Previous lecture

- Atomistic models for diffusion coefficients - ionic crystals

    Intrinsic and extrinsic regimes in stoichiometric material

- Diffusion in nonstoichiometric oxides; the oxygen sensor

Today

- Quick primer on grain boundary structure
- Diffusion spectrum in defective crystals
- Diffusion regimes in defective crystals
- DIGM ("dig-em")

- **Essentials of grain boundary structure**

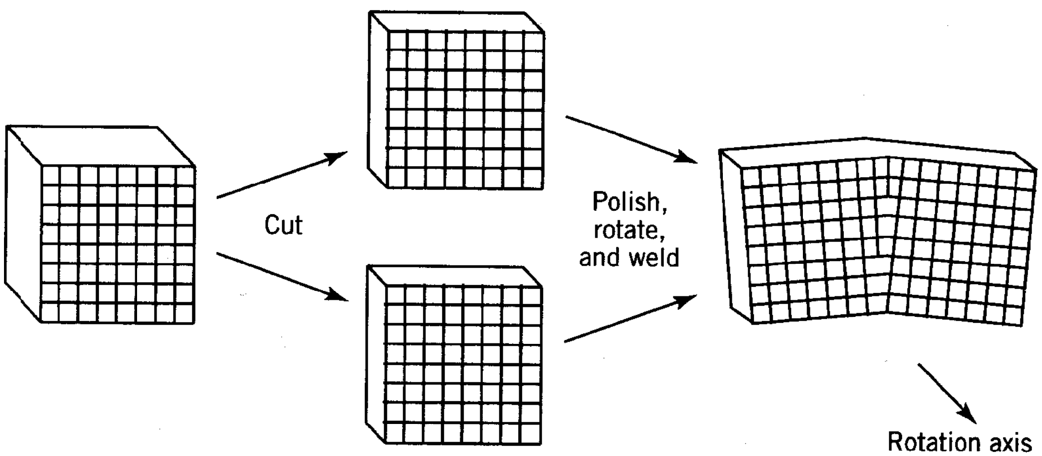
Specification of a grain boundary: five degrees of freedom (at least)

Rotation axis $\hat{\mathbf{r}}$

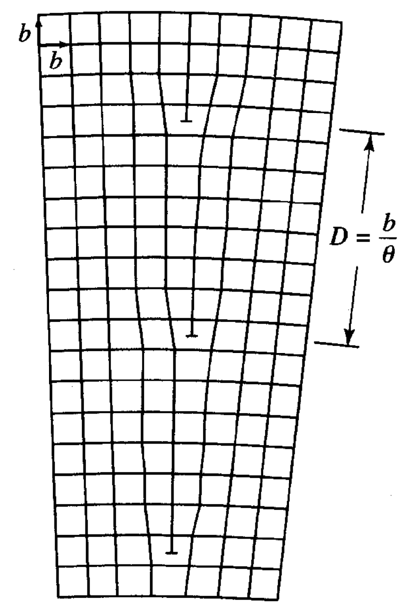
Rotation angle θ

Boundary normal $\hat{\mathbf{n}}$

Example: tilt boundary

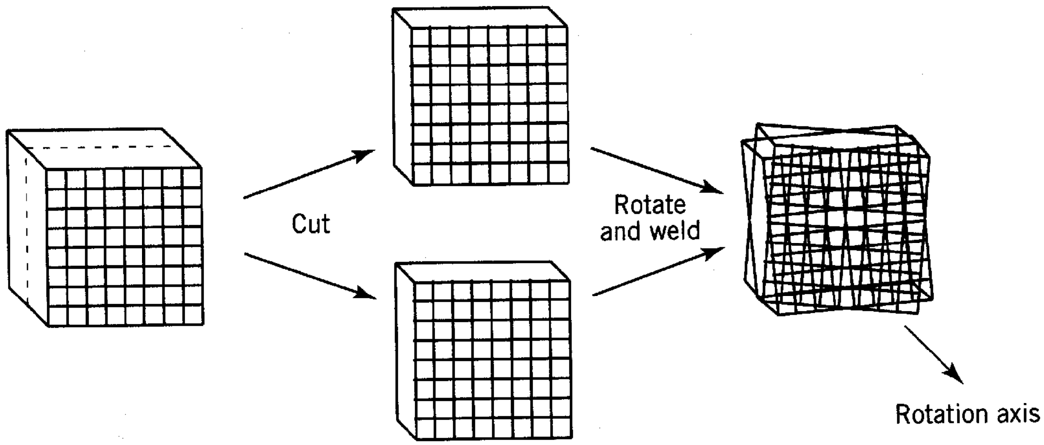


(a)

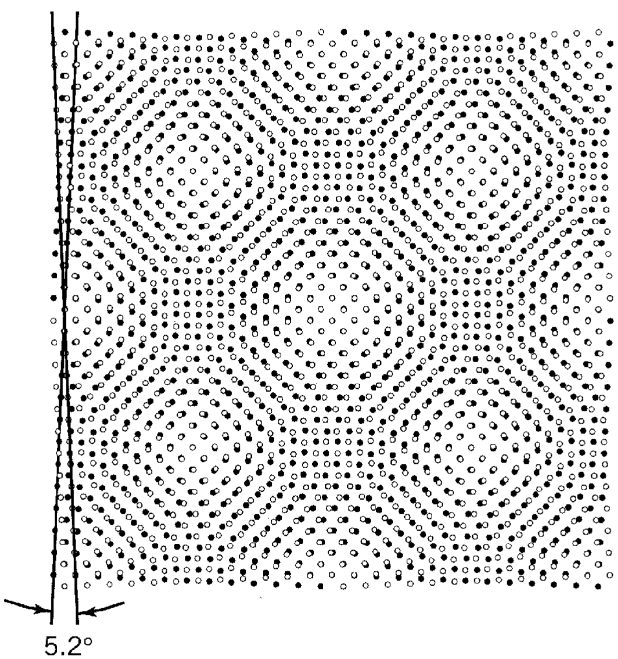


• Essentials of grain boundary structure

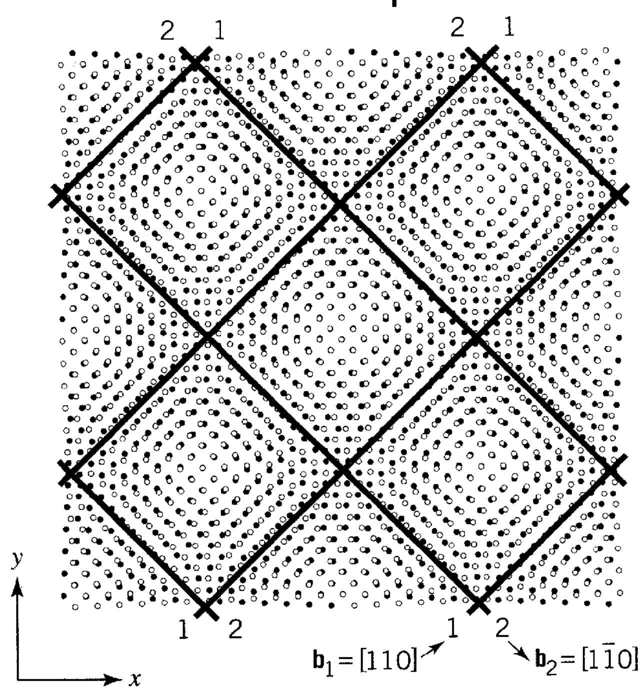
Example: twist boundary



Unrelaxed atom positions



Relaxed atom positions



- **Possible diffusion paths in polycrystals**

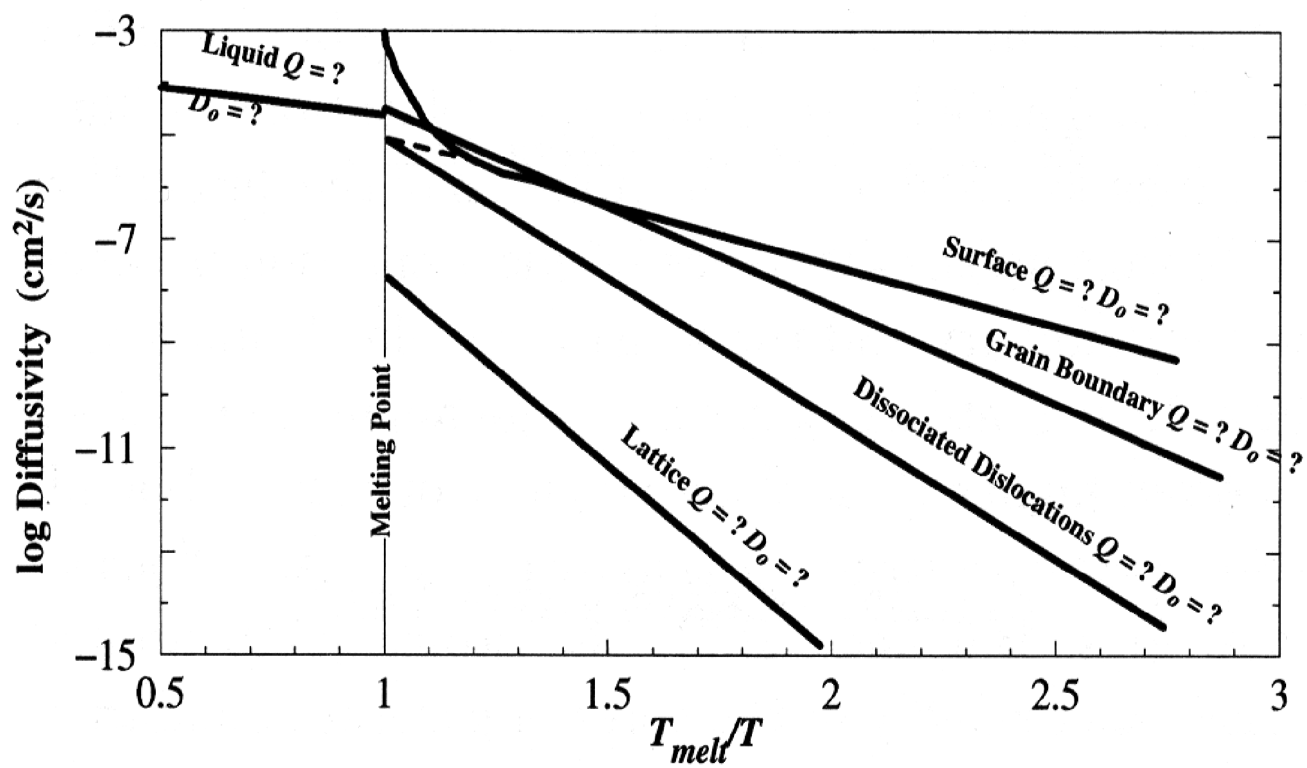
  D^{Bulk}, bulk (lattice) diffusivity

  $D^{Bound}\,\delta$, grain boundary diffusivity

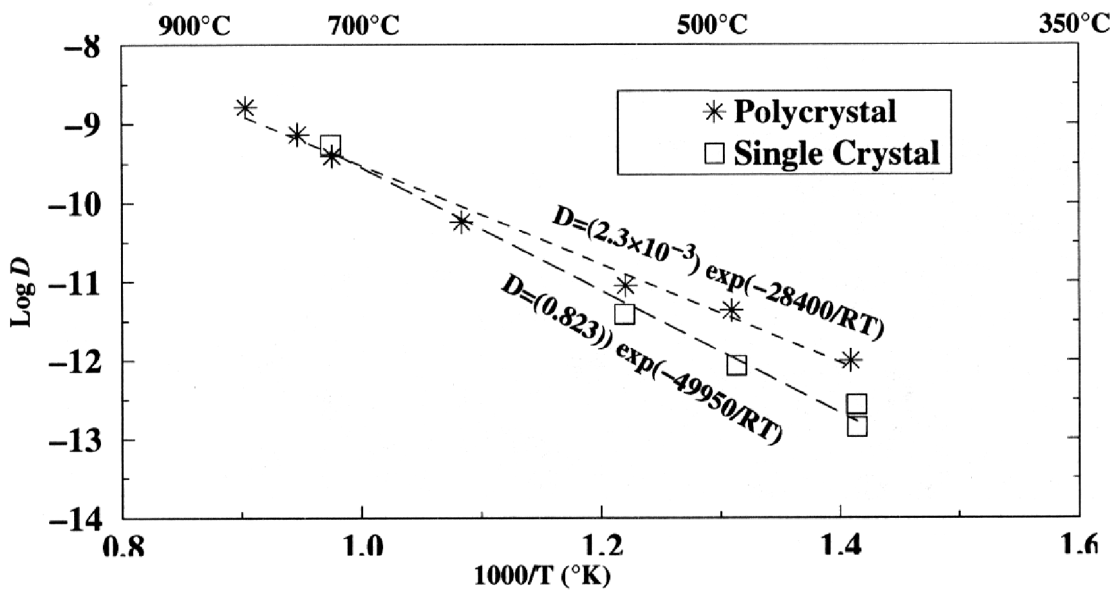
  $D^{Surf}\,\delta$, (free) surface diffusivity

  $D^{Disl}\,\delta$, dislocation diffusivity

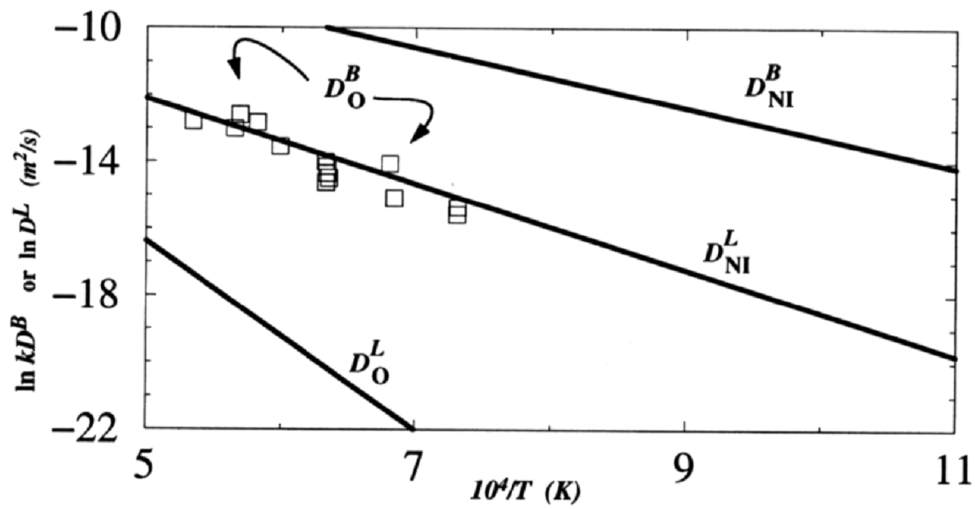
Typical behavior in fcc metals



In Silver



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



Role of grain boundary structure on impurity diffusion

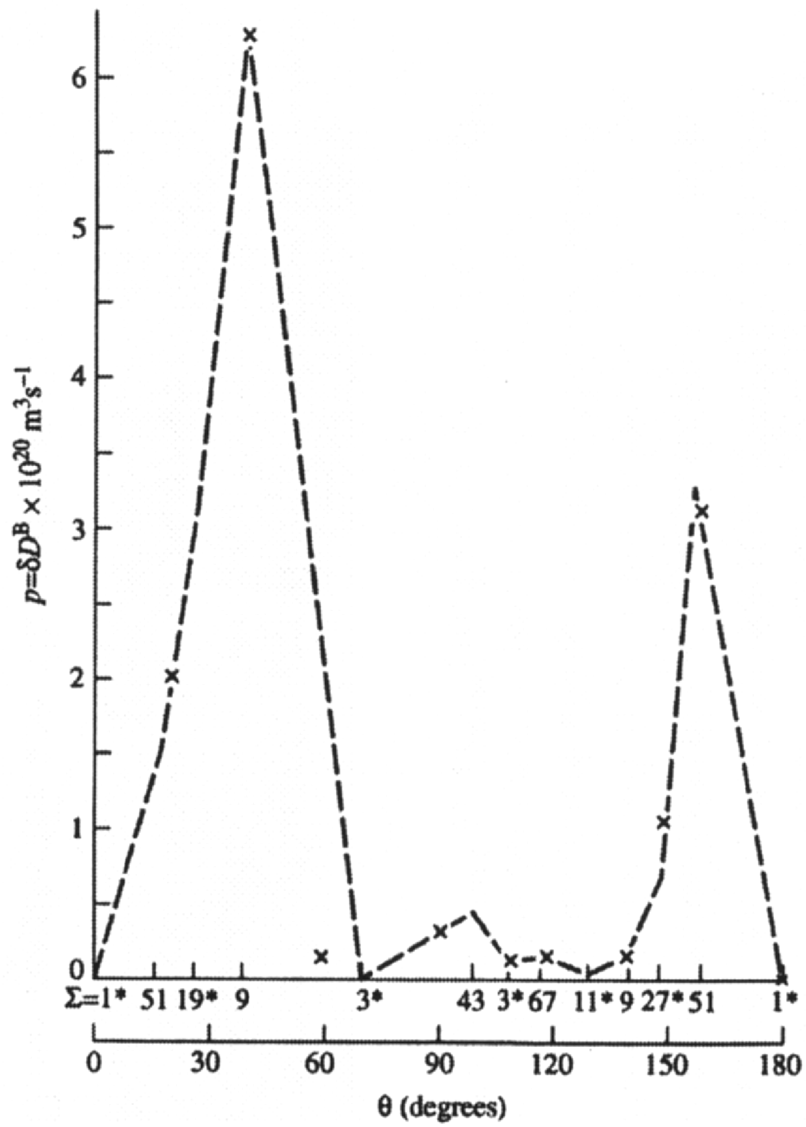
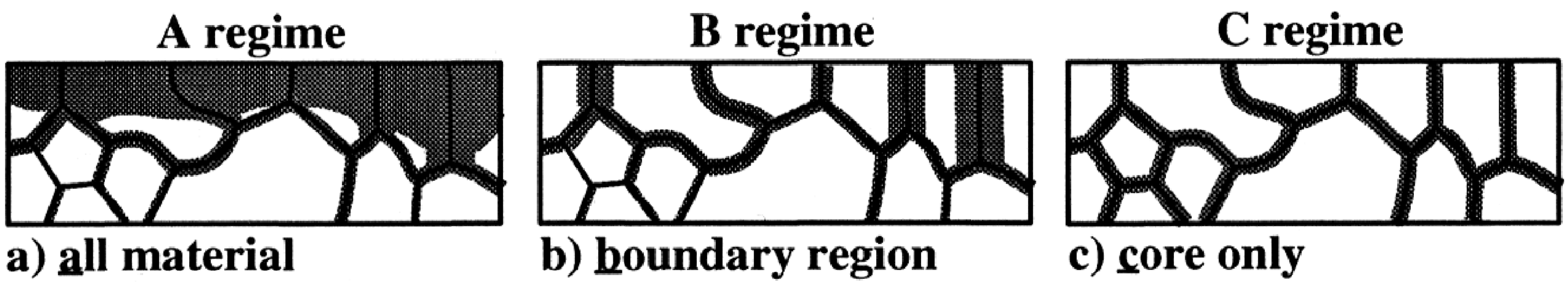


Figure 9.2 Fit of idealized structural unit model to data of Herbeuval and Biscondi (1974) for the diffusion of Zn along the tilt axes [110] symmetric tilt boundaries in Al as a function of tilt angle, θ. The delimiting boundaries chosen are indicated by aster isks, and, from left to right, are Σ1*(110), Σ19*(331), Σ3*(111), Σ11*(113), Σ27*(115), and Σ1*(001).

Regimes of grain boundary "short-circuit" diffusion for stationary boundaries

Diffusing species inititially coats top surface…



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

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

and effective mean squared displacement is $D_{eff} t = D^L (1-\eta) t + D^B \eta t$

and for $\eta << 1,\ D_{eff} = D^L + (3\delta/s) D^B$

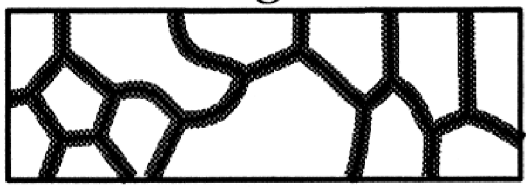
- "Multiple" because diffusing atom visits several grains

• Regimes of grain boundary "short-circuit" diffusion for stationary boundaries (continued)

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

- "Isolated" because a diffusing atom visits only the grain boundaries

C regime

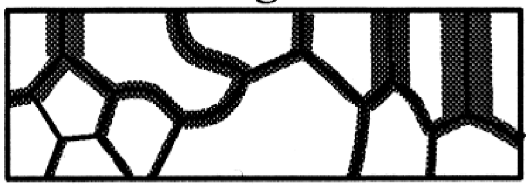


c) core only

Case B: Intermediate regime where $\lambda^2 < D^{Bulk} t < s^2$

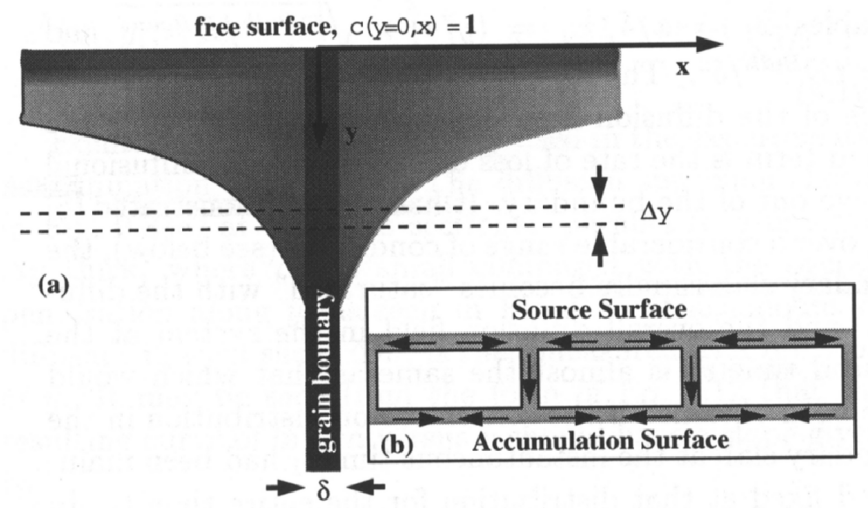
- "Isolated" because a diffusing atom visits only a single grain

B regime



b) boundary region

• Analysis of Type-B regime for Stationary Boundaries



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

$$\frac{\partial c^B}{\partial t} = \frac{\partial^2 c^B}{\partial y_1^2} + 2\left(\frac{\partial c^L}{\partial x_1}\right)_{x_1=0}$$

with $x_1 = x/\delta$, $y_1 = (y/\delta)\sqrt{D^{Bulk}/D^{Bound}}$, and $t_1 = D^{Bulk}t/\delta^2$

• Analysis of Type-B regime for Stationary Boundaries (continued)

For wide range of conditions

- g.b. acts like a source with erf solution off to the sides

$$c^L(x_1,y_1,t_1) = 0 = c^B(y_1,t_1)\left[1-\operatorname{erf}\left(\frac{x_1}{2\sqrt{t_1}}\right)\right]$$

- g.b is effectively "saturated" and steady-state solution to diffusion equation applies in the boundary

$$\frac{\partial c^B}{\partial t} = 0 = \frac{\partial^2 c^B(y_1,t_1)}{\partial y_1^2} - 2c^B(y_1,t_1)\left[\frac{\partial}{\partial x_1}\operatorname{erf}\left(\frac{x_1}{2\sqrt{t_1}}\right)\right]_{x_1=0}$$

and thus

$$c^B(y_1,t_1) = \exp\left[-\left(\frac{4}{\pi t_1}\right)^{1/4} y_1\right]$$

and so the final solution is

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

References for additional study:

KPIM Chapter 9

KPIM Appendix B, Structure of Interfaces Involving Crystalline Materials (background on structure)

Allen and Thomas, *The Structure of Materials*, 1999

Section 5.3, Surface Imperfections (background on grain boundaries, stacking faults, etc.)

R W Balluffi and A Sutton, *Interfaces in Crystalline Materials*, 1995

Chapter 8 on Diffusion at Interfaces - goes into more advanced topics than KPIM