

Lecture 14

Sintering

$$\sigma_1 = \frac{4\gamma}{D}$$

↗ surface energy
↓ surface tension

$$\sigma_2 = \gamma \left[\frac{2}{D} - \frac{4D}{\lambda^2} \right]$$

↘ necking

compressive stress
being exerted due to
necking

$\Delta\sigma = \sigma_1 - \sigma_2$ → this triggers atomistic
stress gradient mechanisms of diffusion.
hence sintering takes place.

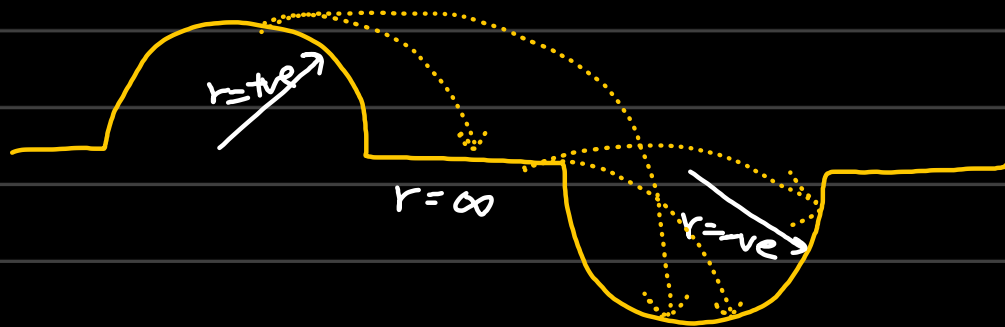
$$\sigma_1 \propto \frac{1}{X}, \quad \sigma_2 \propto \frac{1}{D}$$

→ As sintering progresses : $X \uparrow$ so $\sigma_1 \downarrow$ so $\sigma_2 \downarrow$
↳ $\Delta\sigma \downarrow$

Kinetics of Sintering:

* Evaporation & Condensation:

↳ decided by diff in radius of curvature.



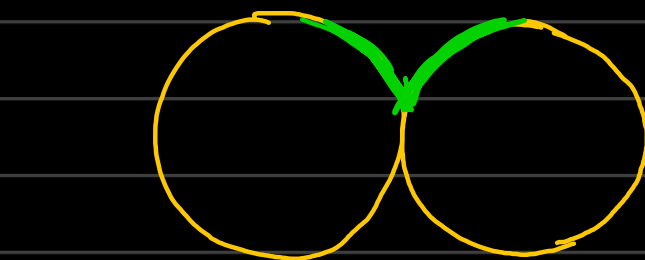
$$r = +ve \Rightarrow \Delta P = +ve$$

{ partial pressure gradients analogous to stress gradient }

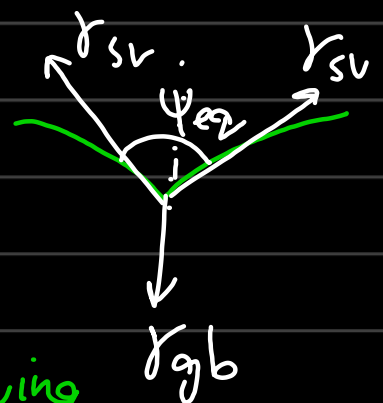
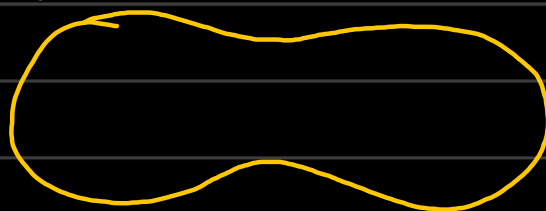
↳ mass transport from here

$$r = \infty \Rightarrow \Delta P = 0$$

$$r = -ve \Rightarrow \Delta P = -ve$$



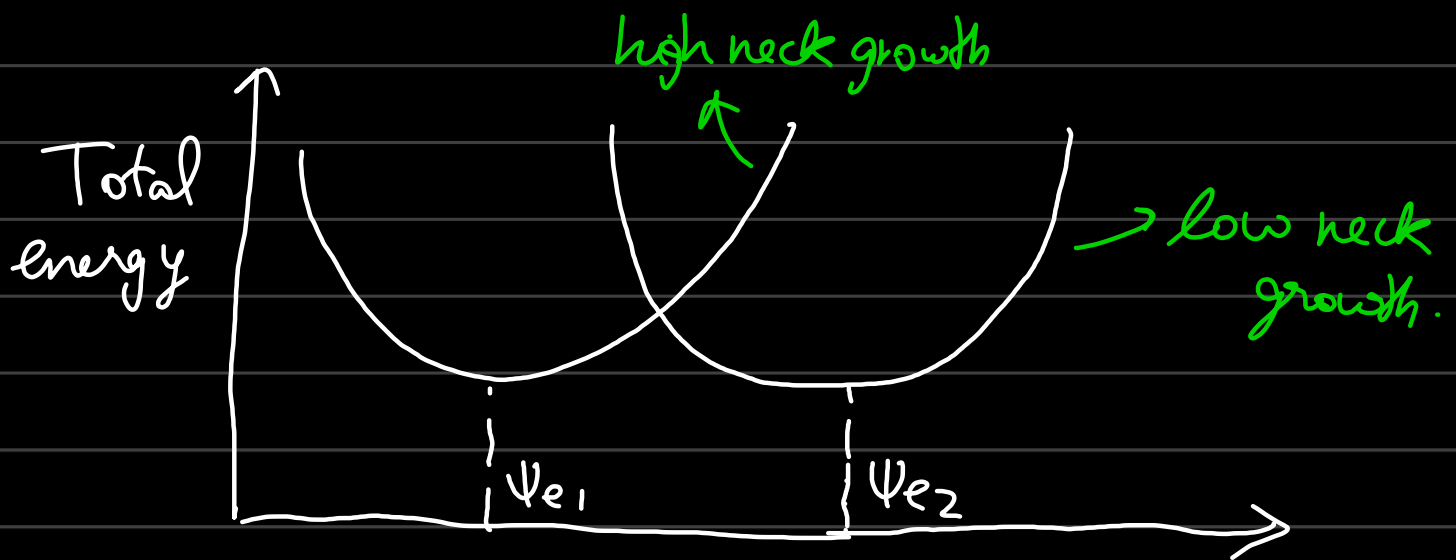
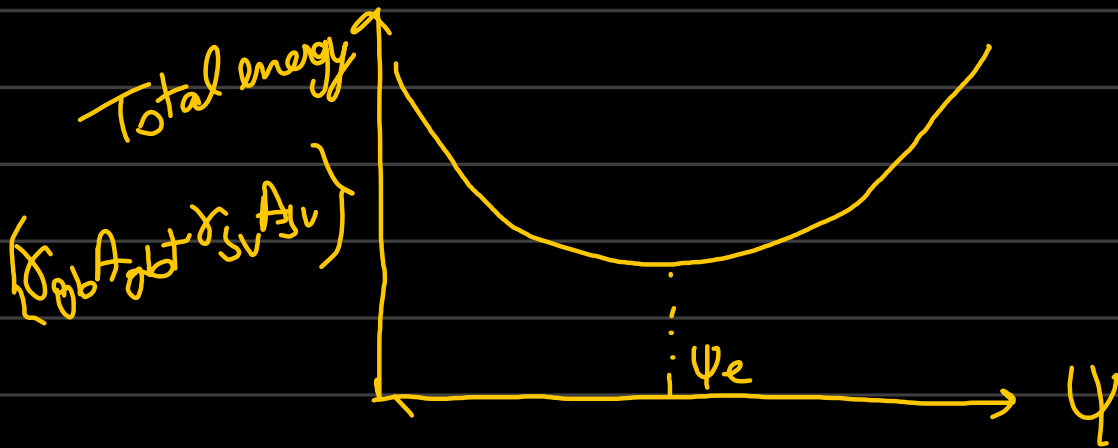
sintering



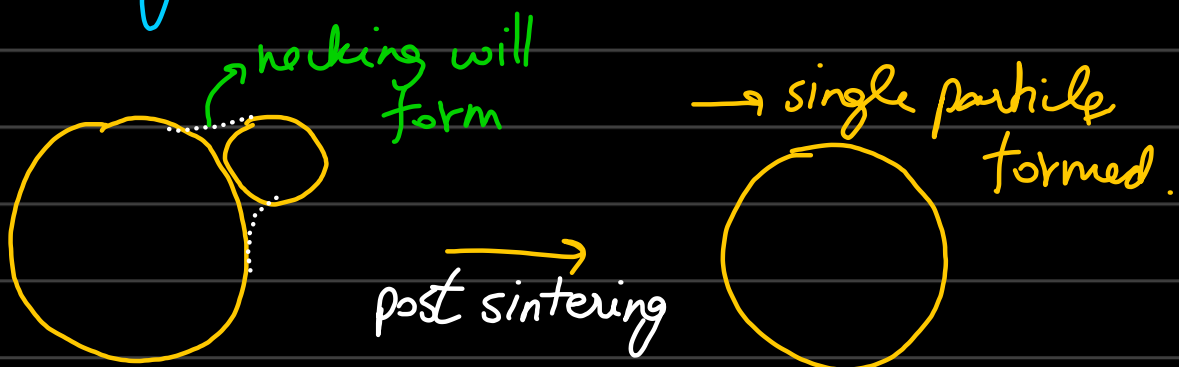
* Equilibrium achieved when driving

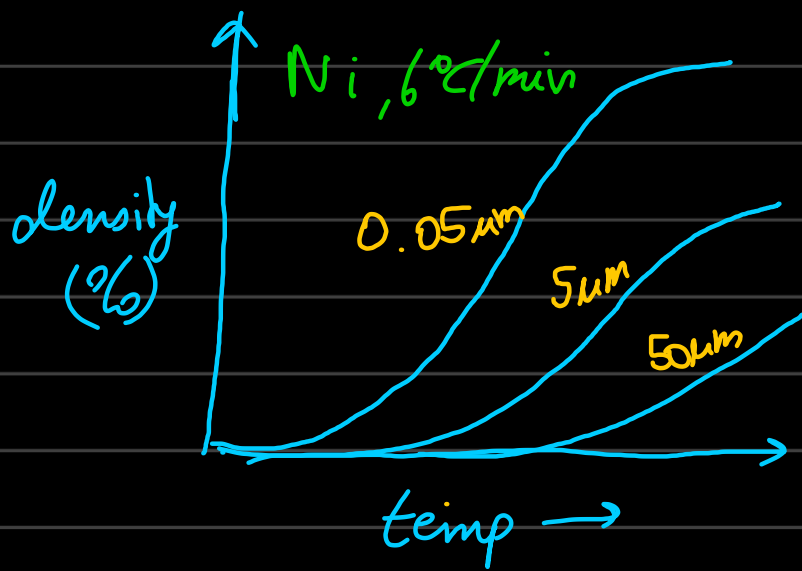
force is minimised st atomistic diffusion ceases.

$$\gamma_{gb} = 2\gamma_{sv} \cos\left(\frac{\psi_e}{2}\right)$$



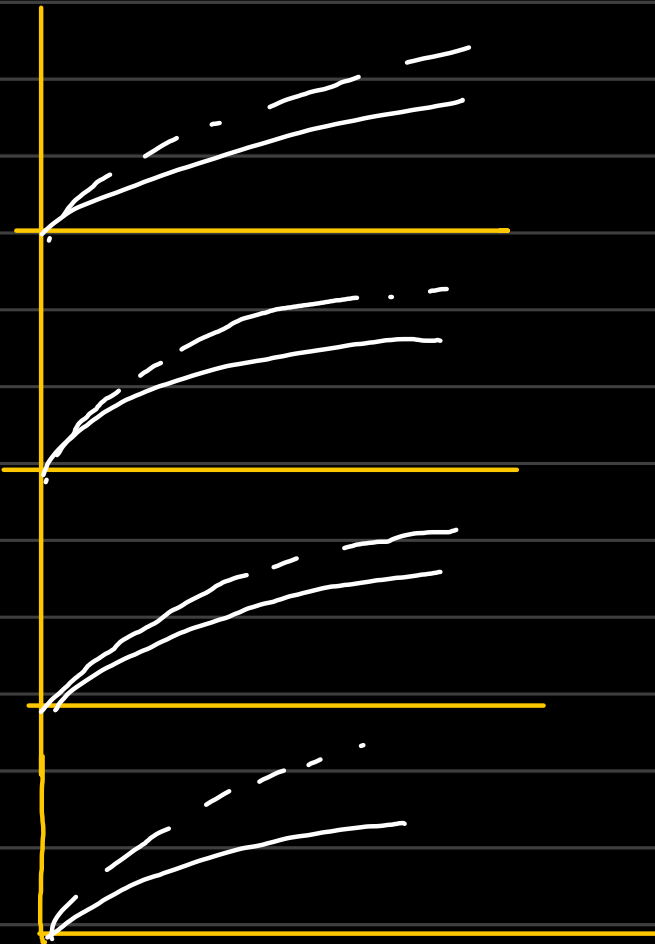
→ reflecting upon the sintering process which is happening.





densification $\propto \frac{1}{D}$

densification rate $\propto \frac{1}{D}$



Stages of Sintering:

- i) Initial Stage: Neck formation, pore formation
- ii) Intermediate stage: Pore rounding, grain growth and some densification
- iii) Final stage: Sintering occurs with closed pores.

* $\left(\frac{X}{D}\right)^n = \frac{Bt}{D^m}$

Annotations:
- B : constant
- t : sintering time.
- n and m : exponents
- \Rightarrow initial stage of sintering

* n & m dictated by mechanism.

* B thermally varying constant

B can change upon changing mechanism.

* The above equation holds true for $\frac{X}{D} < 0.3$
for $\frac{X}{D} \geq 0.3 \rightarrow$ eqn collapses.

* Sintering rate can be measured easily in terms of shrinkage rather than neck size reduction

Intermediate Stages.

→ tetrakaidecahedron. (14-sided)

↳ formation of pore structure network.

↳ highly interconnected cylindrical pores on edges of tetrakaidecahedron.

→ densification takes place by diffusion of vacancies away from pores.

$$\rho_s = \rho_I + B_I \ln \left(\frac{t}{t_s} \right)$$

constant $\propto \frac{1}{\text{grain size}}$

ρ_s → fractional density after stage II

ρ_I → fractional density start stage II

t_s → time of start stage II

end of stage II

Final Stage:

↳ characterized by spherical monosized pores at corners at corners of tetrakaidecahedron grains.

↳ pores are closed and isolated.

→ pores grow by Ostwald Ripening

* If pore has trapped gas, it slows or prevents pore elimination.

↳ Sintering performed in vacuum eliminates this problem.

→ For the final stage of sintering:

densitification rate. $\frac{dS}{dt} = \frac{12 D_v \Omega}{K T G^2} \left[\frac{4\gamma}{dp} - P_g \right]$

Volume diffusivity

Ω = atomic volume

K = Boltzmann const.

dp = size of pore

G = grain size

γ = Solid-vapour Surface energy.

P_g = pressure exerted by pore due to gas entrapment.

→ over time $\frac{dS}{dt} \rightarrow 0$: saturation in densification.

* Pores at grain boundary are stable

Example:

Q) $P = 10^5 \text{ N/m}^2$; $d_p = 20 \mu\text{m}$

final pore diameter that can be achieved.
assuming ideal gas law.

$$\gamma = 2 \text{ J/m}^2 \quad ; \quad D_v = 5 \times 10^{-5} \text{ m}^2/\text{s}$$

$$\Omega = 125 \text{ A}^3$$

From ideal gas law: $P_1 d_1^3 = P_2 d_2^3$

→ Final size attained when $\frac{d\gamma}{dP} = 0$

$$\frac{4\gamma}{d_p} = P_G$$

$$\frac{4\gamma}{d_p} = \frac{P_1 d_1^3}{d_p^{3/2}}$$

$$d_p^2 = \frac{P_1 d_1^3}{4\gamma}$$

$$d_p^2 = \frac{10^5 \times (20 \times 10^{-6})^3}{4 \times 2}$$