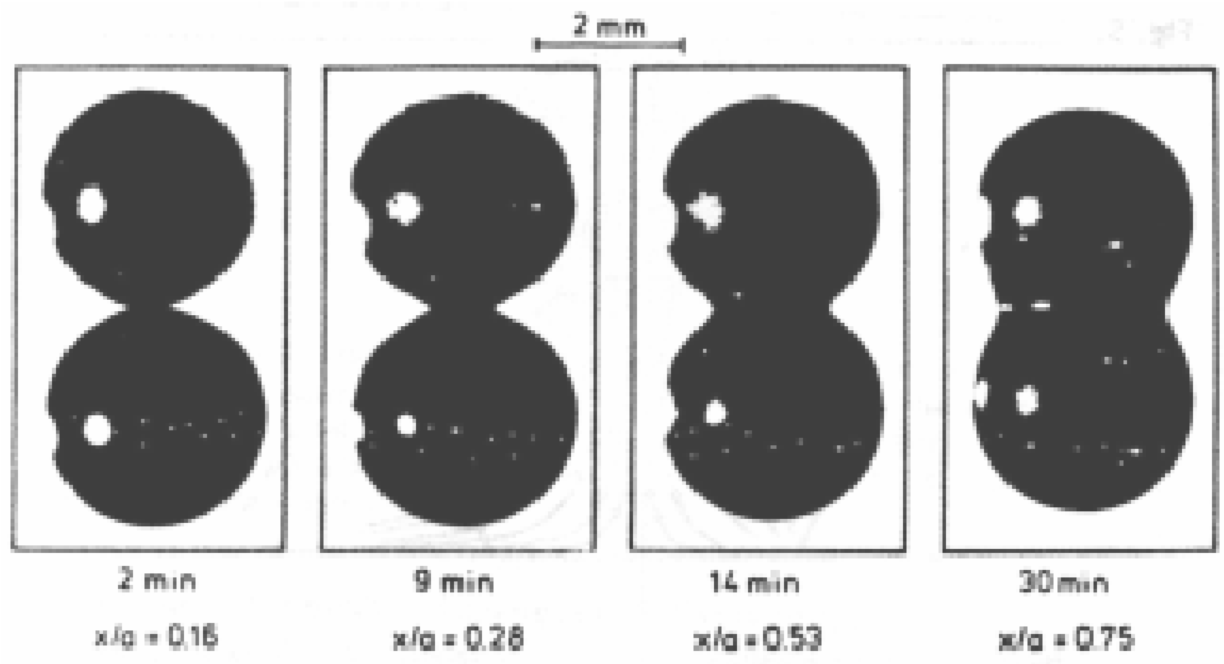
IX. Sintering

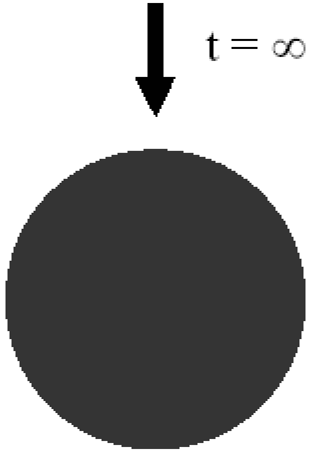
- General Phenomena

Sintering is a process of densification driven by interfacial energy. Sintering is a thermodynamically spontaneous process.



x: radius of neck

a:radius of particle



γ_{SV} : surface tension of solid-vapor interface

At t=0, we have two balls with $r_i = a_0$ and the surface energy is

$$G_0 = 2\gamma_{SV}(4\pi a_0^2) = 8\pi a_0^2 \gamma_{SV}$$

At t=∞, we have one ball with $r_f = 2^{1/3} a_0$, and

$$G_f = \gamma_{SV}(4\pi r_f^2) = 4 \times 2^{2/3} \pi a_0^2 \gamma_{SV}$$

$$\Rightarrow \quad \Delta G = G_f - G_0 = 4(2^{2/3} - 2)\pi a_0^2 \gamma_{SV} < 0$$

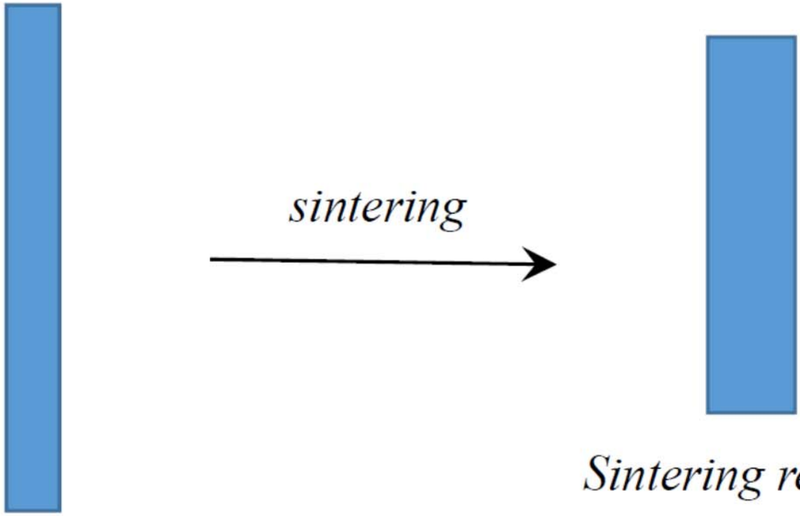
- Viscous Sintering (Noncrystalline Materials)

Energy Balance and Sintering Rate

Long cylinder:

L in length and

a in radius



Sintering reduces the length

(and increases radius)

The rate of dissipation of energy during the movement of material is:

$$E_f = (3\mu\varepsilon_Z^2)(\pi a^2 L)$$

where μ : viscosity of solid

ε_Z : strain rate in L direction

$$\varepsilon_Z = \left(\frac{1}{L}\right)\left(\frac{dL}{dt}\right)$$

The rate of the energy change due to the reduction in surface area is:

$$E_S = \gamma_{SV}\left(\frac{dS}{dt}\right)$$

Neglecting the end surfaces, we have $S = 2\pi aL$

$$\frac{dS}{dt} = 2\pi aL\left[\left(\frac{1}{a}\right)\left(\frac{da}{dt}\right) + \left(\frac{1}{L}\right)\left(\frac{dL}{dt}\right)\right] = 2\pi aL\left[\varepsilon_r + \varepsilon_Z\right] = \pi aL\varepsilon_Z$$

(Note: for incompressible cylinder, $\varepsilon_r = -\varepsilon_Z / 2$)

Energy balance gives

$$E_f + E_S = 0$$

$$\varepsilon_Z = -\gamma_{SV} / 3a\mu$$

Sintering rate ↑ as
- particle or pore size ↓
- surface energy ↑
- viscosity ↓

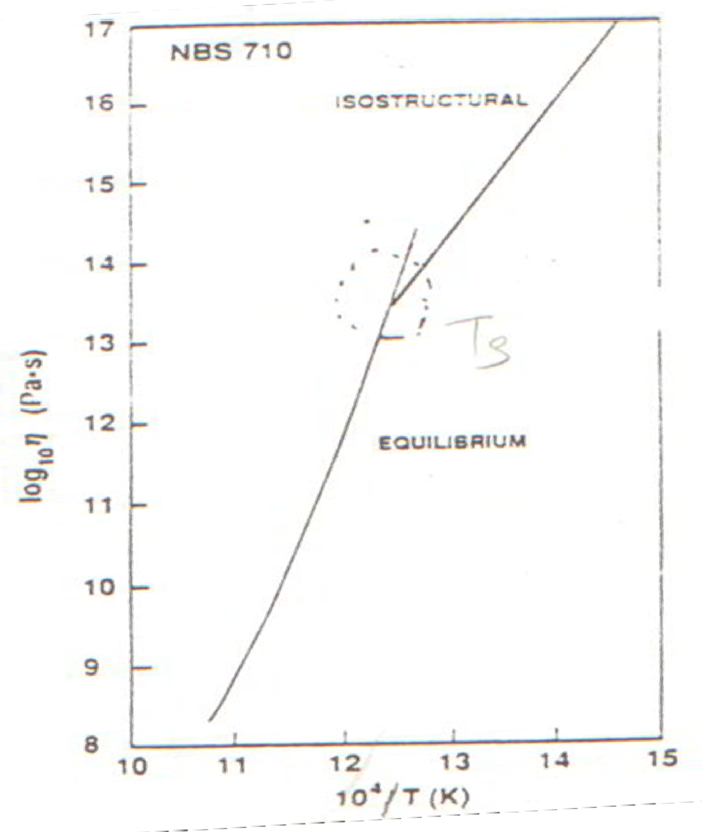
Temperature Dependence of Viscosity and Surface Tension

Viscosity decreases by an order of magnitude for every 20-40°C increase in temperature.

$$\mu = \mu_0 \exp[A/(T - T_0)]$$

Or over a narrow range of temperature

$$\mu = \mu_0 \exp(-E/RT)$$



Surface energy of glass is weakly dependent on temperature.

- Cylindrical Model for Microstructure Gel

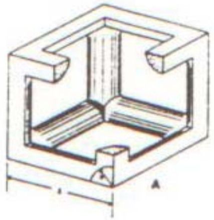
ρ : density of porous gel

ρ_0 : green density of gel (sub "0" is for gel before sintering)

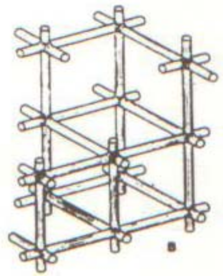
ρ_S : theoretical density of gel after complete densification

ρ / ρ_S : relative density

Unit cell of gel



Relative density=0.1



Relative density=0.5

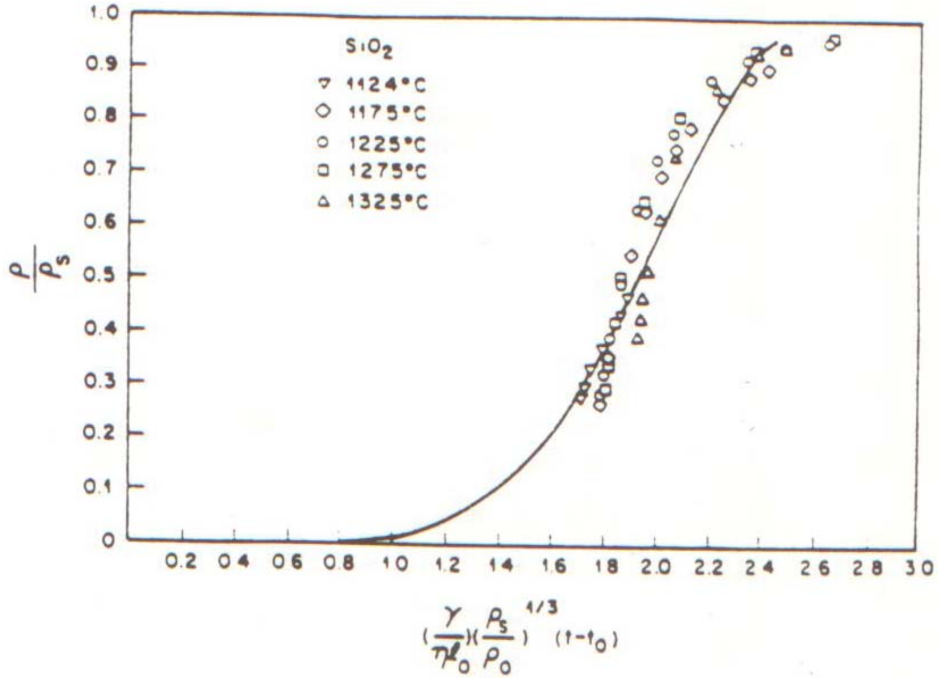
a - radius of cylinder
l - cell length
x =a/l

For the cylindrical model, the relative density can be correlated to the size of cylinder by:

$$\rho / \rho_S = x^2 (3\pi - 8\sqrt{2}x)$$

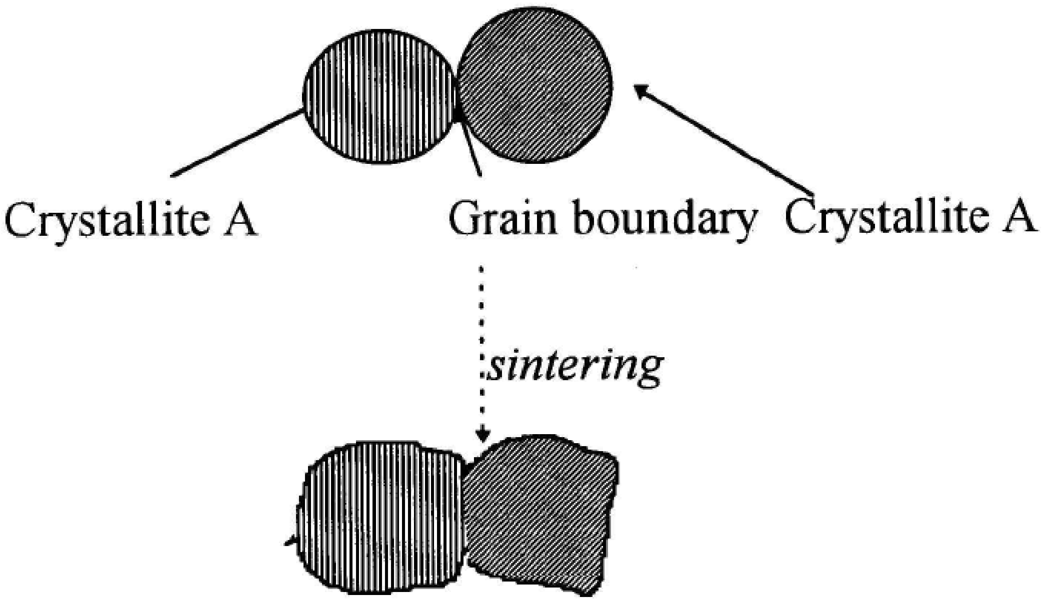
and x is a function of sintering time as:

$$\int_{x_0}^{x} \frac{2dx}{(3\pi - 8\sqrt{2x})^{1/3} x^{2/3}} = \frac{\gamma_{SV} \rho_s^{1/3} t}{\mu l_0 \rho_0^{1/3}}$$



SINTERING OF CRYSTALLINE MATERIALS

- General Phenomena



Driving force is reduction of total surface energy; There is an additional interfacial energy γ_{gb} at the grain boundary; During sintering grains grow, surface/volume ratio decreases; interfacial energy decreases.

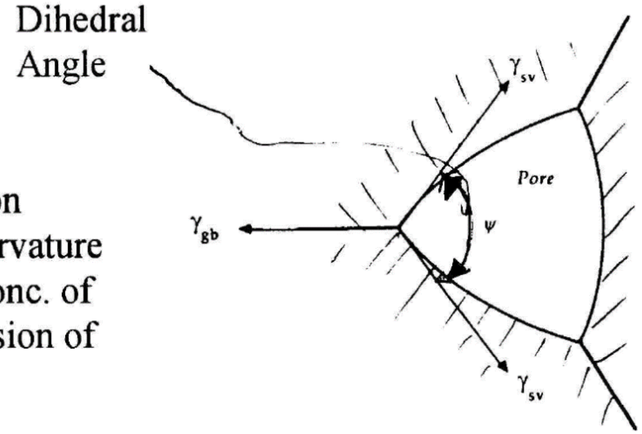
- Energy Balance:

$$E_f + E_s + E_{gb} = 0$$

Energy consumed to transfer materials (E_f)

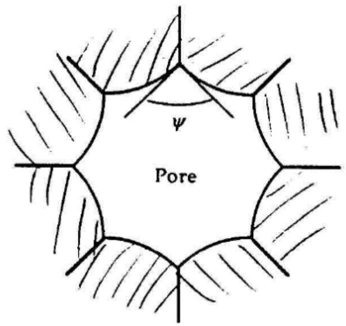
Energy change due to decrease in surface energy (E_s)

Energy change due to change in the grain boundary area (E_{gb})



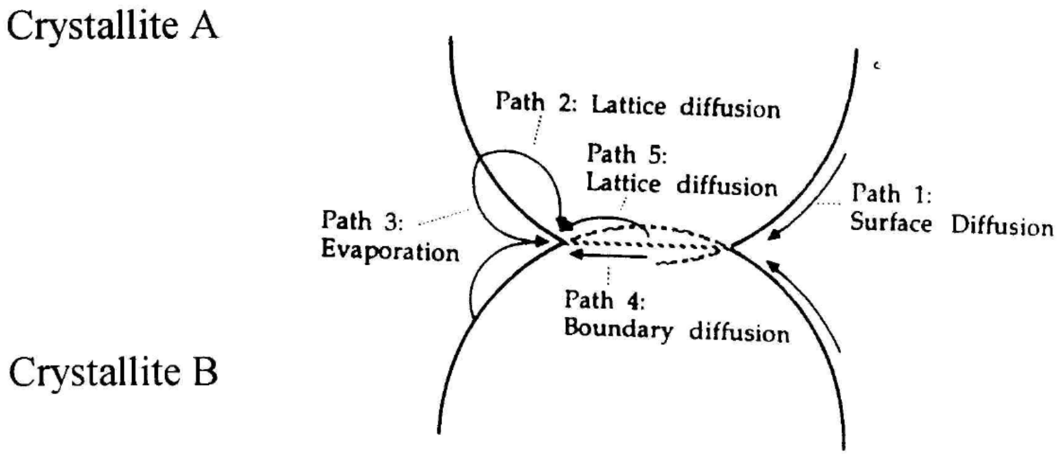
$\gamma_{gb} = 2\gamma_{sv} \cos(\psi/2)$

. 3 grains => pore formation
. negative V/S interface curvature
. tension creating higher conc. of vacancies, favoring diffusion of solid => pore shrinks



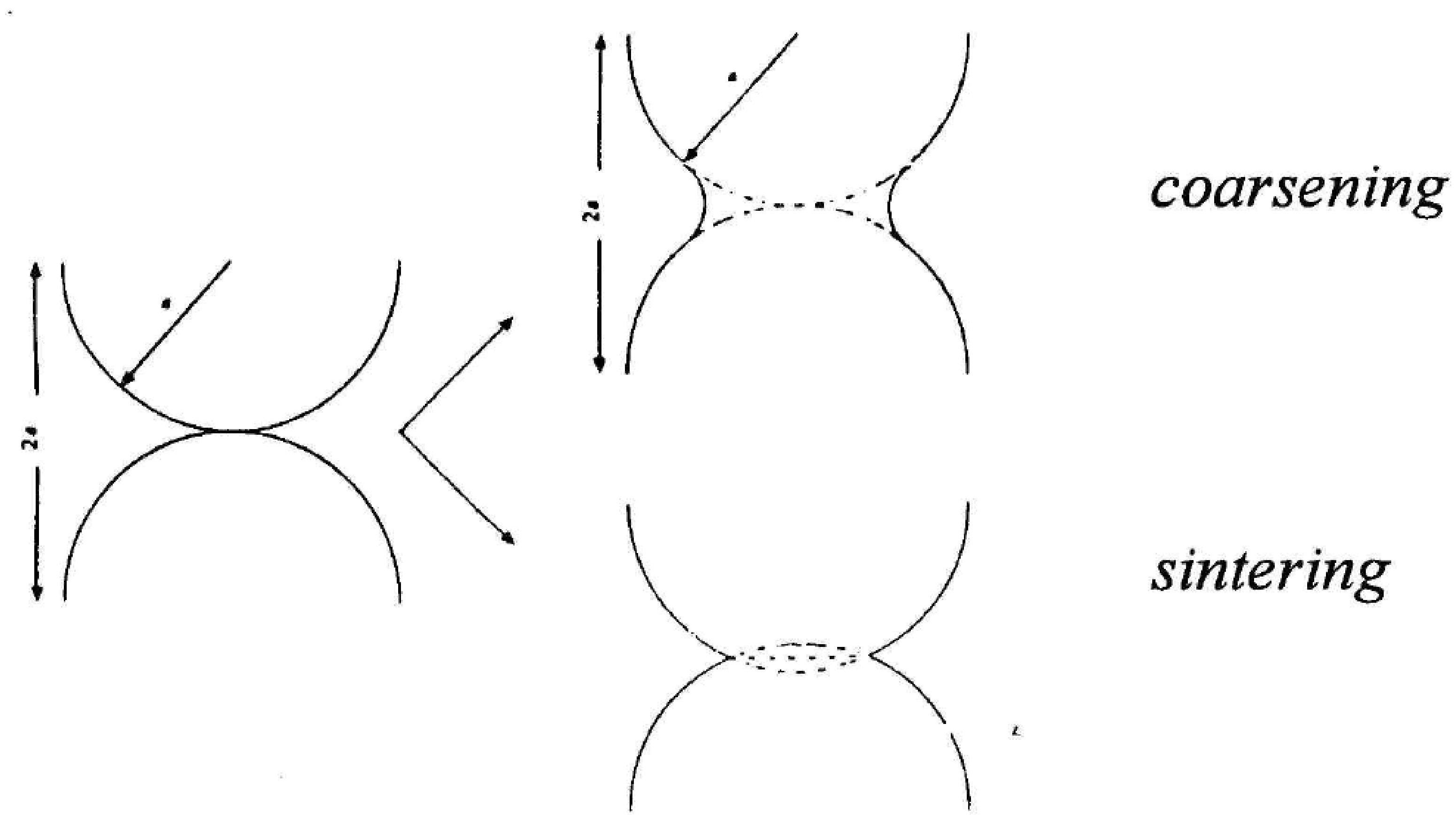
. more than 3 grains
. positive V/S interface curvature
. diffusion of solid from pores
. pore grows

- Sintering Paths



<u>Five Paths for Solid Transport</u>

Path 1	Surface diffusion, D_s	Coarsen the body by making the necks, pores may grow
Path 2	Lattice diffusion, $D_{L(I)}$	
Path 3	Evaporation	
Path 4	Boundary diffusion, D_{gb}	Grain boundary changes, decrease in distance between particles, pores shrink
Path 5	Lattice diffusion II, $D_{L(II)}$ (volume diffusion)	


coarsening
sintering