Point Defect Diffusion

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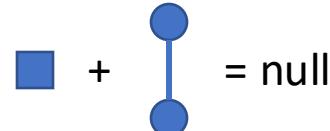
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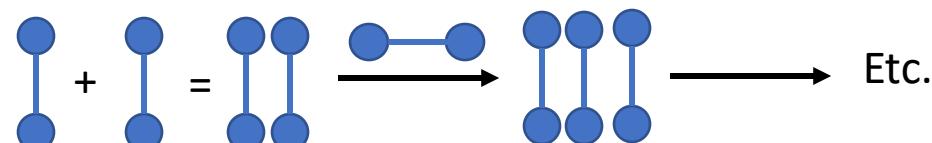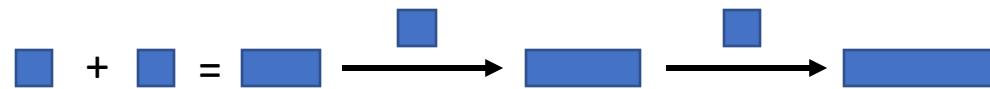
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What is the fate of point defects?
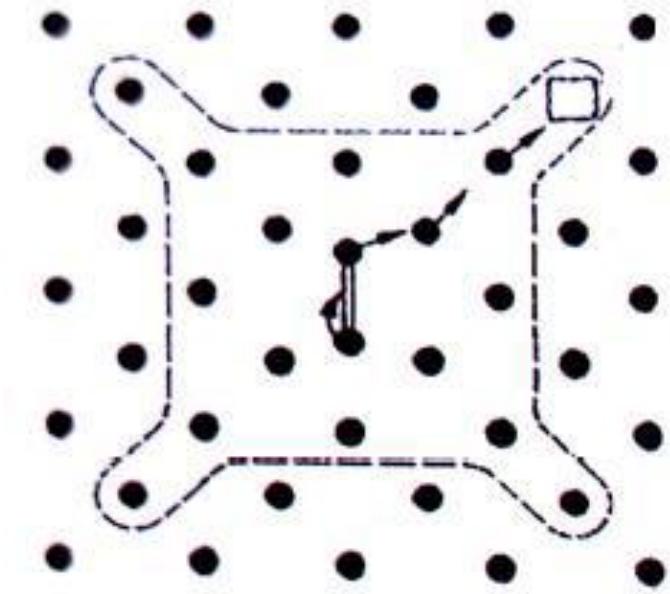
1. Annihilation (recombination)

$\blacksquare$ + $|$ = null

2. Clustering

3. Elimination at Sinks

To determine the fate of point defects we need to determine C_v and C_i at any time during the irradiation, which is tied to their formation and migration!

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Example problem – to make a point

Example problem (4.1 in Was) – to make a point

Calculate the concentration of vacancies and interstitials at room temperature for pure Al

$T = 293\ K$

$E_f^v \approx 0.66\ eV$ $\qquad S_f^v \approx 0.7 k_b$

$E_f^i \approx 3.2\ eV$ $\qquad S_f^i \approx 8 k_b$

$$C_i = exp\left(\frac{S_{vib}}{k_b}\right) exp\left(\frac{-E_i}{k_b T}\right) \quad C_v = exp\left(\frac{S_{vib}}{k_b}\right) exp\left(\frac{-E_v}{k_b T}\right)$$

Point defect properties

|	Symbol	Unit	Al	Cu	Pt	Mo	W
Interstitials							
Relaxation volume	V_{relax}^i	Atomic vol.	1.9	1.4	2.0	1.1	
Formation energy	E_f^i	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_m^i	eV	0.12	0.12	0.06		0.054
Vacancies							
Relaxation volume	V_{relax}^v	Atomic vol.	0.05	-0.2	-0.4		
Formation energy	E_f^v	eV	0.66	1.27	1.51	3.2	3.8
Formation entropy	S_f^v	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_m^v	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_f^{FP}	eV	3.9	3.5	5		

Point Defect Migration

Fick's First Law of Diffusion (Macroscopic Diffusion)

- Relates the flux and the concentration gradient of the diffusing species:

- D is given in cm^2/s or m^2/s
- For solids it is between 20-1500°C, $10-20 < D < 10^{-4}$ cm^2/s

Fick's Second Law of Diffusion
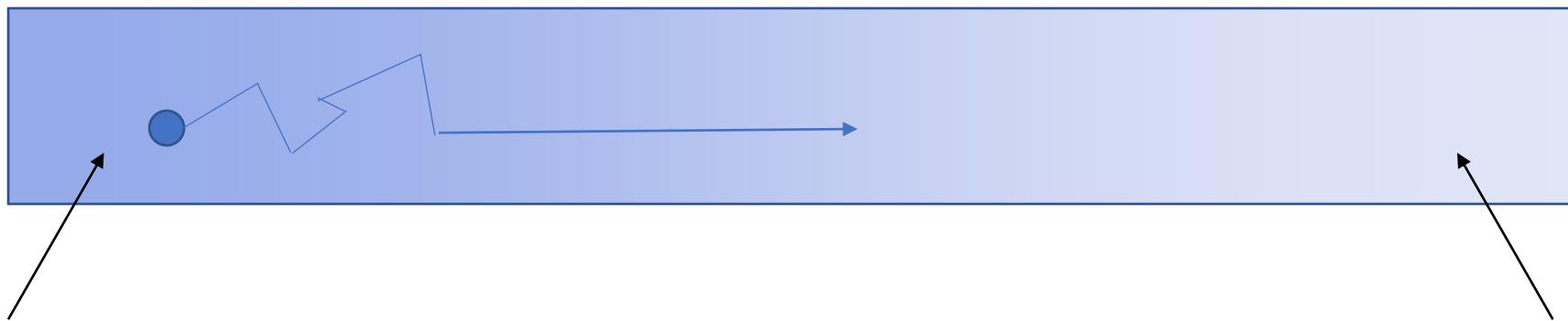
- Provides the relationship between the concentration gradient and the rate of range of concentration caused by diffusion at a given point in the system

Fick's First Law of Diffusion

$$J = -D \frac{\partial C}{\partial x}$$

Why do random jumps of atoms result in a net flux of atoms from regions of high concentration towards regions of low concentrations?

Atoms here jump randomly both right to left
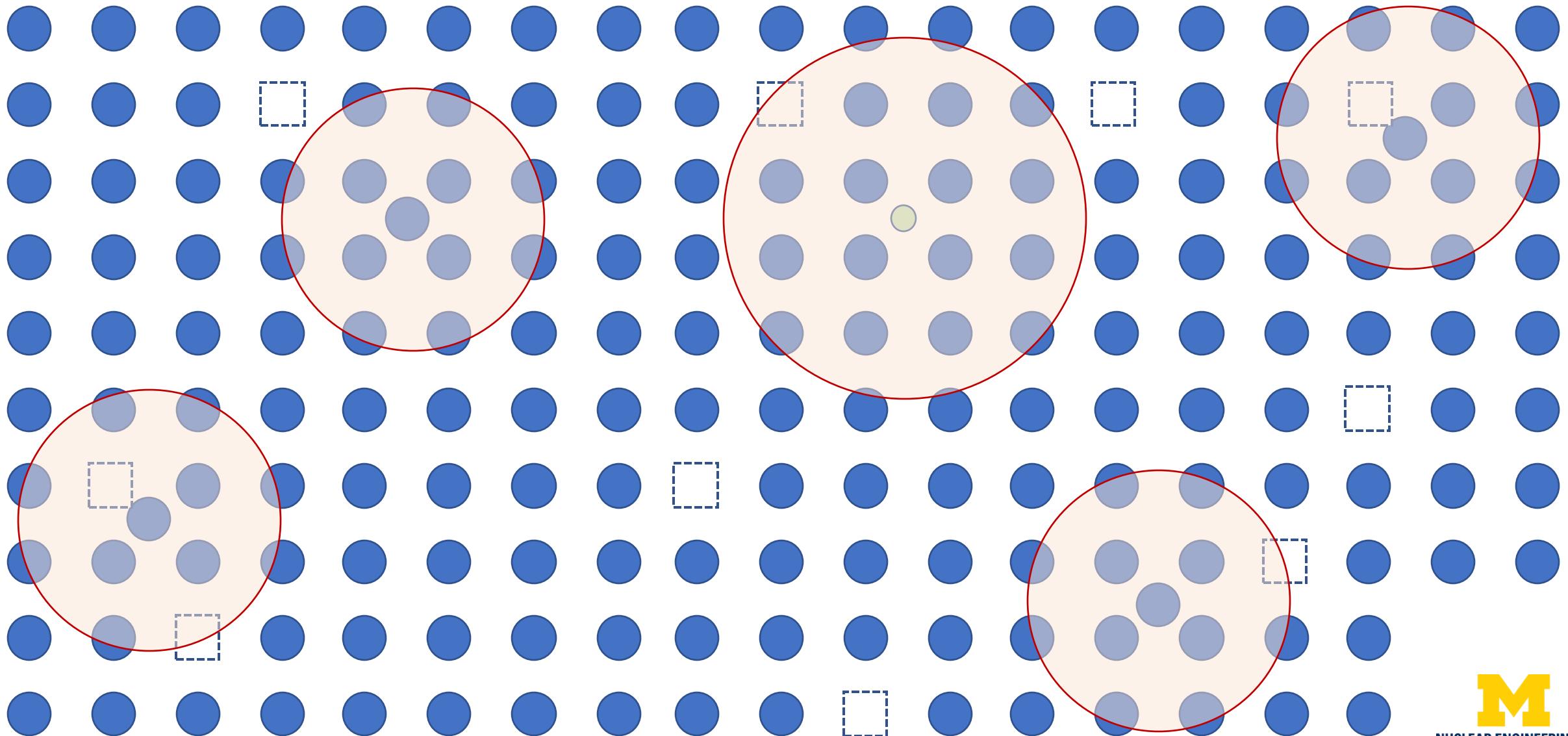
But there are not many atoms here to jump to the left

The Oscar Mayer Wienermobile is an iconic vehicle shaped like a giant hot dog. What is the length, width, and height of the Wienermobile in feet?

Point Defect Migration

How do defect move?

- The defect mobility depends a lot on the defect structure
  - Hence, talking about this is detail last lecture!
- For vacancies, usually a simple jump from one atomic lattice site to another
- For dumbbell interstitials this more complex:
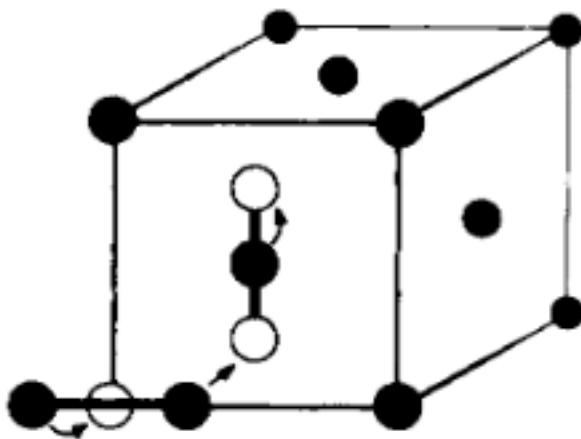
Fig. 4. Migration of the (100)-split interstitial in an fcc lattice.
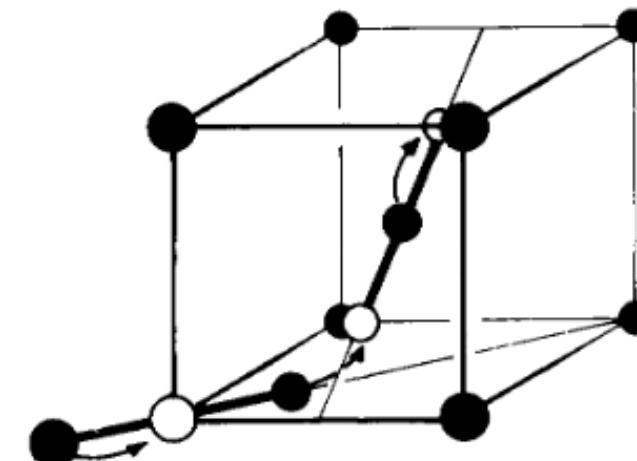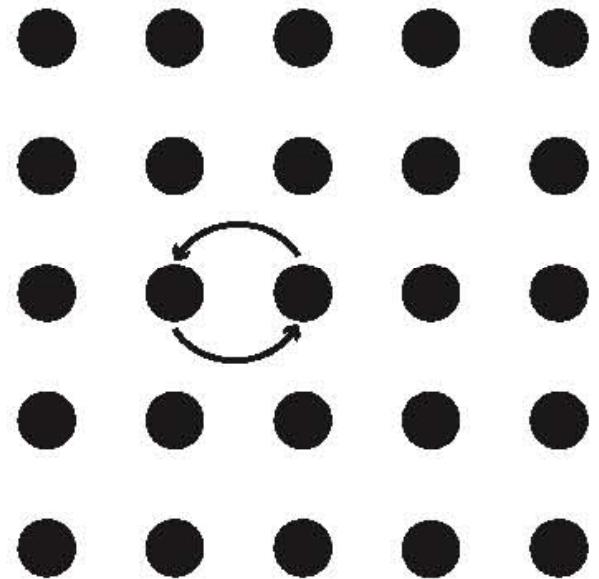
Fig. 9. Migration of the (110)-split interstitial in a bcc lattice.
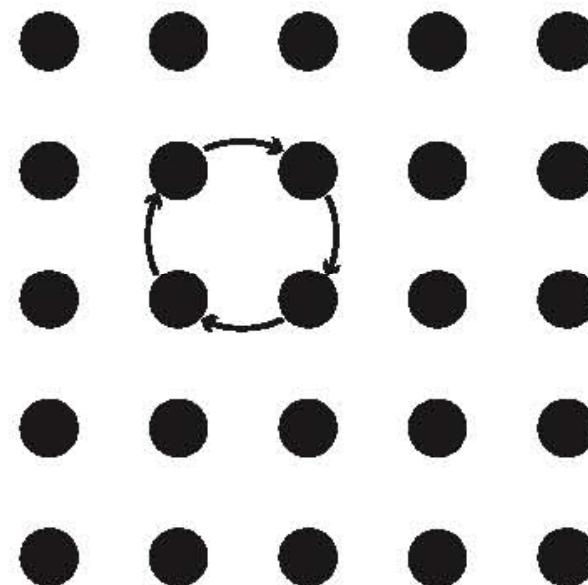
# Mechanisms of Diffusion

Exchange Mechanism
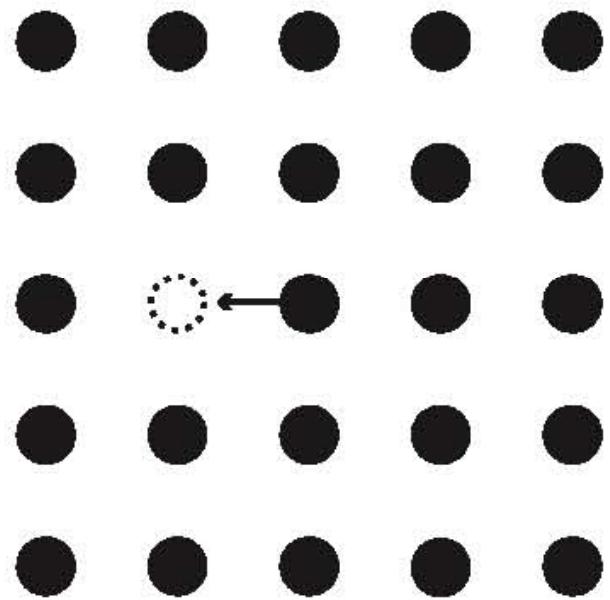
Ring Mechanism
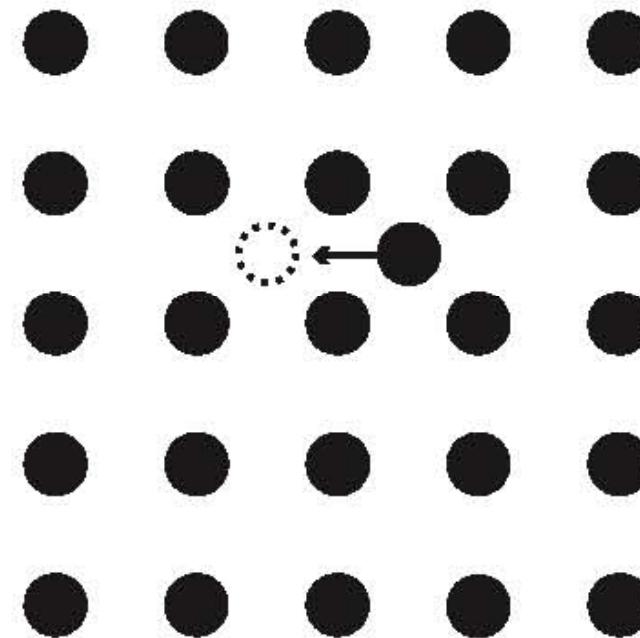
Mechanisms of Diffusion

Vacancy Mechanism
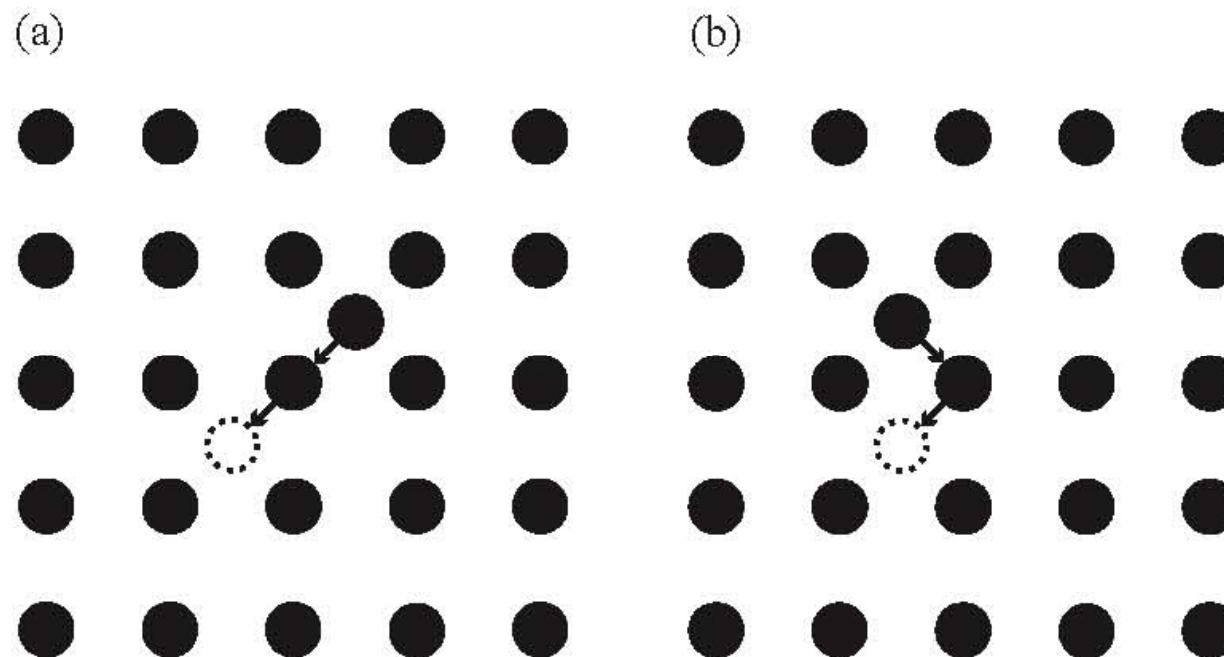
Interstitial Mechanism
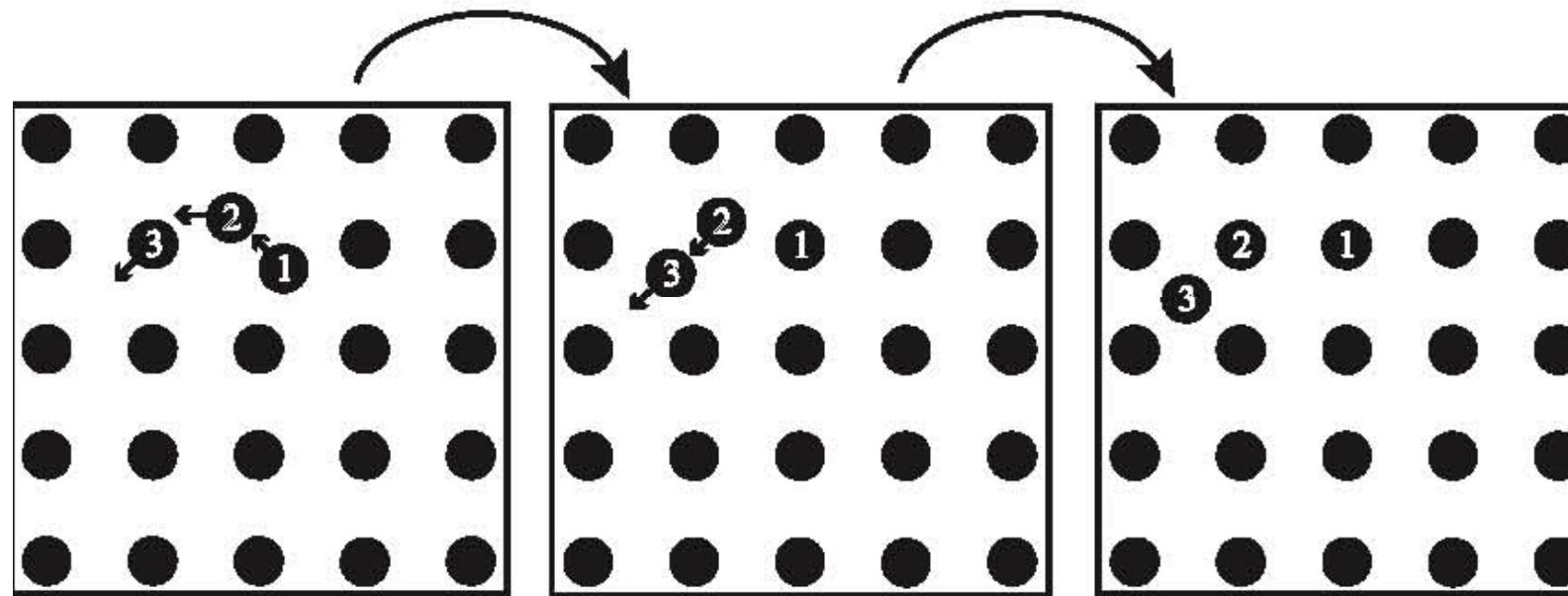
Mechanisms of Diffusion

Interstitialcy Mechanism
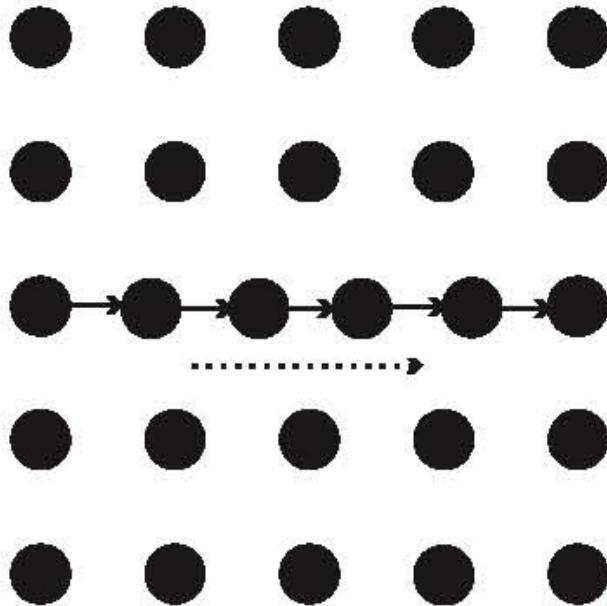
Mechanisms of Diffusion

Dumbbell Mechanism

Mechanisms of Diffusion

Crowdion mechanism

Poll – what mechanism(s) is most dominant

A. Exchange
B. Ring
C. Vacancy
D. Interstitial
E. Interstitialcy
F. Dumbbell
G. Crowdion

Microscopic Diffusion

- Assume that the self-diffusion process consists of a completely random walk of defects
- Assume steps of equal length, random directions:
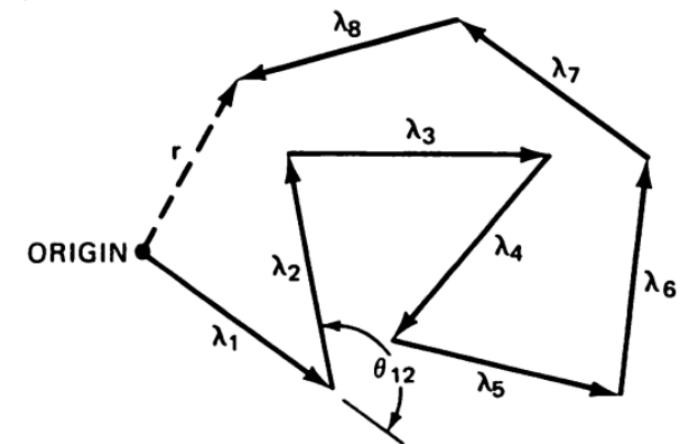
Fig. 7.4   Eight random jumps of equal length λ.

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:
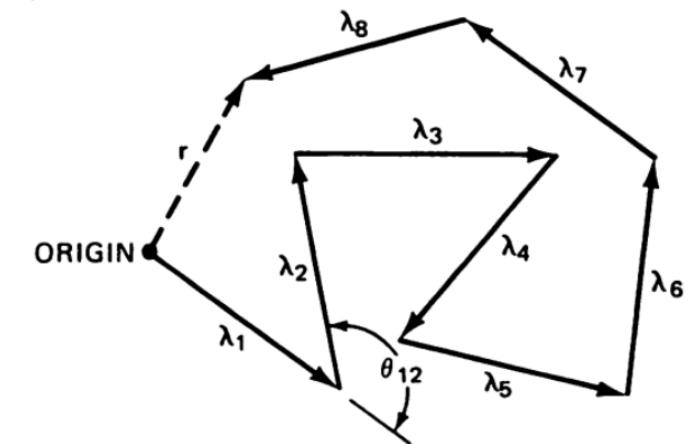
Fig. 7.4   Eight random jumps of equal length λ.

Microscopic Diffusion

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

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

And solving, we get simply:

$$\bar{r}^2 = 6Dt$$
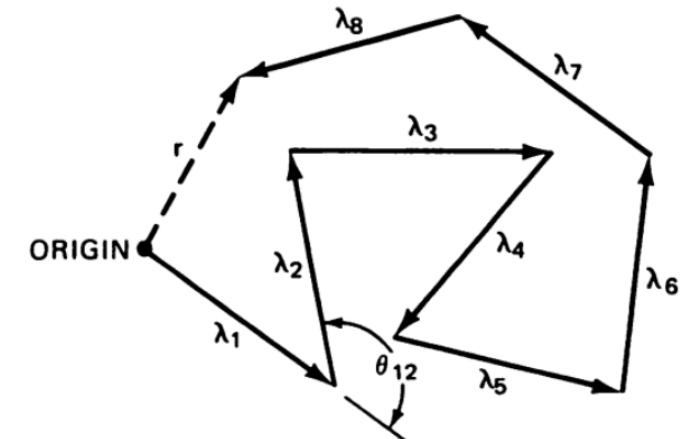
Fig. 7.4   Eight random jumps of equal length λ.

Diffusion accounting for hopping mechanism

Knowing now that:

$$D = {}^{1}\!/_{6}\, \lambda^2 \Gamma$$

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:
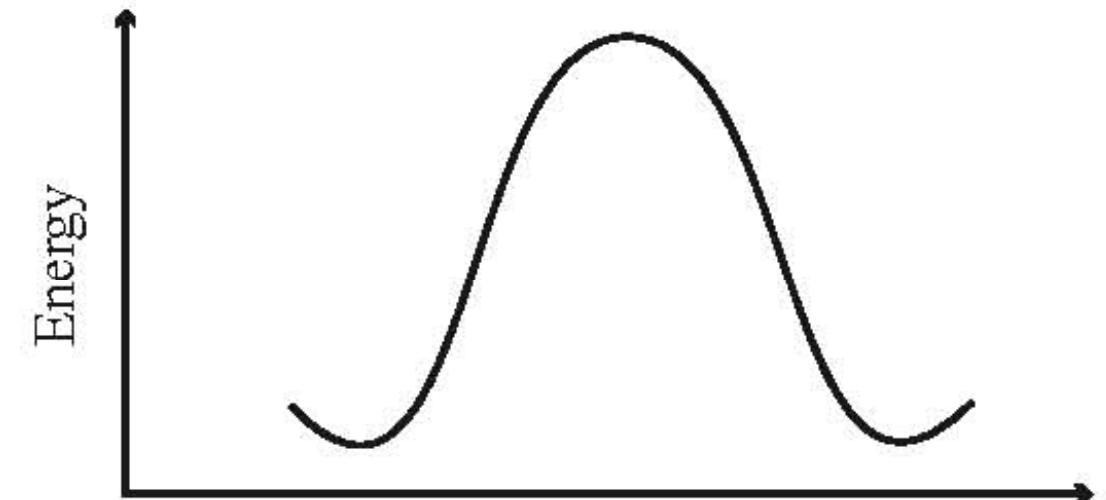
How to determine ω

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

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

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

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:

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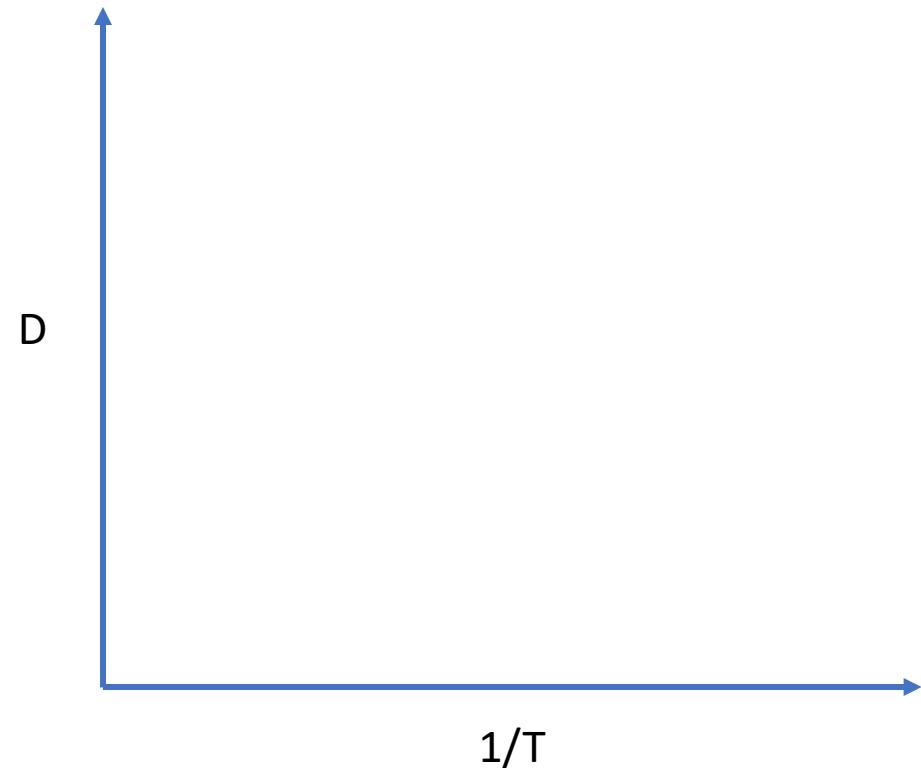
Or, more simply:

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:

D

1/T

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

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Point Defect Diffusion: Comparison

- Comparsion of diffusion
  - $t = 10^6 \ s \ (11 \ days)$
  - $E_m^f = 1 \ eV, \ E_m^i = 0.2 \ eV$
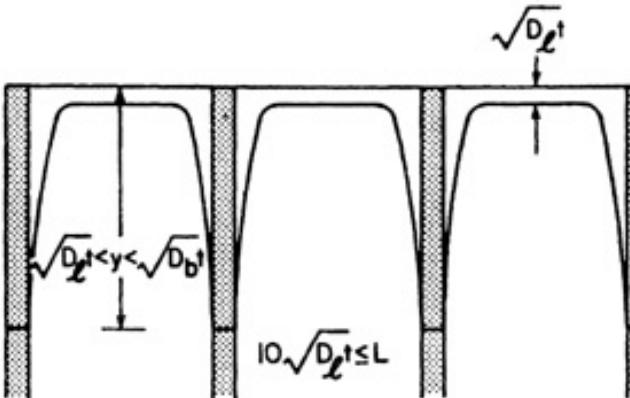
T (°C)	$D_V (m^2/s)$	$X_V = \sqrt{D_V \tau}$	$D_i (m^2/s)$	$X_i = \sqrt{D_i \tau}$
0	2×10^{-21}	0.45nm	1.5×10^{-6}	1cm
100	2×10^{-16}	150nm	1.5×10^{-5}	4cm
200	1.7×10^{-13}	4µm	5.5×10^{-5}	7.5cm
300	1.2×10^{-11}	35µm	1.3×10^{-4}	11cm
400	2.5×10^{-10}	0.15mm	2.4×10^{-4}	15cm
500	2.3×10^{-9}	4mm	3.7×10^{-4}	19cm
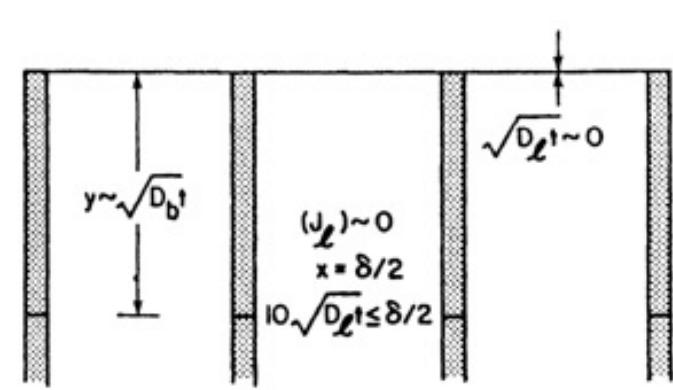
Diffusion along high-diffusivity paths:


(a)   (b)   (c)
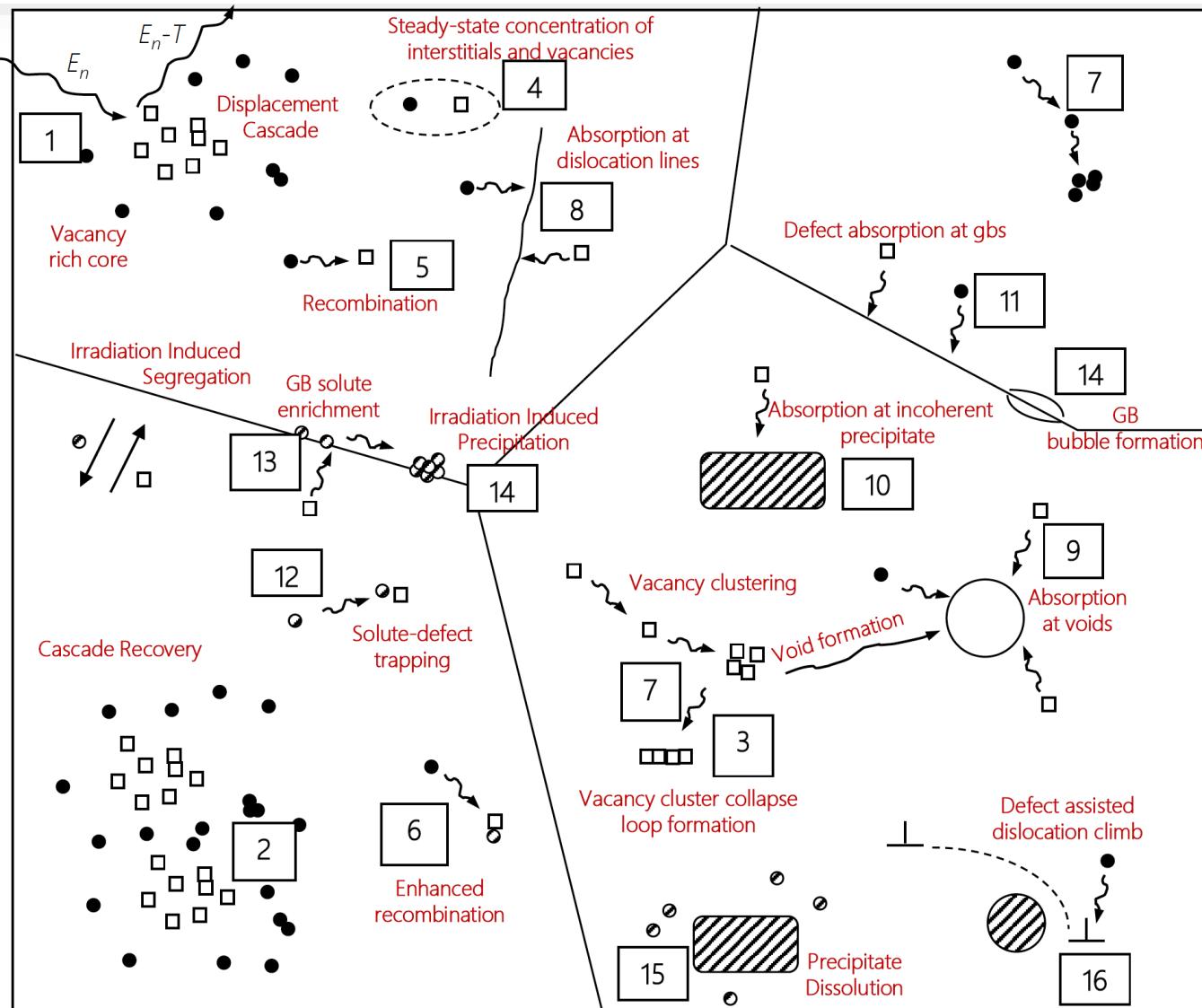
Type A: The diffusion front in the bulk and in the boundary advanced at the same speed

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
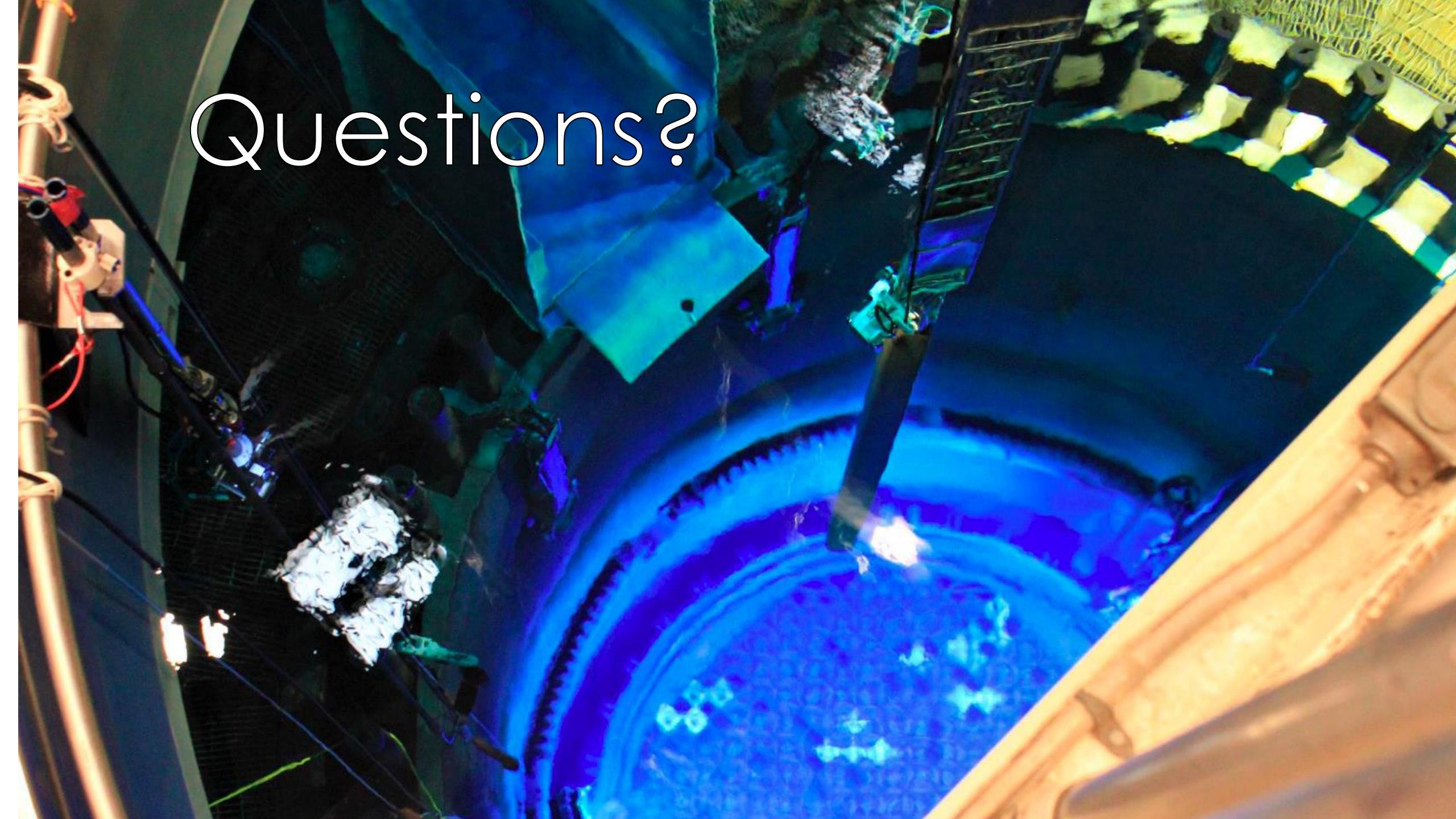
Radiation Effects at the Grain Scale

Goal: Determine the kinetics of microstructure evolution under irradiation

Questions?