

# Lecture Notes from Monday 04/22/2020

## Hi-Temp

### Topics

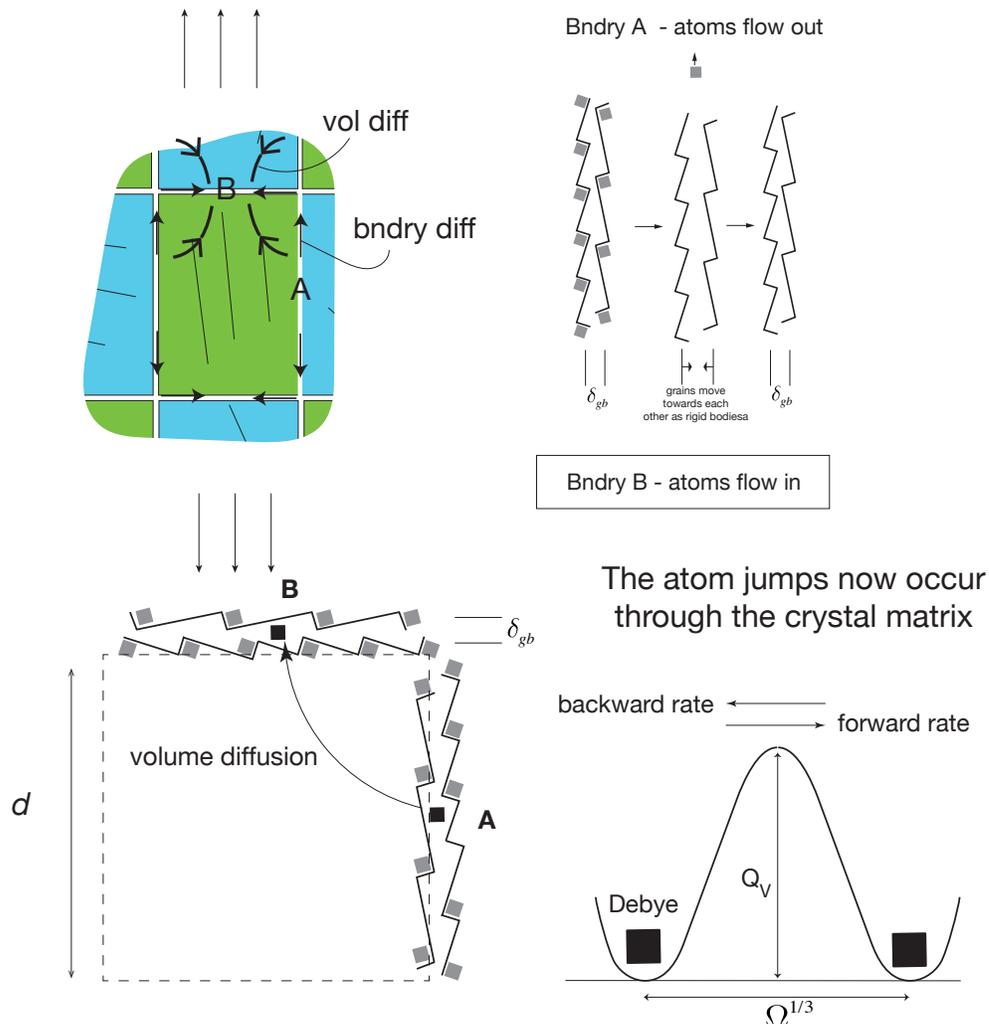
- (i) The mechanism for Volume Diffusion
- (ii) The Coefficient of Volume Diffusion
- (iii) Strain rate by Volume Diffusion

### (i) The Mechanism of Volume diffusion

Notable differences between boundary and lattice diffusion

(i) The coefficient for volume diffusion will be slower since it is more difficult for atoms to make jumps since the atoms are tightly packed within the crystal. The activation barrier to diffusion will be greater in volume diffusion.

Diffusion Transport by "Volume Diffusion"  
that is, by diffusion through the grain matrix crystal

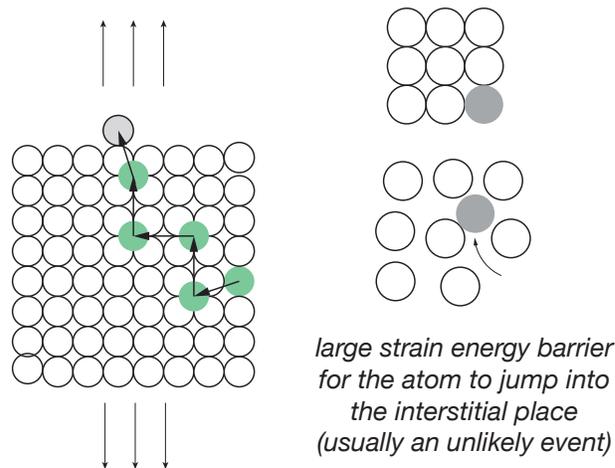


(ii) The cross section for boundary diffusion was determined by the effective width of the grain boundary, i.e.  $\delta_{gb}$ , while the cross section for volume diffusion is much greater and determined by the grain size,  $d$ . The total cross section for diffusion taking into account the perpendicular dimension will be  $\delta_{gb}d$  and  $d^2$ , for boundary and volume diffusion.

## (ii) The Coefficient of Volume Diffusion

The derivation for the coefficient of volume diffusion

$$D_V \text{ m}^2\text{s}^{-1}$$



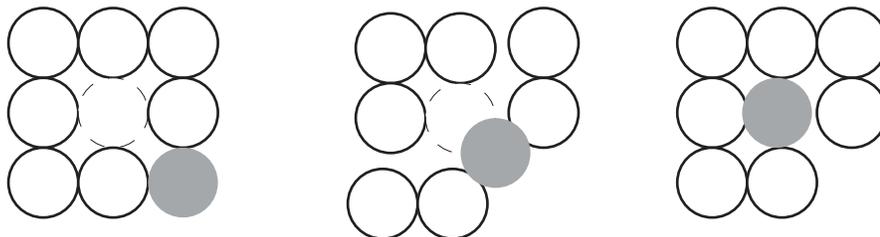
is similar to the case of boundary diffusion except for the activation barrier for atom jumps, which as shown above is very large.

Crystals contain within them vacant sites that exist in thermodynamic equilibrium (stabilized by their entropy). The equilibrium concentration of vacancies is given by

$$x_{vac} = e^{-\frac{\Delta H_{vac}}{RT}}$$

where  $x_{vac}$  is the molar concentration of vacancies, and  $\Delta H_{vac}$  is the enthalpy of formation of vacancies (per mole)

It is easier for atoms to jump into an adjacent vacancy



However, the jumps become possible if the atom can jump into an adjacent atom site which is vacant (occupied by a vacancy). Therefore the coefficient of volume diffusion is described by

$$D_V = D_V^0 e^{-\frac{Q_{vac}}{RT}} x_v$$

The exponential term is the probability of an atom being able to jump into an adjacent vacant site, and  $x_v$ , equal to the molar concentration of vacancies, is the probability of finding a vacancy next to the atom which makes the jump.

The Equation above can be expressed as

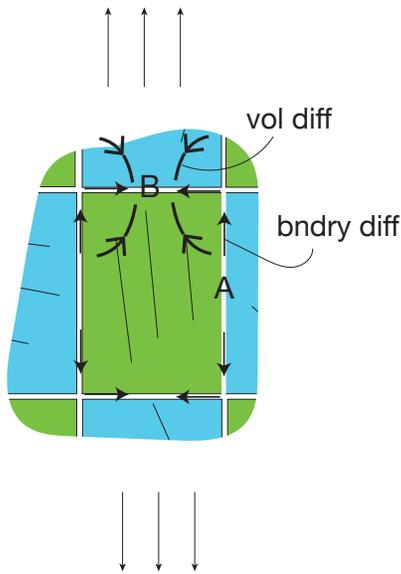
$$D_V = D_V^0 e^{-\frac{Q_V}{RT}}$$

Where

$$Q_V = Q_{vac} + \Delta H_{vac}$$

For our purposes the phenomenological equation above is enough.

### (iii) Strain Rate by Volume diffusion



As seen on the left there are two pathways to transport atoms from face B to face A: (i) boundary diffusion travelling through the thickness of the boundary, and (ii) lattice or volume diffusion where mass travel through the crystalline grain matrix.

Other than the above distinction between the boundary diffusion and volume diffusion mechanisms, the physics of diffusion induced strain rate is the same.

So, we ask what will change in the strain rate equation we had derived for the boundary diffusion case, which is repeated below

$$\dot{\epsilon}_{gb} = 4 \frac{\sigma \Omega}{k_B T} \frac{\delta_{gb} D_{gb}}{d^3} \quad (22.1)$$

It is now "intuitively obvious" that the main difference between the two pathways is the magnitude of the coefficient of diffusion, differentiated by  $D_{gb}$  and  $D_V$ , and, also by the cross section available to the flux of atoms from A face to the B face. This cross section for boundary diffusion is the slab of the interface layer with a cross section of  $\delta_{gb} d$ , where the boundary width is shown in the figure and  $d$  is the broadside of the slab, normal to the plane of the paper.

The cross section for volume diffusion is given, approximately, by  $\frac{d}{2}$ ,

where  $d/2$  is the approximate scale seen in the figure and  $d$  as for the case of boundary diffusion is the other dimension of the cross section normal to the plane of the paper.

We may now draw an equivalence between the boundary and volume diffusion mechanisms by taking the product of the coefficient of diffusion and the cross section of diffusion. The argument is that the diffusion flux is given by

$$J = \frac{D_{gb}}{\Omega k_B T} \frac{d\Delta\mu}{dx}$$

It is proportional to the coefficient of diffusion, and the total transport is equal to the product of the flux and the cross sectional area for diffusion. Therefore we assert that

$\delta_{gb} dD_{gb}$  for boundary diffusion is equivalent to

$\frac{d}{2} dD_v$  for volume diffusion.

Therefore the strain rate for volume diffusion can be drawn from Eq. (22.2) just above by making this substitution

$$\dot{\epsilon}_v = 4 \frac{\sigma \Omega}{k_B T} \frac{\delta_{gb} D_{gb}}{d^3} \cdot \frac{\frac{d}{2} dD_v}{\delta_{gb} dD_{gb}}$$

With the final result that

$$\dot{\epsilon}_v = 2 \frac{\sigma \Omega}{k_B T} \frac{D_v}{d^2}. \quad (22.2)$$

A comparison between the equation for boundary diffusion and volume diffusion predicts that

- (i) The activation energy for diffusion will change
- (ii) The linear relationship between stress and strain rate is retained
- (iii) The boundary diffusion mechanism is more sensitive to the grain size ( $d^{-3}$ ) than the volume diffusion mechanism ( $d^{-2}$ )

Equations (22.1) and (22.2) can be used to anticipate how the dominant mechanism will change with temperature and the grain size. This effect can be seen by plotting the log of the strain rate against  $(1/T)$  – an Arrhenius plot for the two mechanisms – since volume diffusion has a significantly higher activation energy, you will find that volume diffusion will dominate at higher temperatures, and boundary diffusion will prevail at the lower temperatures.

Similarly, a plot of the log of the strain rate vs. the log of the grain size will show that the smaller grain size promotes the dominance of boundary diffusion. This is important since it asks that superplastic deformation is more likely to be viable with a small grain size.