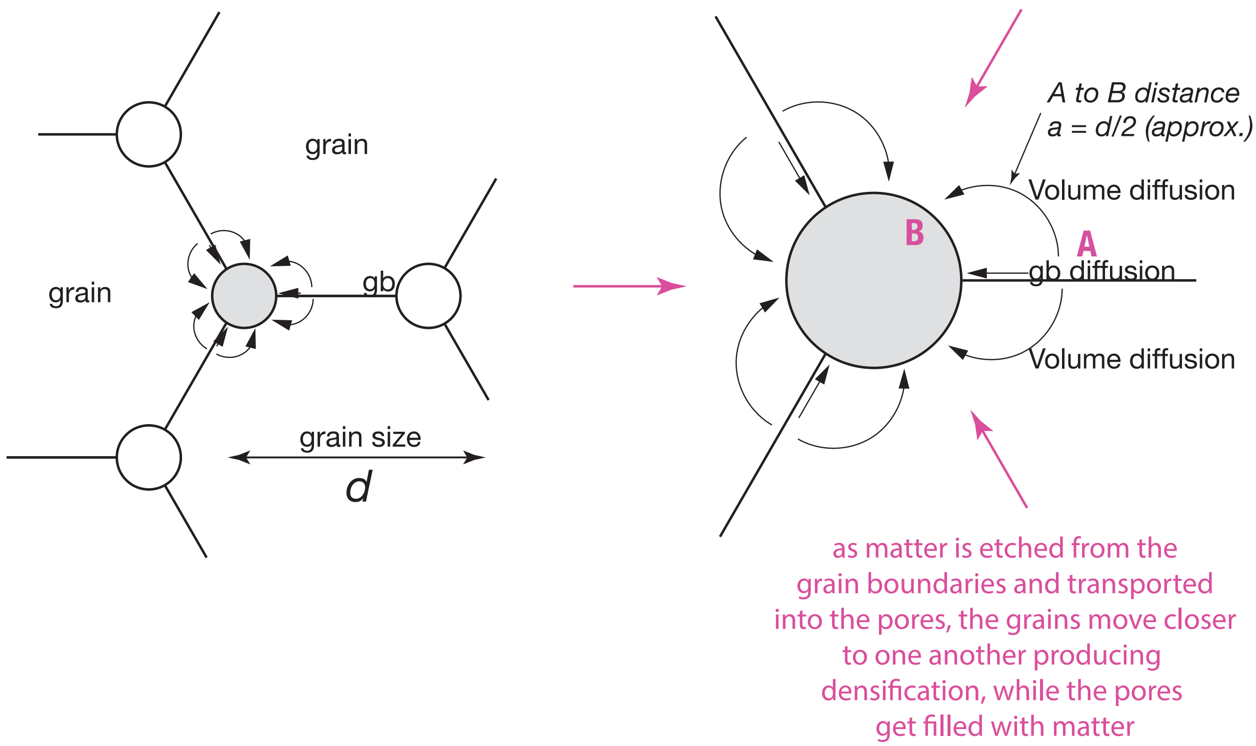
01F The Sintering Equation



•Mass from the grain boundaries can be transported simultaneously along two paths, one through the grain matrix (volume diffusion) and the other along the grain boundary.

•We shall consider the grain boundary diffusion is the dominant mechanism for mass transport.

The Method

The method is prescribed by the flow diagram shown on the next page. It begins with the prescription of the chemical potential of the species at points A and B. When divided by the distance between these points the gradient of the chemical potential is obtained, which then leads to the diffusion flux.

We must now consider the cross section for the flow of atoms across the grain boundary, which will give the number of atoms transported into the pore (after multiplying the number of grain boundaries that are feeding the pore).

Multiplying above by the volume per atom (or molecule) gives the volume of matter being fed into the pore per unit time.

Now dividing the initial pore volume by above will give the approximate sintering time.

Please note that the species here is the chemical unit that must be transported. In copper for example it is the copper atoms. However in zirconia, ZrO_2, it is the molecule ZrO_2. Therefore, Ω, will now refer to the volume per ZrO_2 molecule.

I Calculate the Gradient in the Chemical Potential between the Source, A and the sink B $\longrightarrow$

$$\frac{d\Delta\mu}{dx} = \frac{\sigma\Omega}{d/2} = \frac{\frac{2\gamma_S}{r}\Omega}{d/2}$$

next

II Calculate the flux in units of atoms transported through a unit area per unit time $\longrightarrow$

$$j = \frac{D}{\Omega k_B T}\frac{d\Delta\mu}{dx}$$

next

III Calculate the number of atoms flowing from one grain boundary into the pore $\longrightarrow$

$$N_{gb\rightarrow pore} = j * (\text{cross section of diffusion})$$

next

IV Multiply by the number of boundaries feedingn one pore (assume grains to be in the shape of cubes). Three gb aplanes are feeding one pore $\longrightarrow$

$$N_{total} = 3 * N_{gb\rightarrow pore}$$

next

V Calculate the total volume of atoms flowing into the pore per second $\longrightarrow$

$$\phi = N_{total}\Omega \; m^3 s^{-1}$$

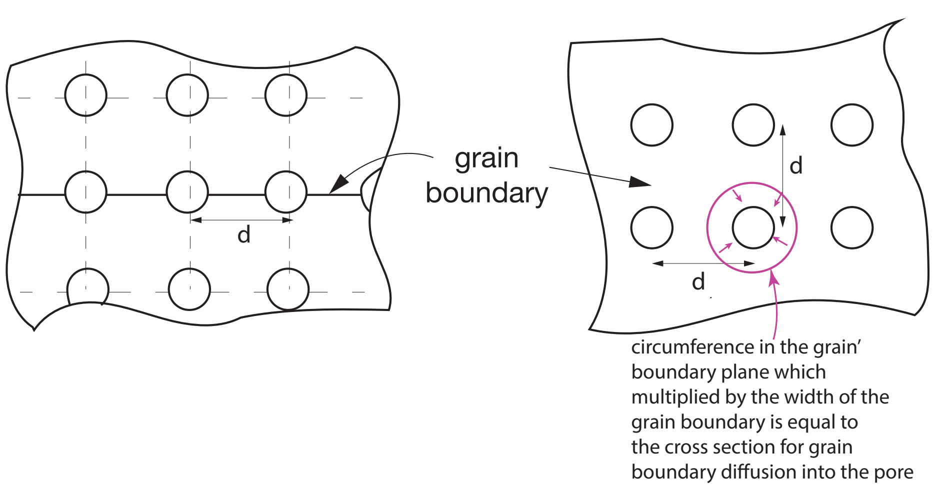
next

VI Sintering time = volume of the pore divided by the volume of mass flowing into it per second $\longrightarrow$

$$t_S = \frac{pore\ volume}{\phi}$$

Caveats:

- **We are assuming the "r" remains unchanged but it becomes smaller as the pore fills**
- **The grains are actually not cubes as assumed here**
- **The radius of curvature of the pores will scale as the grain size, therefore we may write it as being proportional to the grain size.**



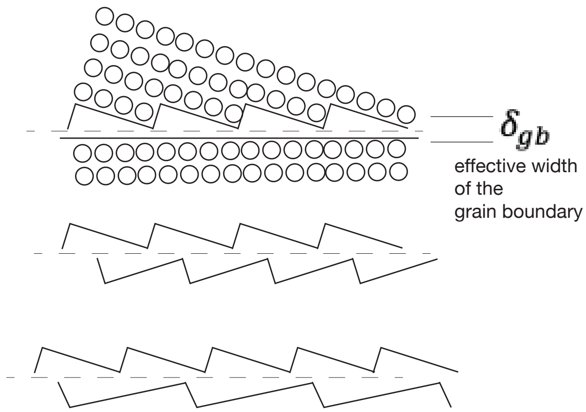
Let us now proceed with the above steps.

Cross section for diffusion in one grain boundary plane

$$\text{Cross section of one boundary feeding the pore} = 2\pi \frac{d/2}{2}\delta_{gb}$$

Number of gb planes feeding one pore: three planes.

•Here δ_{gb} is the effective width of the grain boundary as in



The volume of mass flowing into the pore per unit time is

flux*cross-section*number of boundaries feeding one pore*volume per atom or molecule), that is

$$\phi = \frac{D_{gb}}{\Omega k_B T}\frac{\frac{2\gamma_S}{r}\Omega}{d/2} * 2\pi \frac{d/2}{2}\delta_{gb} * 3 * \Omega$$ volume of mass flowing into the pore per second

therefore the time for sintering

$$t_S = \frac{\text{Pore volume}}{\phi}$$ seconds

Pore volume$=\frac{4}{3}\pi r^3$

$$t_S = \frac{4}{3}\pi r^3 \frac{1}{\frac{D_{gb}}{\Omega k_B T}\frac{\frac{2\gamma_S}{r}\Omega}{d/2} * 2\pi \frac{d/2}{2}\delta_{gb} * 3 * \Omega} = \frac{2}{9} r^4 \frac{k_B T}{\delta_{gb} D_{gb} \gamma_S \Omega}$$ has units of seconds.

How do we estimate a value for r. The pore size will scale as the grain size.

$r = \alpha d$

Where α is less than one (may be 0.25, or 0.5)

$$t_S = \frac{2\alpha^4}{9}\frac{k_B T d^4}{\delta_{gb} D_{gb} \gamma_S \Omega}$$

if $\alpha = 0.3$

$$t_S = \frac{1}{450}\frac{k_B T d^4}{\delta_{gb} D_{gb} \gamma_S \Omega}$$

Typical values

$\gamma_S = 1 Jm^{-2}$

$k_B = 1.38x10^{-23}$ J K^{-1} $atom^{-1}$

$\Omega = \frac{M_{wt}}{\rho N_A}$ m^3

d is the grain size or the particle size.

NOte that the time for sintering decreases as the fourth power of the particle size.

So for example if it takes 10 h to sinter with a particle size of 100 nm (0.1 μm) then a particle size of 50 nm will accelerate the sintering to 0.5 h.

What about $\delta_{gb} D_{gb}$?

Scales as $e^{-\frac{Q}{RT}}$. That is it is very sensitive to temperature.

$$D = D_O e^{-\frac{Q}{RT}}$$

This is called and Arrhenius equation. It is discussed in the next lecture.