

3.21 Kinetics of Materials—Spring 2006

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Lecture 5: Effects of Capillarity and Stress on Diffusion.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Sections 3.4–3.5.

Key Concepts

- “Capillarity” refers broadly to phenomena arising from the fact that surfaces and interfaces possess an excess free energy per unit area γ (numerically equal to surface tension for fluids). A capillary driving force arises from the tendency of surfaces and interfaces to make adjustments of position and orientation so as to minimize the total interfacial free energy.
- When γ is isotropic, a corrugated surface with linear parallel grooves will spontaneously tend to smooth so as to reduce the surface area and total surface free energy.
- When a curved surface moves normal to itself, the area change per volume swept out by the interface is $\Delta A/\Delta V = (K_1 + K_2)$, where $K_1 + K_2 \equiv \kappa$ is the sum of the principal curvatures. The product $\gamma(K_1 + K_2)$ is the driving force for capillarity-induced interfacial motion, equal to the energy change per unit volume swept out by the interface as it moves.
- The diffusion potential for a species i at a curved surface is $\Phi_i^S = \mu_i^\circ + \gamma\kappa\Omega_i$.
- *KoM* Fig. 3.7 illustrates the variation of chemical at the surface of an undulating surface and the direction of the resulting diffusion fluxes. As shown in the text, the local equilibrium concentration of vacancies depends on surface curvature (see Eq. 3.74) and the resulting fluxes determine the rate of surface smoothing.
- Stresses in solids can affect diffusion in a variety of ways, including via the mobility, its effect on diffusion potential, and via influencing the boundary conditions for diffusion.
- Even a uniform state of stress may break symmetry and cause jumps in certain directions in the material to be favored and modify the mobility (see *KoM* Eq. 3.78).
- For a crystal in a state of hydrostatic stress a “misfitting” solute atom with an excess atomic volume $\Delta\Omega_1$ will require work against pressure when it moves and causes a concentration change. This work is $dw = -P\Delta\Omega_1dc_1$ and the resulting diffusion potential is $\Phi_1 = \mu_1 + \Delta\Omega_1P$.
- In an alloy crystal in a state of nonuniform stress the solute concentration field will also be nonuniform at equilibrium in order to make the diffusion potential uniform. *KoM* Fig. 3.8 illustrates an edge dislocation and its hydrostatic stress field is given by Eq. 3.80. Such defects are common in real crystals and their interactions with solute atoms has profound effects on mechanical behavior.

Related Exercises in *Kinetics of Materials*

Review Exercise 3.8, pp. 72–73.