Point Defect Diffusion

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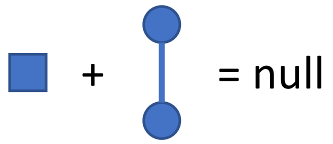
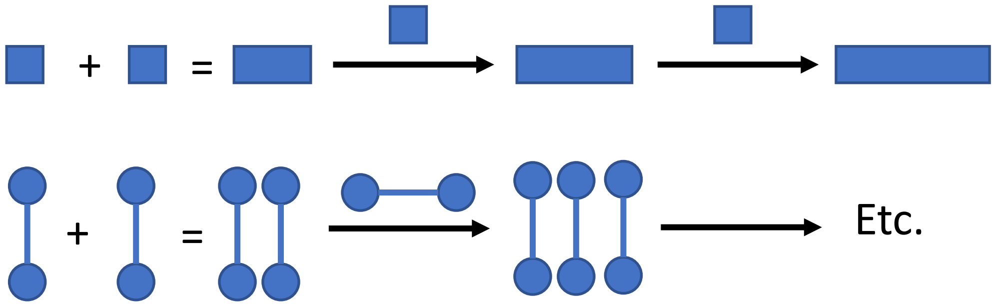
What is the fate of point defects?

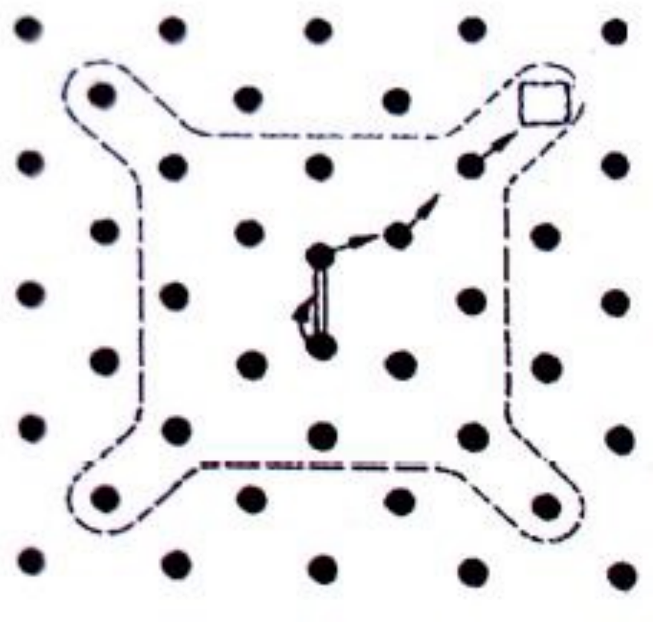
1. Annihilation (recombination)



2. Clustering



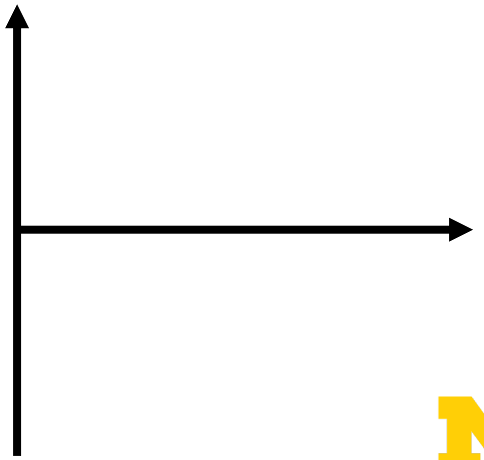
3. Elimination at Sinks



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!

Point Defects Formation: Vacancy

- **Vacancy formation:**
  - The Gibbs energy, G_v, of a solid containing N_v moles of vacancies and N moles of atoms is:



Point Defects Formation: Interstitial

- **Interstitial formation:**
  - Using the same analysis, we then get:

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

$T = 293\ K$

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

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

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

Point defect properties

	Symbol	Unit	Al	Cu	Pt	Mo	W
Interstitials							
Relaxation volume	V^{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		

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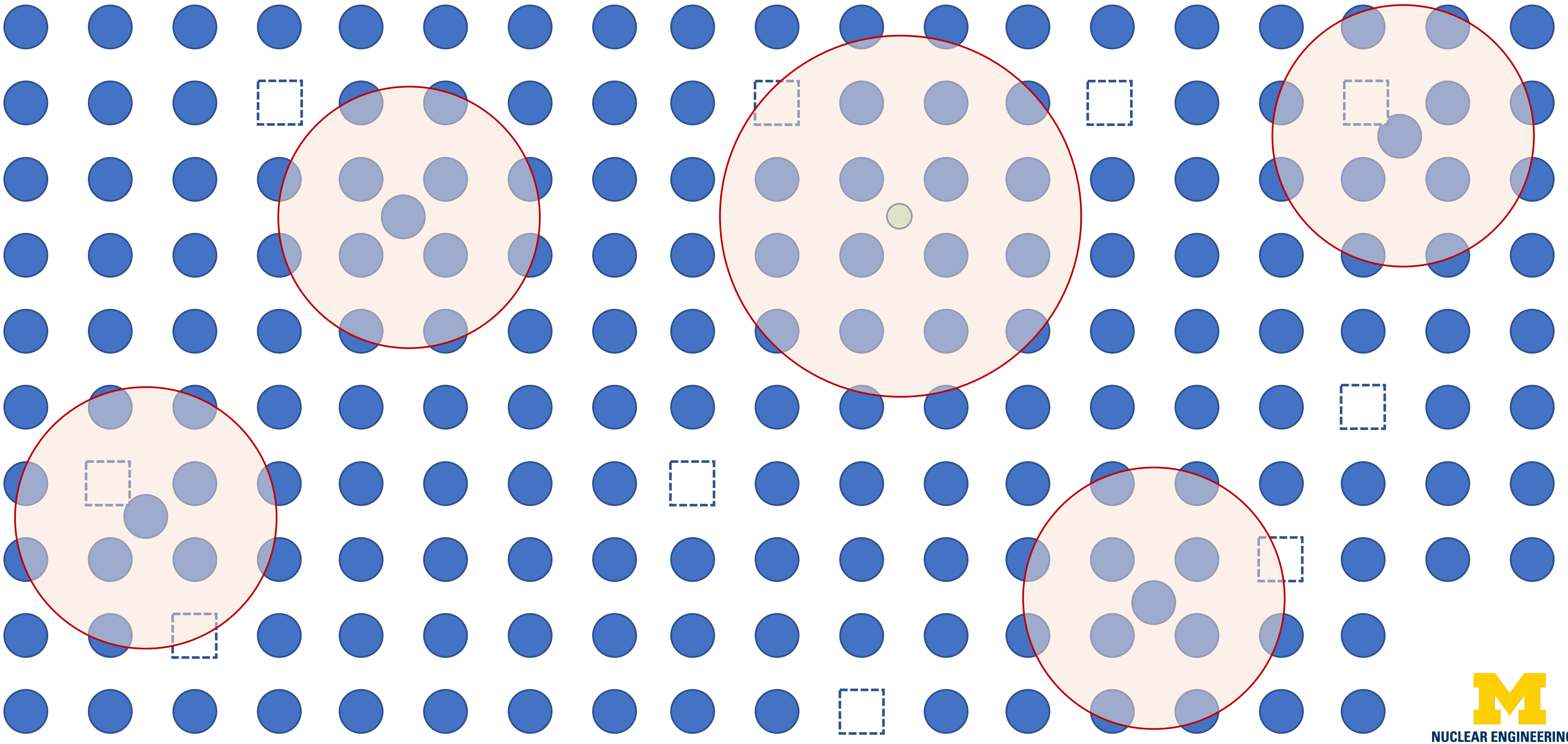
Point Defect Migration



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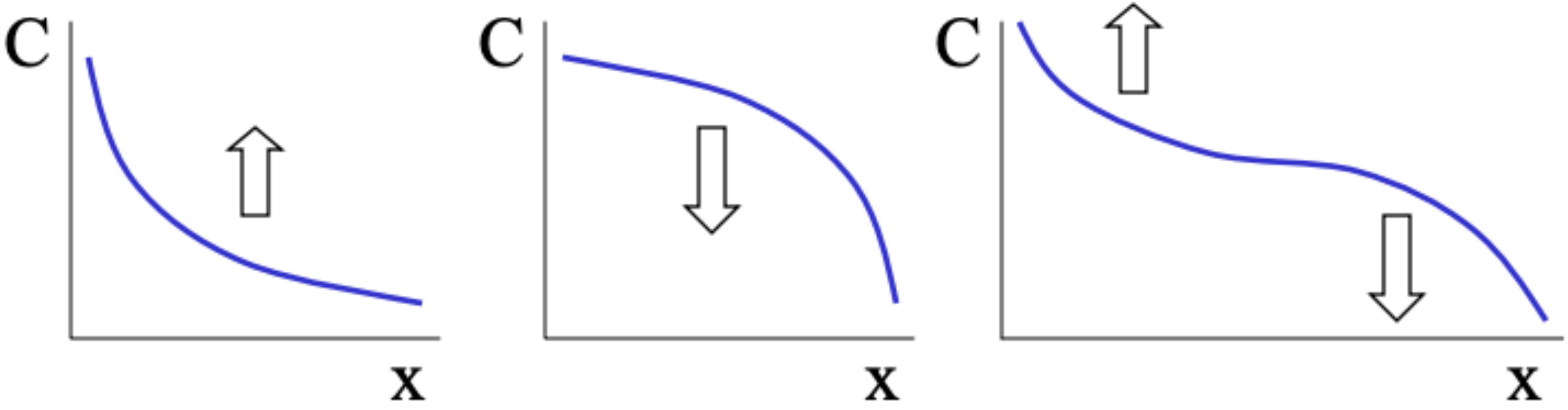
Fick’s First Law of Diffusion (Macroscopic Diffusion)

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

- 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



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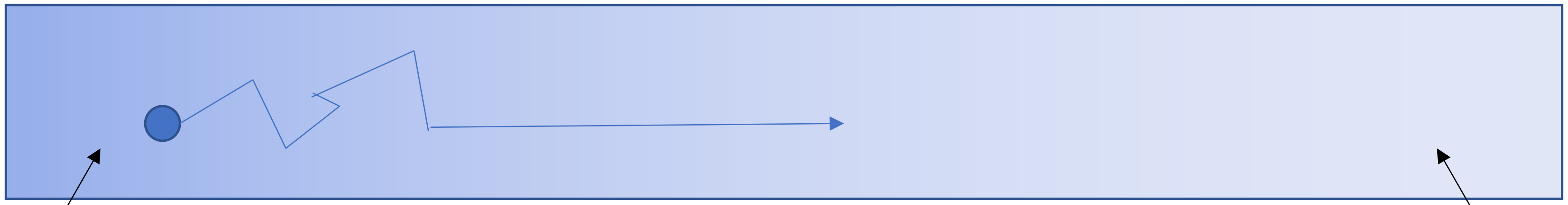
Fick’s First Law of Diffusion

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

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

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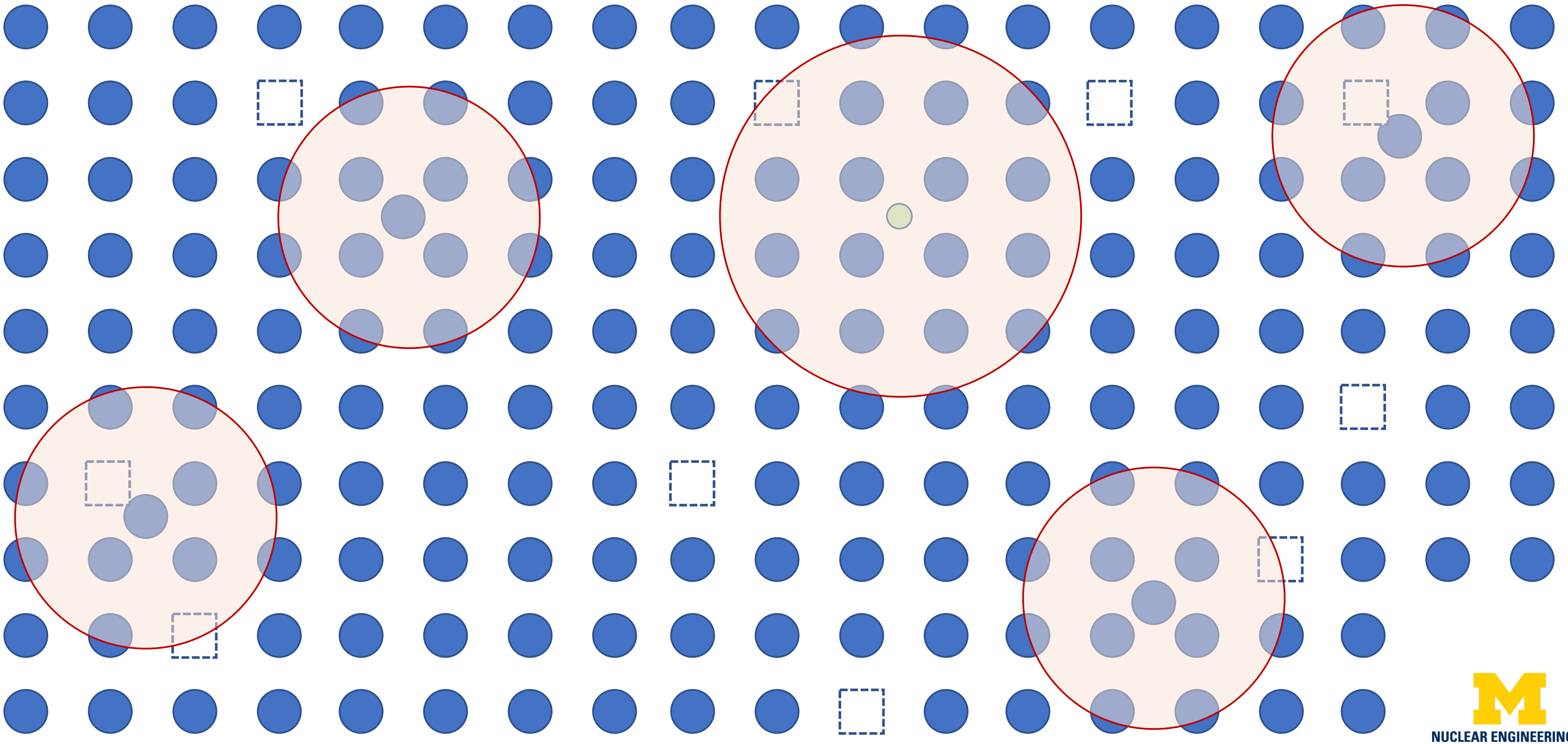
In December of 2016, the record for the world's longest squash rally was made. Simon Boughton and Mark James rallied for one hour, four minutes, and 28 seconds at Edinburgh Sports Club, completing how many shots ?

Point Defect Migration



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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:

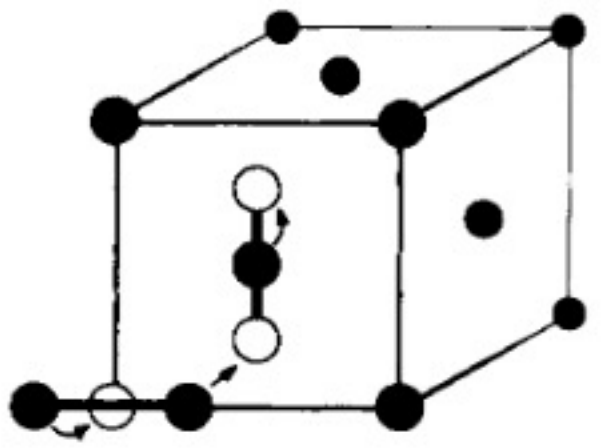

Fig. 4. Migration of the (100)-split interstitial in an fcc lattice.

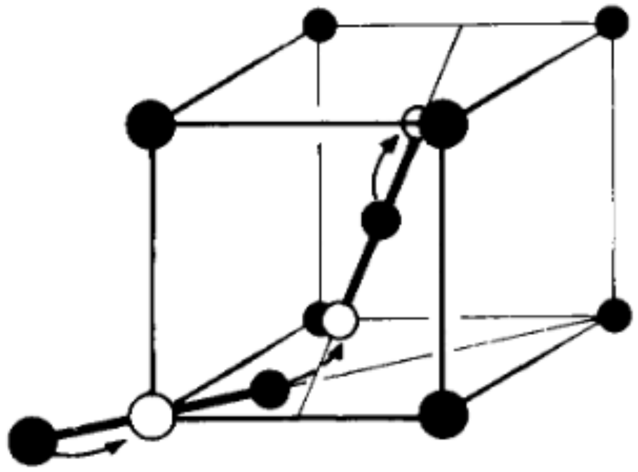

Fig. 9. Migration of the (110)-split interstitial in a bcc lattice.

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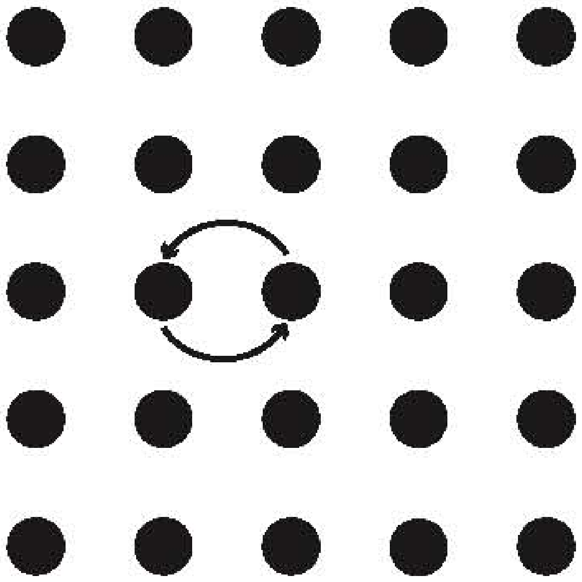
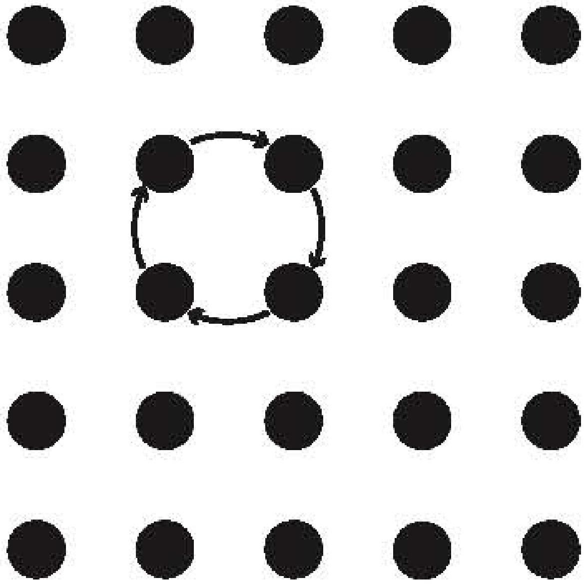
Mechanisms of Diffusion

Exchange Mechanism



Ring Mechanism



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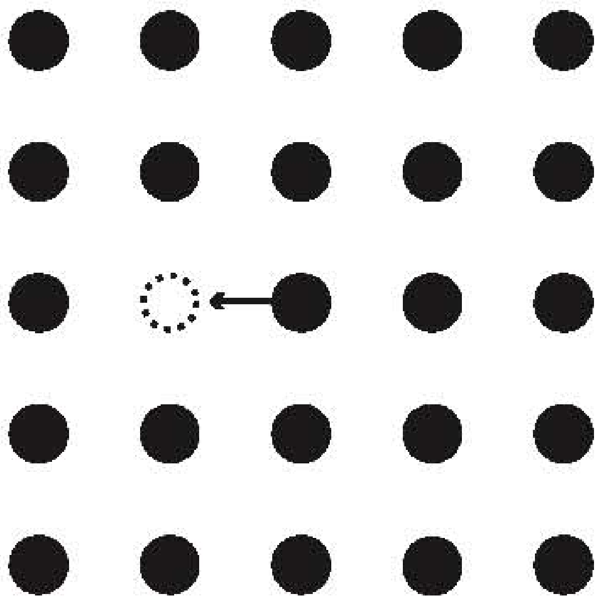
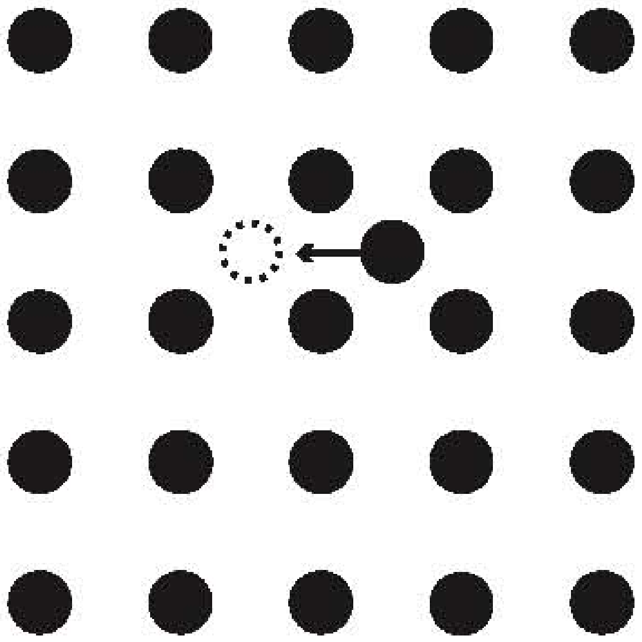
Mechanisms of Diffusion

Vacancy Mechanism

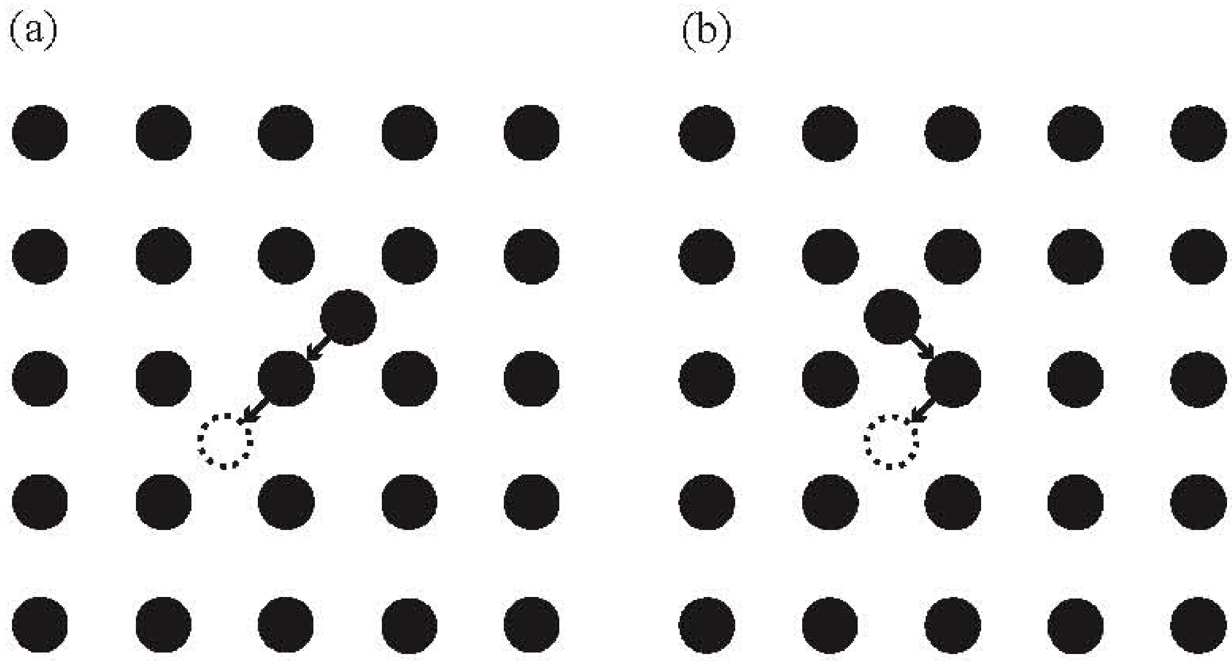


Interstitial Mechanism



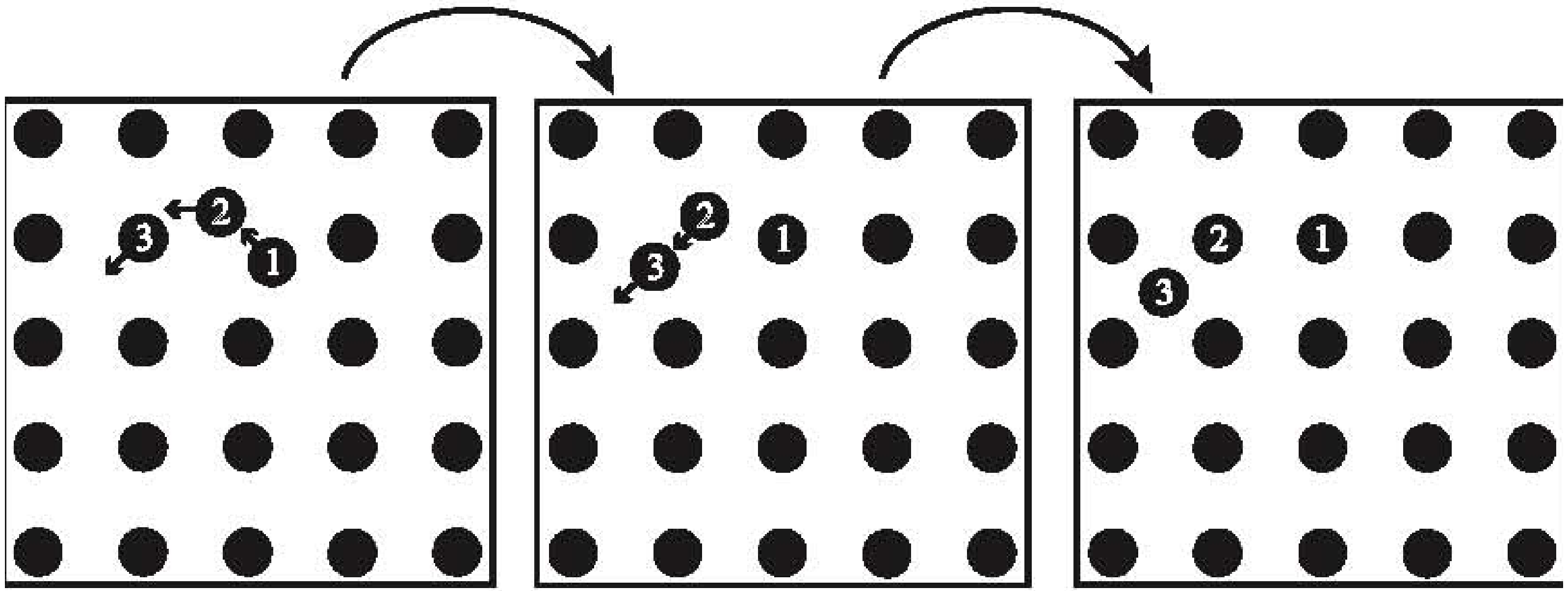
Mechanisms of Diffusion

Interstitialcy Mechanism



Mechanisms of Diffusion

Dumbbell Mechanism



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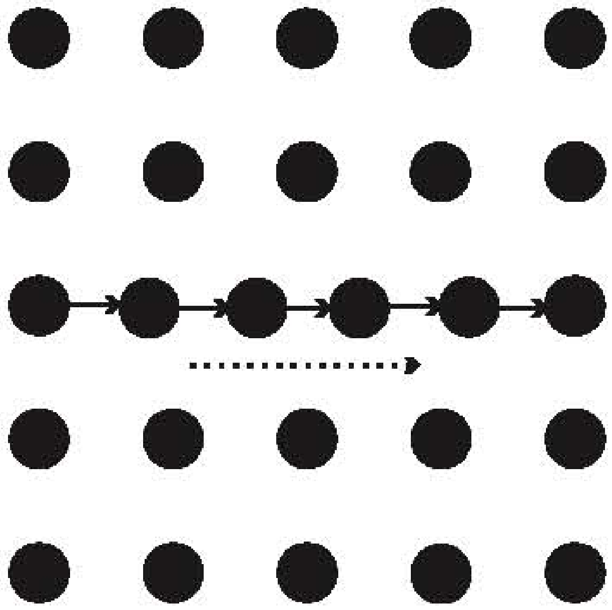
Mechanisms of Diffusion

Crowdion mechanism



Poll – what mechanism(s) is most dominant

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

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Microscopic Diffusion

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

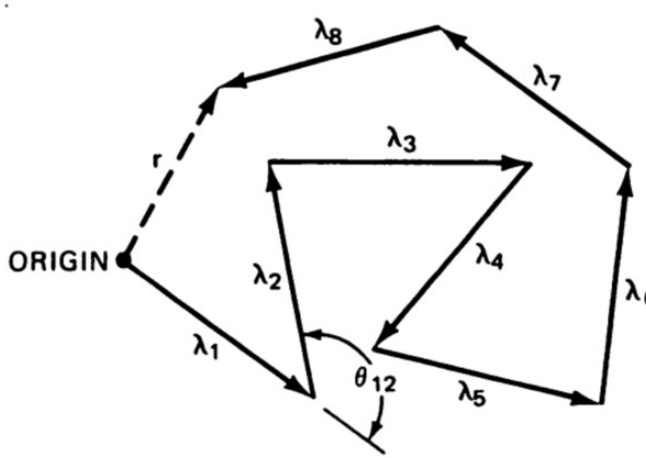

Fig. 7.4 Eight random jumps of equal length λ.

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:

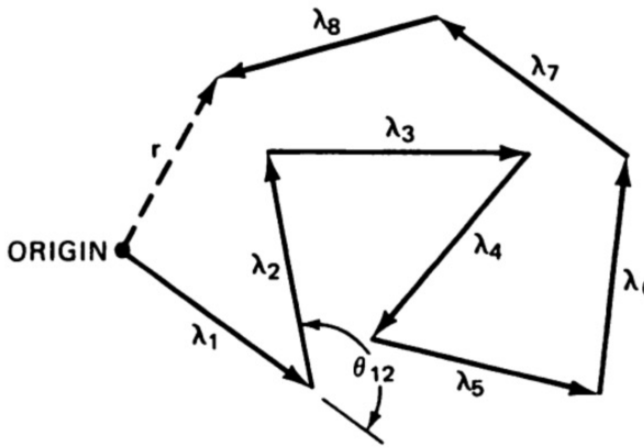

Fig. 7.4 Eight random jumps of equal length λ.

Microscopic Diffusion

Both the macroscopic and microscopic 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:

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

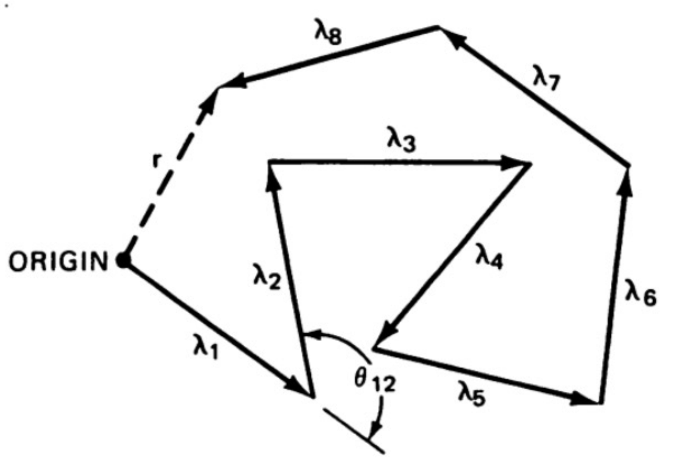

Fig. 7.4 Eight random jumps of equal length λ.

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Diffusion accounting for hopping mechanism

Knowing now that:

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

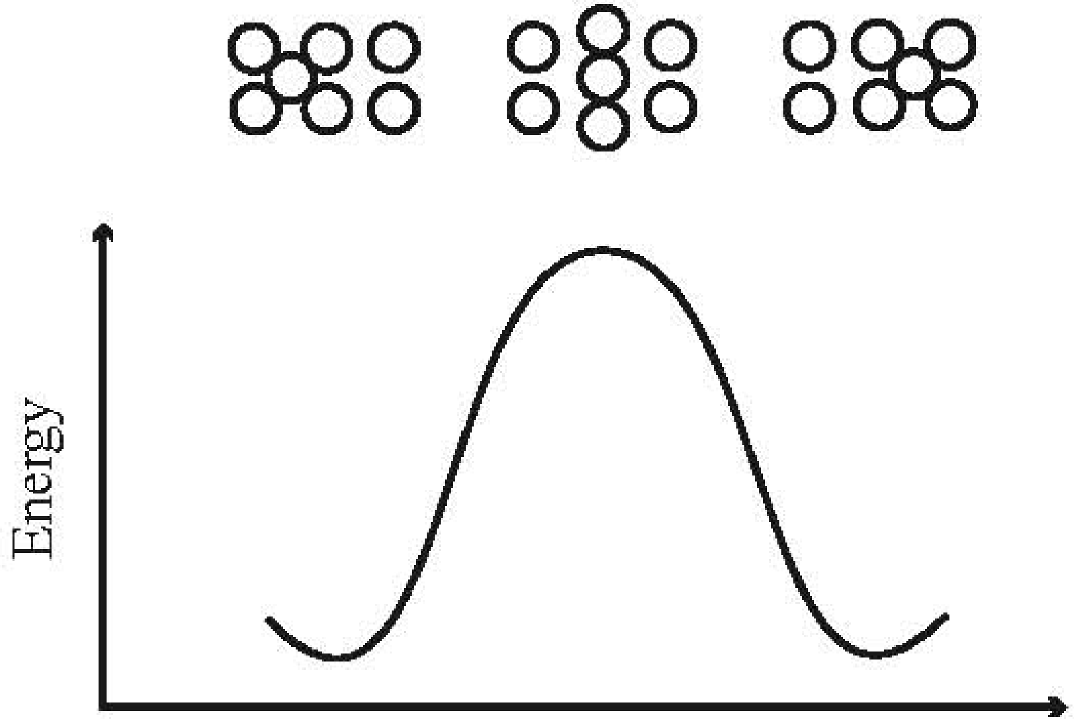
We need to determine the jump frequency for a given jump mechanism. This is dependent on the probability a jump site is open, ρ_j, the number of nearest neighbors, z, and the frequency of a given jump type, ω:

How to determine ω

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

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

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



Pulling it together to get the diffusion equations:

Diffusion of vacancies:

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

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

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

Diffusion of interstitials:

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

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

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

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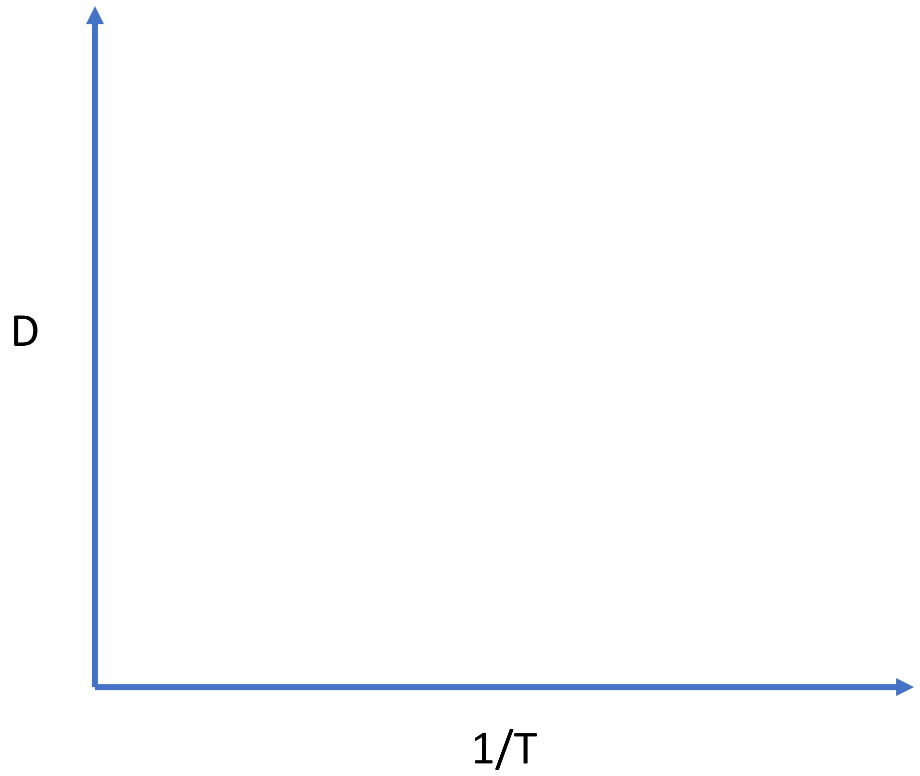
Or, more simply:

We can use an Arrhenius relationship:

$$D = D_0 exp\left({}^{-Q}/_{k_b T} \right)$$

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



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

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Point defect properties

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Frenkel pairs							
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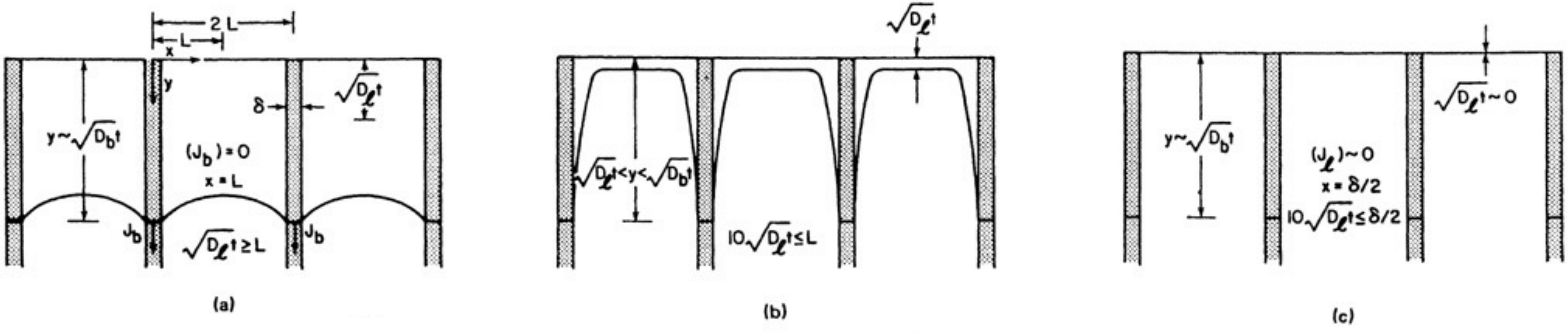
Point Defect Diffusion: Comparison

- 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:

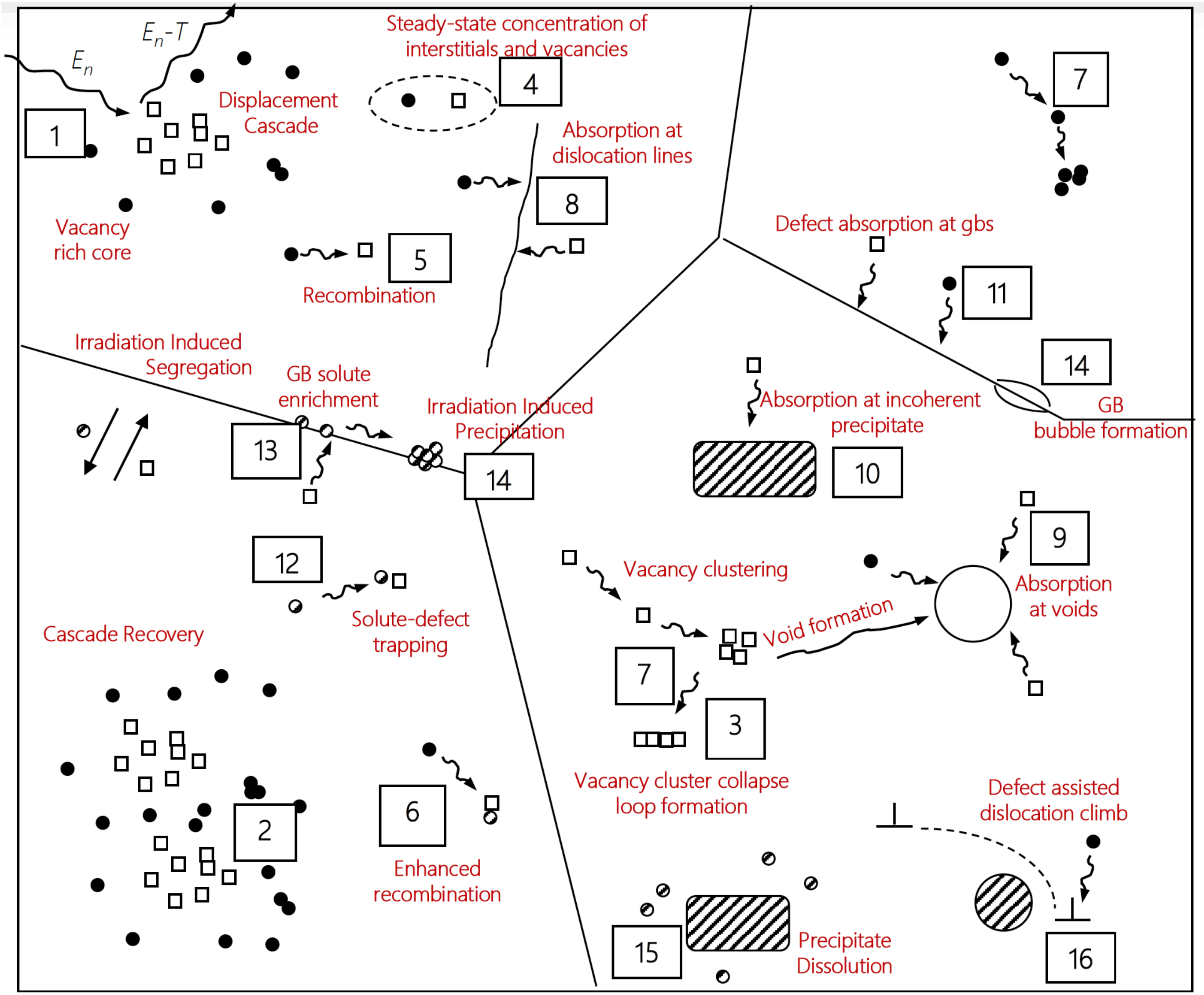


Type A: The diffusion front in the bulk and in the boundary advanced at the same speed

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



<u>Goal</u>: Determine the kinetics of microstructure evolution under irradiation

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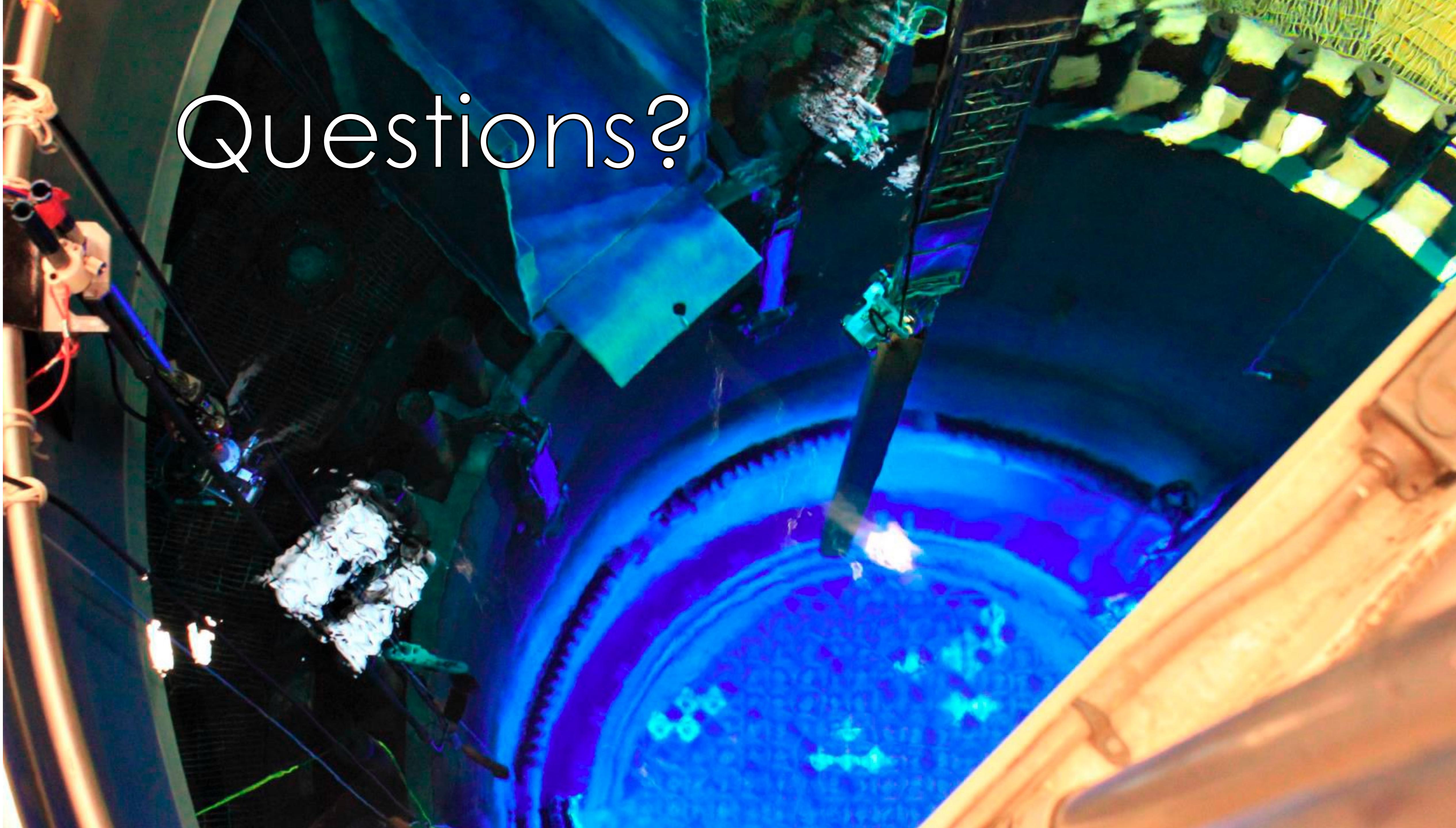
Questions?