Short-Circuit Diffusion in Crystals

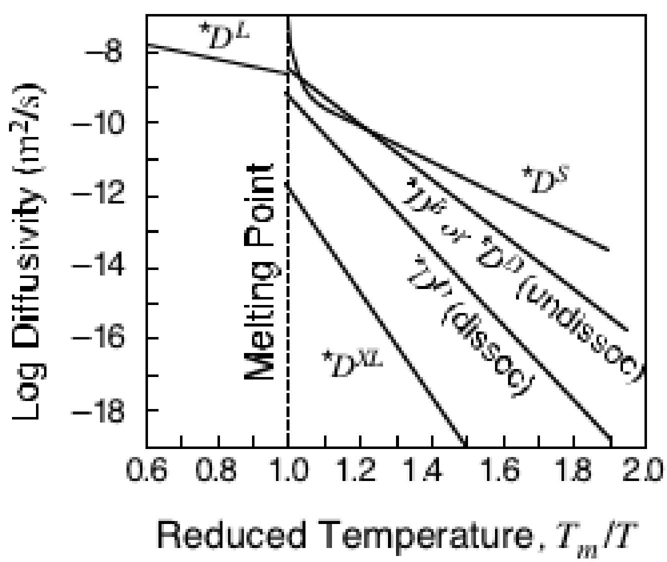
Today's topics:

- Diffusion spectrum in defective crystals
- Dislocation core structure and dislocation "short circuits"
- Grain boundary structure
- Grain boundary diffusion mechanisms and phenomena
- Some phenomena where short-circuits are important

Diffusion Paths in Polycrystals

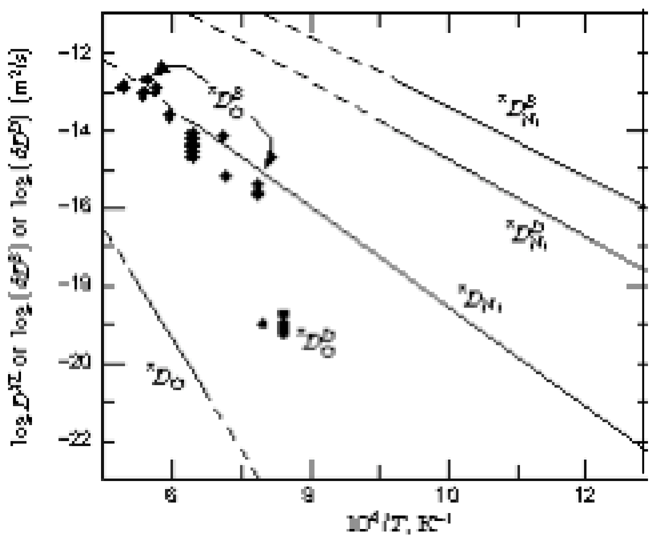
- D^{XL}, bulk (lattice) diffusivity
- D^{B}, grain boundary diffusivity
- D^{S}, (free) surface diffusivity
- D^{D}, dislocation diffusivity

Typical behavior in fcc metals



Grain Boundary Diffusion in NiO

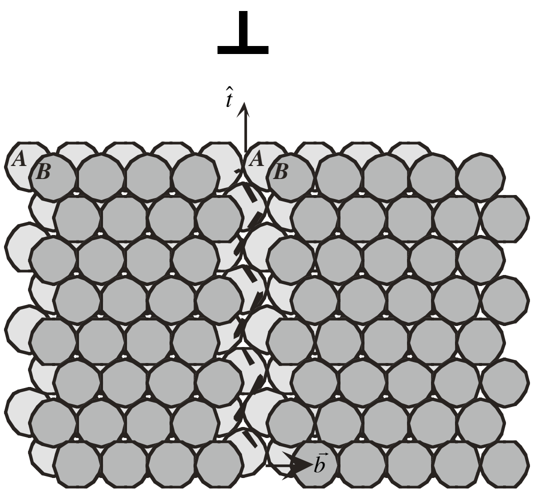
- **Diffusion data from NiO, comparing rates of bulk diffusion and grain boundary diffusion**



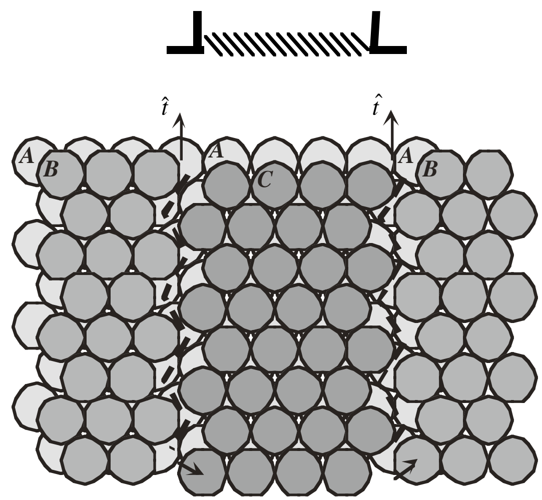
Dislocation "Pipe" Diffusion

Dislocations, especially edge dislocations, can act as short-circuit diffusion paths.

Dissociated dislocations have cores that are more spread out, connected by a ribbon of stacking fault:



Perfect dislocation



Partial dislocation

Grain Boundary Structure

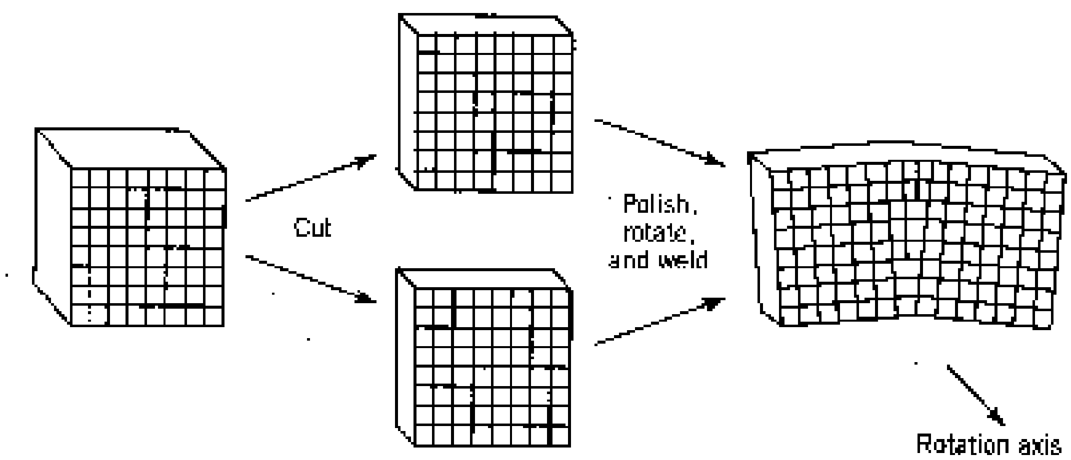
Specification of a grain boundary: five degrees of freedom (at least)

Rotation axis $\hat{r}$

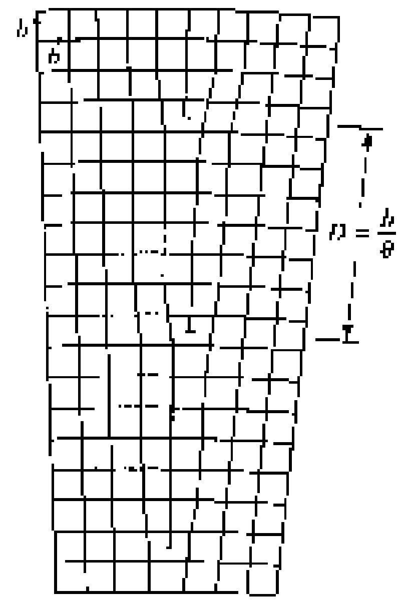
Rotation angle θ

Boundary normal $\hat{n}$

Example: tilt boundaries

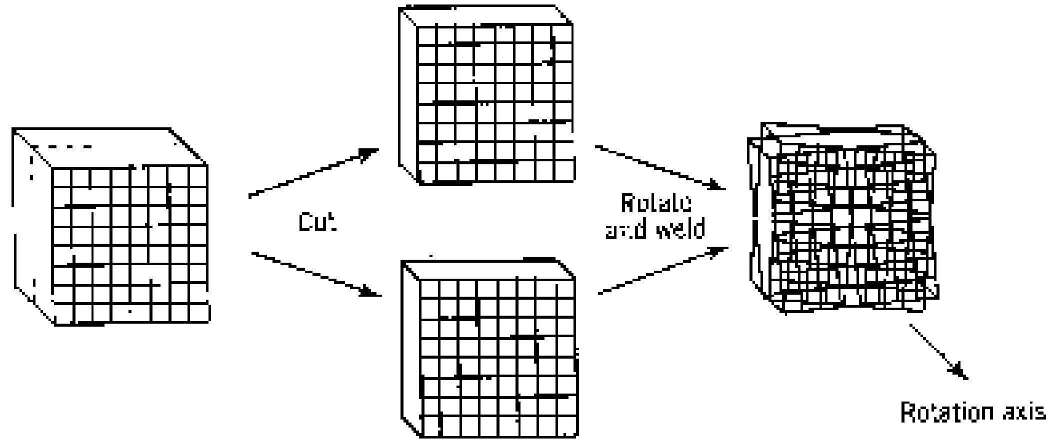


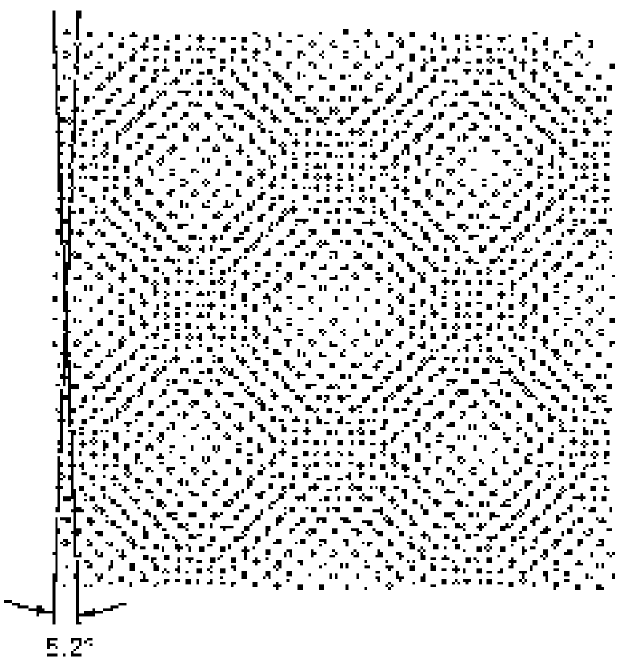
(a)



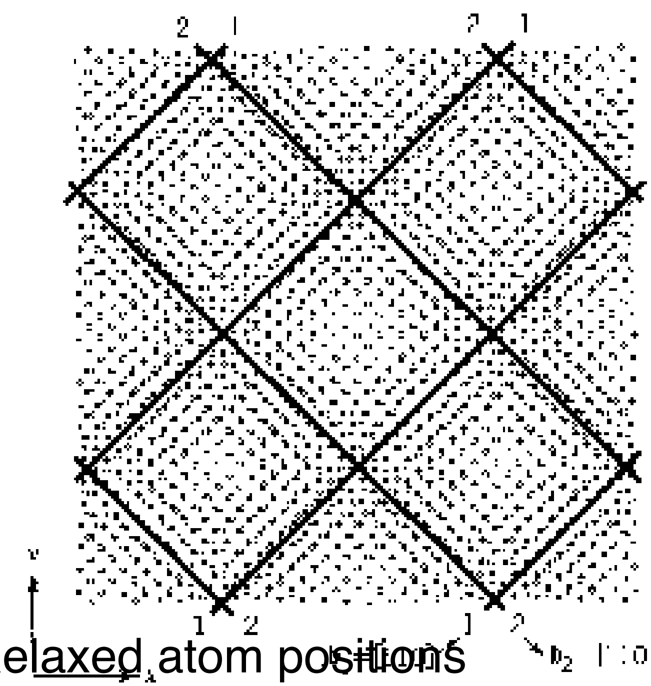
Grain Boundary Structure, cont'd

Twist boundaries





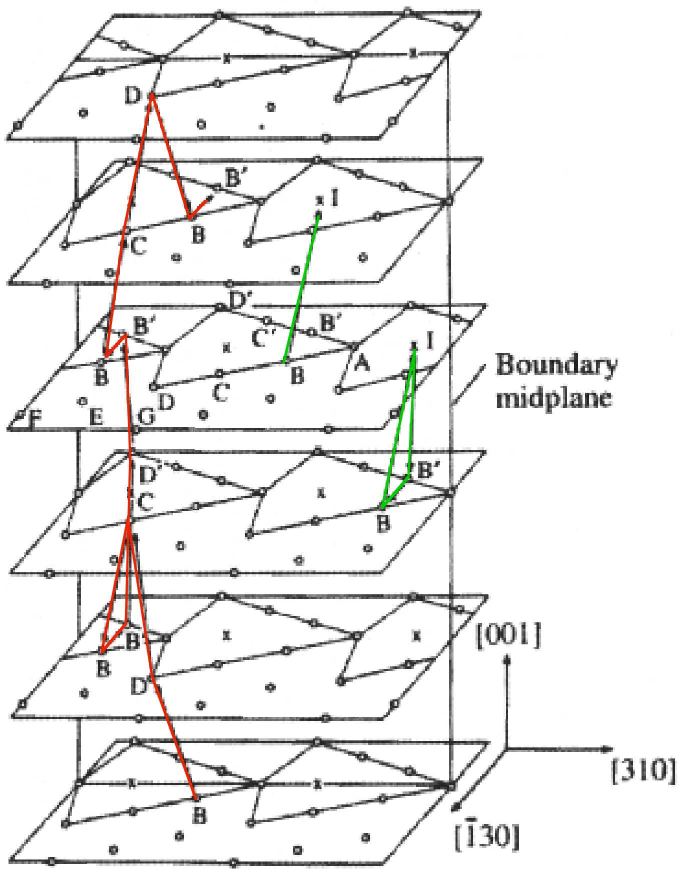
Unrelaxed atom positions



Relaxed atom positions

Mechanism of Grain Boundary Diffusion

Vacancies and self-interstitials



Atom jumping events in Σ 5<001>(310) symmetric tilt boundary in b.c.c.-Fe calculated by molecular dynamics using pair-potential model. The ratios of the scales used in the drawing are

$$[\bar{1}30]:[310]:[001]=1:1:5$$

vacancy trajectory, confined to grain boundary sites

vacancy/interstitial pair creation

Grain Boundaries and Impurity Diffusion

- Diffusivity of Zn along the tilt axes [110] symmetric tilt boundaries in Al as a function of tilt angle, θ.

- Orientations near the center of the plot, where the boundary diffusivity is small, correspond to orientations with a high density of coincidence sites. Peaks in the plot are orientations corresponding to general boundaries with more open structure.

See Figure 9.2 in Balluffi, Robert W., Samuel M. Allen, and W.Craig Carter. *Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Diffusion on Stationary G.B.s

- Diffusing species initially coats top surface…

A regime
all material

B regime
boundary region

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See Figure 9.4 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter. *Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

C regime
core only

Grain Boundary Diffusion, cont'd

- **Regime A**: Characteristic diffusion distance in bulk > grain size s.

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See Figure 9.4 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter.
Kinetics of Materials. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

Fraction of atomic sites in grain boundaries is $\eta \approx 3\delta/s$

Effective mean squared displacement is

$$\langle D \rangle t = D^{XL}(1-\eta)t + D^{B}\eta t$$

and for $\eta << 1$, $\langle D \rangle = D^{XL} + (3\delta/s)D^{B}$

Grain Boundary Diffusion, cont'd

Case C: Characteristic diffusion distance in bulk < atomic spacing < characteristic diffusion distance in grain boundary.

- a diffusing atom visits only the grain boundaries

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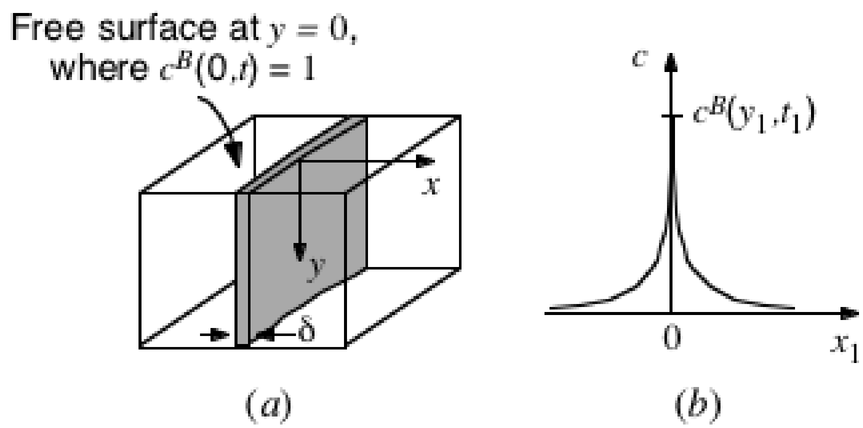
See Figure 9.4 in Balluffi, Robert W., Samuel M. Allen, and W. Craig Carter. *Kinetics of Materials*. Hoboken, NJ: J. Wiley & Sons, 2005. ISBN: 0471246891.

- **Case B**: Intermediate regime where

$$\lambda^2 < D^{XL} t < s^2$$

  - a diffusing atom visits only a single grain

B-Type Diffusion, Stationary g.b.s



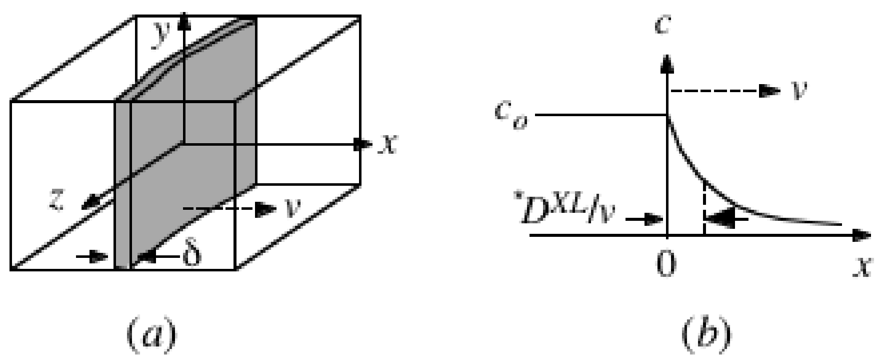
- Solve two-dimensional diffusion problem for fast boundary diffusion and relatively slow bulk diffusion, with constant concentration of diffusant at the surface as illustrated.

$$c^{XL}(x_1, y_1, t_1) = \exp\left[-\left(\frac{4}{\pi t_1}\right)^{1/4} y_1\right]\left[1 - \mathrm{erf}\left(\frac{x_1}{2\sqrt{t_1}}\right)\right]$$

B-Type Diffusion, Stationary g.b.s

$$c^{XL}(x_1, y_1, t_1) = \exp\left[-\left(\frac{4}{\pi t_1}\right)^{1/4} y_1\right]\left[1 - \operatorname{erf}\left(\frac{x_1}{2\sqrt{t_1}}\right)\right]$$

Moving Grain-Boundary Diffusion Source



Steady-state diffusion with respect to a frame at the interface migrating at velocity *v* :

$$-\nabla \cdot \vec{J} = -\frac{d}{dx}\left(-D^{XL}\frac{dc}{dx} - vc\right) = 0$$

which has the solution

$$c(x) = c_0 \exp\left[\left(-v/D^{XL}\right)x\right]$$

Phenomena Involving Short Circuits…

Chiang, Birnie, and Kingery *Physical Ceramics,* 1997 Section 5.3 on "Single-Phase Sintering"

R W Balluffi and A Sutton, *Interfaces in Crystalline Materials*, 1995, p. 762–763 explains theory of Coble creep

Nieh, Wadsworth, and Sherby, *Superplasticity in Metals and Ceramics*, Cambridge University Press, 1997. Chapter 3 provides an overview of mechanisms of superplasticity