Point Defect Diffusion + Defect Reactions

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Microscopic Diffusion

4.3.3 was ←

5.2 & 5.4 0&M

- Assume that the self-diffusion process consists of a completely random walk of defects
- Assume steps of equal length, random directions:

$\rightarrow \lambda$

$$\bar{r} = \sum_{i=1}^{n} \lambda_i$$

∴

mean square displacement

math ☺

$$\bar{r}^2 = n \lambda^2$$

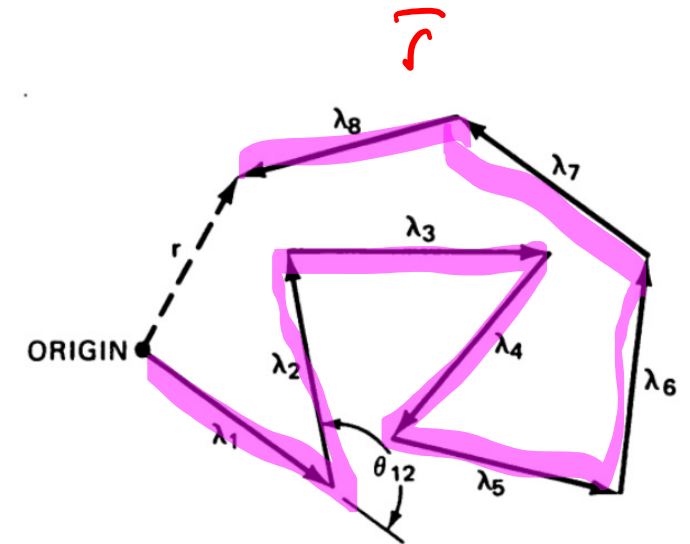hop distance

hops

Brownian

Fig. 7.4 Eight random jumps of equal length λ.

Microscopic Diffusion

$$\bar{r}^2 = n\lambda^2$$

We need to now convert this to a function of time, t. We can do this by considering the frequency of each jump, Γ, and the time allowed for hopping, then we get:

We now need to equate this to the macroscopic diffusion, D. To do this we use Ficks second law of diffusion to describe the probability of finding a spherical shell surrounding an origin:
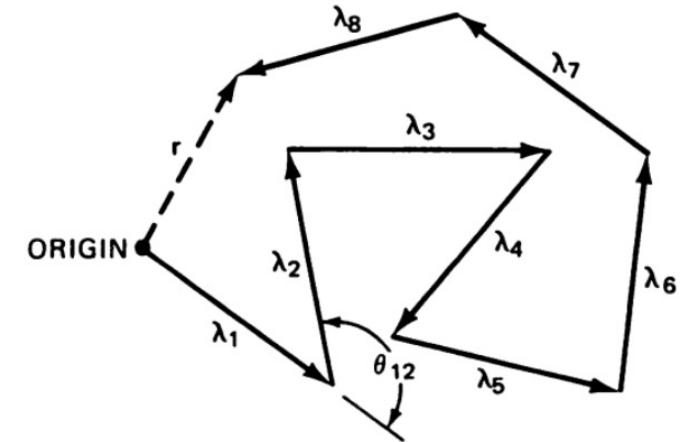

Fig. 7.4 Eight random jumps of equal length λ.

Microscopic Diffusion

Both the macroscopic and microscopic eqautions can be equated together based on both can be defined based on the probability, p_t. To do this, we substitute $p_t(r)$ into:

$$\bar{r}^2 = 4\pi \int_0^\infty r^4\, p_t(r)\mathrm{dr}$$

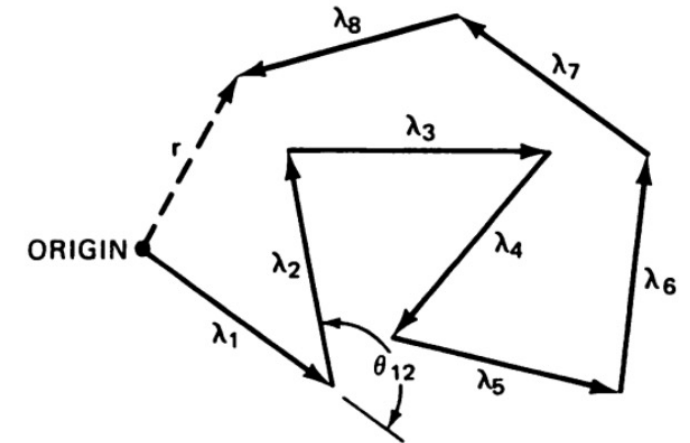And solving, we get simply:

$$\bar{r}^2 = 6Dt$$

Fig. 7.4   Eight random jumps of equal length λ.

Diffusion accounting for hopping mechanism

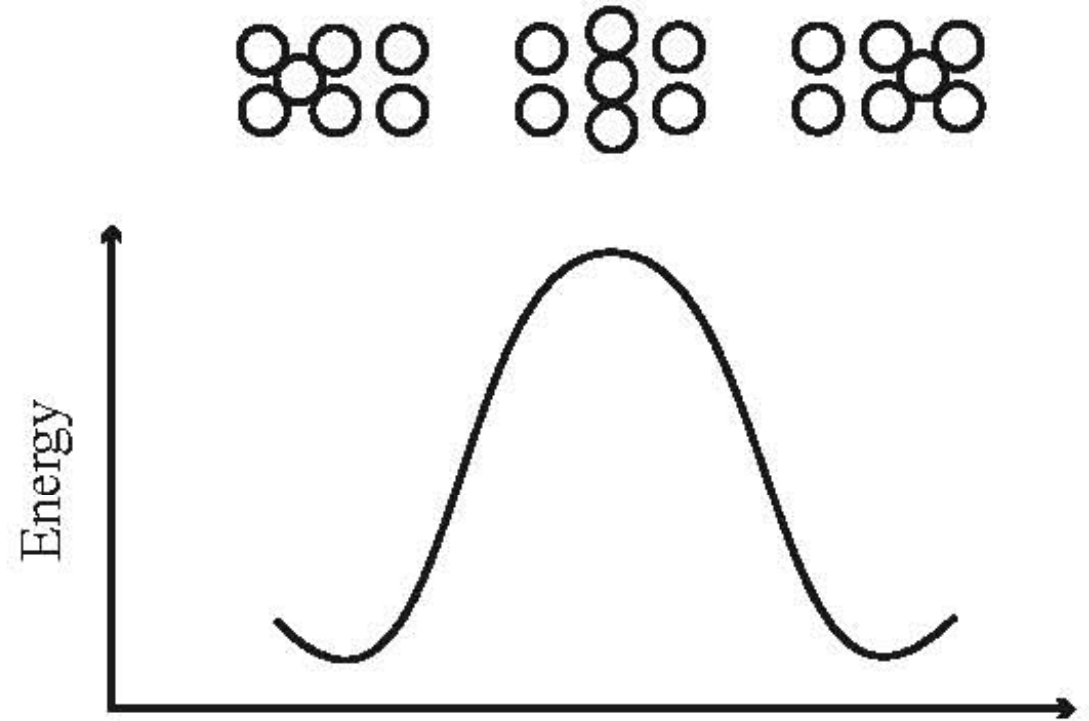Knowing now that:

$$D = \frac{1}{6}\lambda^2\Gamma$$

We need to determine the jump frequency for a given jump mechanism. This is dependent on the probability a jump site is open, ρ_j, the number of nearest neighbors, z, and the frequency of a given jump type, ω:

How to determine ω

$$\omega = v\ exp\left(\frac{-\Delta G_m}{k_b T}\right)$$

$$\omega = v\ exp\left(\frac{-S_m}{k_b}\right) exp\left(\frac{-\Delta H_m}{k_b T}\right)$$

$$\omega = v\ exp\left(\frac{-S_m}{k_b}\right) exp\left(\frac{-\Delta E_m}{k_b T}\right)$$

Pulling it together to get the diffusion equations:

Diffusion of vacancies:

$$D_v = \alpha a^2 \omega = \alpha a^2 v \exp\left(\frac{S_m^v}{k}\right)\exp\left(\frac{-E_m^v}{kT}\right)$$

Diffusion of atoms by way of vacancies – vacancy self-diffusion:

$$D_a^v = \alpha a^2 v \exp\left(\frac{S_f^v + S_m^v}{k}\right)\exp\left(\frac{-E_f^v - E_m^v}{kT}\right).$$

Diffusion of interstitials:

$$D_i = \alpha a^2 v \exp\left(\frac{S_m^i}{k}\right)\exp\left(\frac{-E_m^i}{kT}\right).$$

Diffusion of atoms by way of interstitials – interstitial self-diffusion:

$$D_a^i = \alpha a^2 v \exp\left(\frac{S_f^i + S_m^i}{k}\right)\exp\left(\frac{-E_f^i + -E_m^i}{kT}\right).$$

Or, more simply:

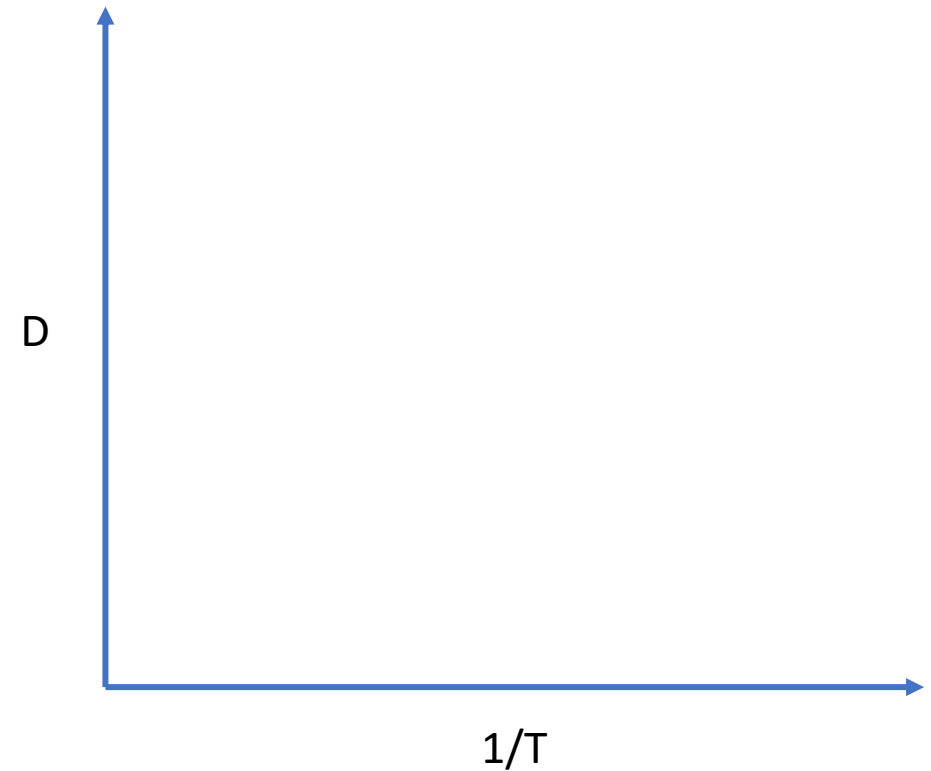We can use an Arrhenius relationship:

$$D = D_0 exp\left(-Q/k_bT\right)$$

Where D_o and Q are given but incorporate the discussed factors:

Mechanism	D_o	Q
Vacancy Diffusion (D_v)	$\alpha a_o^2 \nu exp\left(\dfrac{S_m^v}{k_b}\right)$	E_m^v
Vacancy Self Diffusion (D_a^v)	$\alpha a_o^2 \nu exp\left(\dfrac{S_f^v + S_m^v}{k_b}\right)$	$E_f^v + E_m^v$

D

1/T

Point defect properties

|	Symbol	Unit	Al	Cu	Pt	Mo	W
Interstitials							
Relaxation volume	V^i_{relax}	Atomic vol.	1.9	1.4	2.0	1.1	
Formation energy	E^i_f	eV	3.2	2.2	3.5		
Equilibrium concentration at T_m*	$C_i(T_m)$	-	10^{-18}	10^{-7}	10^{-6}		
Migration energy	E^i_m	eV	0.12	0.12	0.06		0.054
Vacancies							
Relaxation volume	V^v_{relax}	Atomic vol.	0.05	-0.2	-0.4		
Formation energy	E^v_f	eV	0.66	1.27	1.51	3.2	3.8
Formation entropy	S^v_f	k	0.7	2.4			2
Equilibrium concentration at T_m*	$C_v(T_m)$	-	9×10^{-6}	2×10^{-6}			4×10^{-5}
Migration energy	E^v_m	eV	0.62	0.8	1.43	1.3	1.8
Activation energy for self diffusion	Q_{vSD}	eV	1.28	2.07	2.9	4.5	5.7
Frenkel pairs							
Formation energy	E^{FP}_f	eV	3.9	3.5	5		

Point Defect Diffusion: Comparison

- Comparsion of diffusion
  - $t = 10^6 \, s \, (11 \, days)$
  - $E_m^f = 1 \, eV, \, E_m^i = 0.2 \, eV$

| T (°C)	$D_V(m^2/s)$	$X_V = \sqrt{D_V \tau}$	$D_i(m^2/s)$	$X_i = \sqrt{D_i \tau}$
0	2×10^{-21}	0.45nm	1.5×10^{-6}	1cm
100	2×10^{-16}	150nm	1.5×10^{-5}	4cm
200	1.7×10^{-13}	4μm	5.5×10^{-5}	7.5cm
300	1.2×10^{-11}	35μm	1.3×10^{-4}	11cm
400	2.5×10^{-10}	0.15mm	2.4×10^{-4}	15cm
500	2.3×10^{-9}	4mm	3.7×10^{-4}	19cm

Diffusion along high-diffusivity paths:
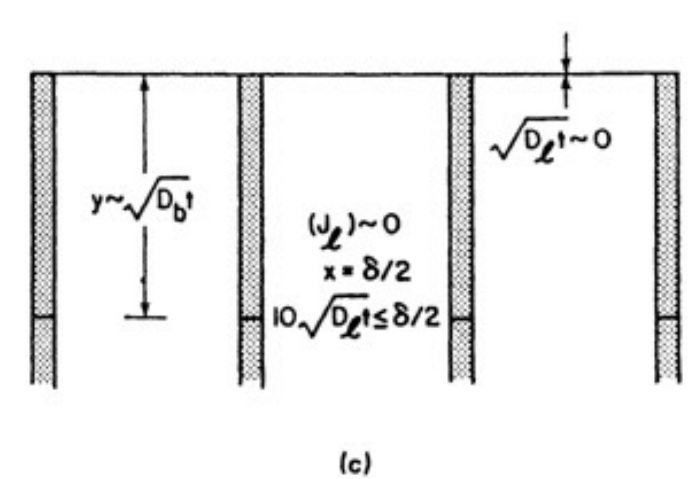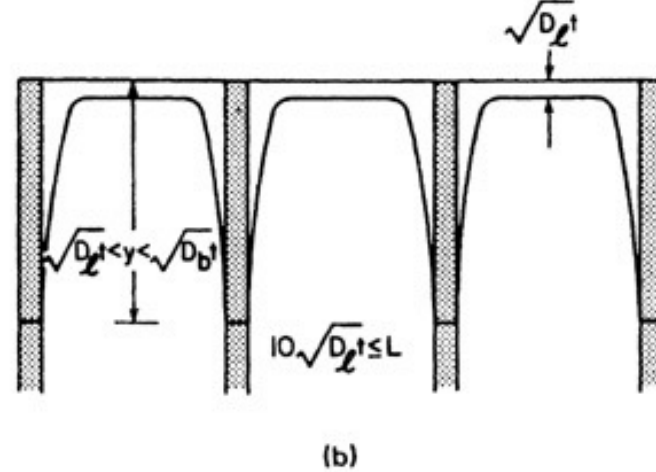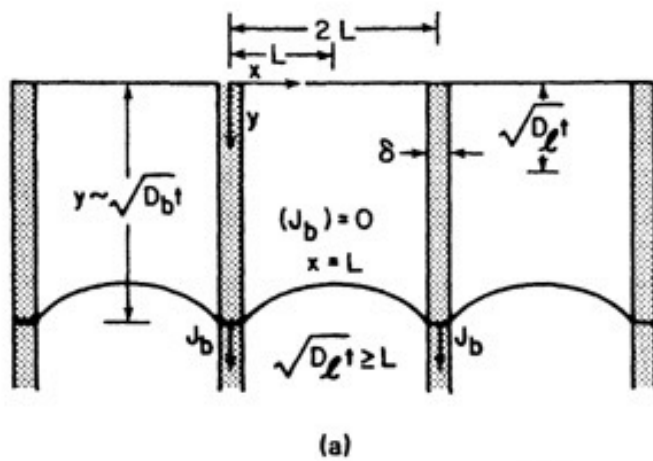
Type A: The diffusion front in the bulk and in the boundary advanced at the same speed

Type B: The diffusion in the grain boundary is faster than in the bulk

Type C: The diffusion in the bulk is negligible and grain boundary diffusion is only active

Radiation Effects at the Grain Scale

Goal: Determine the kinetics of microstructure evolution under irradiation
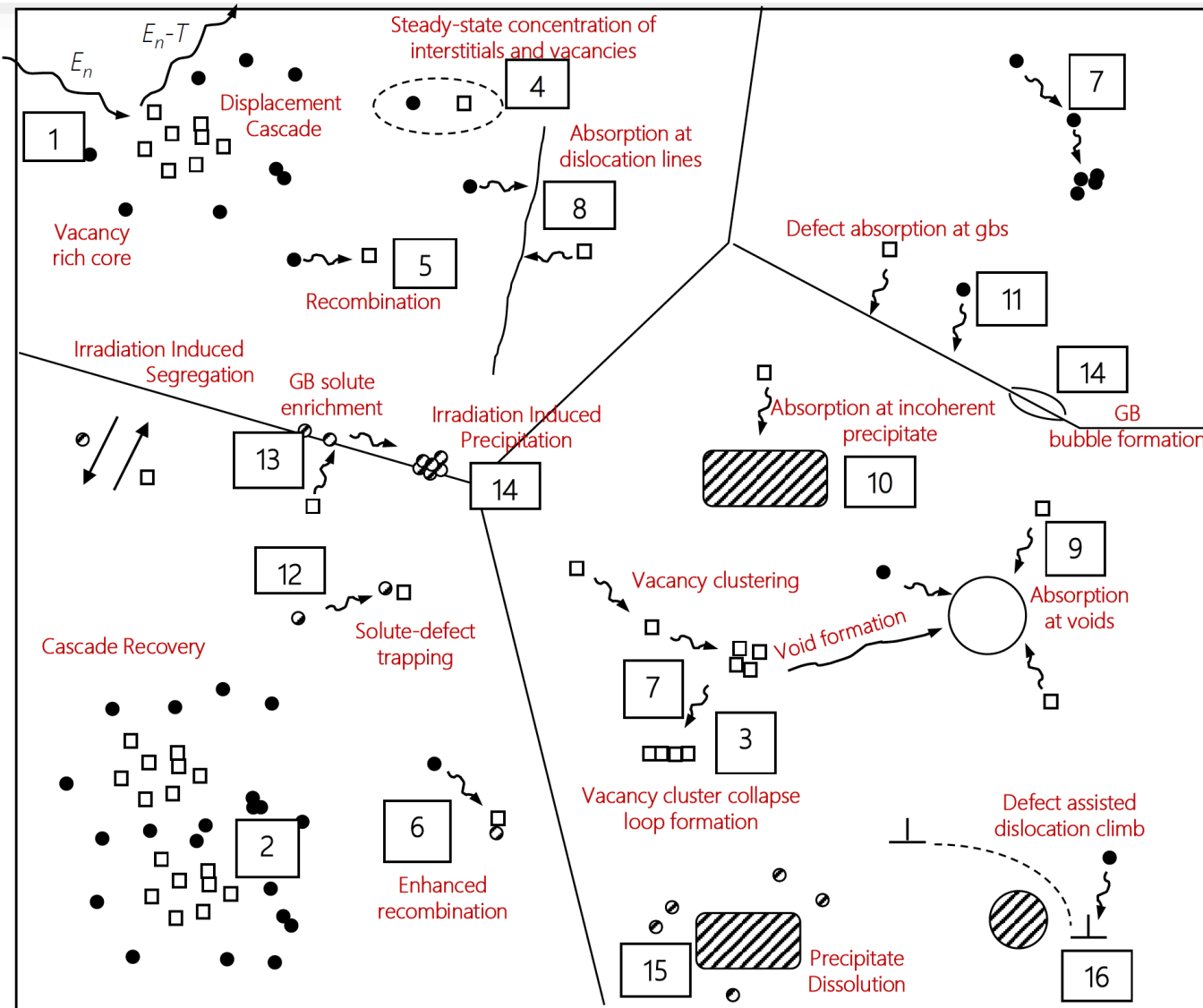
We now do point defect accounting

Change = | Gain | - | Loss |

- What are the possible gain terms?

- What are the possible loss terms?

Gain Terms

- Defect production rate:

$$K_0 = \left(\frac{dpa}{s} \right) \times \varepsilon$$

- Reaction production rate:

$$R_0 = \sum_{d=1}^{n} Rxn_d$$

Loss Term: Recombination

- Inherently, random walk of defects means there is a probability and thus a rate of recombination

- Must be related to the defect concentration

Loss Term: Diffusion

- Inherently, random walk of defects means there is a probability and thus a local loss of defects due to diffusion

- Use macroscopic description for diffusion (Fick's Law):

Loss Terms: Sinks

- Non-perfect crystals have trapping sites for point defects where annihilation or recombination is promoted, these are defect sinks

- The effectiveness (or rate) of a sink in promoting loss is the *sink strength*, K_s

Let's play a quick game:

Change =	Gain	-	Loss

Sinks

Diffusion

Recombination

Production

Gain

Loss

$$K_0 = \left(\frac{dpa}{s}\right)\varepsilon$$

$$\frac{\partial C_{i,v}}{\partial t} = -\sum_{s=1}^{all\ sinks} K_s C_{i,v} C_s$$

$$\frac{\partial C_{i,v}}{\partial t} = K_{iv} C_i C_v$$

$$\frac{\partial C_{i,v}}{\partial t} = \nabla D_{i,v} \nabla C_{i,v}$$

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Pulling it together: Point Defect Kinetic Equations

- If we neglect clustering:

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

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

Point Defect Kinetic Equations

- If we neglect clustering:

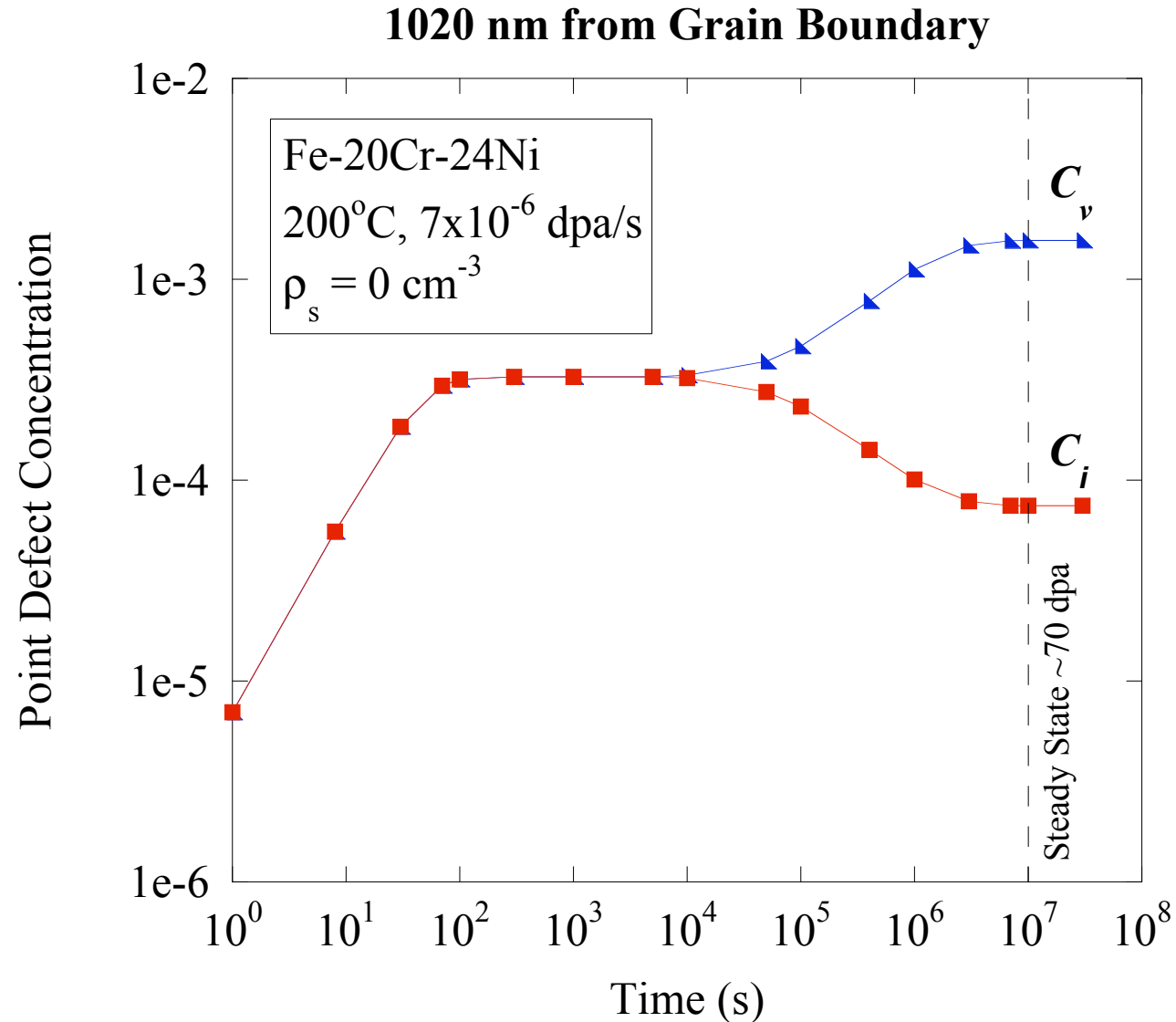$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v - \sum_s K_{vs}C_vC_s + D_v\nabla^2 C_v$$

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

- Example of defect absorption to cavities and dislocations:

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

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

Results from MIK code for Fe-20Cr-24Ni at a damage rate of 7 x 10^{-6} dpa/s, T=200°C

1020 nm from Grain Boundary

To solve these, we subject these equations to limitations

1. The model applies to pure metals. No binding of defects to atomic species
2. Sink concentration and strength are time-independent
3. Other than mutual recombination, defect-defect interactions(e.g. formation of di-vacancies or di-interstitials) are ignored
4. Bias factors for diffusion of defects to sinks are set to unity (no preferential absorption of specific point defects at specific sinks)
5. Diffusion loss terms in and out of the observation volume are not considered
6. Thermal equilibrium vacancy concentration is neglected

We can now look at several cases...

Low Temperature, Low Sink Density

1. Initially, defect concentrations build up according to $dC/dt = \varepsilon K_0$ with $C_i \sim C_v$ so $C_i = C_v = C = \varepsilon K_0 t$

   - Concentrations are too low for either recombination or sinks to have an effect

2. Build up will start to level off when the production rate is compensated by the recombination rate. Quasi-steady state concentrations are:

We can find the time at which the defect concentrations level off by equating this concentration with that during build:

Low Temperature, Low Sink Density

3. C_i and C_v remain approximately equal until a time, t_2, which is the time constant for the process of interstitials reacting with sinks. Because $D_i > D_v$, more interstitials are lost to sinks than vacancies, which is described by:

Vacancies and interstitials build up and decay (respectively) to:

$$C_v(t) = \left[\frac{K_0 K_{is} C_s t}{K_{iv}}\right]^{1/2} \qquad C_i(t) = \left[\frac{K_0}{K_{iv} K_{is} C_s t}\right]^{1/2}$$

The time at which this occurs is given by:

Low Temperature, Low Sink Density

4. After awhile, true steady state is achieved due to interaction of vacancies with sinks. Solving for the steady state concentrations of vacancies and interstitials by setting $dC_v/dt = dC_i/dt = 0$, gives:
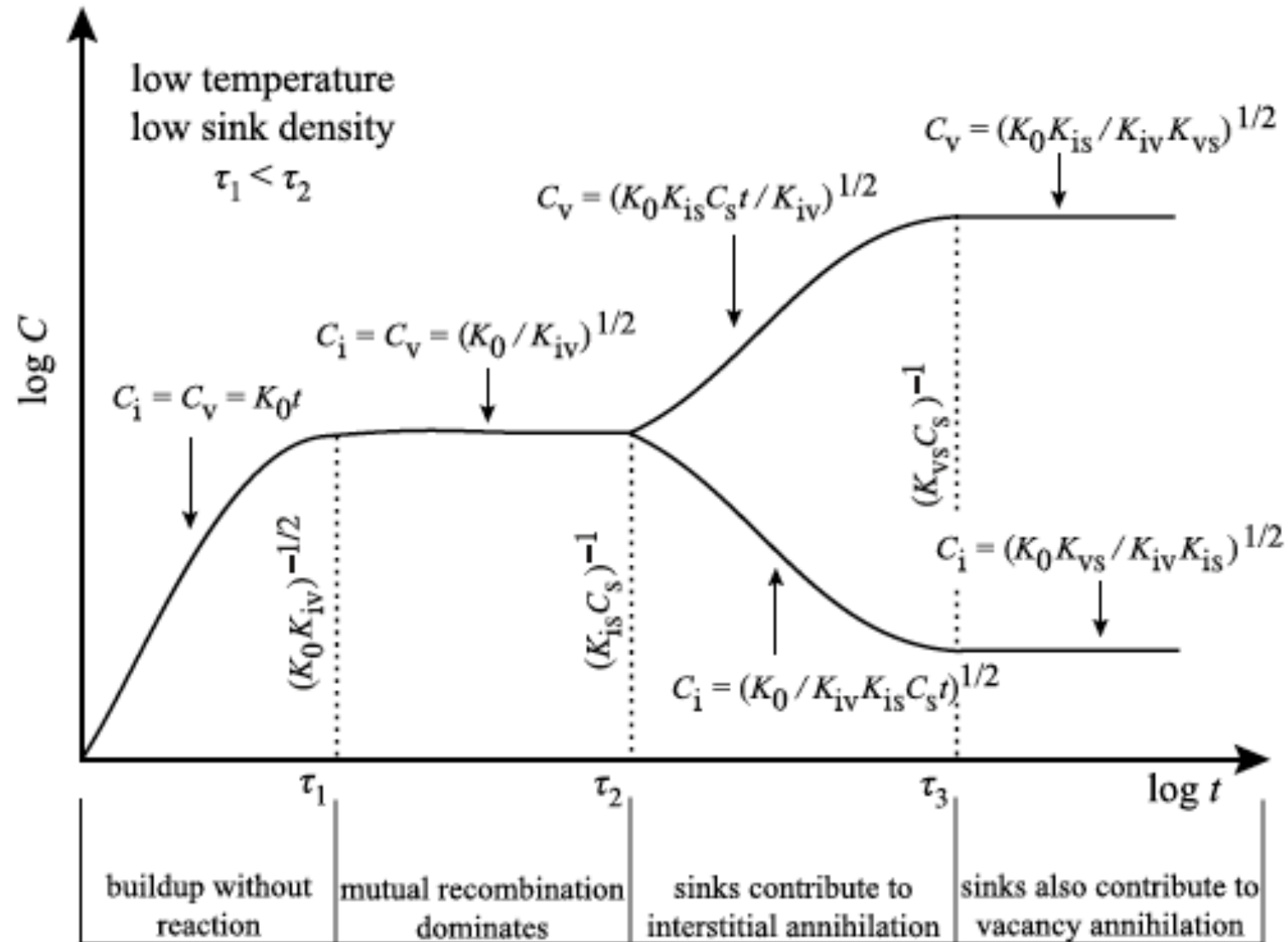
$$C_v^{SS} = -\frac{K_{is}C_s}{2K_{iv}} + \left[\frac{K_0 K_{is}}{K_{iv}K_{vs}} + \frac{K_{is}^2 C_s^2}{4K_{iv}^2}\right]^{1/2} \qquad C_i^{SS} = -\frac{K_{is}C_s}{2K_{iv}} + \left[\frac{K_0 K_{vs}}{K_{iv}K_{is}} + \frac{K_{vs}^2 C_s^2}{4K_{iv}^2}\right]^{1/2}$$

For the case of low temperature and low sink density, C_s is small:

Low Temperature, Low Sink Density

We can solve for the time to steady state in a similar manner to that of the quasi steady state by equating the previous region (build up) to the steady state regime:

Low Temperature, Low Sink Density

low temperature
low sink density

$\tau_1 < \tau_2$

$C_i = C_v = K_0 t$

$C_i = C_v = (K_0 / K_{iv})^{1/2}$

$C_v = (K_0 K_{is} C_s t / K_{iv})^{1/2}$

$C_v = (K_0 K_{is} / K_{iv} K_{vs})^{1/2}$

$C_i = (K_0 K_{vs} / K_{iv} K_{is})^{1/2}$

$C_i = (K_0 / K_{iv} K_{is} C_s t)^{1/2}$

$(K_0 K_{iv})^{-1/2}$

$(K_{is} C_s)^{-1}$

$(K_{vs} C_s)^{-1}$

τ_1 τ_2 τ_3 $\log t$

buildup without reaction | mutual recombination dominates | sinks contribute to interstitial annihilation | sinks also contribute to vacancy annihilation

Example calculation for BCC Fe

- Problem: Calculate the typical times of the different stages of C_v and C_i for BCC Fe using the following parameters:

293K neutron irradiation

Lattice parameter (a_0) of 2.82 Å

Dislocation density (p_d) of 10^8 cm^{-2}

Interstitial migration energy (E_m^i) of 0.65 eV

Vacancy migration energy (E_m^v) of 1.5 eV

Capture radius (r_{iv}) of $10a_0$

Displacement rate (K_0) of 10^{-7} dpa/s

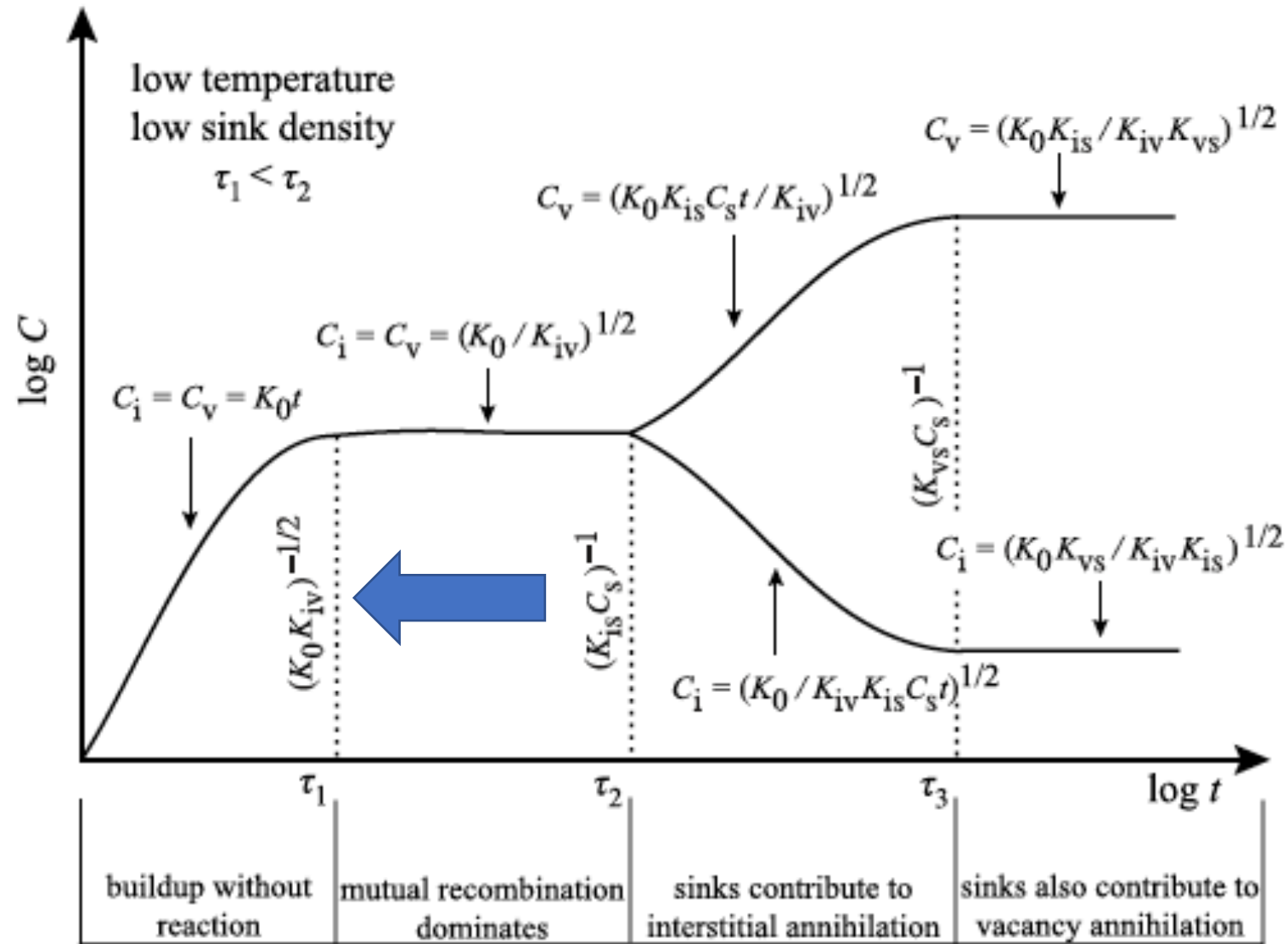Vibration frequency (v) of 10^{13} Hz

Example calculation for BCC Fe

- Problem: Calculate the typical times of the different stages of C_v and C_i for BCC Fe using the following parameters:
    - Step 1: Calculate the recombination constant:

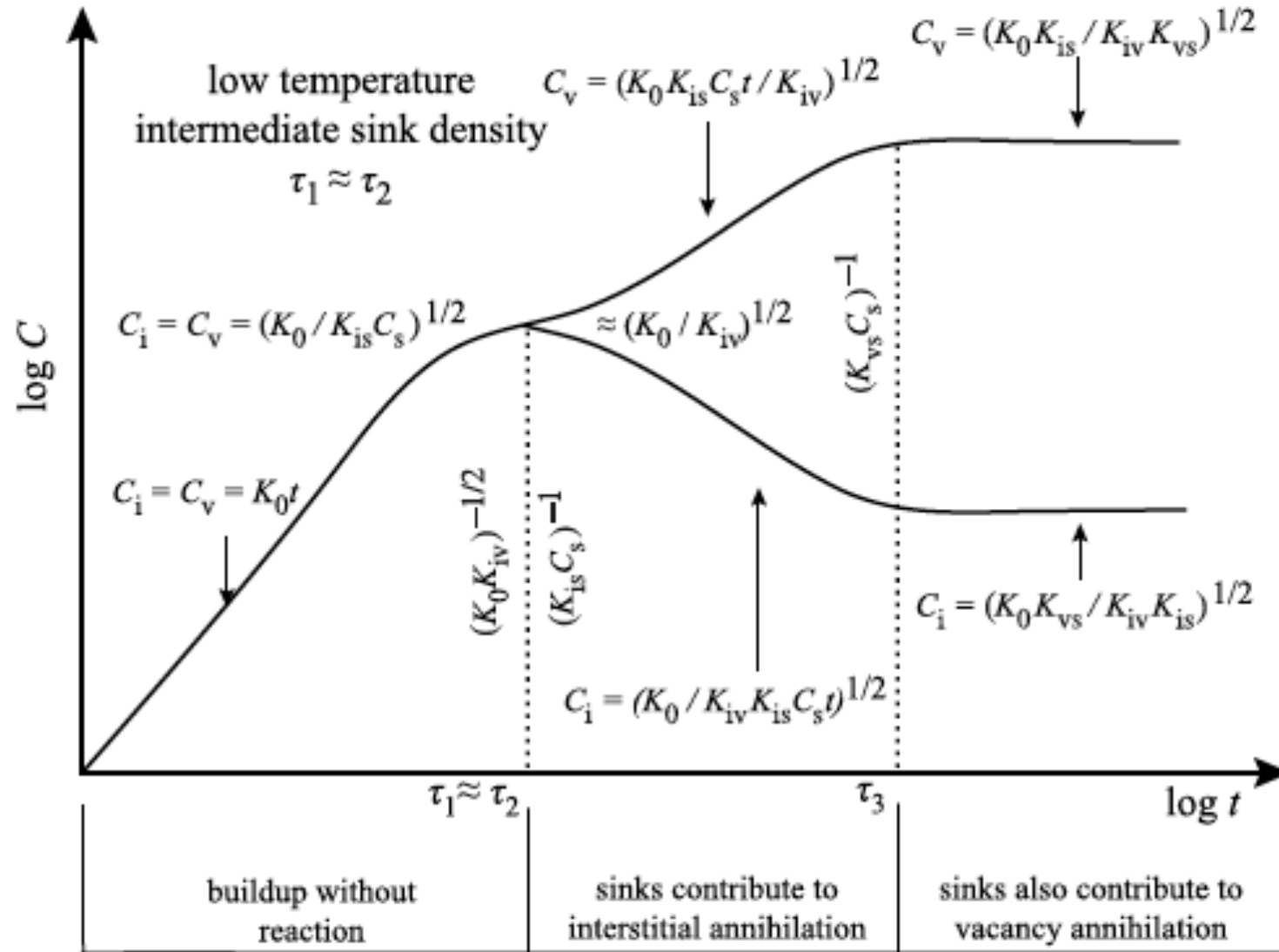   - Now calculate the time for recombination to become significant

Example calculation for BCC Fe

- Problem: Calculate the typical times of the different stages of C_v and C_i for BCC Fe using the following parameters:
    - Step 2: Calculate the time for interstitials to arrive sinks using D_i from before:

    - Step 3: Calculate the time when vacancies arrive at sinks to determine steady state:
        - Must calculate D_v

Low Temperature, Increasing Sink Density

low temperature
low sink density

$\tau_1 < \tau_2$

$C_i = C_v = K_0 t$

$C_i = C_v = (K_0 / K_{iv})^{1/2}$

$C_v = (K_0 K_{is} C_s t / K_{iv})^{1/2}$

$C_v = (K_0 K_{is} / K_{iv} K_{vs})^{1/2}$

$C_i = (K_0 K_{vs} / K_{iv} K_{is})^{1/2}$

$C_i = (K_0 / K_{iv} K_{is} C_s t)^{1/2}$

$(K_0 K_{iv})^{-1/2}$

$(K_{is} C_s)^{-1}$

$(K_{vs} C_s)^{-1}$

τ_1 τ_2 τ_3 $\log t$

buildup without reaction | mutual recombination dominates | sinks contribute to interstitial annihilation | sinks also contribute to vacancy annihilation

log C

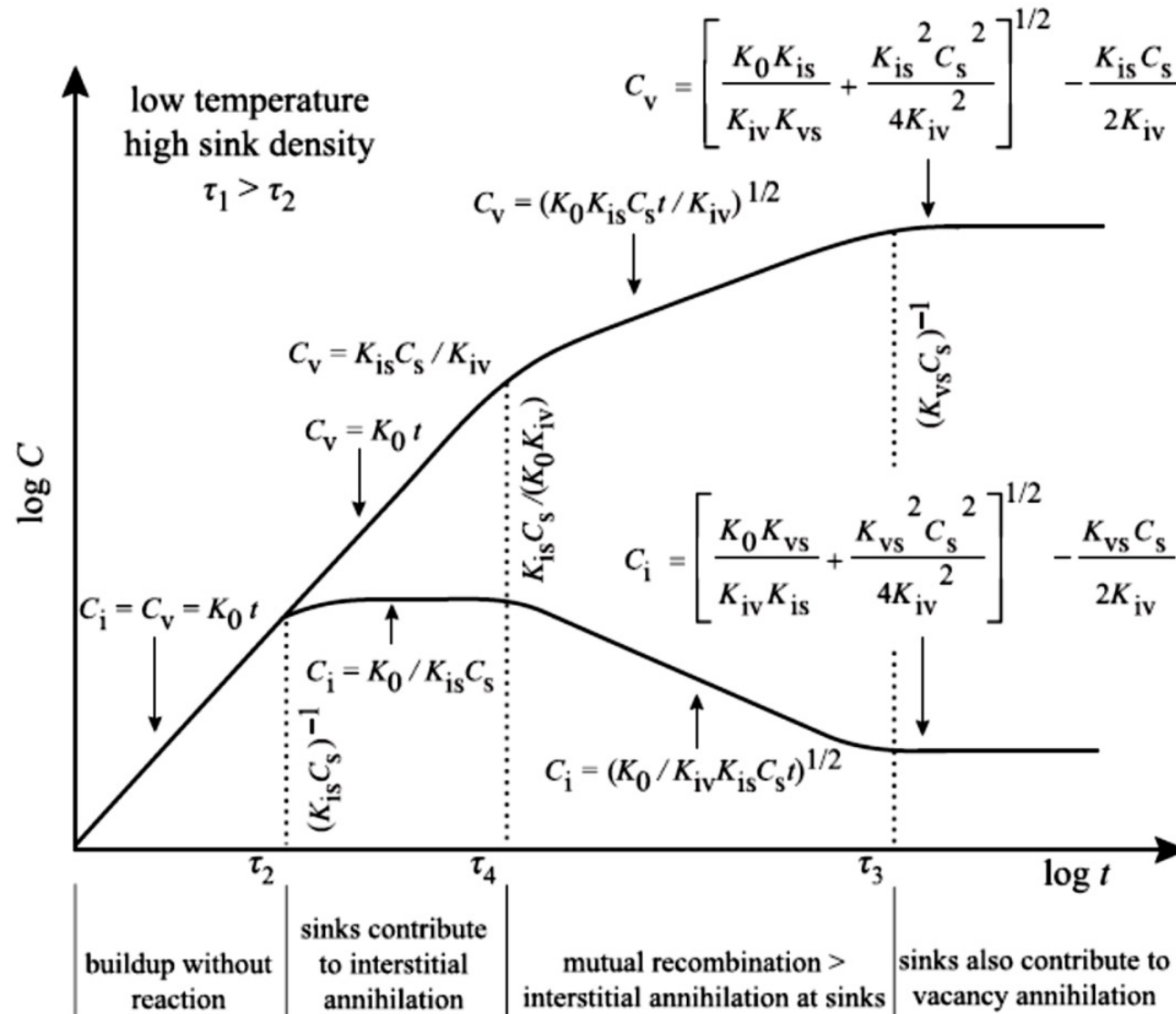# Low Temperature, Increasing Sink Density

Low T, High C_s

- In this case, the interstitial concentration comes into a quasi-steady state with production and annihilation at sinks:

- Equating the interstitial concentrations in the linear buildup regime with the quasi-steady state regime:
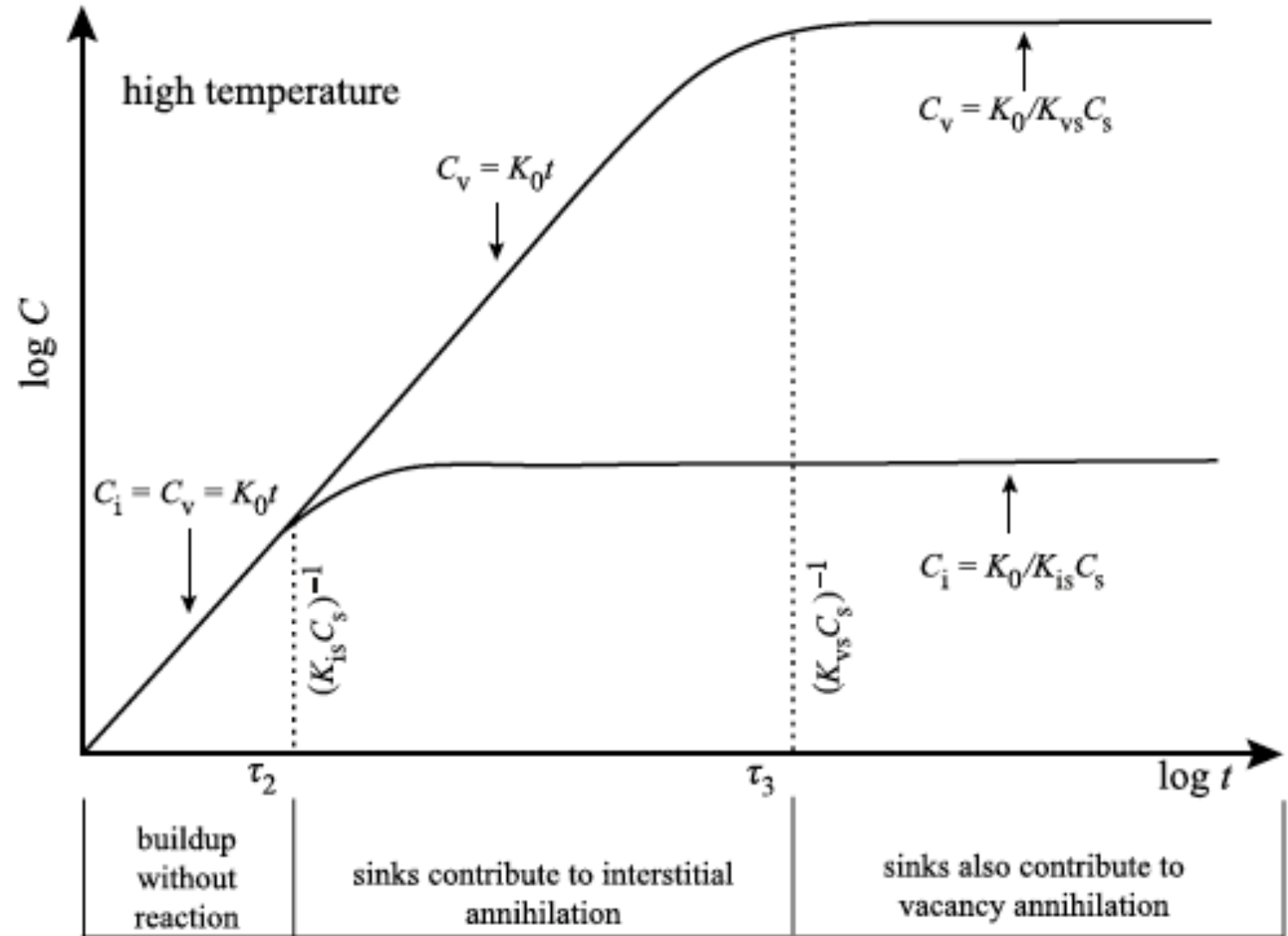
Low T, High C_s

- A competition soon arises between the annihilation of interstitials at sinks and recombination with vacancies, such that:

- Yielding the time constant for the transition between the regimes where interstitials go to sinks and mutual recombination dominates:

Low T, High C_s

low temperature
high sink density
$\tau_1 > \tau_2$

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

$C_v = (K_0 K_{is} C_s t / K_{iv})^{1/2}$

$C_v = K_{is} C_s / K_{iv}$

$C_v = K_0 t$

$C_i = C_v = K_0 t$

$C_i = K_0 / K_{is} C_s$

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

$C_i = (K_0 / K_{iv} K_{is} C_s t)^{1/2}$

$\log C$

$\log t$

$(K_{is} C_s)^{-1}$

$K_{is} C_s / (K_0 K_{iv})$

$(K_{vs} C_s)^{-1}$

τ_2 τ_4 τ_3

| buildup without reaction | sinks contribute to interstitial annihilation | mutual recombination > interstitial annihilation at sinks | sinks also contribute to vacancy annihilation |

High Temperature

Properties of point defect balance equations

1. If there is only one type of sink, then the net absorption rate at that sink is zero:

$$K_{is}C_i = K_{vs}(C_v - C_v^0)$$

2. Even if we have more than one type of sink, if the sinks have the same "strength" for vacancies and interstitials ($z_i = z_v$), then the net flow to any sink is zero

3. In the absence of sinks and thermal vacancies, C_v can be exchanged with Ci, that is, $C_v = C_i$ at any instant

$$\frac{\partial C_v}{\partial t} = K_0 - K_{iv}C_iC_v \qquad\qquad \frac{\partial C_i}{\partial t} = K_0 - K_{iv}C_iC_v$$

Since $D_{rad}=d_iC_i+d_vC_v$ & $C_i=C_v$, but since $d_i>>d_v$, then interstitials contribute more to atom mobility than do vacancies

4. Inclusion of sink terms violates the symmetry with respect to C_i and C_v because of different values of K_s ($K_{vs}\neq K_{is}$)

 - Symmetry is present in the steady state with regard to d_iC_i and d_vC_v since K_{is} and K_{vs} are proportional to d_i and d_v, respectively
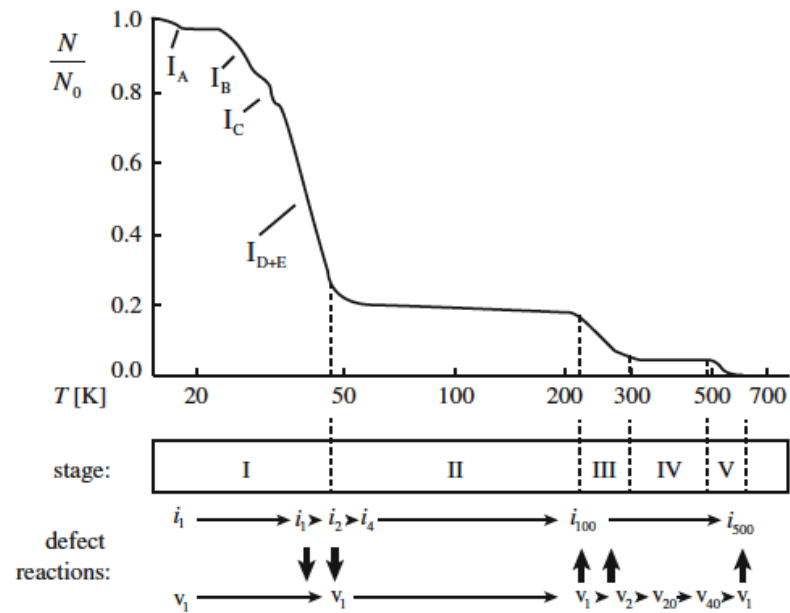
Note on vacancy concentration

- C_v must be accounted for thermal vacancies:

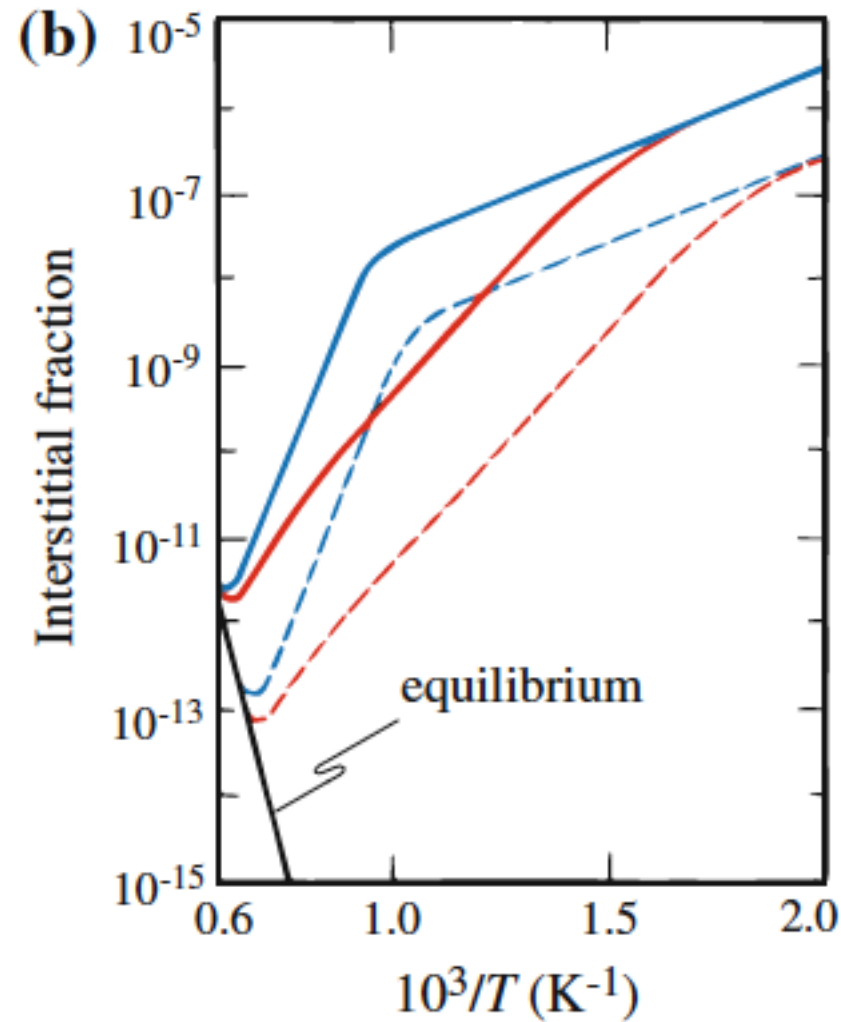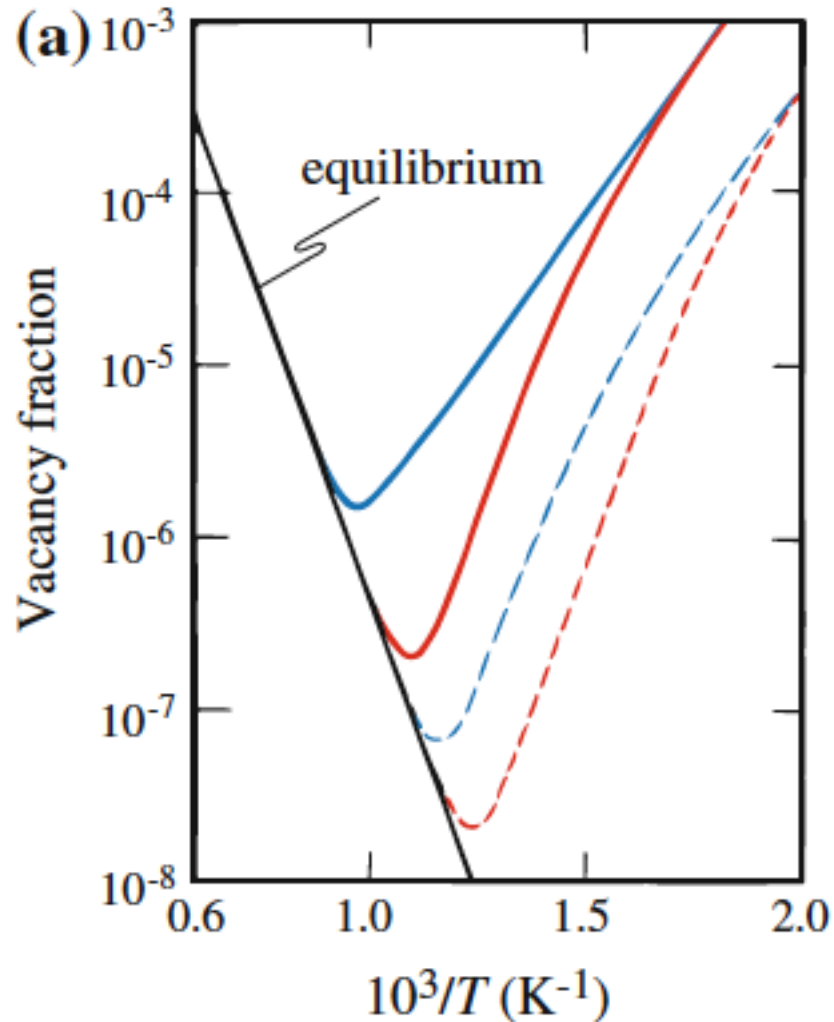- Why are we ignoring this for interstitials?!

Post-irradiation annealing

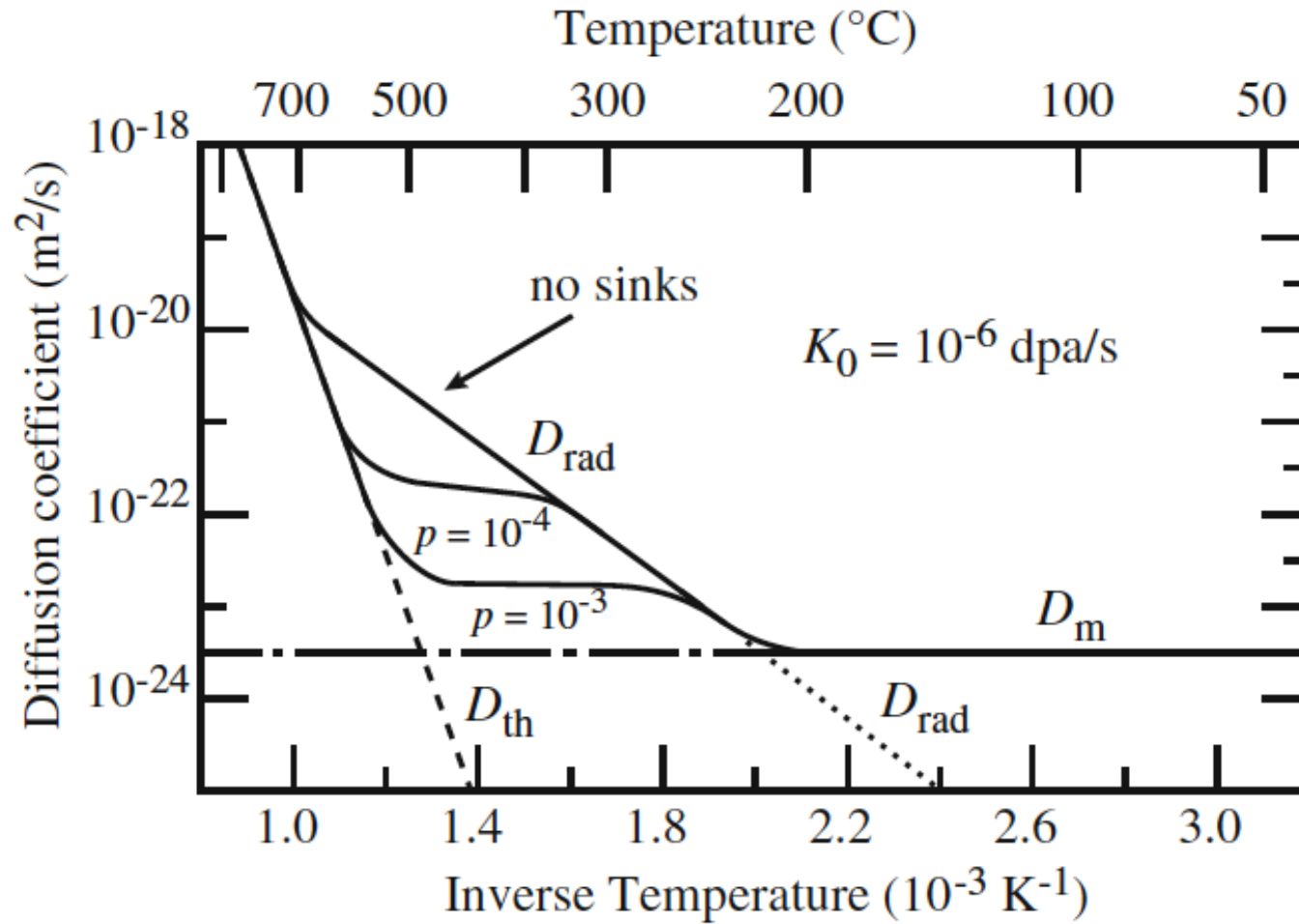- No diffusion, no sinks, no irradiation:
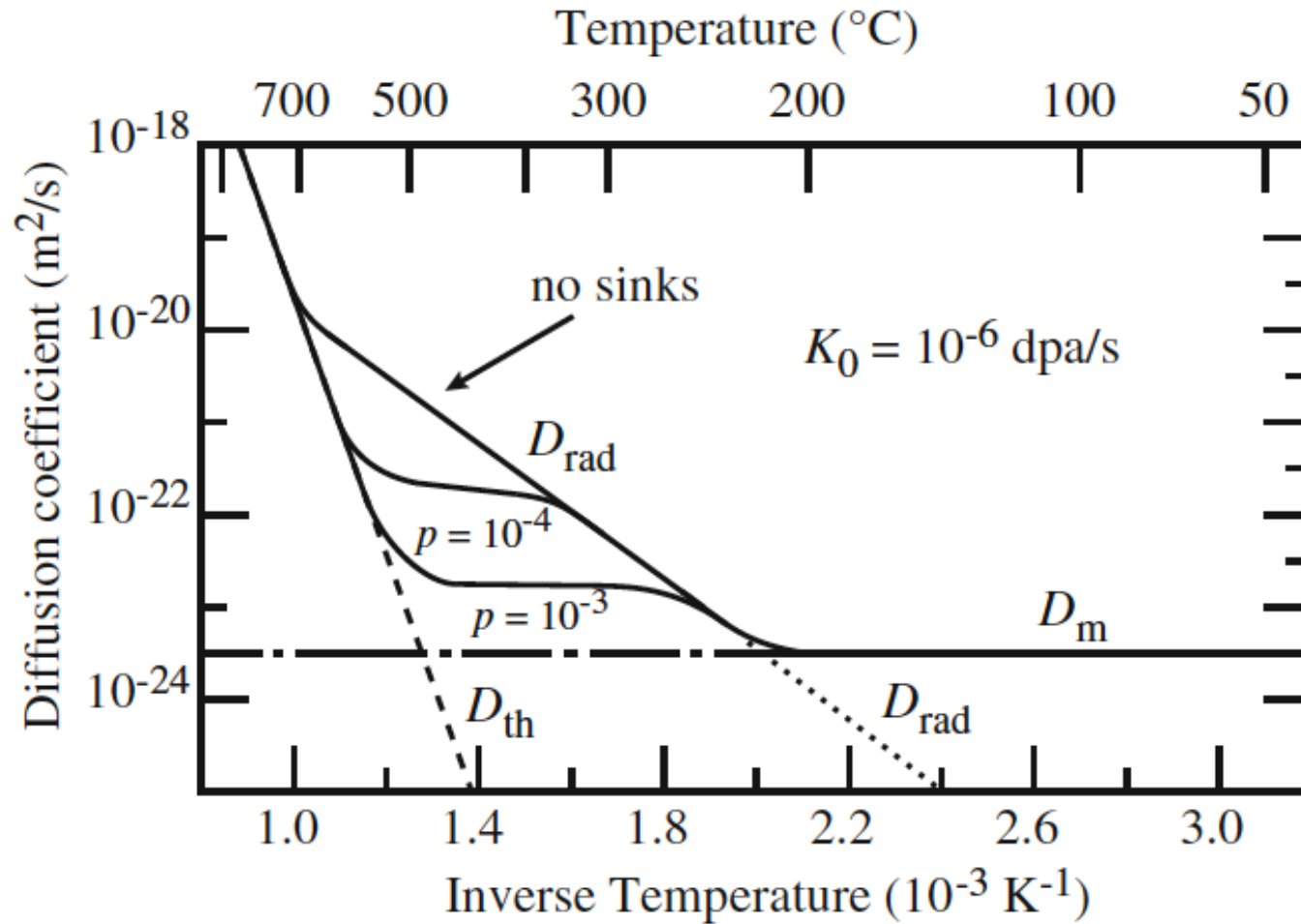
- Integrating:

- Then:

Pulling this now together:

Pulling this now together:

Pulling this now together:

The critical temperature below which mutual recombination will dominate, above which loss to sinks will dominate:

$$T_c = \frac{E_m^v}{k\ln\dfrac{2D_0^v C_s^2 K_{is}' K_{vs}'}{K_0 K_{iv}'}}$$

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

Questions?