

# 04D: The Strain Rate Equation

## Overview

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

$$\dot{\epsilon} = A \frac{\sigma^n}{d^p} e^{-\frac{Q}{RT}} \quad (1)$$

The equation represents how the strain rate ( $\dot{\epsilon}$ ) varies with stress ( $\sigma$ ), the grain size ( $d$ ), and temperature  $T$ (K).

In this section (04C) we will discuss the temperature dependent activation energy term from an atomistic point of view.

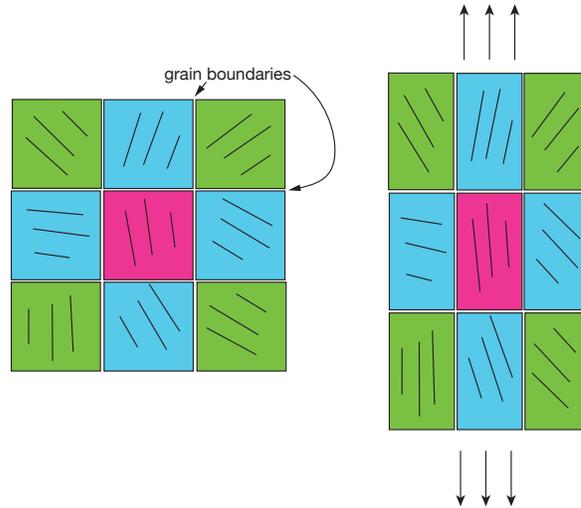
The atomistic point of view recognizes that mass must be transported through the polycrystal in order to change its shape. this concept requires two elements

In this class we will begin to derive Eq. (1) using the following elements:

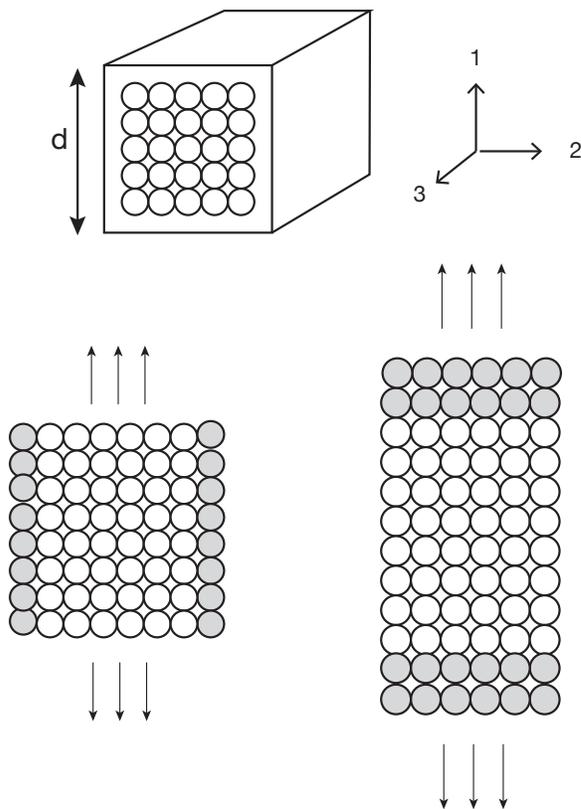
- i. The geometry of the flow lines for (a) boundary diffusion, and (b) volume diffusion
- ii. The stress induced driving force for diffusional flow - the concept of the chemical potential
- iii. The combination of the driving force and the diffusion coefficient written as the flux of mass transport, that is the number of atoms being transported per unit area
- iv. The cross section of diffusion which depends on the grain size
- v. Predictions from the strain rate equation

# From previous lecture

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



## Relationship between the transport of atoms and tensile strain



The schematic shows entire layers of atoms moving from the side to the top.

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 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

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

## 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  $\frac{\text{one atom}}{\text{number of atoms in one layer}}$

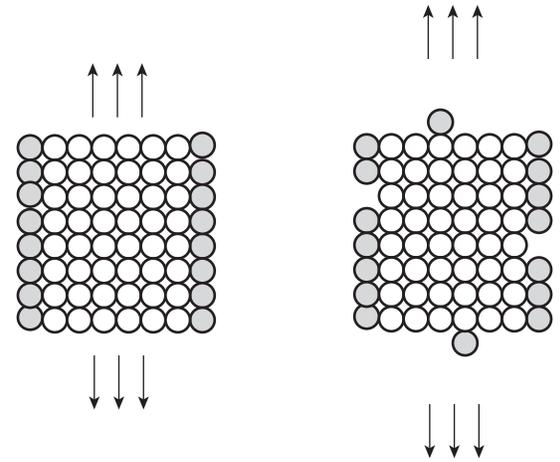
The denominator is equal to  $\frac{d^2}{\Omega^{2/3}}$  (note that it is dimensionless)

Therefore, the weighting factor is  $\frac{\Omega^{2/3}}{d^2}$ .

The strain in Eq. (1) now becomes

$$\Delta \epsilon = \frac{2\Omega^{1/3}}{d} * \frac{\Omega^{2/3}}{d^2} = \frac{2\Omega}{d^3} \quad (2)$$

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

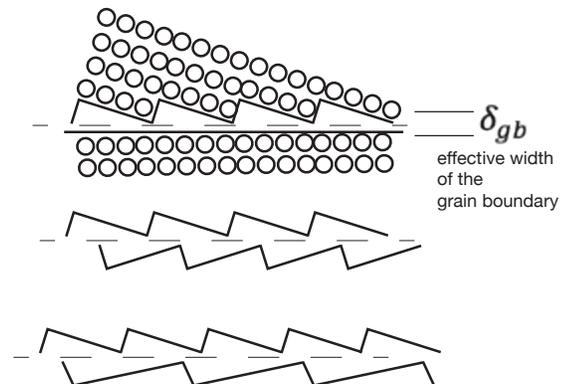


Remember that the factor of (4/2) arises because four side faces serve as the source of atoms while the atoms are plated onto two faces of the cube.

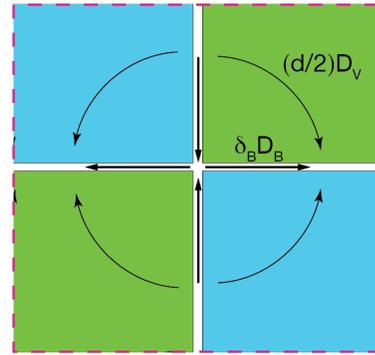
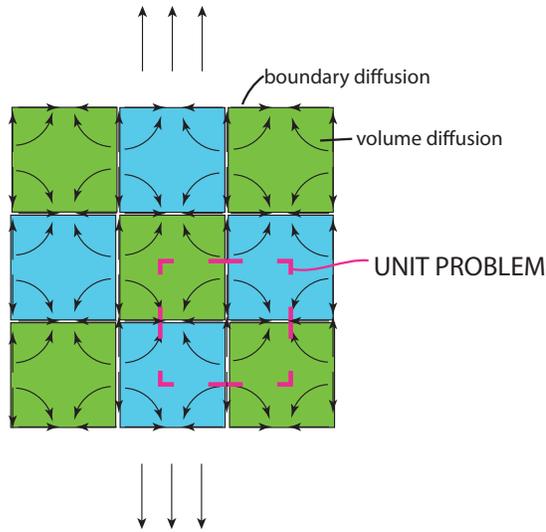
## Diffusion, the Mechanism of Mass Transport

There are two fundamental issues related to the model presented just above.

- (i) Grain Boundaries as the Source and Sink for Atoms
- (ii) Atoms are transported from the side faces of the cube to the two faces under a tensile stress by solid-state diffusion.



# Grain Boundary and Lattice (or Volume) Diffusion



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

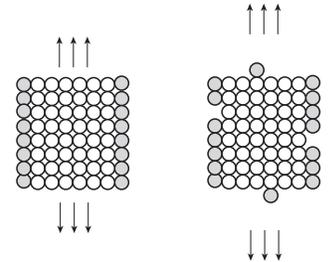
• Mass transport occurs via two parallel paths: (i) volume diffusion and (ii) grain boundary diffusion. matrix.

Note that difference between the picture just above and the description of strain from transport in an open single crystal as shown on the right.

In the polycrystal the flow of atoms from the side face is divided into two side crystals.

Therefore, the strain from the transport of one atom is actually given by Eq. (3) - not Eq. (2):

$$\Delta \epsilon = \frac{\Omega}{d^3} \quad (3)$$



## 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

(i) The jump frequency:  $\Gamma = \nu e^{-\frac{Q}{RT}}$

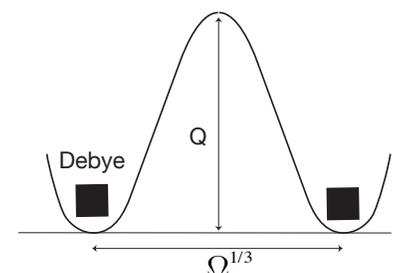
and,

(ii) the jump distance  $a \approx \Omega^{1/3}$

It can be shown that the coefficient of diffusion for mass transport in the solid-state is given by



(4) backward rate  $\leftarrow$  forward rate  $\rightarrow$



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

•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  $\text{m}^2\text{s}^{-1}$ , or early on in CGS units  $\text{cm}^2\text{s}^{-1}$ .

•The diffusion coefficient may not be expressed as

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

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

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

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

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

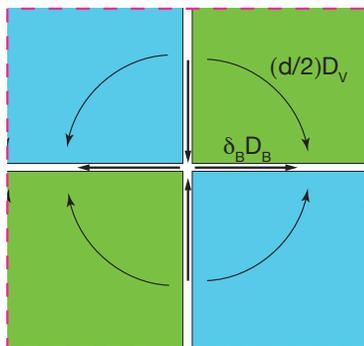
It is perhaps "intuitively obvious" that  $Q_B < Q_V$

In fact, in metals the following empirical relationship is found

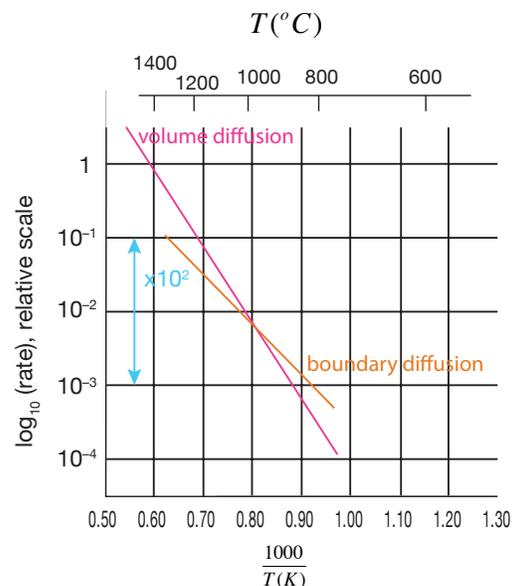
$$Q_B \approx 0.6Q_V \quad (7)$$

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

Note that volume and boundary diffusion are additive mechanisms for the strain rate since they are parallel paths for diffusion.



In three dimensions  
 (d)  $\delta_{gb} D_B$   
 (d)(d/2)  $D_V$



Let us now derive  $\dot{\epsilon} = A \frac{\sigma^n}{d^p} e^{-\frac{Q}{RT}}$

The strain rate is related to the rate of transport of atoms.

Rate Process (solid state)  $\propto$  (rate of diffusion)\*(Driving force for the transport)

A general diffusion equation for flux of atoms

(Consider a flow-in-a-pipe analogy where the flow rate, that is the mass transport is related to the pressure difference between the ends, and rate at which the atoms and move:

- the pressure difference is the driving force
- the flow rate is proportional to the viscosity of the fluid (viscosity of a liquid is related to the coefficient of diffusion)
- the geometry of the pipe - its area of cross section)

## The Driving Force

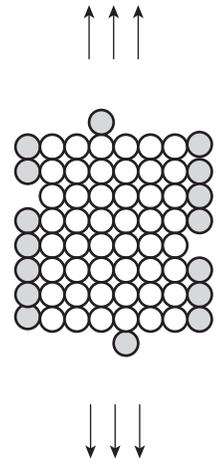
The uniaxial tensile stress  $\sigma$  somehow produces a driving force for the atoms to move from the side face (which is under zero stress) to the upper face which is under a tensile stress,  $\sigma$ .

We need to derive this driving force from thermodynamics.

Chemical potential and its gradient at the driving force for diffusion.

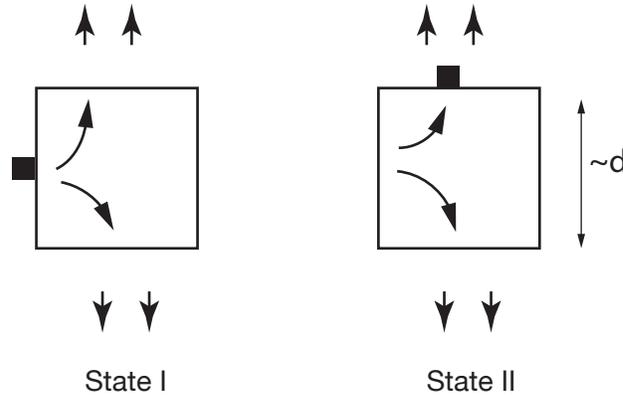
Peculiarities of chemical potential:

- We can talk about the chemical potential only of a specific species (here it is atom species of the crystal which is deforming)
- If we consider (hypothetically) that the species exists in two different states then the difference in the chemical potential of that species between these two states speaks about the amount work that is exchanged with the surroundings when that particular species is transferred from one state to the other state.
- The great usefulness of the chemical potential is that the work can be mechanical, electrical, chemical etc. etc. Thus the chemical potential is unifying approach to analyze seemingly disparate phenomena. For example in battery, the chemical potential of the Li-ion (the species) is higher at the anode than at the cathode. This difference then can be immediately related to the voltage of the battery since the work done to move the ion from the anode to the cathode = voltage difference\*electrical charge on the species).



•In another application for example consider H<sub>2</sub>O (species) in two states: as water and as ice. Chemical potentials in these two state can be written as  $\mu_{ice}^{H_2O}$  and  $\mu_{water}^{H_2O}$ . In these two states are in equilibrium then  $\mu_{ice}^{H_2O} = \mu_{water}^{H_2O}$  (which gives the melting point). If  $\mu_{ice}^{H_2O} < \mu_{water}^{H_2O}$ , then water would tend to freeze, that the work which is equal to the latent heat of fusion of water would be released to the environment (exothermic process).

In the present problem:



What is the difference in the chemical potential of "my" species between the two states?

$$\mu^{II} - \mu^I = \Delta\mu = \text{work done by the applied stress to move the atom from State I to State II}$$

$$\text{This mechanical work} = (\text{force}) * (\text{displacement}) = (\text{applied stress} * \text{area}) * (\text{one atom size}) = \sigma\Omega^{2/3} * \Omega^{1/3} = \sigma\Omega$$

It is a positive quantity because the work had been done by the environment on the system.

$$\mu^{II} - \mu^I = \Delta\mu = \sigma\Omega \quad (A)$$

The driving force is the gradient of the chemical potential, that is  $\frac{d\mu}{dx}$ .

recall that, Rate Process (solid state)  $\propto$  (rate of diffusion)\*(Driving force for the transport)

The equation for atom flux in terms of the driving force and the coefficient of diffusion is given by

$$J = \frac{D_V}{\Omega k_B T} * \frac{d\mu}{dx} \quad (B)$$

Here:

J is the atom flux (it is like the water flowing through a pipe per unit cross section area of the pipe).

Units for  $J$  are atoms  $m^{-2} s^{-1}$ . Units on the right-hand side.  $D_V$   $m^2 s^{-1}$ ,  $\Omega$   $m^3$ ,  $k_B T$  has units of energy per atom  $J \text{ atom}^{-1}$ ,  $dx$  is  $m$ ,  $\mu$ , chemical potential work done per atom  $J \text{ atom}^{-1}$ .

Applying these units to the right-hand side in equation (B)... $m^{-2}s^{-1}$ .

$$\mu'' - \mu' = \Delta\mu = \sigma\Omega \quad (A)$$

$$\frac{d\mu}{dx} = \frac{\Delta\mu}{d/2} \quad (B)$$

$$J = \frac{D_V}{\Omega k_B T} * \frac{d\mu}{dx} \quad (C)$$

Total number of atoms transported per second from the side faces to the top and bottom faces =  $4*(J)*(cross \text{ section for diffusion} = d^2)$

$$\phi = 4 * Jd^2 \quad (D)$$

here  $\phi$  is the number of atoms being transported as described above. The factor of 4 arises from the four side-faces contributing to the atom flux.

The strain from one atom is given by  $\frac{\Omega}{d^3}$ , therefore the strain rate from diffusive

transport of atoms under a mechanical force (expressed as chemical potential) will be given by

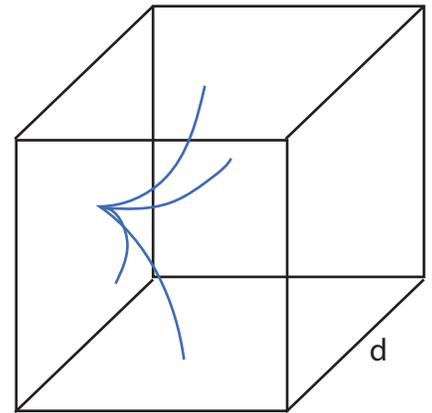
$$\dot{\epsilon} = \phi \frac{\Omega}{d^3} \quad (E)$$

$$\dot{\epsilon} = \frac{\Omega}{d^3} 4d^2 \frac{D_V}{\Omega k_B T} \frac{\sigma\Omega}{d/2}$$

$$\dot{\epsilon} = 8 \frac{\sigma\Omega}{k_B T} \frac{D_V}{d^2} \quad (F)$$

Check the units. LHS is  $s^{-1}$ . As does the RHS since  $\frac{\sigma\Omega}{k_B T}$  is dimensionless and  $D_V$  has units of  $m^2s^{-1}$

The exact result is given by  $\dot{\epsilon} = 14 \frac{\sigma\Omega}{k_B T} \frac{D_V}{d^2}$ , which is within a factor of 2 of the approximate derivation.



# Boundary Diffusion?

The two mechanisms of transport, volume diffusion and boundary diffusion, act in parallel, that is they add together to give the total strain rate.

The equivalence between volume and boundary diffusion is related to

- i. The rate of diffusion, that is,  $D_B$  versus  $D_V$
- ii. Cross section for volume and boundary diffusion. The cross-section for volume diffusion was  $d^2$ , and the cross section for boundary diffusion will be  $\delta_{gb}d$

Therefore, the relative flux by boundary versus volume diffusion will be given by

$$\delta_{gb}dD_B \text{ versus } d^2D_V$$

(that the equivalence is the product of the diffusion mechanism multiplied by the cross for diffusion for that mechanism)

Therefore to obtain the equation for the strain rate by boundary diffusion replace  $D_V$  by  $\frac{\delta_{gb}dD_B}{d^2} \equiv D_V$

Replace  $D_V$  by  $\frac{\delta_{gb}}{d}D_B$

$$\dot{\epsilon}_B = 8 \frac{\sigma\Omega}{k_B T} \frac{1}{d^2} \frac{\delta_{gb}D_B}{d} = \dot{\epsilon}_B = 8 \frac{\sigma\Omega}{k_B T} \frac{\delta_{gb}D_B}{d^3}; \text{ Exact analysis gives: } \dot{\epsilon}_B = 8\pi \frac{\sigma\Omega}{k_B T} \frac{\delta_{gb}D_B}{d^3}$$

The total strain rate is then the sum of volume and boundary

$$\begin{aligned} \dot{\epsilon}_{tot} &= 8 \frac{\sigma\Omega}{k_B T} \left( \frac{D_V}{d^2} + \frac{\delta_{gb}D_B}{d^3} \right) \\ &= 8 \frac{\sigma\Omega}{k_B T} \frac{D_V}{d^2} \left( 1 + \frac{\delta_{gb}D_B}{dD_V} \right) \end{aligned} \quad (G)$$

Predictions:

- the "n" value in the original equation is predicted to be 1
- The grain size dependence is different for volume and boundary diffusion
- Since the activation energy for boundary diffusion is lower we expect the boundary diffusion mechanism to be dominant at lower temperatures.

THE PREDICTIONS CAN BE VALIDATED BY EXPERIMENTS SINCE THE CONTROL VARIABLES IN EQ. (G) CAN BE SEPARATED EXPERIMENTALLY. FOR EXAMPLE, THE INFLUENCE OF GRAIN SIZE CAN BE INVESTIGATED BY HOLDING T AND  $\sigma$  CONSTANT AND VARYING THE GRAIN SIZE.

