MATE 664 Lecture 11

Diffusion in Defect and Material Imperfections

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Recap of Lecture 10

Key ideas from last lecture:

- Diffusion equations for solids
- Link Einstein's equation to Arrhenius equation
- Emergence of activation enthalpy / entropy
- Vacancy formation free energy and diffusion

Learning Outcomes

After this lecture, you will be able to:

- Apply the free energy-dependent diffusion equations to systems with defects and material imperfections
- Understand how intrinsic and extrinsic defect in ionic materials are formed
- Analyze intrinsic / extrinsic diffusion regimes in ionic materials
- Understand material imperfections as the diffusion shortcuts

What Does Diffusion In Real Materials Look Like?

- Real solids are not perfect crystals
- Defects control transport properties
- Ionic diffusion shows rich temperature dependence
- Same Einstein framework, new physics inside

Base Line: Vacancy-Mediated Diffusion In Metals

- Diffusion = random walk of atoms via vacancies
- Diffusivity related to both vacancy density (controlled by G_v^f) and vacancy jumping (controlled by G_v^m)

$$D_A = \frac{z\langle r^2\rangle\nu}{6}\exp\left(\frac{S_v^f + S_v^m}{k_B}\right)\exp\left(-\frac{H_v^f + H_v^m}{k_B T}\right) f \tag{1}$$

Defect-Mediated Diffusion In Ionic Crystals

- Defects in ionic crystals are more complex than in metal
- Charge neutrality has to be conserved
- More than one single defect species are involed
- In other words, defects always come in **pairs** in ionic solids

Schottkey and Frenkel Defects In Ionic Crystals

- Shottkey defects: missing both positive and negative species
- Frenkel defects: one charged species moved to other site

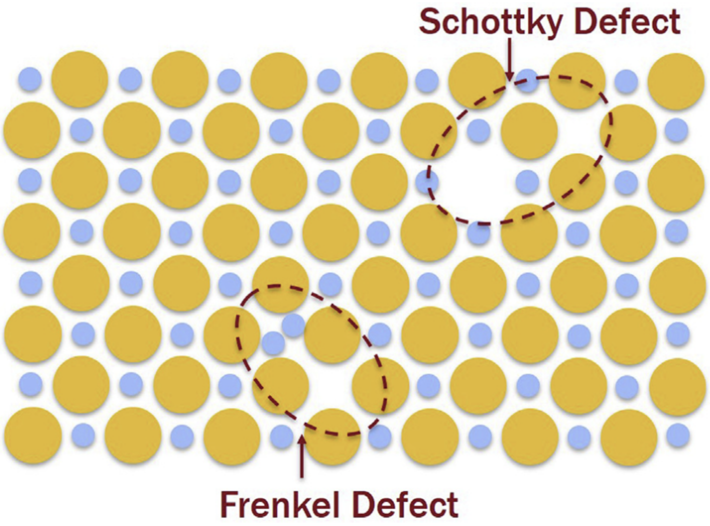


Figure 1: Comparison between Schottkey and Frenkel defects

Ionic Defects: Kröger-Vink (KV) notation

- Formula X_Y^Z
- X = what is at the site (Element or Vacancy)
- Y = what site is defective (Element or i)
- Z = effective charge at the site ($\bullet$ = +; '= −)

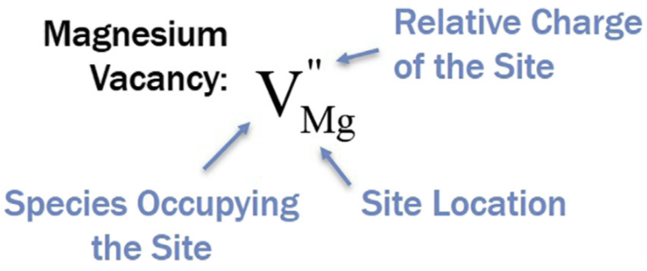


Figure 2: Example of KV notation

KV Notation For Schottky Defects

Example: Schottky defects in MgO (anion + cation vacancies)

- Formation reaction

$$\text{null} \rightarrow V''_{\text{Mg}} + V_{\text{O}}^{\bullet\bullet}$$

- Equilibrium condition
    - G_S^f: formation free energy for Schottky defects (per reaction)

$$K_S = [V''_{\text{Mg}}][V_{\text{O}}^{\bullet\bullet}] = \exp\left(-\frac{G_S^f}{kT}\right)$$

- Charge neutrality

$$[V''_{\text{Mg}}] = [V_{\text{O}}^{\bullet\bullet}]$$

KV Notation For Frenkel Defects

Example: Frenkel pairs in LiF (Lithium escaping to interstitial sites)

- Formation reaction

$$\mathrm{Li}_{\mathrm{Li}}^{\times} \rightarrow V_{\mathrm{Li}}' + \mathrm{Li}_i^{\bullet}$$

- Equilibrium condition
  - G_F^f: formation free energy for Schottky defects (per reaction)

$$K_F = [V_{\mathrm{Li}}'][\mathrm{Li}_i^{\bullet}] = \exp\left(-\frac{G_F^f}{kT}\right)$$

- Charge neutrality
  $[V_{\mathrm{Li}}'] = [\mathrm{Li}_i^{\bullet}]$

Intrinsic vs Extrinsic Defects

- **Intrinsic** defects are those controlled by thermodynamics G_S^f, G_F^f or G_V^f
- **Extrinsic** defects are those defects added to the ionic crystal via doping

Example of Extrinsic defects: $\mathrm{CdCl_2}$ in NaCl

- Dopant incorporation reaction

$$\mathrm{CdCl_2} \rightarrow \mathrm{Cd}_{\mathrm{Na}}^{\bullet} + 2\,\mathrm{Cl}_{\mathrm{Cl}}^{\times} + V_{\mathrm{Na}}'$$

- Extrinsic defect concentration

$$[V_{\mathrm{Na}}']_{\mathrm{ext}} = [\mathrm{Cd}_{\mathrm{Na}}^{\bullet}] = [\mathrm{CdCl_2}]$$

- Total vacancy concentration

$$[V_{\mathrm{Na}}'] = [V_{\mathrm{Na}}']_s + [V_{\mathrm{Na}}']_{\mathrm{ext}} = \exp\left(-\frac{G_S^f}{2kT}\right) + [\mathrm{CdCl_2}]$$

Diffusivity of Ionic Species

- We can still use the vacancy exchange mechanism for the diffusivity of ionic species
- E.g. Na^+ exchanges with its own vacancy $V_{\mathrm{Na}}^{'}$
- $[V_{\mathrm{Na}}^{'}]$ depends on the T-regime!

$$\begin{aligned} D_{\mathrm{Na}} &= [V_{\mathrm{Na}}^{'}]\, f\, \lambda^2\, \nu \exp\left(-\frac{G_{\mathrm{Na}}^m}{kT}\right) && (2) \\ &= f \lambda^2 \nu \left[\exp\left(-\frac{G_S^f}{2kT}\right) + [\mathrm{CdCl_2}]\right] \exp\left(-\frac{G_{\mathrm{Na}}^m}{kT}\right) && (3) \end{aligned}$$

Intrinsic vs Extrinsic Regimes

- Extrinsic: vacancy dominated by doped materials
  - Low-T regime (high $1/T$)

$$D_{\mathrm{Na,ext}} = [\mathrm{CdCl_2}]\, f\, \lambda^2\, \nu \exp\left(\frac{S_{\mathrm{Na}}^m}{k}\right) \exp\left(-\frac{H_{\mathrm{Na}}^m}{kT}\right) \tag{4}$$

- Intrinsic: vacancy dominated by thermal dissociation
  - High-T regime (low $1/T$)

$$D_{\mathrm{Na,int}} = f\, \lambda^2\, \nu \exp\left(\frac{S_S^f}{2k}\right) \exp\left(\frac{S_{\mathrm{Na}}^m}{k}\right) \exp\left(-\frac{H_S^f}{2kT}\right) \exp\left(-\frac{H_{\mathrm{Na}}^m}{kT}\right) \tag{5}$$

Two-Regimes In The Arrhenius Plot

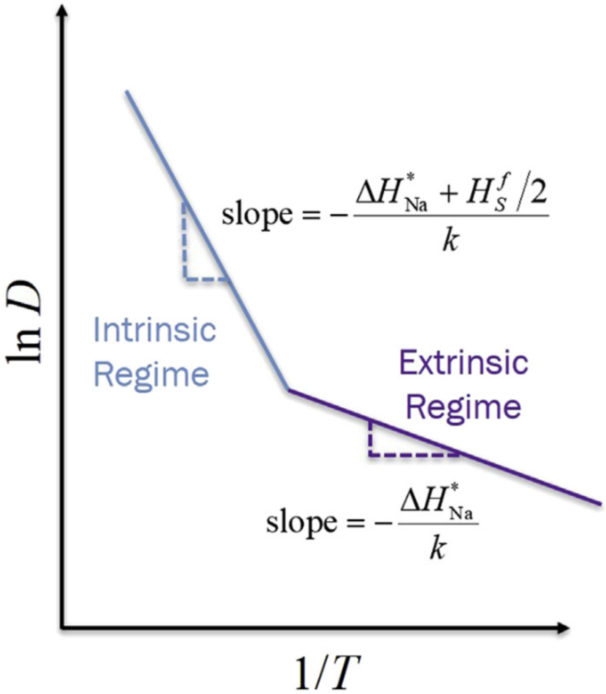
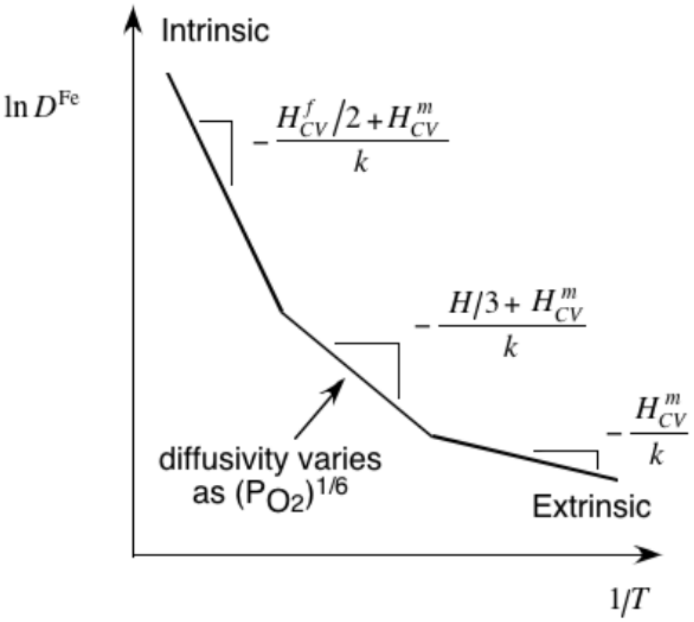


Figure 8.9 Intrinsic and extrinsic regimes of diffusion. The crossover between the two regimes occurs where the number of defects is equal from the intrinsic and extrinsic defect mechanisms.

More Regimes In Arrhenius Plot

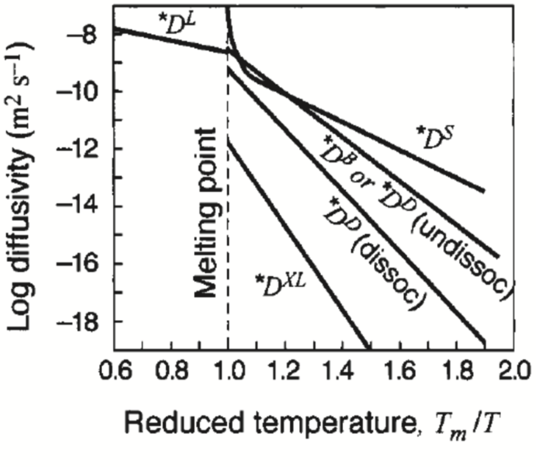
- Example: cation diffusion in FeO during oxidation
- Equilibrium depends on both G^f and $p(O_2)$
- Multiple regimes!

Cation diffusivity Arrhenius plot



Position of middle segment will depend on oxygen pressure, hence this region will not be observable at low oxygen pressures or high impurity contents

Multiple Regimes Diffusion In Polycrystalline Materials



D^D : diffusivity along a dislocation core

D^B : diffusivity along a grain boundary

D^S : diffusivity along a free surface

D^{XL} : diffusivity in a bulk crystal

D^L : diffusivity in a liquid

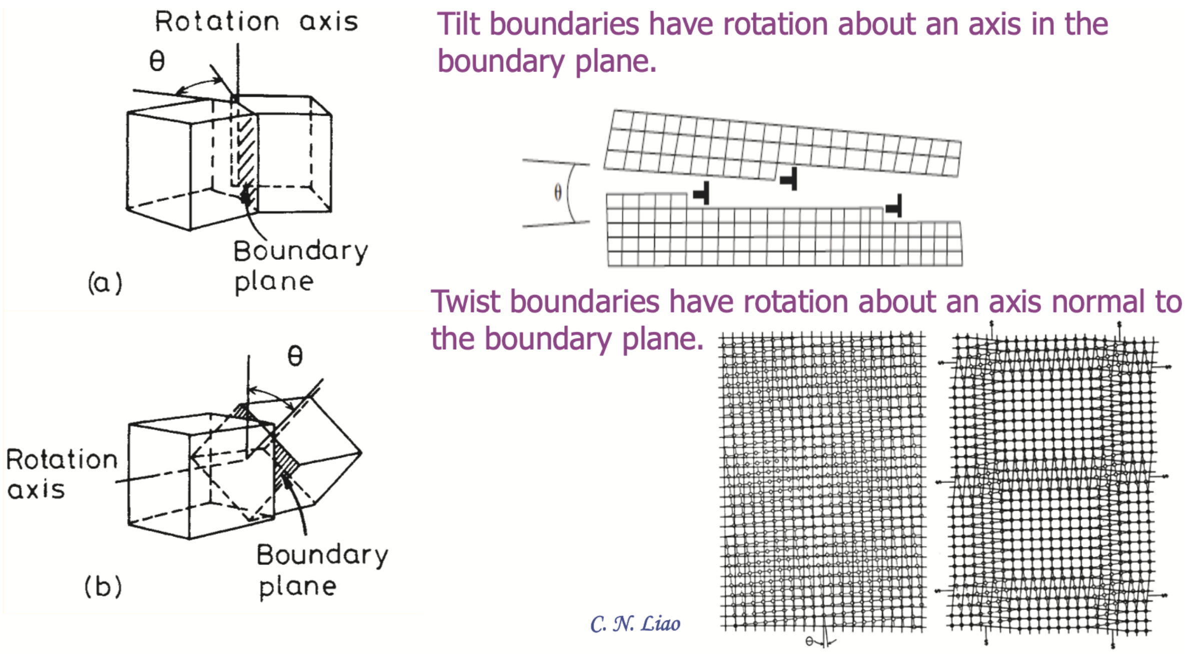
$$D = D_0 \exp\left(-\frac{\Delta H}{kT}\right) \approx D_0 \exp\left(-\frac{T_m}{T}\right)$$

Figure 3: Arrhenius plot for diffusion on imperfections

Diffusion Paths At Crystal Imperfections

- Diffusion can occur along non-bulk pathways
- Typical crystal imperfections
  - Grain boundary and interface diffusion: 2D
  - Free surface diffusion: 2D
  - Dislocation (pipe) diffusion: 1D
  - Vacancy / defect: 0D
- Imperfections are associated with lower migration / activation energy!
- Think as “shortcuts” during diffusion

Imperfection 1: Grain Boundaries

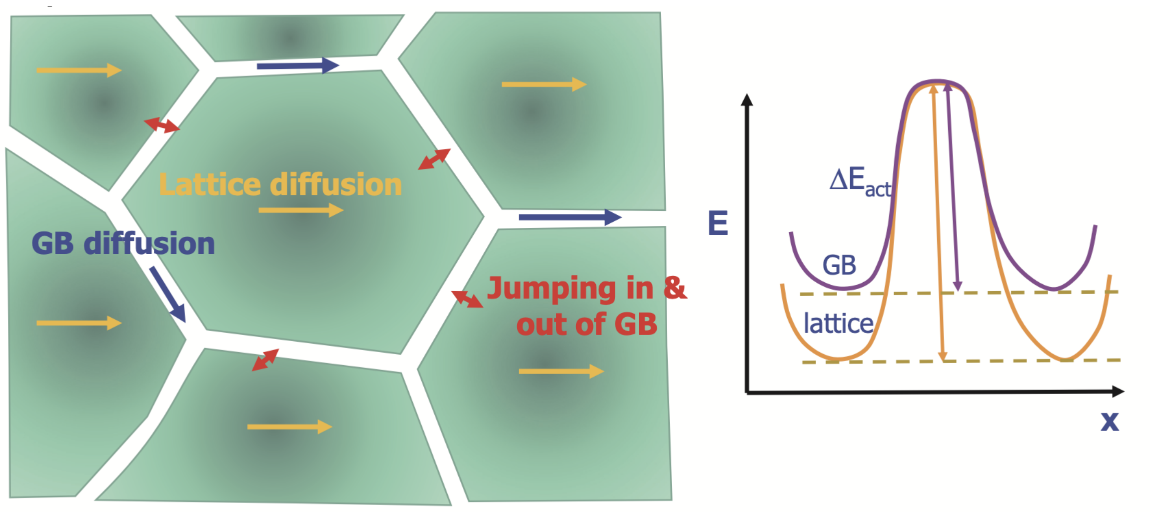


Tilt boundaries have rotation about an axis in the boundary plane.

Twist boundaries have rotation about an axis normal to the boundary plane.

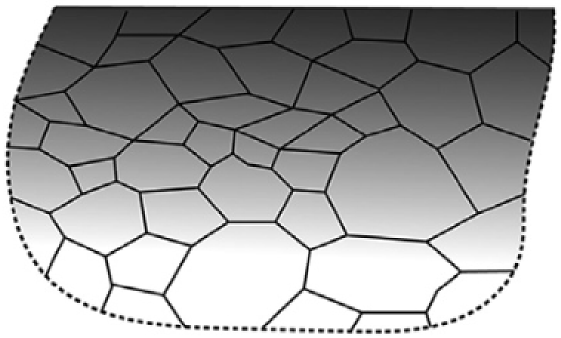
C. N. Liao

Grain Boundary Diffusion

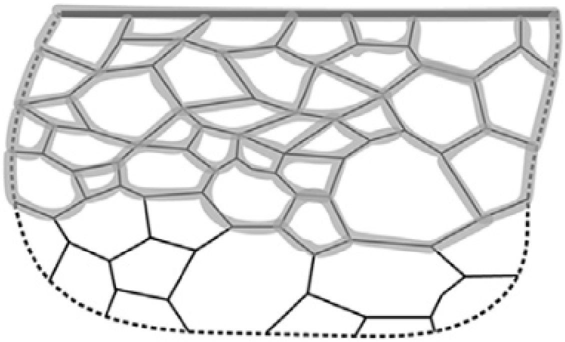


Harrison’s ABC Model For GB Diffusion

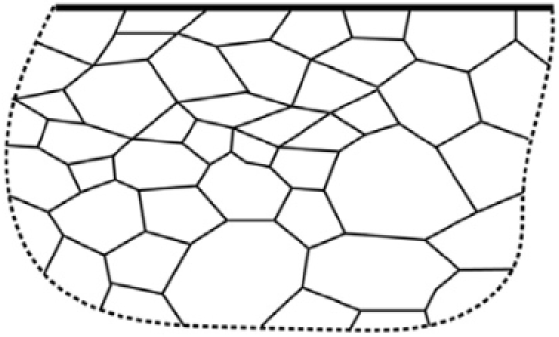
- A regime
  - $D_{XL}t > l^2$
  - $D_B t > l^2$
  - fast diffusion everywhere
- B regime
  - $D_{XL}t \gg l^2$
  - $D_B t < l^2$
  - coupled short-circuit and bulk diffusion
- C regime
  - $D_{XL}t < l^2$
  - $D_B t < l^2$
  - diffusion confined to imperfections



A regime
(a) All material



B regime
(b) Boundary region



C regime
(c) Core only

Dislocation Imperfections (Line Defect)

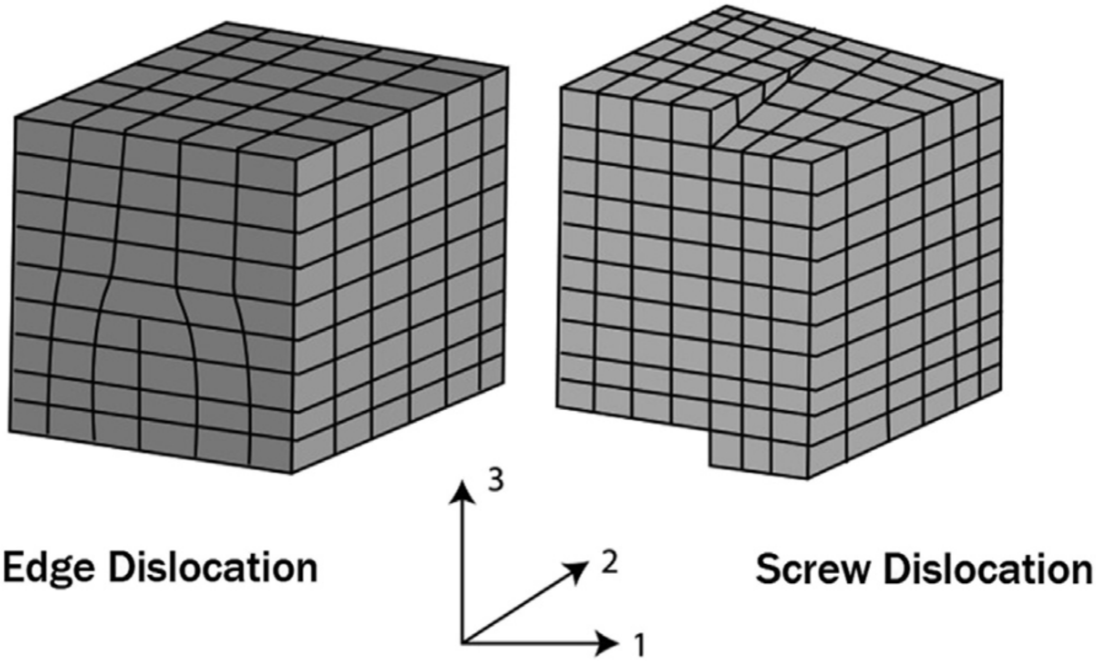


Figure 4: Edge and screw dislocations

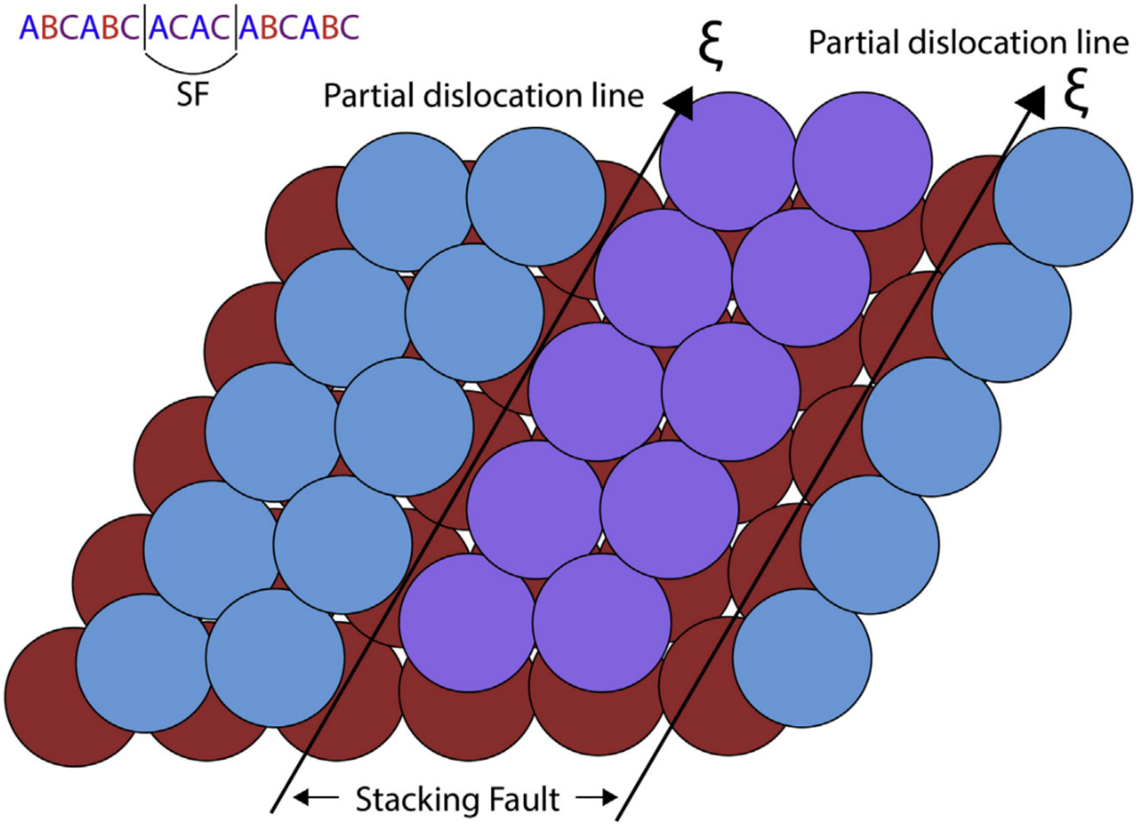


Figure 5: Partial dislocations

Example of Diffusion Along Imperfection: Deposition on Graphene

- See Vagli and Tian et al. *Nat Commun* 2025, 16, 7726.
- Diffusivity change on free graphene surface can be probed by deposition geometry!

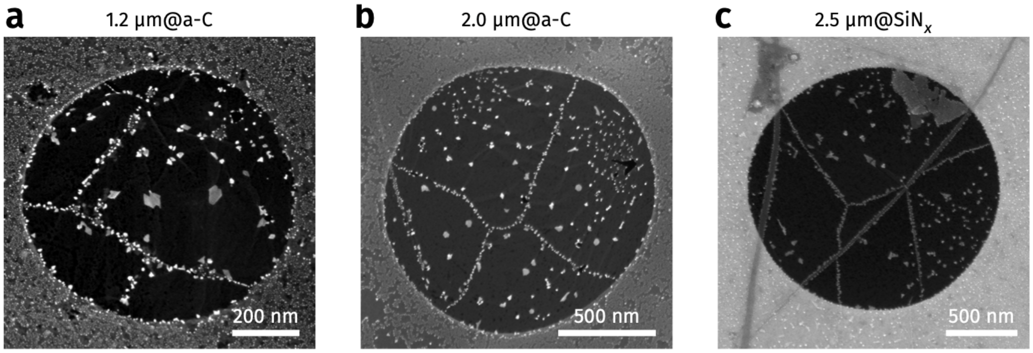
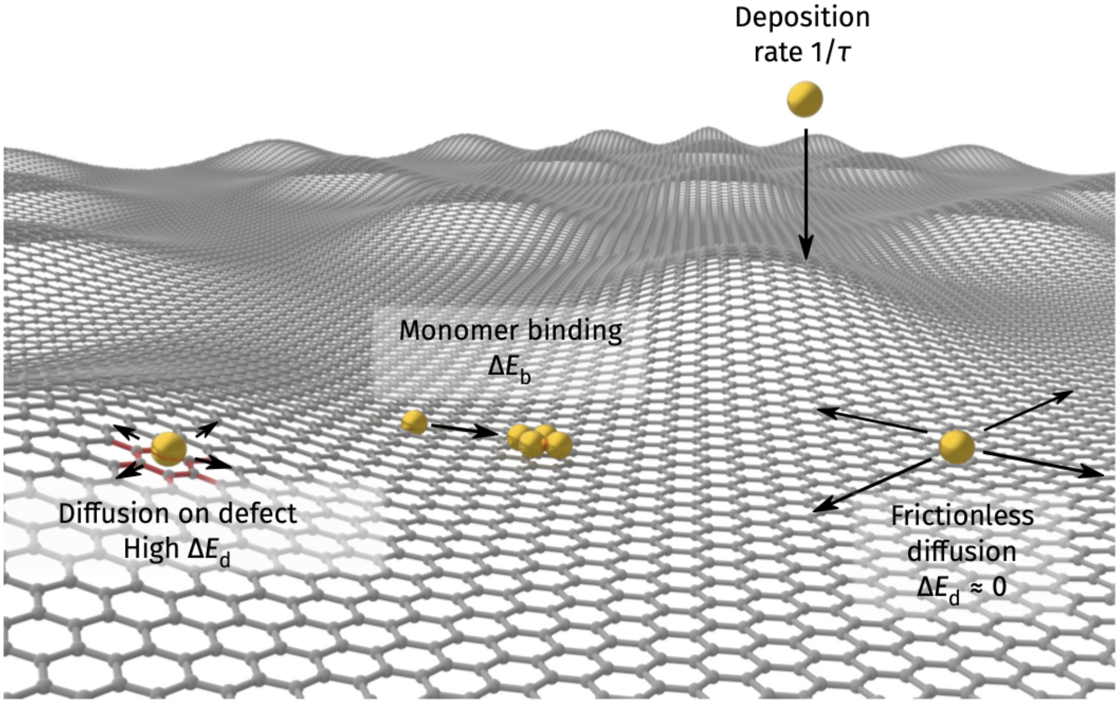


Figure S5: **SEM images of Au deposited on graphene-covered holes on various pore sizes and substrates: a** 1.2 μm pore on a-C support, **b** 2.0 μm pore on a-C support, and **c** 2.5 μm pore on SiN$_x$ support.

Deposition on Graphene - Theoretical Simulations

- Kinetic Monte Carlo (kMC) assuming different diffusion barrier on imperfections
- Faster diffusion direction –> lower density



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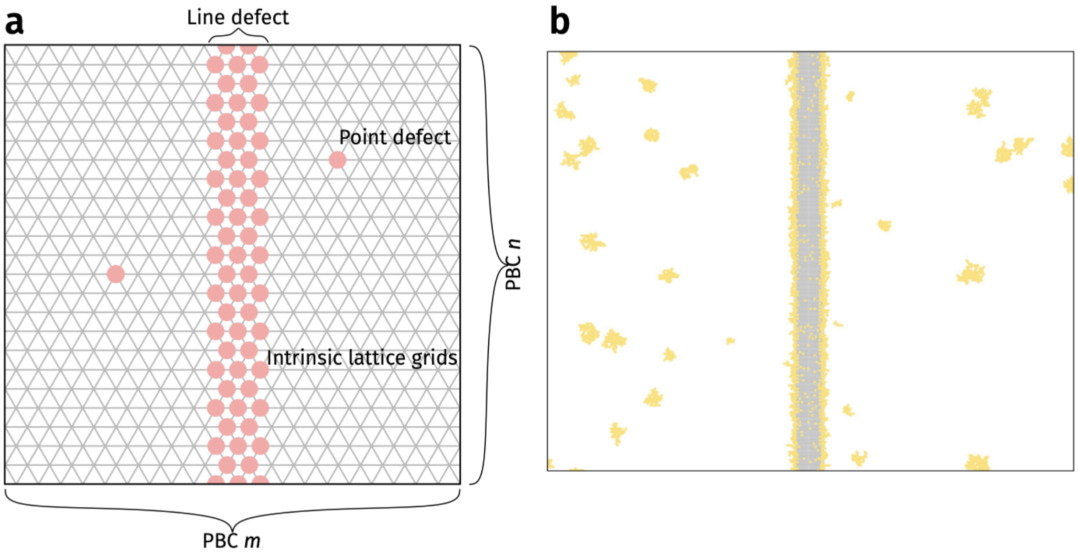
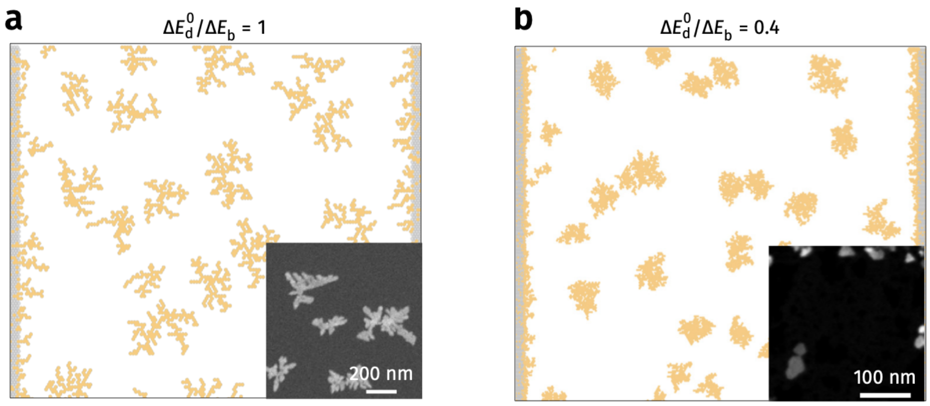


Deposition on Graphene - KMC vs Experiments



Graphite/Au

Vac/Graphene/Au

Figure S21: **Simulated morphology of Au nanostructures on bulk graphite (a) and freestanding graphene (b) surfaces**. The dendritic patterns on graphite are formed as a result of the high $\Delta E_\mathrm{d}^0/\Delta E_\mathrm{b}$ ratio, while hexagonal and triangular structures are observed on freestanding graphene due to lower $\Delta E_\mathrm{d}^0/\Delta E_\mathrm{b}$. Experimental SEM images for Graphite/Au and Vac/Graphene/Au fabricated from Au evaporation at room temperature are shown as insets of **a**