HW Exam on Sintering (due Monday Oct 12, 2020)

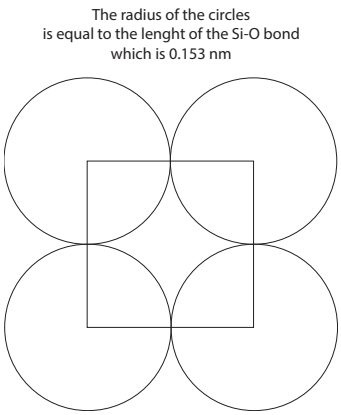
Problems Related to Geometrical Aspects of Sintering

1: Packing of Silica Tetrahedra

The question is to formulate a relationship between the length of the Si-O bond and the density of silica, α, with the assumption that the silica tetrahedra are close packed.

(i) Assume simple cubic packing

Approach:



•One cube contains one sphere since each sphere is shared by eight cubes

•The volume of the sphere is the third power of 2*bond length

•The weight of one cube is give by the sum of the atomic weights of Si (28 g/mol) and two oxygens (2*16), divided by the Avogadro's number (6.02E23 per mole).

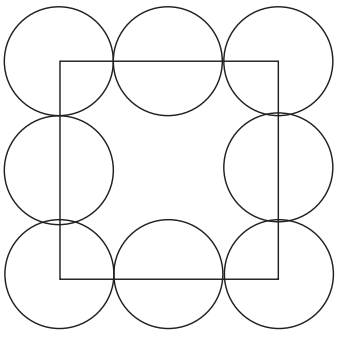
				Avgadro'a No	
				6.03E+23	per mole
bond length	bond len	Vol cube	Mol wt SiO2	One Molecule	density
nm	cm	cm^3	g/mol	g	g/cm^3
0.15	1.50E-08	2.7E-23	60	9.95E-23	3.69

The experimental density of fused (amorphous) silica is 2.2 g/cm^3

Therefore, the packing we have is too severe. Let us pose a different problem. Assume the packing to be as follows

What is the density for the configuration shown on the right and how does it compare with the density of silica which is

2.2 g cm^{-3}



2: Linear Shrinkage Strain and Volumetric Strain

•In a laboratory experiment we measure the linear change in dimensions of a specimen. The problem here is how to convert this measurement into the change in the relative density. The derivation given below gives a start to the problem, but not the final result.

$$\frac{V_f}{V_o}=\left(\frac{L_f}{L_o}\right)^3=\left(\frac{L_0-\Delta L_f}{L_o}\right)^3=\left(1-\frac{\Delta L_f}{L_o}\right)^3$$

Show that the volumetric shrinkage is related to the linear shrinkage, both being expressed as true strains by the following equation

$$\varepsilon_a=3\varepsilon$$

•In sintering we refer to the starting relative density as ρ_g and the sintered relative density as ρ. Show that

3: Relationship between the pore radius and the relative density

•The pore radius can be normalized with respect to the grain size. It is written as a non-dimensional parameter

$$\alpha=\frac{r}{d}$$

Show that

$$\rho=\frac{1}{1+\frac{4\pi}{3}\alpha^3}$$

•Make a plot of $\rho\ vs.\ \alpha$

Explain the significance of the in few words. 06C: Relating Pore Shrinkage to Linear Shrinkage

4: Relationship between Change in Volume, the Linear Strain and the Grain Size

Assume a cubic grain structure.

Assume one spherical pore placed at each corner of the cube.

Show that

$$\frac{\Delta v_p}{\Delta\varepsilon}=8d^3$$

Problems Related to Diffusion

Please refer to the following website for values for the diffusion coefficient, Omega etc. The website is organized into the properties of different classes of materials.. such as face centered cubic, metals, ceramics etc. It does not have an index but you can easily find the content of each chapter by clicking on it.

https://engineering.dartmouth.edu/defmech/

The problems explore different aspects of the diffusion coefficients. So each is given the appropriate heading.

5: The Pre-exponential

From Eq. (1) in the notes on Diffusion we had that

$$\Gamma = \upsilon_D e^{-\frac{Q}{RT}}$$

$$D_{gb} = \frac{1}{4}\Gamma a^2 = \frac{\upsilon_D a^2}{4} e^{-\frac{Q}{RT}} = D_{OB} e^{-\frac{Q_B}{RT}} \quad . \quad D_{OB} \text{ It has units of } m^2 s^{-1}$$

Caveats: (i) Note that boundary diffusion is denoted either by the subscript "gb" or by "B" – they are the same. (ii) the above equation assumes two diffusion in two dimensions in the boundary; in volume diffusion the atom movements is three dimensional so that "4" will be replaced by "6". (iii) The value for the vibration frequency may be assumed to be the Debye Frequency (do not worry about what it is) which is $10^{13} s^{-1}$.. however, this is a very significant approximation. The actual frequency can differ by one or two orders of magnitude.

The interatomic spacing a is given by $a = \Omega^{1/3}$ where Ω is the volume occupied by one atom species in the crystal (it is not the radius of the atom).

Omega is calculated from the molecular wt, the density and the Avogadro's Number,

$$\Omega = \frac{M_W}{\rho N_A}$$ (be very careful with the units).

In W the data for boundary diffusion is given not as D_B but as its product with the boundary width, δ or δ_B *or* δ_{gb} (since diffusion through the boundary always occurs across the boundary width). To a good approximation you can assume that

$\delta_B \approx 1.5\Omega^{1/3}$ which assumes that the width of the boundary is 1.5 times the spacing between the crystal planes within the crystal.

Now answer the following question:

Please go to Chapter 4 in the Website. It gives data for six metals with fcc structure.

(i) It gives data for $\delta_B D_{OB}$. Calculate D_{OB} using $\delta_B \approx 1.5\Omega^{1/3}$, for the six metals. How far do they agree with one another?

(ii) Now compare D_{OB} with D_{OV} the preexponential for volume diffusion. How far do they agree with each other?

Take away: diffusion coefficients can have considerable spread both in experimental measurements and theoretical estimates. Often they can be estimated only to within a factor or ten or one hundred. If you achieve consistent data within a factor of 2 then that is very good.

6: Normalization of the Diffusion Data with the melting Point

(i) Make Arrhenius plots for D_{OV} normalizing the temperature with the melting points (remember to use K) for three metals,

Ni, Cu and Pb. Comment on the degree of agreement shown in this plot.

(ii) Make Arrhenius plots for D_V and D_{OB} (after dividing the given data by the width of the boundary) on the same plot and comment on the difference between their magnitude and their temperature dependence.

Use copper as an example.

(iii) Now make another plot for dD_V where d is the grain size, and $\delta_B D_B$. Assume three values for the grain size, d, 2μm, 0.2 μm and 0.02μm. Comment on the relative shifts between these two plots when you change the grain size.

Problems Related to the Chemical Potential

7: Derive an equation for the change in the chemical potential between states I and II between the chemic

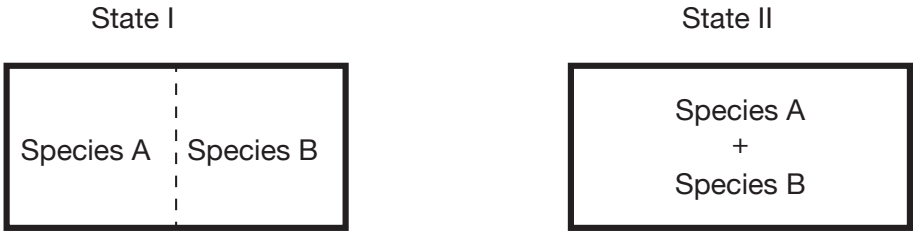
The gas in the above picture consists of species A (just one species). In State II the piston has moved to the right by a distance ΔL. The cross sectional area of the piston is S. Derive and expression for

$\mu_{II}^{A} - \mu_{I}^{A} = ?$

Ideal gas obeys $pV = RT$. Assume that the ambient pressure remains constant and that it is less than p_2.

Hint: your answer should depend on p_1, p_2 and RT.

8: Change in Chemical Potential in a System with Two Species



Assume that the closed chamber contains two gas species, A and B with A having a volume fraction of 30%, and B 70%. The total pressure is p_1 in State I and p_2 in State II. The partition is now removed in State II.

Obtain expressions for the difference in the chemical potential of the two species.

$\mu_{II}^{A} - \mu_{I}^{A} = ?$, and

$\mu_{II}^{B} - \mu_{I}^{B} = ?$

Problems Related to the Sintering Equation

9: The Dominant Diffusion Mechanism: Volume or Grain Boundary

Please look up the values for the material parameters,

$\Omega, D_{OB,} Q_B, D_{OV,} Q_V$ for copper

from the website https://engineering.dartmouth.edu/defmech/ Chapter 4.

Which is the dominant mechanism of mass transport for sintering at a sintering temperature of 750 °C

(i) when the particle size if 10μm, and

(ii) when the particle size is 75 nm

10: The Rate Controlling Species for Overall Diffusional Transport in an Oxide

Consider the problem of calculating the sintering time for Aluminum Oxide. The values for the diffusion coefficients for aluminum ions and oxygen ions, in the boundary and through the lattice are given in Chapter 14.

Assume that the particle size is 50 nm, and sintering is carried out at a temperature of 1500 °C.

Which of the for types of diffusion (aluminum ion through the boundary or the lattice, or oxygen through the boundary or the lattice) will control the sintering process? (Hint, the slowest one.. why?)