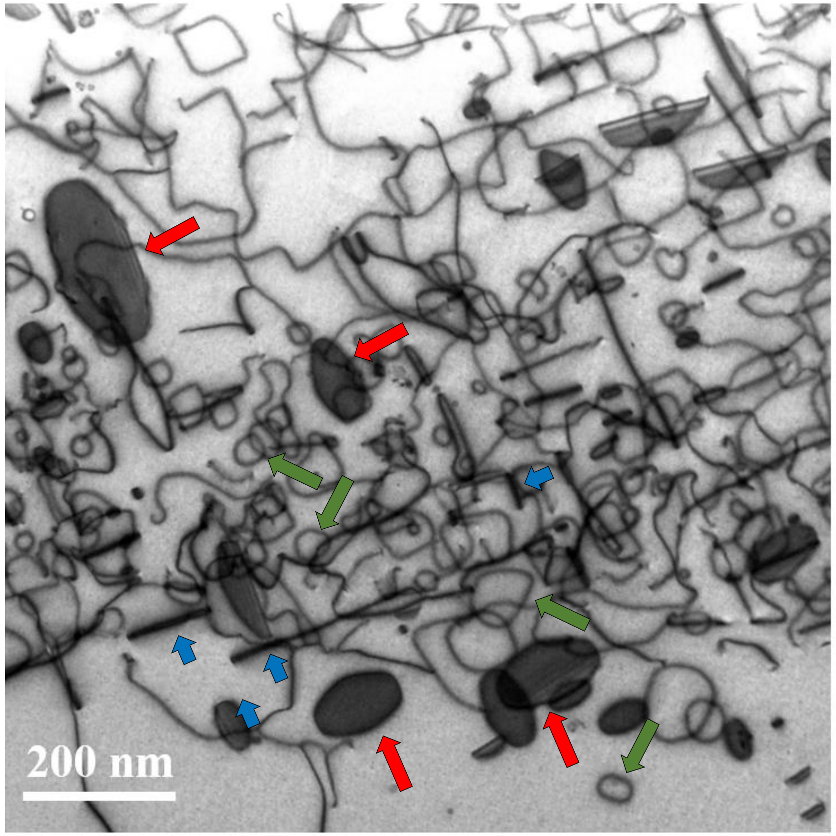




Body Centered Cubic (BCC)

Imaging down the [100] zone





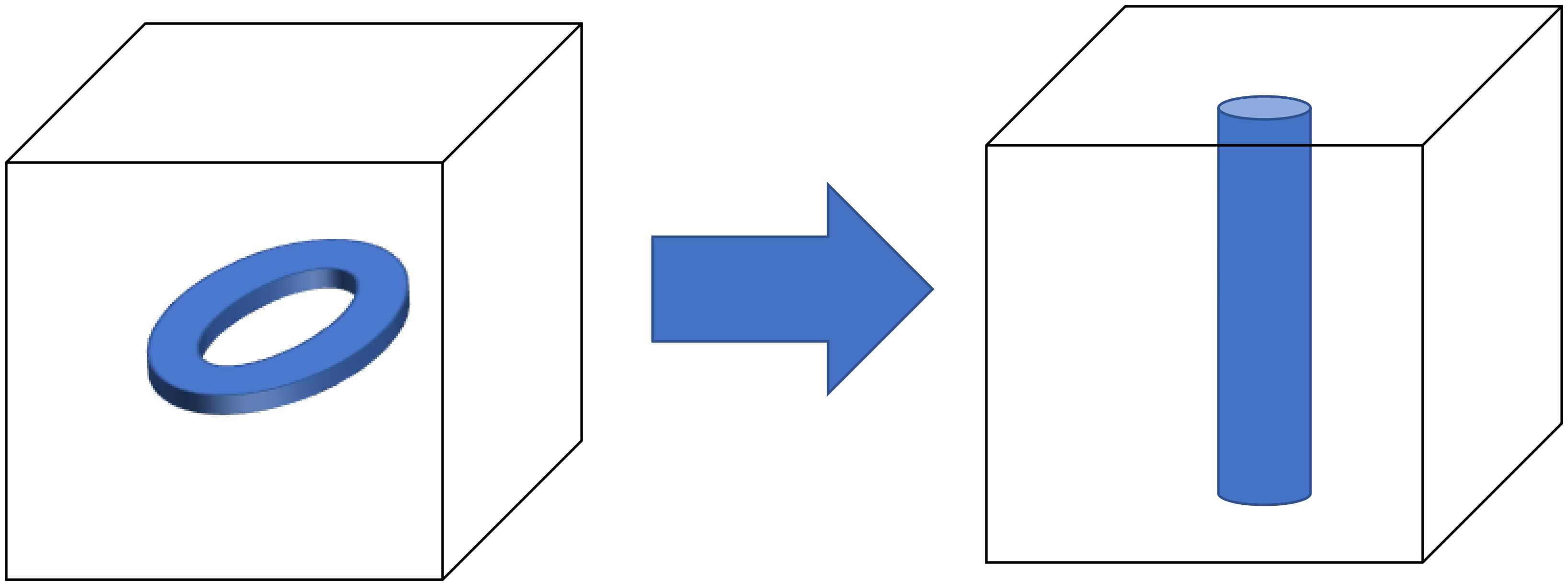
Face Centered Cubic (FCC)

C. Parish, et al., *J. Mat. Res.*, **30**, 2020

P. Xiu, et al., *J. Nuc. Mat.*, **544**, 2021

Accounting for dislocation loops

- We derived the reaction rate and sink strength for dislocation lines, but it is also used for dislocation loops. For loops ρ_d is used but with no consideration of geometry, e.g. the circular dislocation loops are effectively "straightened out"



Sink types

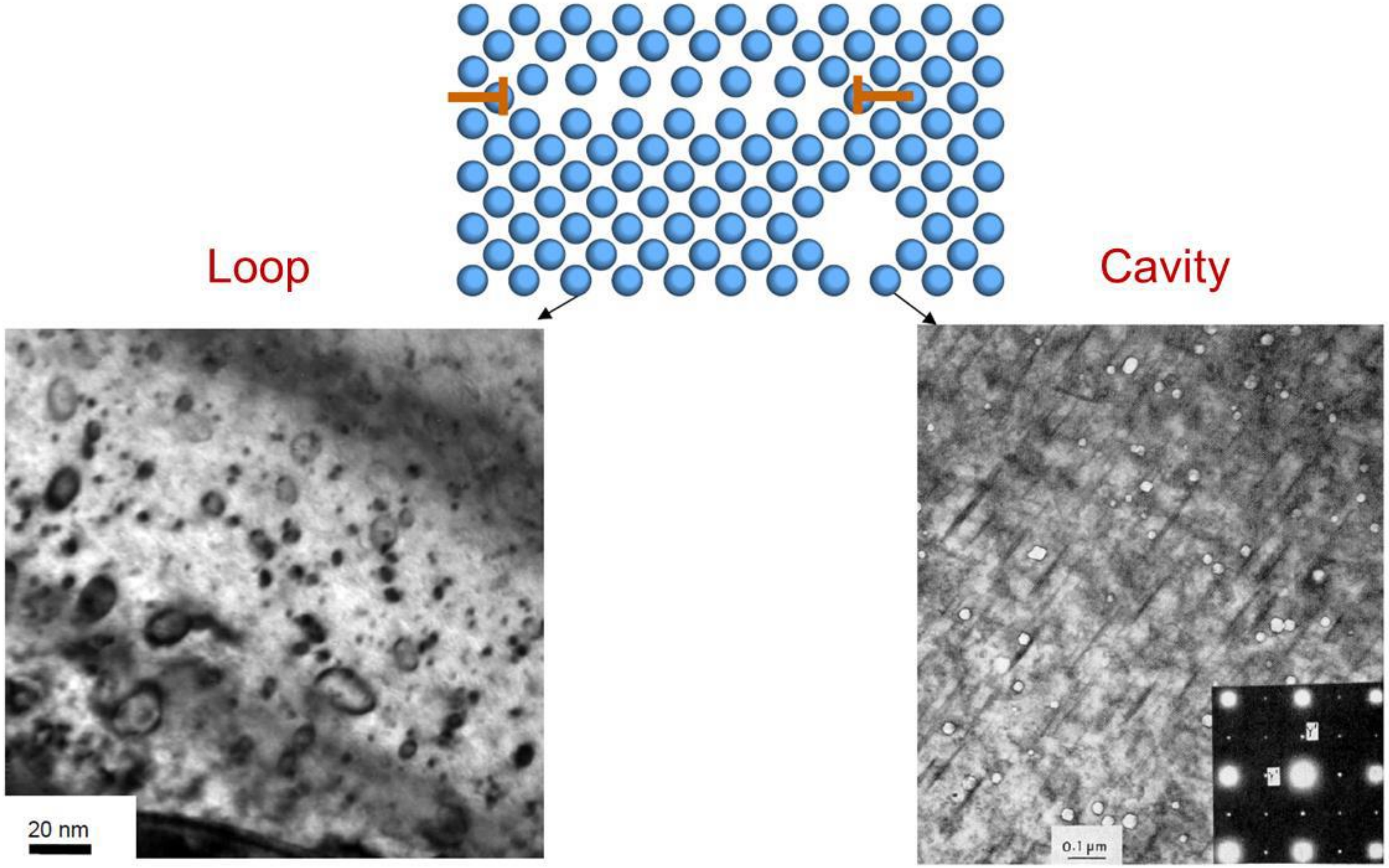
- Sinks can behave differently:
  - **Neutral sinks:** Neutral sinks show no preference for capturing one type of defect over another.
  - **Biased sinks:** Biased sinks show a preferential attraction for one defect over another.
  - **Variable sinks:** Variable sinks act as traps for defects which hold the defect but preserve its identity until annihilation or it is released.

Coherent precipitates

Grain boundaries/Voids

Dislocations

Sink Type II - Cavities



- Cavities are due to vacancies (and possibly gas atoms) diffusing and coalescing together within the matrix
- Can lead to brittle fracture (bad!)

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Sink Type II - Cavities

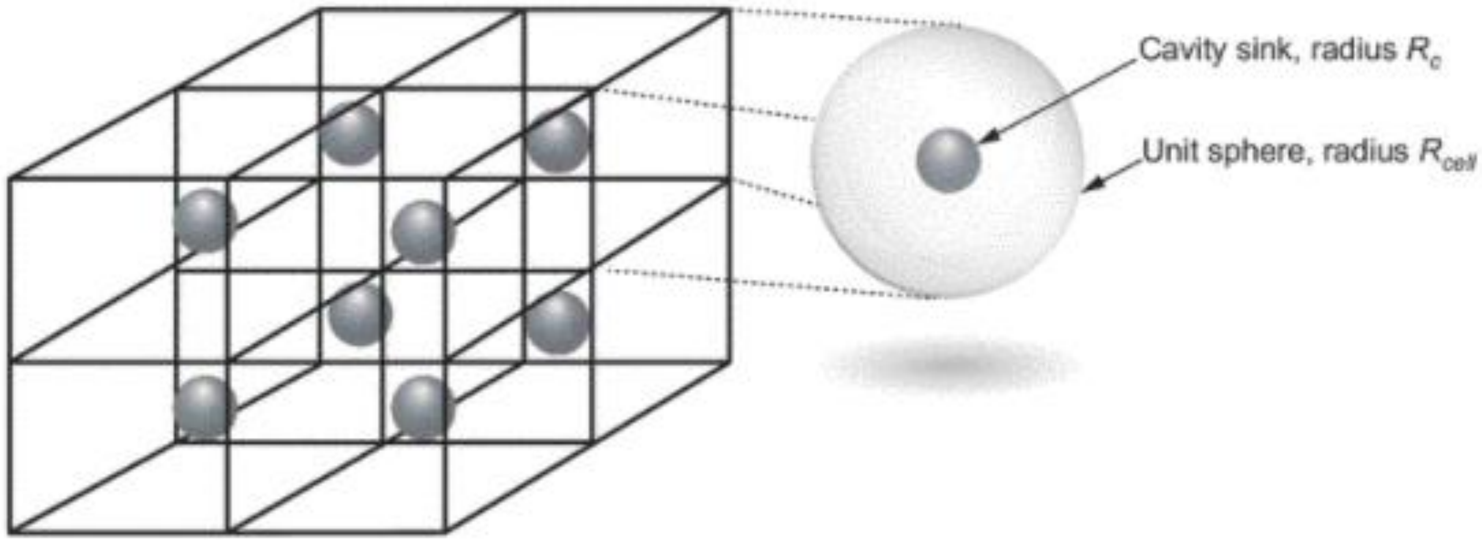

FIGURE 13.8: ***Spherical cavity sinks uniformly distributed in a solid. The cubes are unit cells for each sphere.***

- Similar arguments for point defect absorption can be made in the case of voids:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dC_v}{dr}\right) = 0 \qquad \rightarrow C_v(r) = -\frac{A}{r} + B$$

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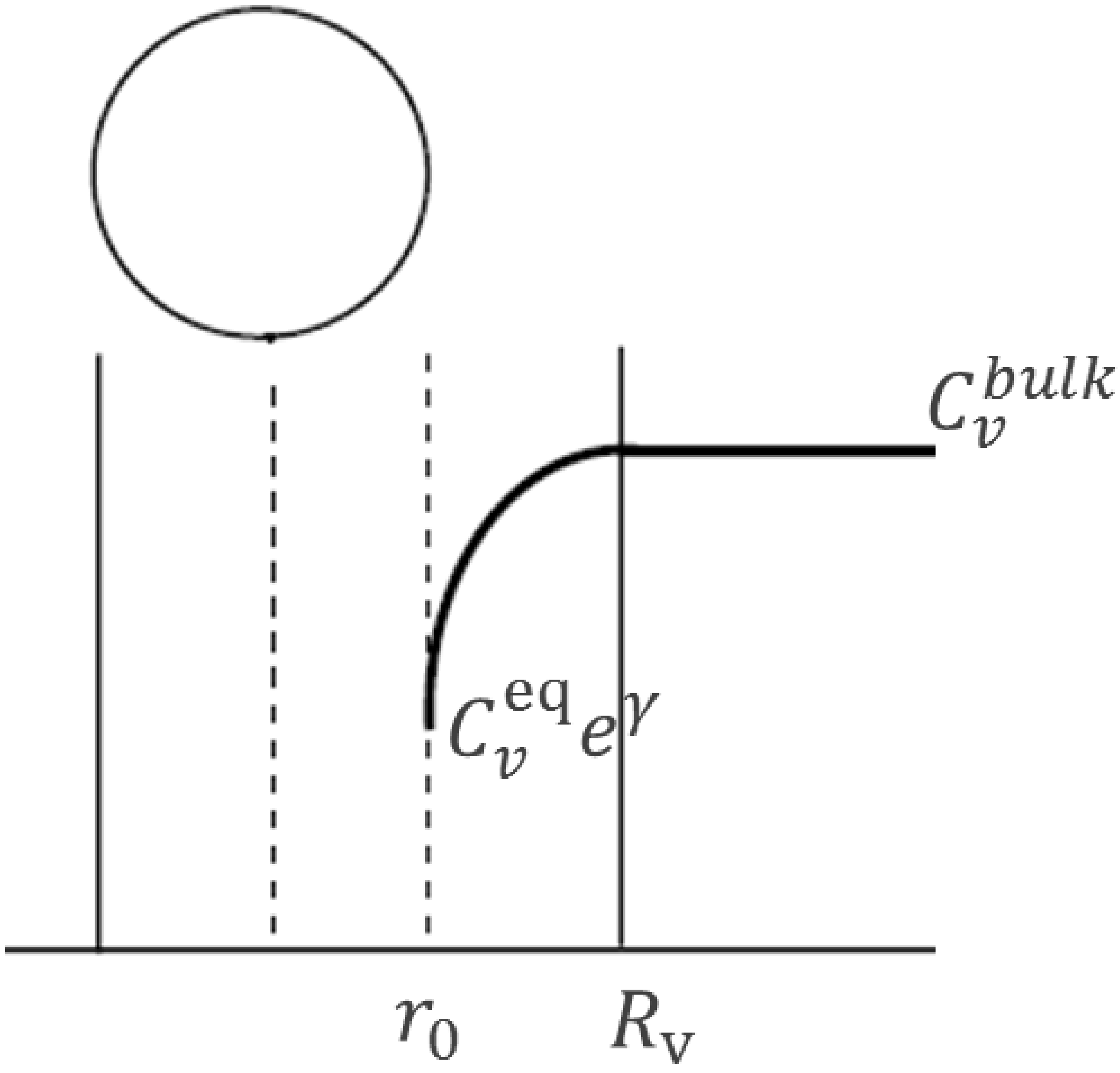
Sink Type II - Cavities



It is assumed that the boundary conditions are:

In these conditions:

$$\frac{C_v(r) - C_v(r_o)}{C_v^{Bulk} - C_v(r_o)} = 1 - \frac{r_o}{r}$$

Sink Type II - Cavities

The rate of absorption per cavity is then given as:

$$j_{i,v}^{Cavity} = 4\pi r_o D_{i,v} C_{i,v}^{bulk}$$

Considering all cavities using N_c (cavities per unit volume), we get:

$$J_v^C = 4\pi r_o N_c D_v C_v^{bulk}$$

$$J_i^C = 4\pi r_o N_c D_i C_i^{bulk}$$

Then:

Point Defect Kinetic Equations

- If we neglect clustering:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{vs}C_vC_s + D_v\nabla^2 C_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{is}C_vC_s + D_i\nabla^2 C_i$$

- Example of defect absorption to cavities:

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - z_v p_d D_v C_v + 4\pi R_c N_c D_v C_v$$

$$\frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v - z_i p_d D_i C_i + 4\pi R_c N_c D_i C_i$$

Sink types

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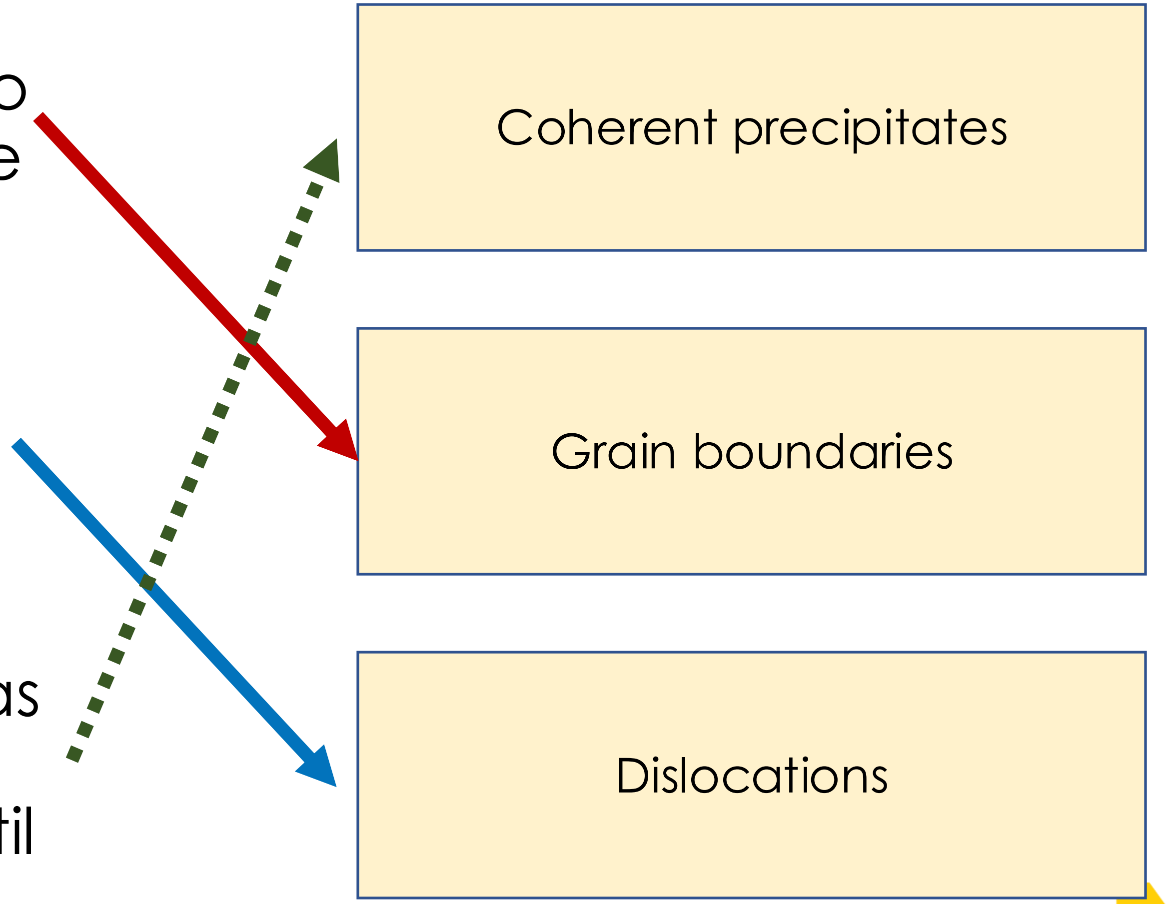
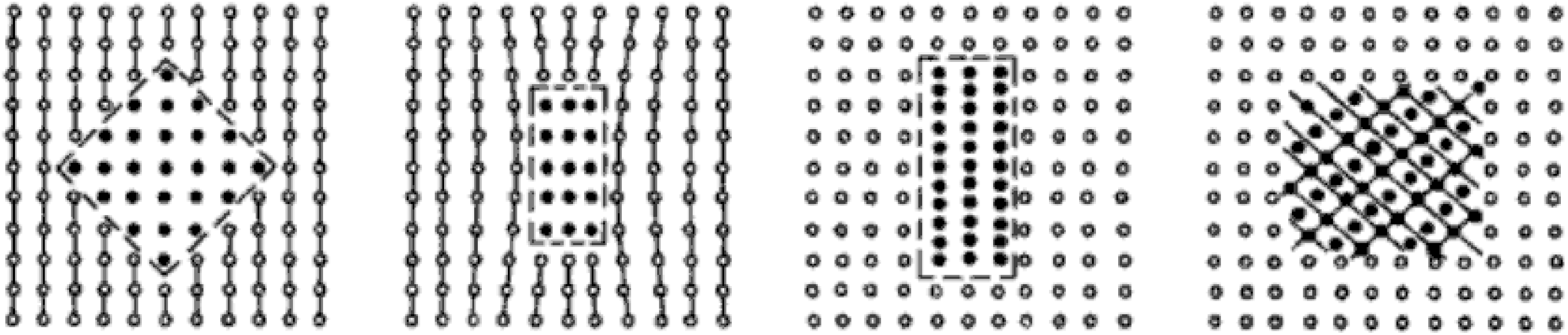


Sink Type III – Coherent Precipitates (PPTs)



a) b) c) d)

- Precipitates are the result of the local solubility limit being reached causing a new phase to form
- Precipitates can be either coherent, partially coherent or incoherent
  - Coherency: a perfect lattice match between the PPT and matrix
  - Coherency affects how dislocations interact with the PPT
  - Coherency can also affect diffusion in and around the PPT

Sink Type III – Coherent Precipitates (PPTs)

- Precipitates impede dislocation motion
- Inclusion of precipitates can strengthen a material

https://www.youtube.com/watch?v=zNZyAN

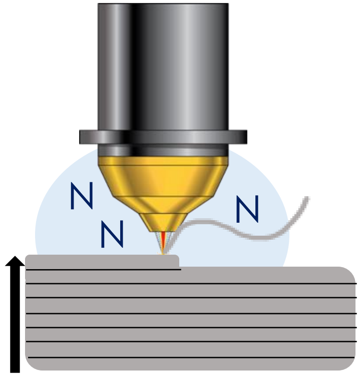
Sink Type III – Coherent Precipitates (PPTs)

- Coherent precipitates act as traps
- Bias to interface depends on the other biased sinks present in the microstructure (such as dislocations!)
- Vacancies and interstitials reduce the strain field at the trap due to the lattice mismatch

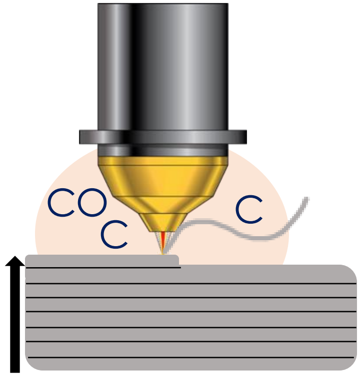
WAAM Grade 91 Experimental Details

Control MX precipitate structure with C and N additions using different shielding gases

99% Ar-1% N_2 Shielding Gas
(Build 99/1)

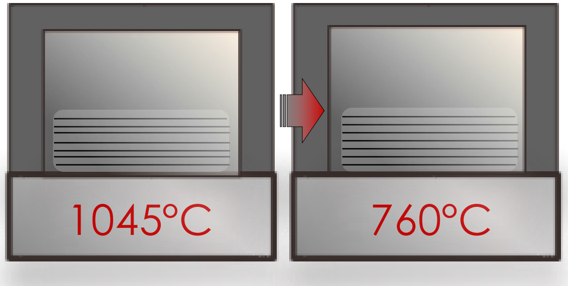


95% Ar-5% CO_2 Shielding Gas
(Build 95/5)

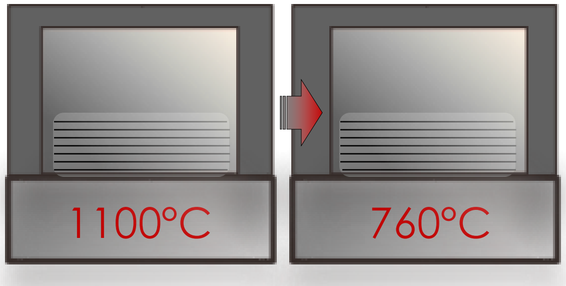


Build

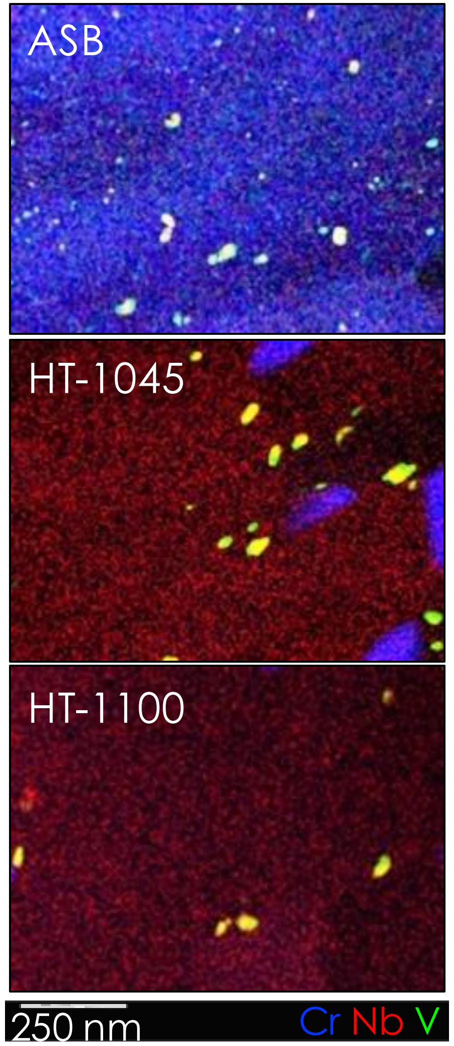
HT-1045



HT-1100



Heat Treat

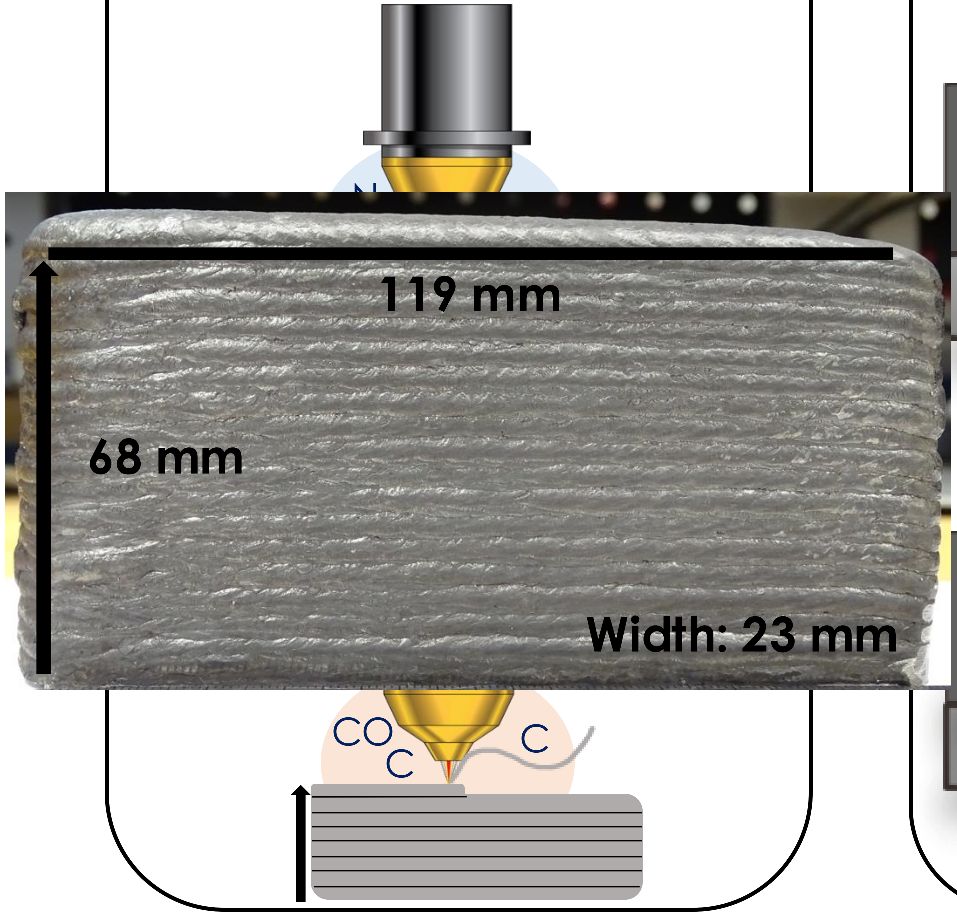


Char

Wire Arc AM Experimental Details

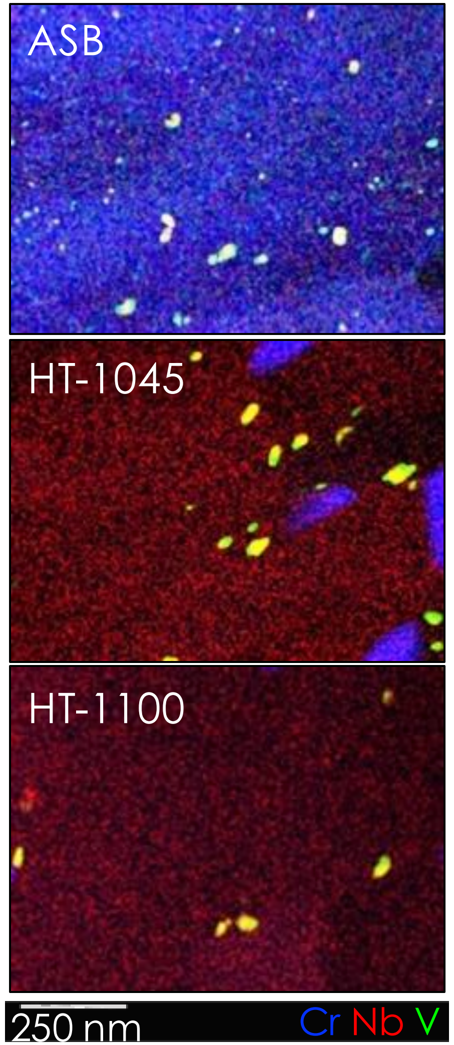
Control MX precipitate structure with C and N additions using different shielding gases

99% Ar-1% N_2 Shielding Gas
(Build 99/1)



Build

Heat Treat



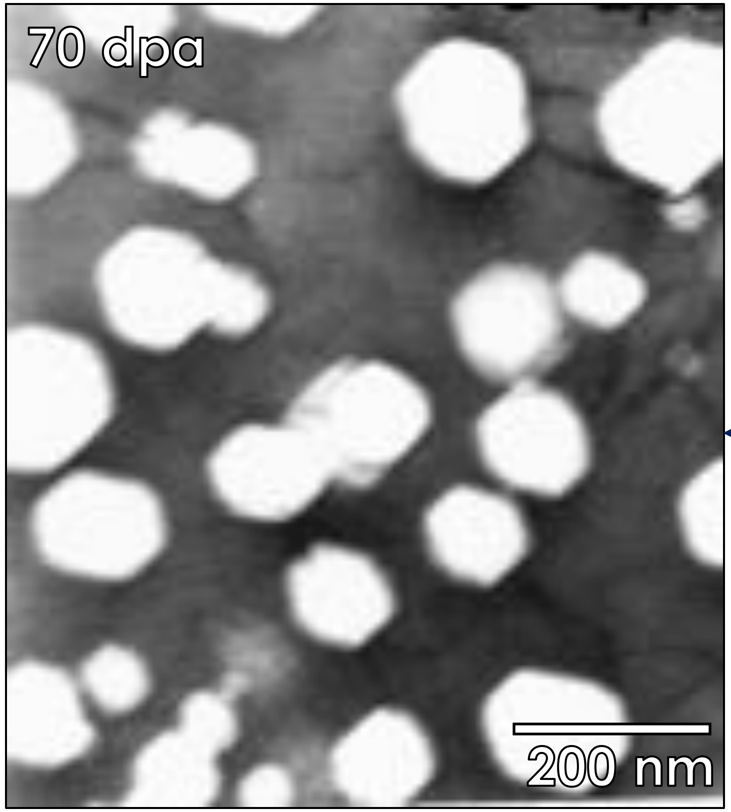
Char

Shielding Gas Effect on Sink Strength

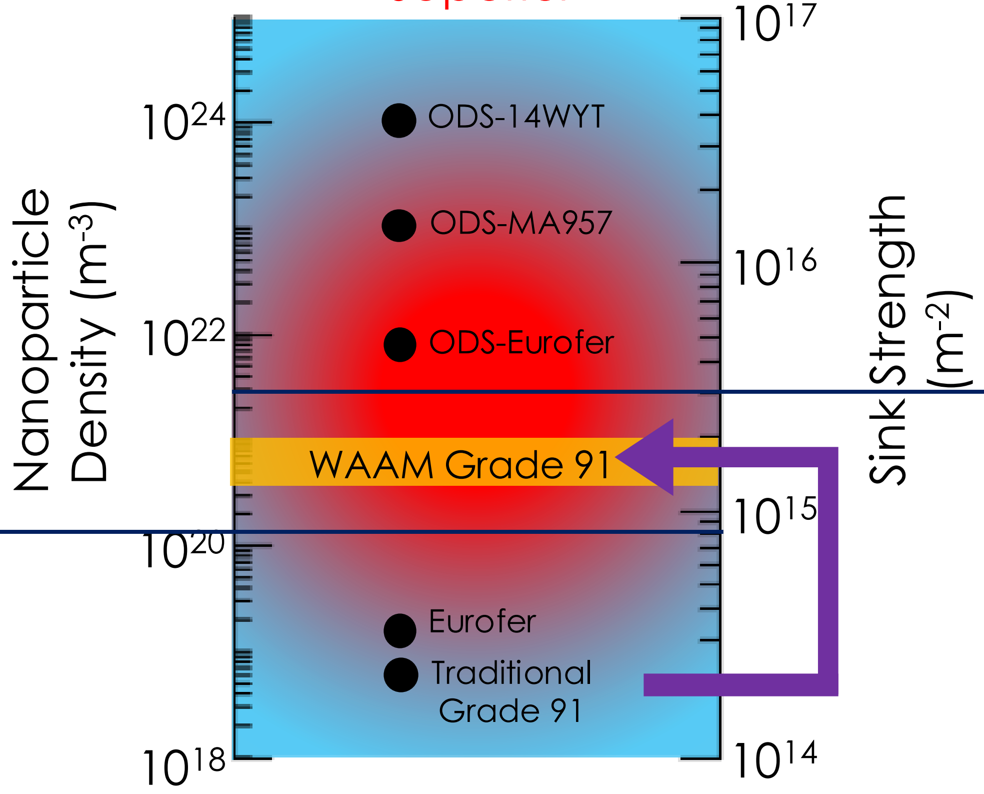
Nanoscale precipitation increases sink strength and hence radiation resistance of a material

$S_{ppt} \sim 4\pi RN$

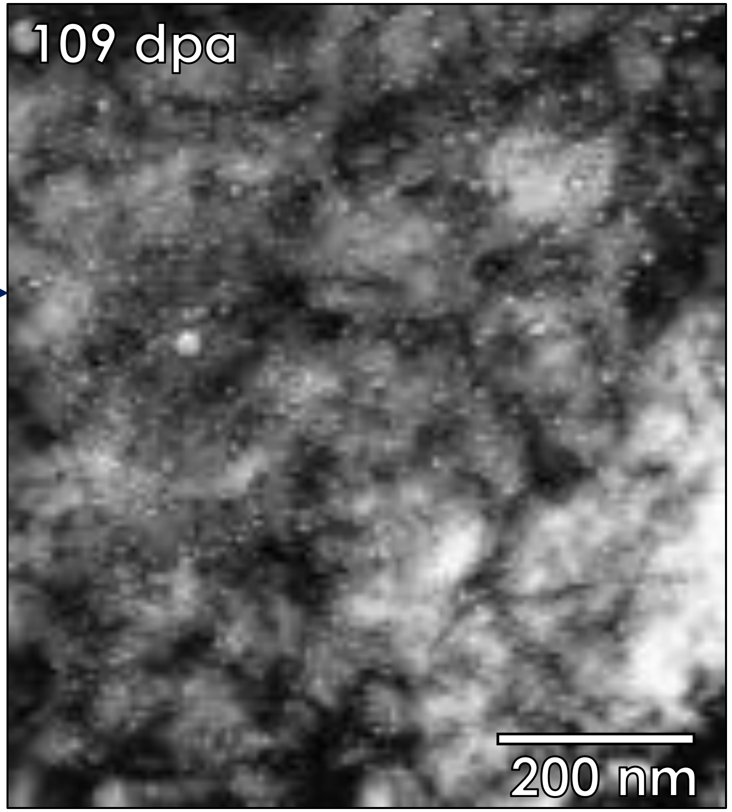
Critical sink strength value to prevent:
- Void swelling : 10^{15} m^{-2}
- Radiation hardening: 10^{16} m^{-2}



22% swelling



Increased gained from shielding gas use



0.5% swelling

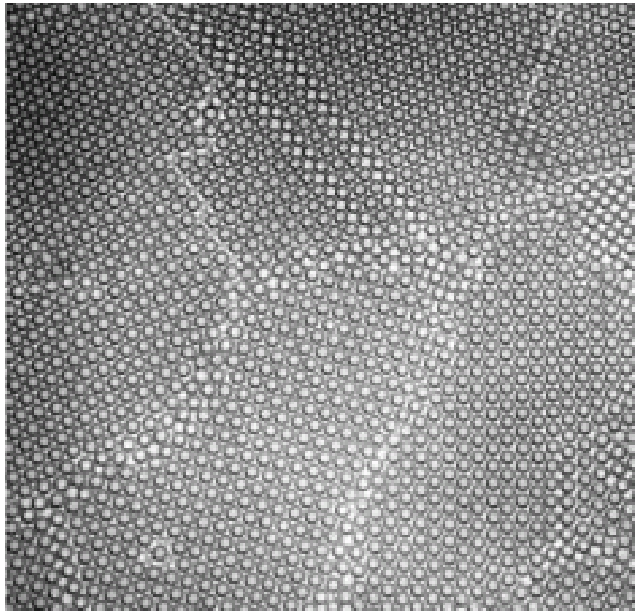
S.J. Zinkle and L.L. Snead, Ann Rev. Mat. Res., 44 (2014) 241

Putting it together:

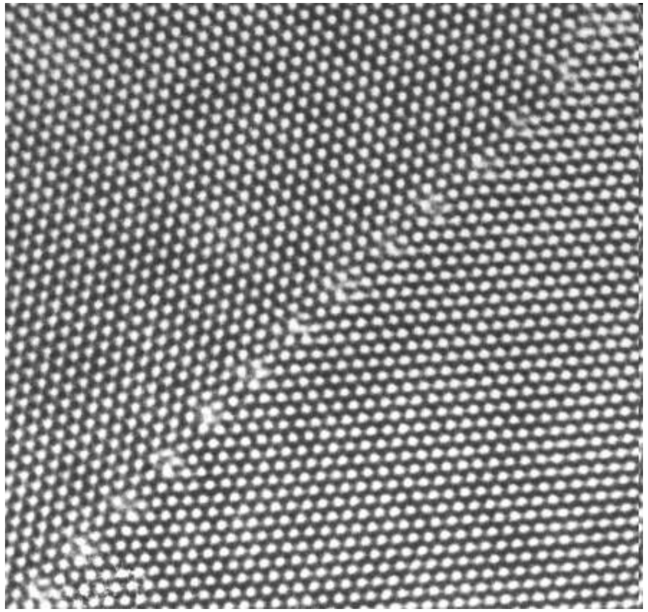
Table 5.2 Reaction rate constants for defect–sink reactions

Reaction	Rate constant	Sink strength	Eq. #
v + v	$K_{2v} = \dfrac{z_{2v}\Omega D_v}{a^2}$	–	Equation (5.58)
i + i	$K_{2i} = \dfrac{z_{2i}\Omega D_i}{a^2}$	–	Equation (5.58)
v + i	$K_{iv} = \dfrac{z_{iv}\Omega D_i}{a^2}$	–	Equation (5.61)
v, i + void			
Reaction rate control	$K_{vV} = \dfrac{4\pi R^2 D_v}{a} \quad K_{iV} = \dfrac{4\pi R^2 D_i}{a}$	$k^2_{vV} = k^2_{iV} = \dfrac{4\pi R^2 \rho_V}{a}$	Equation (5.65)
Diffusion control	$K_{vV} = 4\pi R D_v \quad K_{iV} = 4\pi R D_i$	$k^2_{vV} = k^2_{iV} = 4\pi R \rho_V$	Equation (5.84)
Mixed rate control	$K_{vV} = \dfrac{4\pi R D_v}{1+\dfrac{a}{R}} \quad K_{iV} = \dfrac{4\pi R D_i}{1+\dfrac{a}{R}}$	$k^2_{vV} = k^2_{iV} = \dfrac{4\pi R \rho_V}{1+\dfrac{a}{R}}$	Equation (5.102)
v, i + dislocation			
Diffusion control	$K_{vd} = \dfrac{2\pi D_v}{\ln(\mathscr{R}/R_{vd})} \quad K_{id} = \dfrac{2\pi D_i}{\ln(\mathscr{R}/R_{id})}$	$k^2_{vd} = \dfrac{2\pi \rho_d}{\ln(\mathscr{R}/R_{vd})} \quad k^2_{id} = \dfrac{2\pi \rho_d}{\ln(\mathscr{R}/R_{id})}$	Equations (5.99, 5.100)
Reaction rate control	$K_{vd} = z_{vd} D_v \quad K_{id} = z_{id} D_i$	$k^2_{vd} = z_{vd}\rho_d \quad k^2_{id} = z_{id}\rho_d$	Equation (5.67)
Mixed rate control	$K_{vd} = \dfrac{D_v}{\dfrac{1}{z_{vd}} + \dfrac{\ln(\mathscr{R}/R_{vd})}{2\pi}} \quad K_{id} = \dfrac{D_i}{\dfrac{1}{z_{id}} + \dfrac{\ln(\mathscr{R}/R_{id})}{2\pi}}$	$k^2_{vd} = \dfrac{\rho_d}{\dfrac{1}{z_{vd}} + \dfrac{\ln(\mathscr{R}/R_{vd})}{2\pi}} \quad k^2_{id} = \dfrac{\rho_d}{\dfrac{1}{z_{id}} + \dfrac{\ln(\mathscr{R}/R_{id})}{2\pi}}$	Equation (5.104)
v, i + grain boundary			
Diffusion control	$K_{vgb} = 4\pi D_v d \quad K_{igb} = 4\pi D_i d$ $K_{vgb} = \pi k D_v d^2 \quad K_{igb} = \pi k D_i d^2$	$k^2_{gb} = 24/d^2, \quad d < 10^{-3}$ cm $k^2_{gb} = 6k/d, \quad d > 10^{-3}$ cm	Equation (5.115) Equation (5.116)
v, i + coherent ppt	$K_{vCP} = 4\pi R_{CP} D_v Y_v, \quad K_{iCP} = 4\pi R_{CP} D_i Y_i$	$k^2_{vCP} = 4\pi R_{CP}\rho_{CP} Y_v, \quad k^2_{iCP} = 4$	

Sink Type IV – Grain Boundaries



Bubble Raft Model of Grain Boundaries

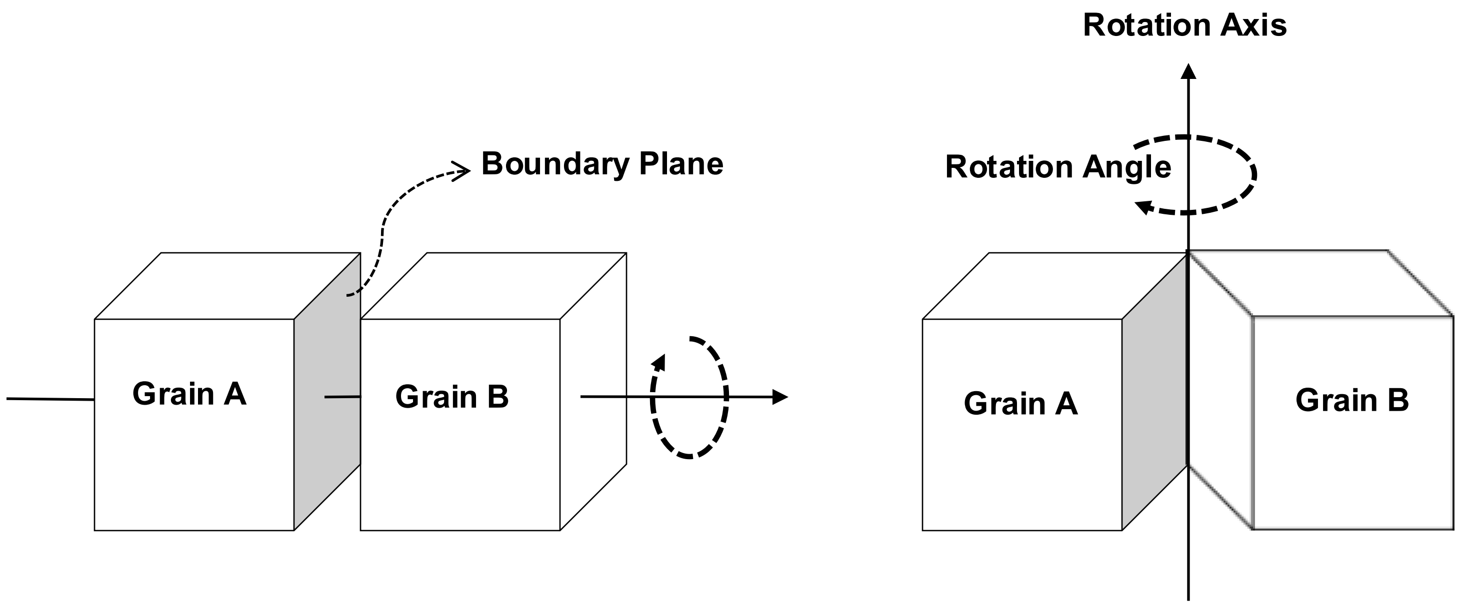


HRTEM image of a Σ19 GB in Al

- A Grain Boundary is a general planar defect that separates regions of different crystalline orientation (i.e. *grains*) within a polycrystalline solid
- Grain boundaries can affect creep strength, yield strength, and diffusion

http://www.allenjhall.com/content/category/work/materials-science-and-engineering/

Sink Type IV – Grain Boundaries



a) Twist Grain Boundary

b) Tilt Grain Boundary

- Grain boundaries can have twist, tilt, or mixed character
- Variations in the degree of misalignment between two adjacent grains are possible

Questions?