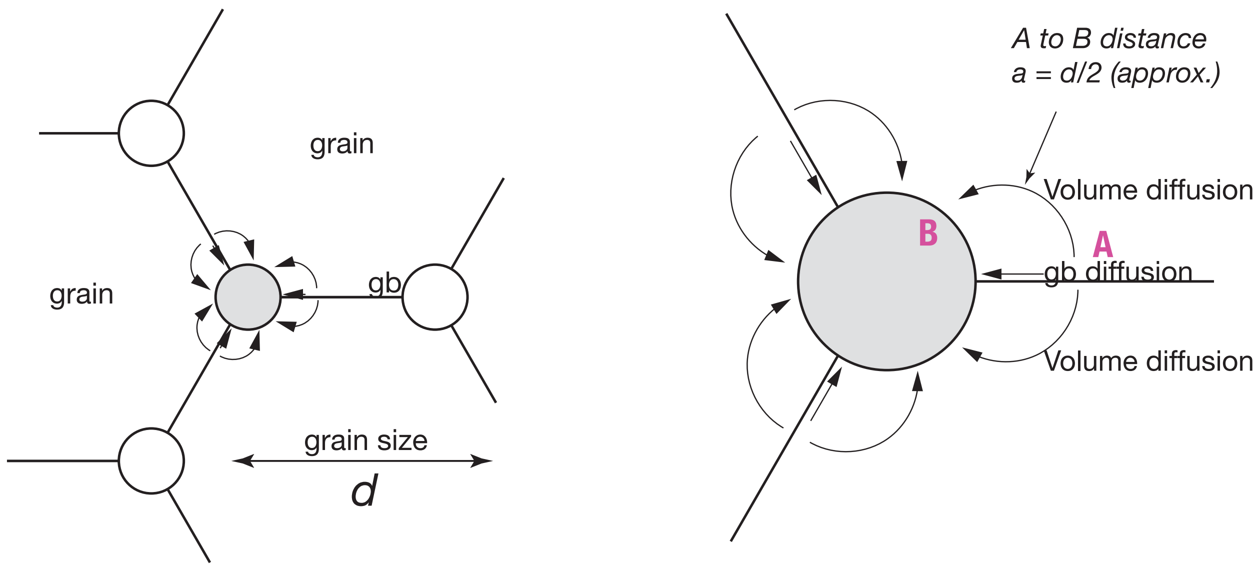
01D Solid State Diffusion

The Structure and the length scale



Length Scales

The elements of diffusional transport in the solid state can be conceptualized with a fluid mechanics example where fluid flows through a pipe with a high pressure at one end and a lower pressure at the other end. Here there are two length scales: the length of the pipe (which is equivalent to the diffusion distance - discussed below), and the cross section of the pipe. The flux is the mass flowing per unit area of the pipe cross section. The total current is the product of the flux and the cross sectional area.

The microstructural length scale

• The grain size: it describes the diffusion distance. Larger grain size will take longer to transport mass. How much longer?

• What is the cross section of diffusion? We shall consider it later.

The atomistic length scale

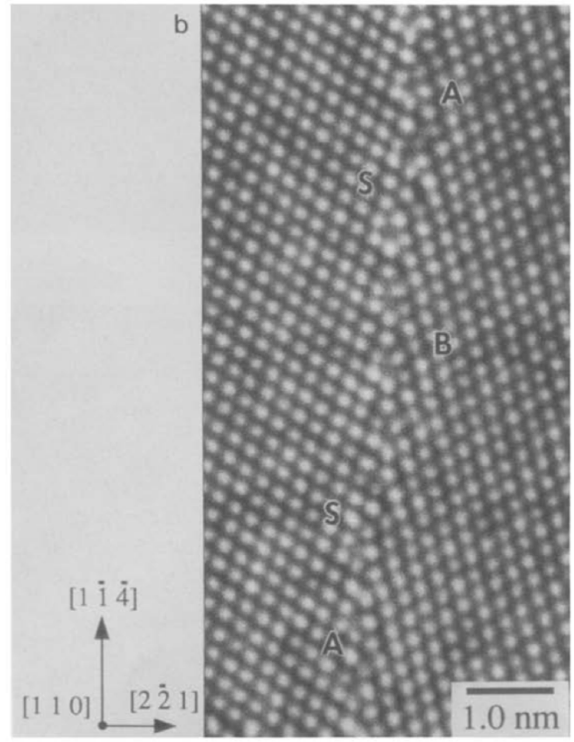
• The atomic level structure of the grain boundaries: The *grain boundaries* serve as the place were atoms begin their journey to the pores. The question is what is the peculiar nature of the atomic structure of the grain boundaries that allows it to serve as a source of atoms without coming apart, that is, serving as a source without changing its structure.

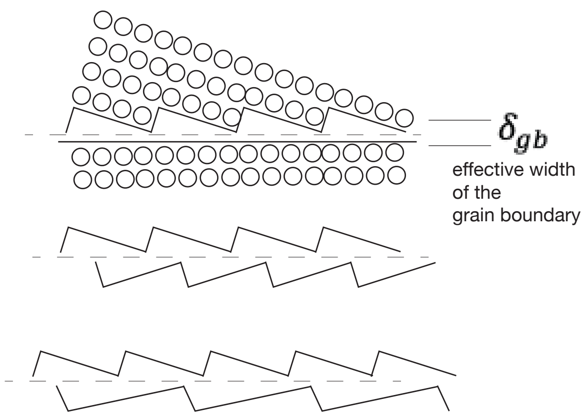
The Nature and the Structure of Grain Boundaries

A very interesting and critical property of grain boundaries emerges from their structure. The grain boundary is a plane where two crystals of different orientation meet.

The boundary is where two grains slightly misoriented with respect to one another meet. It is an interface in two dimensions. The surface of each crystal consists of ledges where the crystal planes emerge from within the crystal, as shown below.

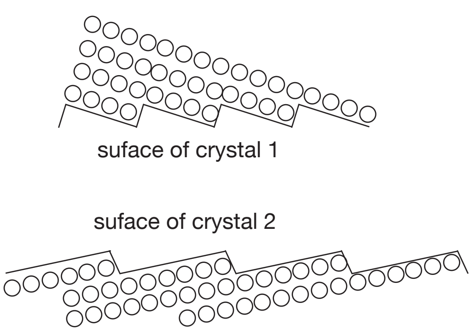
In relative orientations of the two crystals will vary from one boundary to another, but in all instances at least one of the crystals will be ledge emerging at the interface (the other crystal may have an atomically flat orientation - however if both were flat that the grain boundary vanishes and both crystals merge into one crystal.

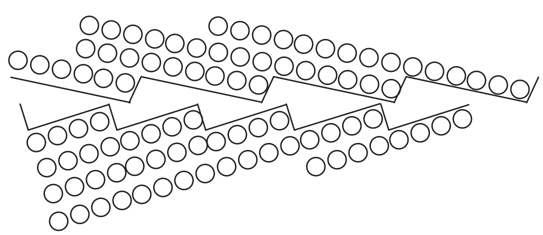




The figure on left shows two instance of grain boundary structure. In one case one of the crystal surface is flat, in the other both surfaces have ledges. Therefore, the structure of the boundaries depends on the misorientation between the grains, but no matter the boundary structure can be represented by ledges.

The following sketches show the construction of a grain boundary by bringing together the surfaces of two crystal misoriented with respect to one another.





Note that surfaces and grain boundaries have interface energies given by $\gamma_S, and, \gamma_{gb}$ respectively. Bonding between atoms across the grain boundary is reflected by $\gamma_{gb} < 2\gamma_S$. Each has units of J m^{-2}. The atoms on the surface have bonds with atoms lying below the surface. The atoms in the grain boundary form bonds both into the crystal and across to the other crystal. Therefore, the energy of the boundary is lower that that of the surface.

A general description of diffusion?

Here we are concerned with diffusion of mass in the solid state. But diffusion occurs in many physical phenomena. In each case however, we deal with a "particle" moving in jumps with the overall "diffusion" being the collective motion of several jumps.

In addition to solid state diffusion, here are some other examples of diffusion"

•**Heat transport.** Here the particles can be electrons or phonons that carry heat. A phonon is defined by lattice vibrations; it is analyzed in physics as a particle whose energy is the energy of the lattice vibration.

•**Interdiffusion of gases.** Gases can interdiffuse. Imagine two chambers with gases I and II separated by a membrane. If the membrane is remove then the gases will diffuse into one another until the composition becomes a uniform mixture of I and II. There is a practice HW problem on this point).

•**Electronic conductivity in a conductor.** Electrons carry charge which produces electrical current. The transport of electrons is stochastic, i.e. the travel some distance until they collide with another electron.

•**Viscous flow in water.** The molecules of H_2O are always moving and running into one another.

All of the above problems (including that of solid state diffusion) has the following two characteristics,

(i) There is a time between collisions, or time between successive jumps.

(ii) There is a characteristic "jump distance" (note the length scale!).

Quantitative description of diffusion

Diffusion is described by a coefficient of diffusion, D. Note that,

•We must speak of diffusion of a specific species within a specific host. For example,

Silicon crystals are doped with elements to make then into n and p type conductors. The doping is done by depositing the "dopant" on the surface. The inward diffusion of the dopant is the given by the diffusion coefficient of the dopant within the crystal of silicon. For example, the coefficient of diffusion of Al in Si or D_{Al}^{Si}

•In the sintering problem the species and the host are made of the same atoms. We call it self-diffusion, and it suffices to simply refer to it as D since the species are the same.

•The diffusion coefficients are material parameters; they are available in handbooks.

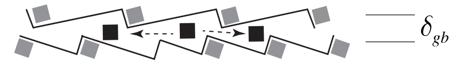
•The coefficient of diffusion, for any situation, always has units of m^2s^{-1}. It depends on the square of a length scale and time.

The time refers to the jump frequency and the length scale refers to the jump distance. These quantities were discussed in the previous section.

Atomistic Description of Diffusion

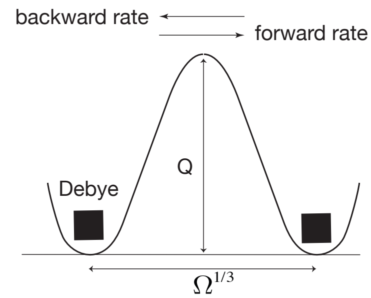
Consider diffusion of atoms within a grain boundary, as shown on the next page. Without any driving force, they move randomly back and forth. If there is a driving force (as in sintering) there is a net flux of atoms in the direction of the force.

Diffusion is characterized by the following parameters,



•The jump distance. This is typically related to the interatomic spacing. We call it

a it has units of distance. Note that $a = \Omega^{1/3}$ where Ω is the volume occupied by one atom (or molecule) in the crystal. The crystal is assumed to be packed with cubes, each cube representing one atom.



•The vibration frequency. It is the frequency at which the atom sitting at its lattice position vibrates from thermal energy. It is equal to the number of times the atom makes and attempt to jump to the adjacent lattice site. This frequency is usually called the Debye frequency, we call it

υ_D it has units of frequency (per sec). It has a typical value of 10^{13} s^{-1}.

•The energy barrier to jump to the adjacent site. We call it the activation energy

Q it has units of energy per mole $J\ mol^{-1}$, usually written as kiloJ per mol, $kJ\ mol^{-1}$

•The probability of jump is related to the thermal energy of the atom, written as RT, where R is the Gas Constant

(Probability of Jump) = $e^{-\frac{Q}{RT}}$; note that R has units of J per mol^{-1} K^{-1}, so that $\frac{Q}{RT}$ is dimensionless.

•The number of jumps per second. The number of jumps per second are given by the product of the intrinsic vibration frequency (i.e. the number of attempts to jump per second) multiplied by probability of a successful jump, that is

$\Gamma = \upsilon_D e^{-\frac{Q}{RT}}$ with units of s^{-1}

•The Coefficient of diffusion. It can be shown that the diffusion coefficient it given by

$$D = \frac{1}{4}\Gamma a^2 \qquad (1)$$

Here we are concerned with grain boundary diffusion, which occurs in two dimensions, hence the factor 4 in the denominator.

If diffusion occurs through the lattice (we call it volume diffusion) then it is replaced by 6 since atoms can now migrate in three directions.

•Expansion of Eq. (1) to diffusion on a larger scale. As you can see the diffusion involves a distance and a time as personified by its units: m^2s^{-1}.

In formal analysis of diffusion (in any of the applications that we have discussed) we would like to know how long it takes for a specific species to migrate a given distance in a specific host. That is how is the time and the effective diffusion distance related. The answer is rather simple,

In two dimensional diffusion, as in grain boundaries this relationship is

$$4Dt = L^2 \qquad (2)$$

But for diffusion in three dimensions it is

$$6Dt = L^2 \qquad (3)$$

Of course these are two different diffusion coefficients, one for boundary diffusion and the other for volume diffusion.