

Lecture 6: Other Interface–Response Functions

Interface–Controlled Growth

Consider the transfer of atoms across a grain boundary in a pure material, across a barrier of height G^* , Fig. 1. The probability of forward jumps (*i.e.* jumps which lead to a reduction in free energy) is given by

$$\exp\{-G^*/kT\}$$

whereas that of reverse jumps is given by

$$\exp\{-(G^* + \Delta G)/kT\} = \exp\{-G^*/kT\} \exp\{-\Delta G/kT\}$$

. The rate at which an interface moves is therefore given by

$$v \propto \exp\{-G^*/kT\}[1 - \exp\{-\Delta G/kT\}]$$

Note that this relation is hardly that predicted from irreversible thermodynamics. However, they become identical when ΔG is small, *i.e.* there is not a great deviation from equilibrium. Note that for small x , $\exp\{x\} \simeq 1 + x$. Thus, at small driving forces,

$$v \propto \exp\{-G^*/kT\}[\Delta G/kT]$$

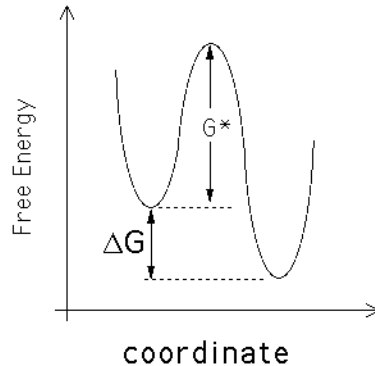


Fig. 1: Activation barrier to the transfer of atoms across a boundary.

Aziz Solute Trapping Function

An interface can move so fast that solute atoms do not have an opportunity to partition. The solute is said to be *trapped* when its chemical potential increases on transfer across the interface. When the concentration of the solute is smaller than expected from equilibrium, it is the solvent that is trapped.

Fig. 2 illustrates a transformation front between the shaded and unshaded crystals, in a binary alloy containing A (solvent) and B (solute) atoms. The smaller solute atoms prefer to be in the parent phase (γ). The atoms in the central layer have to move along the vectors indicated in order to transform into the product phase (α). δ_s is a typical diffusion jump distance for the solute atom; the motions required for the atoms in the interfacial layer to adjust to the new crystal structure are rather smaller.

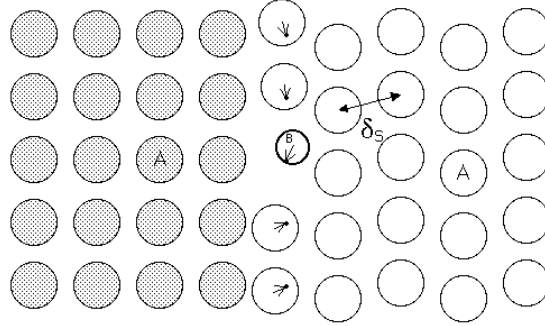


Fig. 2: Choreography of solute trapping, adapted from Aziz (1982). The solvent is labelled A , solute B and the product phase is shaded dark. The transformation front is advancing towards the right.

Solute will be trapped if the interface velocity v is greater than that at which solute atoms can diffuse away. The maximum diffusion velocity is approximately D/δ_s since δ_s is the minimum diffusion distance, so that trapping occurs when $v > D/\delta_s$. In terms of concentrations, solute is said to be trapped when the concentration $C^\alpha > C^{\alpha\gamma}$ where $C^{\alpha\gamma}$ is the concentration in α which is in equilibrium with γ and C^α is the actual concentration.

Consider now a situation where the interface is moving at a *steady rate*. Then the rate at which the solute is absorbed by α as it grows is given by

$$v(C^{\gamma\alpha} - C^\alpha) \tag{1}$$

where $C^{\gamma\alpha}$ is the concentration in γ which is in equilibrium with α . The trapping of solute is opposed by equilibrium so there will be a net flux $J^{\alpha\gamma} - J^{\gamma\alpha}$ tending to oppose trapping. Applying Fick's first law over the thickness of the interface, the flux opposing trapping is

$$J^{\alpha\gamma} - J^{\gamma\alpha} = \frac{D}{\delta_s}(C^\alpha - C^{\alpha\gamma}) \quad (2)$$

where D is the diffusion coefficient. On equating relations (1) and (2) to define the steady-state, we see that

$$v(C^{\gamma\alpha} - C^\alpha) = \frac{D}{\delta_s}(C^\alpha - C^{\alpha\gamma})$$

and writing the equilibrium partition coefficient as

$$k_e = \frac{C^{\alpha\gamma}}{C^{\gamma\alpha}}$$

we get the actual partition coefficient k_p as

$$k_p = \frac{C^\alpha}{C^{\gamma\alpha}} = \frac{\beta_p + k_e}{\beta_p + 1} \quad \text{where} \quad \beta_p = \frac{v\delta_s}{D} \quad (3)$$

This equation enables the composition of a growing phase to be estimated even when it deviates from equilibrium, as long as the velocity of the interface is known.

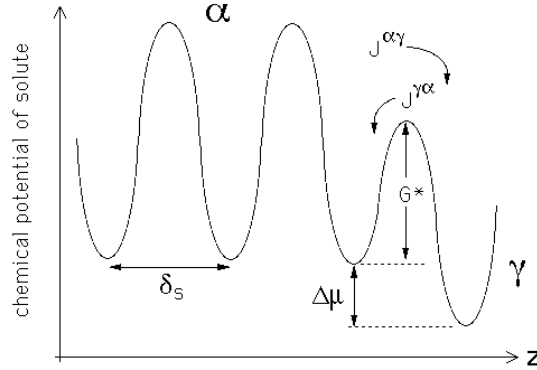


Fig. 2: An illustration of the activation energy barrier G^* for diffusion across the interface, on a plot of the chemical potential of the solute versus distance. Note that this solute potential is lowest in the parent phase γ . The increase in the solute chemical potential as it becomes trapped is $\Delta\mu = \mu^\alpha - \mu^\gamma$.

The Actual Growth Rate

We have seen that there are many processes, including diffusion, which occur in series as the particle grows. Each of these dissipates a proportion of the free energy available for transformation. For a given process, the variation in interface velocity with dissipation defines a function which is called an *interface response function*. The actual velocity of the interface depends on the simultaneous solution of all the interface response functions, a procedure which fixes the composition of the growing particle.

Fig. 3 shows an electrical analogy; the resistors in series are the hurdles to the movement of the interface. They include diffusion in the parent phase, the transfer of atoms across the interface, solute drag *etc.* The electrical-potential drop across each resistor corresponds to the free energy dissipated in each process, and the current, which is the same through each resistor, represents the interface velocity. The relationship between the current and potential is different for each resistor, but the actual current is obtained by a simultaneous solution of all such relations.

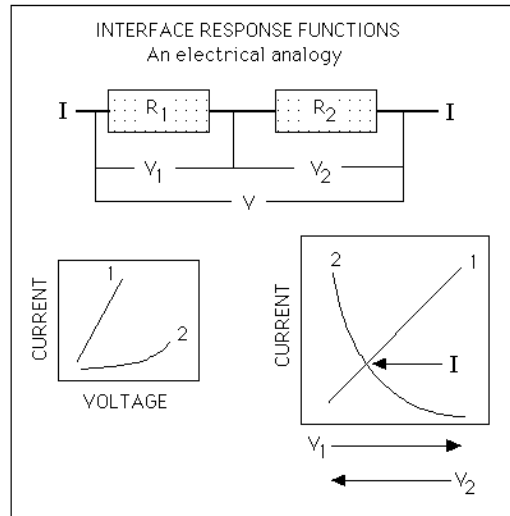


Fig. 3: Electrical analogy of dissipations due to processes which occur in series during interface motion. The resistors in series are the hurdles to the motion of the interface, the voltage the driving force and the current the interface velocity. The way in which voltage (driving force) is dissipated as a function of current (velocity) across each resistor is different. There is one interface so all processes must yield the same velocity, as indicated by the identical current passing through all the resistors.

Following on from this analogy, the available free energy can be partitioned into that dissipated in diffusion ahead of the interface, a quantity expended in the transfer of atoms across the interface, and in any other process (such as solute trapping) determining the motion of the interface.