# 04C: Diffusion and the Deformation-Mechanism

## Overview

So far we have considered the phenomenological equation for time dependent deformation at high temperature which is given by

$$\dot{\varepsilon} = A \frac{\sigma^n}{d^p} e^{-\frac{Q}{RT}}$$

(1)

The equation represents how the strain rate ($\dot{\varepsilon}$) varies with stress ($\sigma$), the grain size ($d$), and temperature $T(\text{K})$.
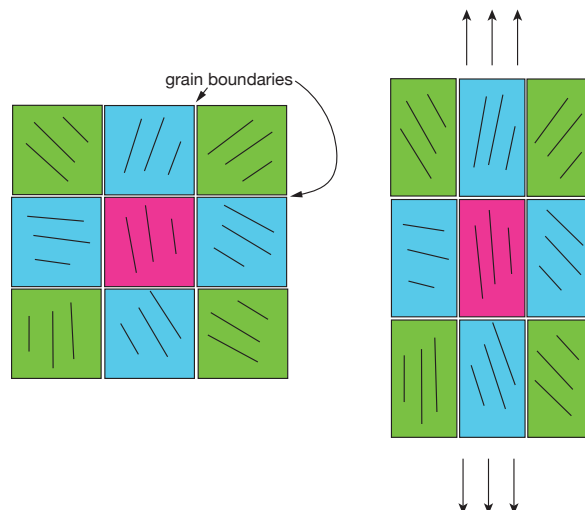
In this section (04C) we will discuss the temperature dependent activation energy term from an atomistic point of view.

The atomistic point of view recognizes that mass must be transported through the polycrystal in order to change its shape. this concept requires two elements

i.    What is the pathway (s) - in other words the geometry of the flow lines - for the transport of atoms which can accomplish a change in the shape of a polycrystal?

ii.   What is the fundamental mechanism for the movement of atoms?

# The Geometry of Flow Lines for Mass Transport to Achieve Change in Shape

The Unit Problem: Deformation of a polycrystal can be analyzed by considering the deformation of one crystal within the polycrystal as shown

The strain is one crystal, shown in red, is also the strain in the whole polycrystal, as it is measured in the laboratory. We may now consider deformation in a one crystal as a unit problem for analyzing high temperature deformation in a polycrystal.

As shown on the right when a tensile stress is applied to the crystal. The crystal can elongate in the tensile direction by the transport of atoms from the sides of the crystal to face across which the tensile stress has been applied.

The schematic on the right shows entire layers of atoms moving from the side to the top. Let us consider strain that will be produced if one atom layer were to be transported from each side face (there are four of them) of the cube to the top face (there are two of them). Let us assume that the area of each face is equal to $d^2$, where $d$ is the grain size. The change in the length of the crystal for the transport of one layer from the side to the top will be equal to $\Delta d = \Omega^{1/3}$ where $\Omega^{1/3}$ is the atom size which is equal to the thickness of one atom layer.

Therefore, the strain for the etching of one atom layer from each of the sides and plating it on the top face of the crystal would be

$$\Delta \varepsilon = \frac{\frac{4}{2}\Omega^{1/3}}{d} \qquad (2)$$

The factor of 4/2 arises because the source of the atoms are the four side faces while the atoms are plated on to just two faces.
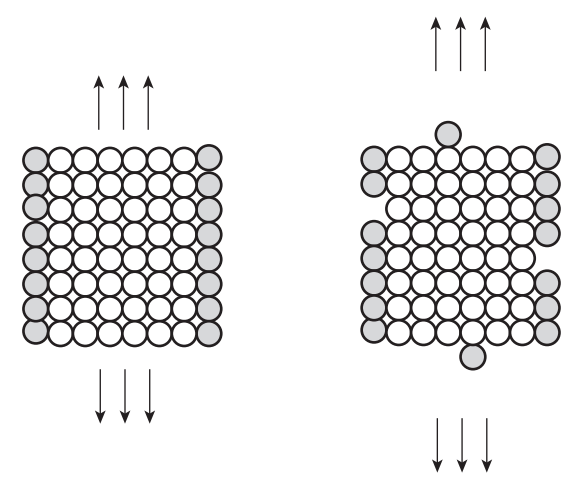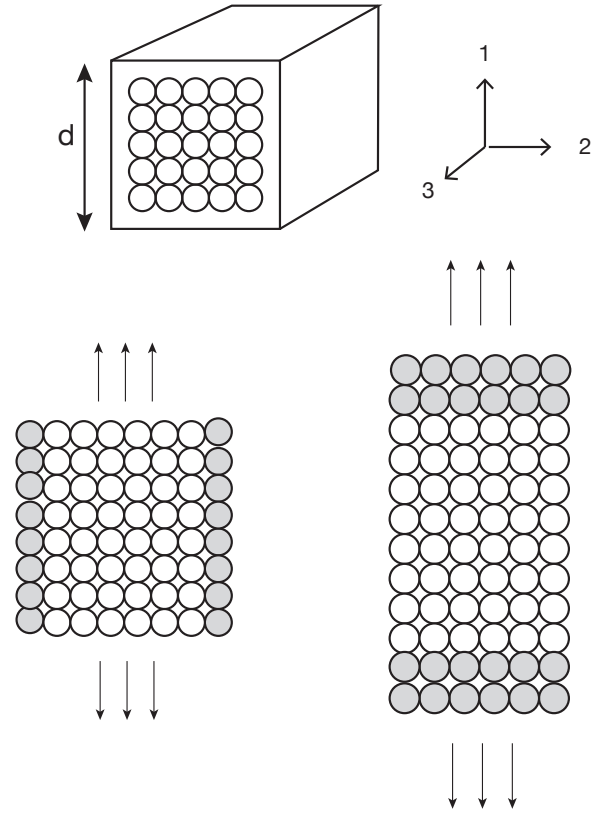
## Atom by atom transport of the layers

Now consider that atoms are transported one at a time as shown on the right, The question is what would be the strain if just one atom, instead of a whole layer is transported across the crystal

The weighting factor would be $\dfrac{\text{one atom}}{\text{number of atoms in one layer}}$

The denominator is equal to $\dfrac{d^2}{\Omega^{2/3}}$ (note that it is dimensionless)

Therefore, the weighting factor is $\dfrac{\Omega^{2/3}}{d^2}$.
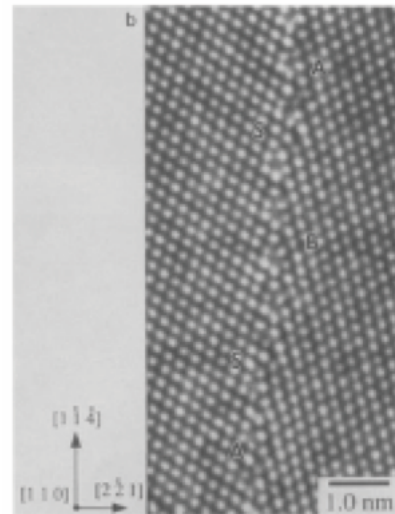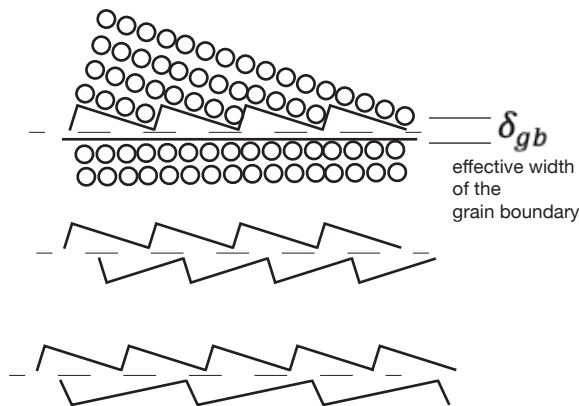
The strain in Eq. (1) now becomes

$$\Delta \varepsilon = \frac{2\Omega}{d^3} \qquad (2)$$

The quantity in Eq. (2) is the strain that would be achieved if <u>one atom</u> from each of the side faces were to be transported to the face across which the tensile stress has been applied.

# Diffusion, the Mechanism of Mass Transport

There are two fundamental issues related to the model presented just above: (i) how can atoms be etched and plated at grain boundaries, and (ii) what are the paths for the transport of atoms. The first is related to the peculiarity of the structure of grain boundaries.
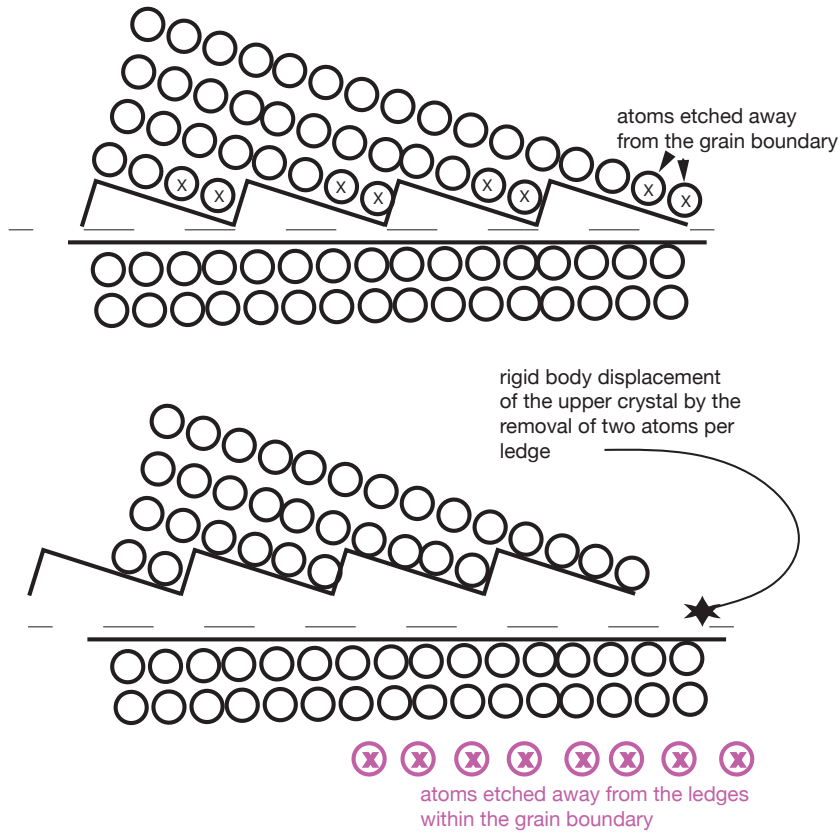
## Grain Boundaries as the Source and Sink for Atoms



The structure of grain boundaries is illustrated by the schematic on the left and the high-resolution image obtained from transmission electron microscopy on the right. Note how the crystals extend into the grain boundary in the form of ledges. While these ledges can have different configurations, in all instances they provide sites where atoms can be added or removed.
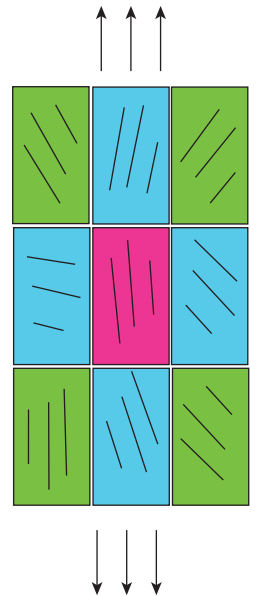
- If the atoms are added to the ledges the crystals "grow" and they move apart to accommodate this growth
- If the atoms are etched from the ledges the crystals shrink and the crystal move towards each other

The above statements are explicitly described by the schematic given below



atoms etched away
from the grain boundary

rigid body displacement
of the upper crystal by the
removal of two atoms per
ledge

atoms etched away from the ledges
within the grain boundary

In this schematic, atoms marked by a cross are etched out of the grain boundary (and transported to the transverse boundary). This removal of these atoms is then accommodated by the two crystals moving closer to one another. The opposite would happen if atoms were to be inserted into the grain boundary - that would cause the crystal to move apart by rigid body motion.
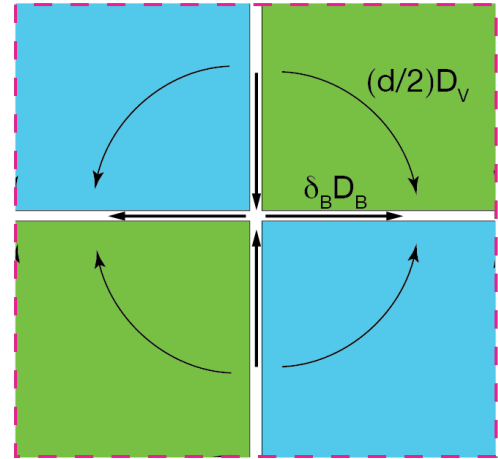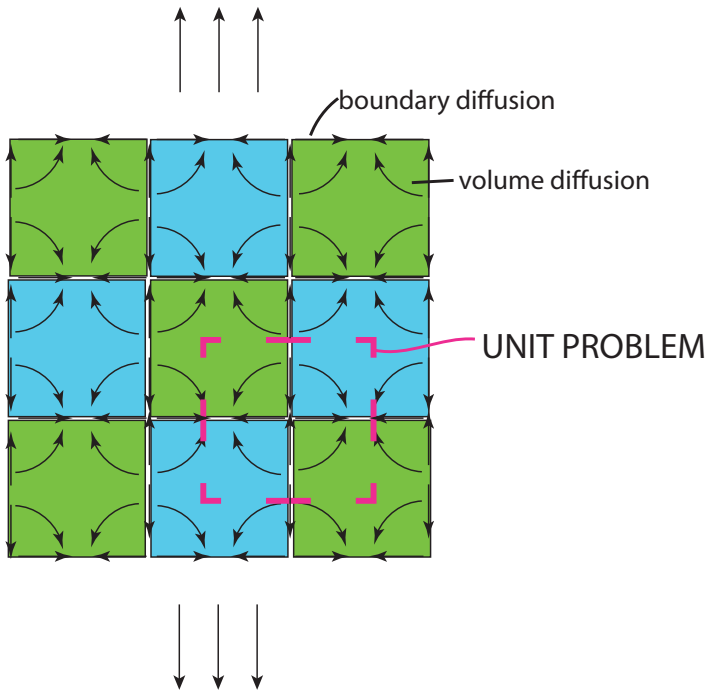
It should now be self-evident how the crystals can shrink in the lateral direction and grow in the transverse direction (in the direction of the applied tensile stress) by the etching and plating of atoms as described above.

# Grain Boundary and Lattice (or Volume) Diffusion

Mass transported across the crystal by atom jumps, also called solid-state diffusion (sometimes called self-diffusion to distinguish it from transport of impurity atoms - as for example in doping of silicon).

The flow lines for atom transport can travel though the matrix of the crystal or along the grain boundaries as shown below

In three dimensions
$(d/2) \delta_B D_B$
$(d/2)(d/2)D_V$

Therefore, there are two paths for mass transport: (i) volume diffusion through the crystal matrix, and (ii) grain boundary diffusion through the crystal matrix. They are given the nomenclature:

$D_V$ and $D_B$

They have units of $\mathrm{m^2 s^{-1}}$, that is, length squared per second.
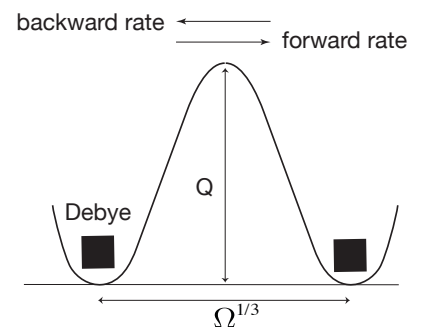
# The Diffusion Mechanism

Let us consider the boundary diffusion mechanism (similar ideas apply for volume diffusion, but that is deferred for the present).

Diffusion involves three essential features:



i.   Each jump occurs in some unit of time, we call it the jump frequency: it is described as $\Gamma$ jumps per second.

ii.  The jump is discreet; it spans a distance that is approximately equal to the interatomic distance $a \approx \Omega^{1/3}$

iii. In the absence of a "driving force" the atoms make jumps in random directions as shown below

Note that the atom jumps have to overcome an energy barrier; this is described as an activation energy, $Q$ and the jump frequency is written as

$$\Gamma = v e^{-\frac{Q}{RT}} \qquad (3)$$

The concept here is that the atoms vibrate in place (that is in their native position) with a frequency $v$ s$^{-1}$, while the probability of an "atom jump" is equal to thus native frequency multiplied by the probability of overcoming the activation barrier given by $e^{-\frac{Q}{RT}}$.

Without going through the formal analysis, it can be shown that the coefficient of diffusion for mass transport in the solid-state is given by

$$D = \frac{1}{6}\Gamma a^2 \qquad (4)$$

•The factor of 6 comes from the three-dimensional possibilities of diffusion, that is, the jump is equally probable in six directions.

•Note that the units for the diffusion coefficient are m$^2$s$^{-1}$, or early on in CGS units cm$^2$s$^{-1}$.

$^a$The diffusion coefficient may not be expressed as

$$D = D_o e^{-\frac{Q}{RT}}, \text{ where } D_o = \frac{1}{6}v a^2 \qquad (5)$$

Approximately it the pre-exponential has a value of about 1 cm$^2$s$^{-1}$ or $10^{-4}$ m$^2$s$^{-1}$.

The form of the diffusion coefficient is the same for volume or boundary diffusion so that we can write

$$D_B = D_{OB} e^{-\frac{Q_B}{RT}} \quad \text{and} \quad D_V = D_{OV} e^{-\frac{Q_V}{RT}} \qquad (6)$$

Note that the activation energy for boundary diffusion is different than the activation energy for volume diffusion.

It is perhaps "intuitively obvious" that $Q_B < Q_V$

In fact, in metals the following empirical relationship is found

$$Q_B \approx 0.6 Q_V \qquad (7)$$

## Additive Nature of Volume and Boundary Diffusion

$$\dot{\varepsilon} = f_V(\sigma, d, D_{OV}) e^{-\frac{Q_V}{RT}} + f_B(\sigma, d, D_{OB}) e^{-\frac{Q_B}{RT}} \qquad (8)$$
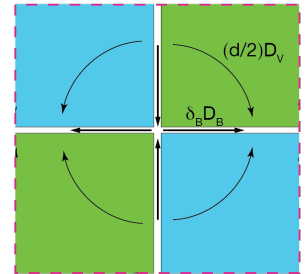
The key feature of the strain rate equation (Eq. 1) is that the activation energy in that equation is specifically related to the coefficient of solid-state diffusion since the temperature dependence of the strain rate equation can only be related to the

coefficient of solid-state diffusion (again recall the separation of variables in the strain rate equation in stress dependent term, grain size dependent term and temperature dependent term).

## Dominance of Grain Boundary and Volume Diffusion in the Temperature Regime

We take note from the figure above, which is repeated here on the right that volume and boundary diffusion are additive mechanisms for the strain rate since they are parallel paths for diffusion.



In three dimensions
(d/2) $\delta_B D_B$
(d/2)(d/2)$D_V$

The interesting point is that the difference in the activation energy for these two diffusion paths (the activation energy is lower for boundary diffusion) leads to the interesting result that is displayed in the Arrhenius plot that shows both terms
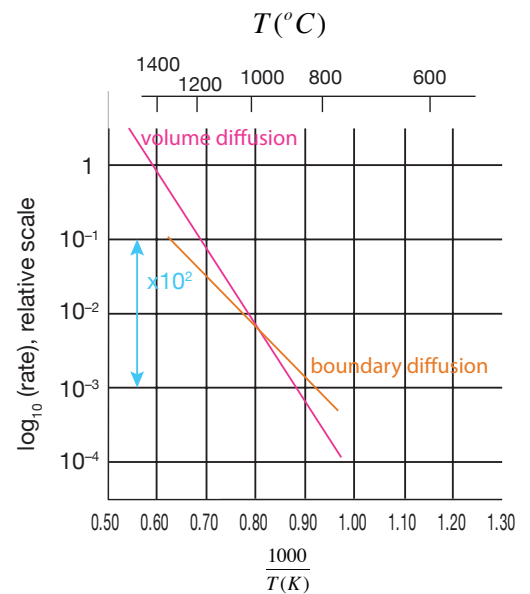
In the Arrhenius plots on the right, boundary diffusion is drawn with a lower slope that volume diffusion since $Q_B \approx 0.6 Q_V$.

•Note that the relative magnitudes of boundary and volume diffusion switches with temperature. At higher temperature the volume diffusion term is larger while the boundary diffusion component is larger at the lower temperature. This switch is simply graphical - it is a consequence of the lower activation energy for boundary diffusion.

•Because of the logarithmic scale the sum of the two mechanisms quickly becomes dominated by the faster mechanism, that is the sum is essentially equal to the rate from the faster mechanism.



As we shall see experimental data for the strain rate plotted Arrheniusly may show this transition which helps to distinguish between the volume and boundary diffusion mechanisms.

Note: As you will note from the diffusion data for copper given in Problem 04C begins to show this transition from volume to boundary diffusion at lower temperature. (Note that the strain rates and diffusion coefficients follow the same relative behavior in the Arrhenius plots because of their similar dependence on activation energy. The preexponential shifts the curves up or down but does not change their slopes. We may or may not see this transition in the plots for the strain rates since the vertical position of the lines may preclude the measurement of this transition - that is, it may be outside the regime of experimental data).