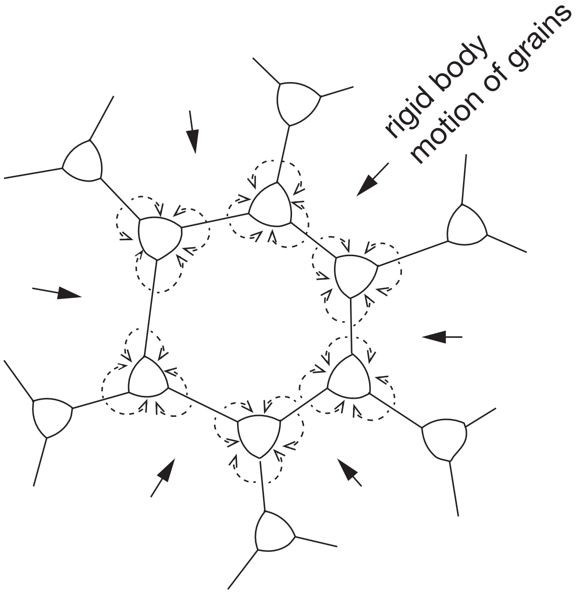
01B Pores - The Driving Force for Sintering



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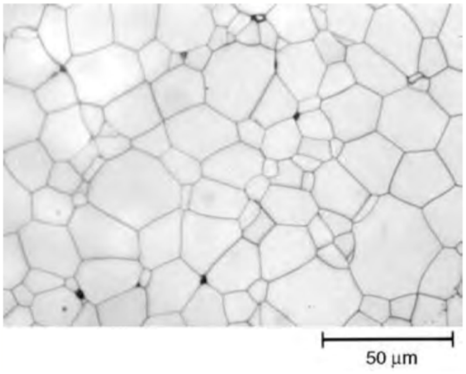


Questions:

Driving Force

Driving force for densification - it must be related to the pores wanting to fill.

Sintering Rate

Sintering rate = (driving force)*(kinetics - rate of the process, here we are concerned with the rate mass transport).

Solid state diffusion

Equation for the flux of atoms in terms of the driving force and the diffusion coefficient.

> (Mathematically the flux equation is the same as in heat transfer and fluid mechanics. In fluid mechanics the driving force is the pressure gradient and the rate is related to the viscosity - viscosity is related to the diffusion, i.e., the movement of atoms/molecules in the liquid).

Diffusion Coefficient

The phenomenon of diffusion or diffusivity is very general. As a result the coefficient of diffusion has the units of $m^2\ s^{-1}$.

Flux

Flux is also a universal quantity. For example in fluid mechanics where there is mass flowing through pipe under a pressure gradient, the flux is written in units of mass area^{-1} time^{-1}.

In diffusional transport mass can be written as moles or the number of atoms (equal to moles times the Avogadro's number)

Description of flux in diffusional mass transport

Volume of Matter

Ω is the volume per molecule (e.g. zirconium oxide)

So, for example:

$$\Omega = \frac{V_M}{N_A}$$

where V_M is the volume per mole, and N_A is the Avogadro's Number

$$N_A = 6.02 * 10^{23} \text{atoms per mol}$$

Note that the molar volumes is given by the ratio of the molecular wt divided by the density:

$$V_M = \frac{M_W}{\rho}$$

If M_W is in units of g mol^{-1} and the density in g cm^{-3}, the the molar volume will be in units of cm^3. You can divide by 10^6 to convert into m^3.

Flux of diffusional mass transport

The symbol is

J in moles per unit area per unit time

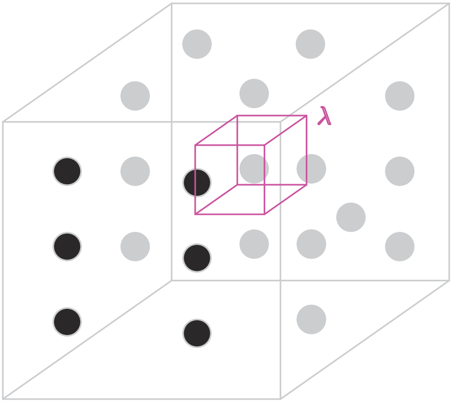
or, in the number of atoms per unit area per unit time.

The volume transported per unit time is then $J\Omega$.

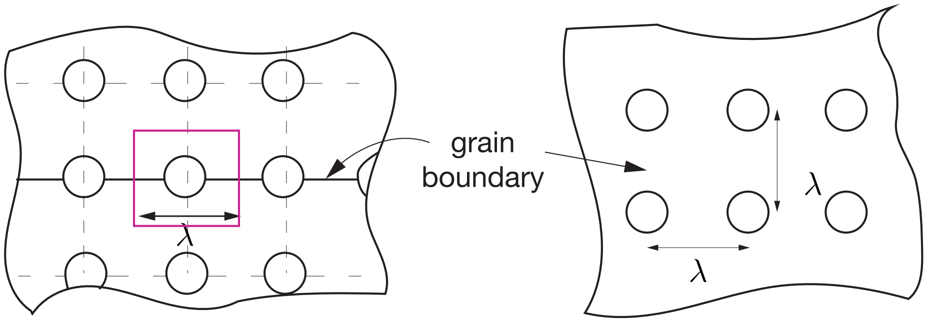
The Driving Force for Sintering

Geometrical Distribution of Pores

We begin with a geometrical distribution of the pores. We idealize the structure as being a packing of cubes where each cube represents one particle, and the size of the cube, λ, is equal to the particle size.



Imagine pores sitting at the corners of the cubes. So that each pore is shared by eight cubes. Define a unit cell which captures this geometry, which we say is a cube with an edge length of λ.



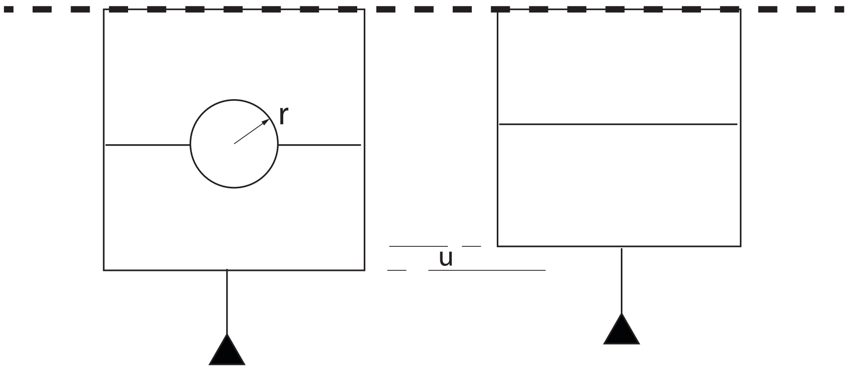
In cross Section
(across the grain boundaries)

Plan view of
the grain boundary

The picture on the left is a cross section of many grains (particles, cubes etc.) The picture of the right is plan view of the grain boundary with the pore spaced a distance λ from one another.

Sintering produced a compressive stress on the body

The driving force for sintering is like a pressure exerted on the body to make it shrink. Consider for example the pore in the figure on the left, just below, being sintered away to give a dense material shown on the right. If a weight were attached to the body then sintering of will the weight, meaning that sintering exerts a compressive force on the body.



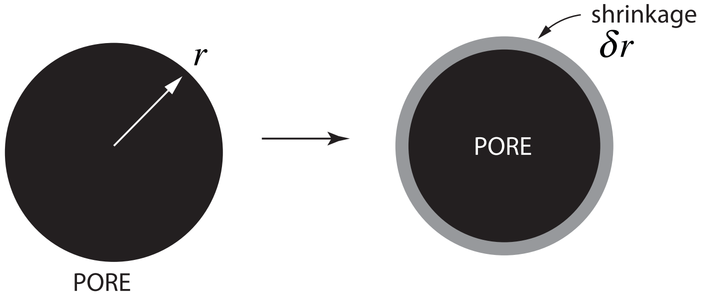
Note that hanging a weight slows the sintering because it pulls in the opposite direction to densification. Indeed, if the applied weight was equal to the sintering pressure (time the cross-sectional area of the sample to convert pressure into a force) then sintering would stop.

Application of the Principal of Virtual work to Calculate the Sintering Pressure

In this approach we equate the mechanical work to the reduction in the surface energy of the pore.

Consider a pore in of radius r to shrink by δr. Assume that there is one pore in a unit cell as described on page 3. Therefore,

δr



The mechanical work done by shrinkage of the pore is given by

$$p_{SX}\delta V_{pore} \qquad (1)$$

where δV_{pore} is the decrease in the volume of the pore.

The mechanical work is provided by the decrease in the surface energy of the pore,

$$\gamma_S \delta S_{pore} \qquad (2)$$

where γ_S is the surface energy with units of J m⁻², $S_{pore} = 4\pi r^2$ that is the surface area of the pore.

From the virtual work principle (i) and (2) must be equal, which gives

$$p_{SX}\delta V_{pore} = \gamma_S \delta S_{pore}$$

i.e.

$$p_{SX}\delta\left(\frac{4}{3}\pi r^3\right) = \gamma_S \delta\left(4\pi r^2\right)$$

which gives that

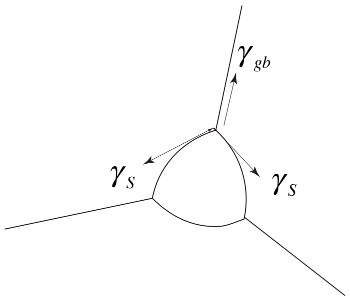
$$p_{SX} = \frac{2\gamma_S}{r} \qquad (3)$$

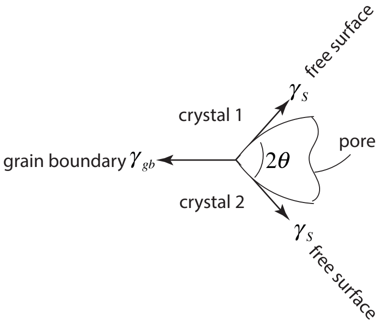
That is, the sintering pressure within a body containing pores is given by the surface energy and the radius of curvature of pore as in Eq. (3).

The Shape of Real Pores in the Grain Boundary: the Contact Angle

Pores at grain boundaries have a "lenticular" shape as shown below:

While the sintering pressure exerted by such a pore is still given by Eq. (3), the radius of curvature is now defined by the contact angle where the free surfaces of the pore meet the grain boundary:





The grain boundary "surface tension" is in equilibrium with the surface tension from the free surface, which defines the contact angle,

$$2\gamma_S \cos\theta = \gamma_{gb} \qquad (4)$$

You can appreciate that the radius of curvature can be constructed from simple geometry for a given value of the contact angle, and for a specific volume of the void.

An interesting feature of such a construction would be that if in the above figure the contact angle becomes less than 30° then the radius of curvature becomes convex and the sintering pressure vanishes.