Powder Technology
course
Autumn semester 2017

Sintering theory

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Semestre d'hiver 2017

Week- DATE	**File. no.**		**Powder Technology – Wednesday 10.15-12.00 – MXG 110**
1- sept 20	1		Introduction - PB
2 – sept 27	2		Powder packing and compaction - 1- PB -
3 – oct 4	3		Powder packing and compaction - 2-PB- and guest lecturer - MS
4 – oct 11	4		Powder packing and compaction -3- PD
5 – oct 18	4		Powder packing and compaction - 4 – PD
6 – oct 25	5		Particle – Particle Interactions 1 - PB
7 – nov1	6		Particle – Particle Interactions 2- PB
8 – nov 8	7		Particle – Particle Interactions - 3-PB
9 – nov -15	8		Introduction to atomistic scale simulations PD
10 – nov 22	9		Compaction, Sintering & Defects in metals at atomistic scale - PD
11 -nov-29	10		Sintering Mechanisms& New Technologies - 1 – PB
12 - dec 6	11		Sintering Mechanisms & New Technologies - 2 - PD
13 – dec 13	11		Sintering Mechanisms &New Technologies -3 PD
14 – dec 20	11		Sintering Mechanisms & New Technologies- and exam 4 – PB
			PB – Prof. Paul Bowen (EPFL), PD – Dr. Peter Derlet (PSI)
			MS- Dr. Mark Sawley (EPFL)

References

- German, R.M. (1994) Powder metallurgy science, in Metal Powder Industries Federation, 2nd edn, Princeton, New York.
- Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure, 1st edn, Butterworth-Heinemann (available via ScienceDirect)
- Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Lecture outline

- General definitions/stages of sintering
- Driving force for sintering – the general framework
    - Reduction of interfacial energy
    - Mass transport
    - Diffusion – the example of a vacancy defect
- Theory of diffusion
    - The diffusion equation and Fick's laws
    - Microscopic diffusion – the case of a vacancy
- Thermodynamics primer
    - 1st law of thermodynamics & thermodynamic Potentials
    - The chemical potential and the drive towards equilibrium
- Interface thermodynamics and the underlying physics in sintering
    - The interface free energy
    - The pressure and chemical potential of two phases with a curved surface
- Two particle sintering models for initial stage sintering
    - General framework and geometry
    - The different diffusion mechanisms
- Intermediate and final stage theory
    - The models of Coble
    - Plasticity & recrystallization
    - Grain growth

General definitions/stages of sintering

Sintering - definition

- Sintering is defined as a thermal treatment of a powder or powder compact at an elevated temperature below the melting temperature.

- The goal of sintering is to increase powder compact strength.

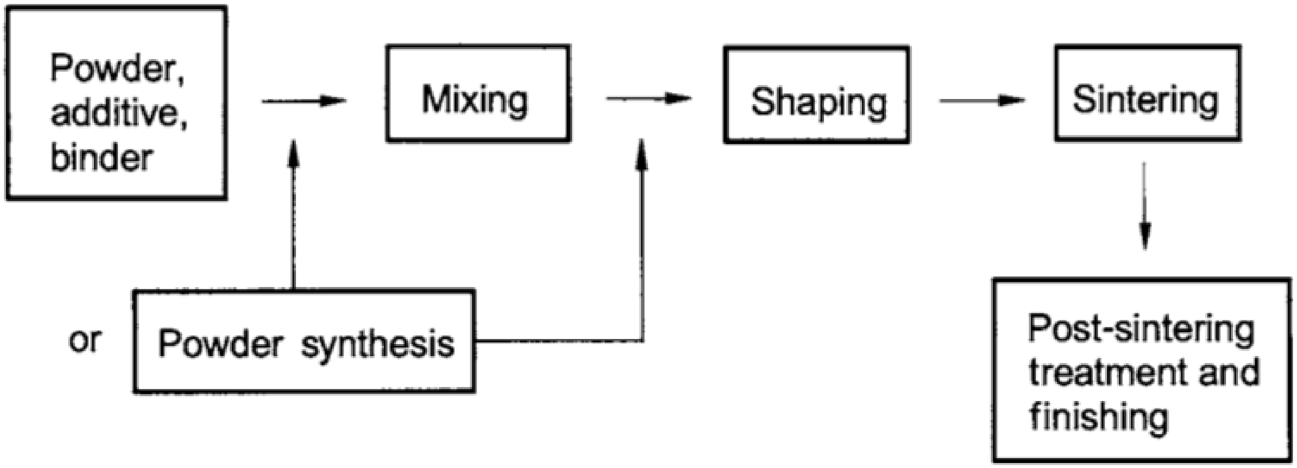


Figure I.2. General fabrication pattern of sintered parts.

Sintering – types

- **Solid phase** sintering – only solid phases are present
- **Liquid phase** sintering – liquid phases are also present
- **Reactive phase** sintering – different phases are present which react to produce new phases

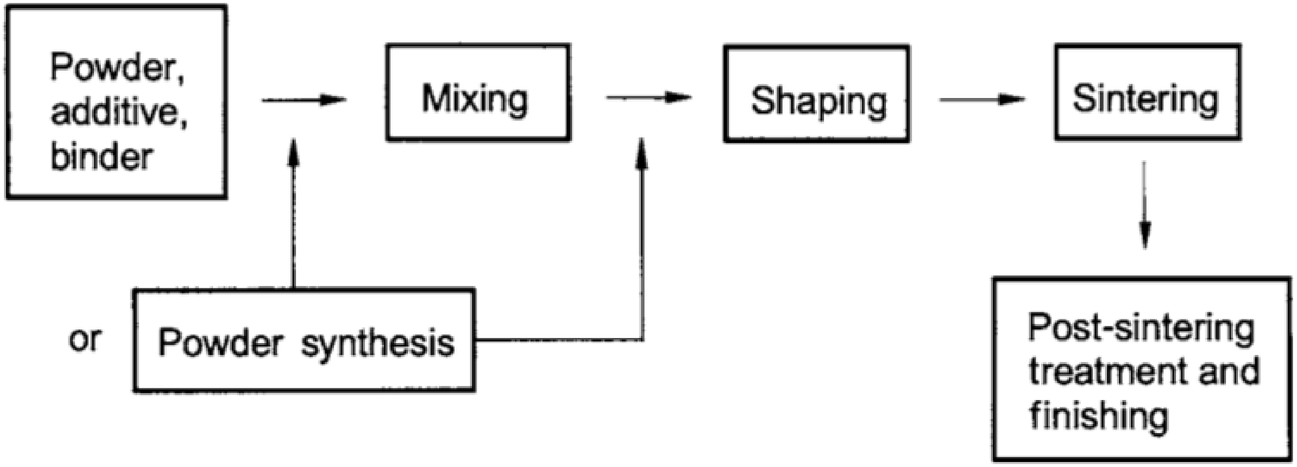
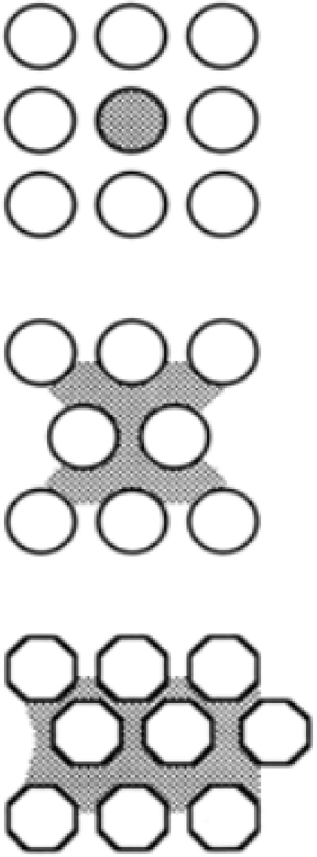


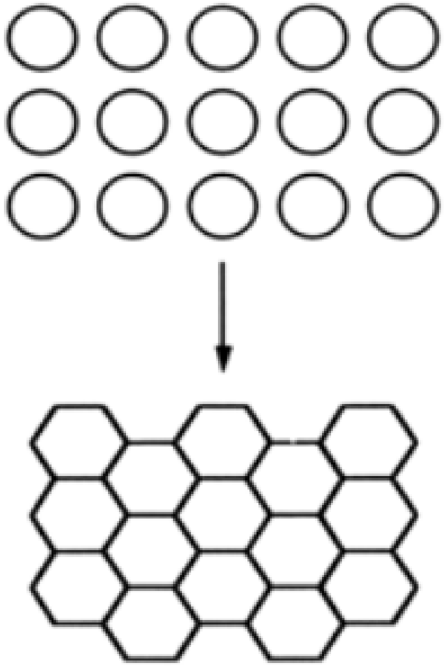
Figure I.2. General fabrication pattern of sintered parts.

Sintering – types

Liquid phase sintering



Solid phase sintering



Sintering – parameters

- Powder compact parameters
  - Shape
  - Shape distribution
  - Degree of agglomeration
  - Presence of impurities
  - Chemical composition

- Sintering condition parameters
  - Temperature
  - Pressure
  - Atmosphere
  - Heating and cooling rate

Sintering – stages

'A "stage" of sintering may be described as an interval of geometric change in which the pore shape change is totally defined (such as rounding of necks during the initial stage of sintering), or an interval of time during which the pore remains constant in shape while decreasing in size (such as shrinkage of spherical pores during the final stage of sintering).'

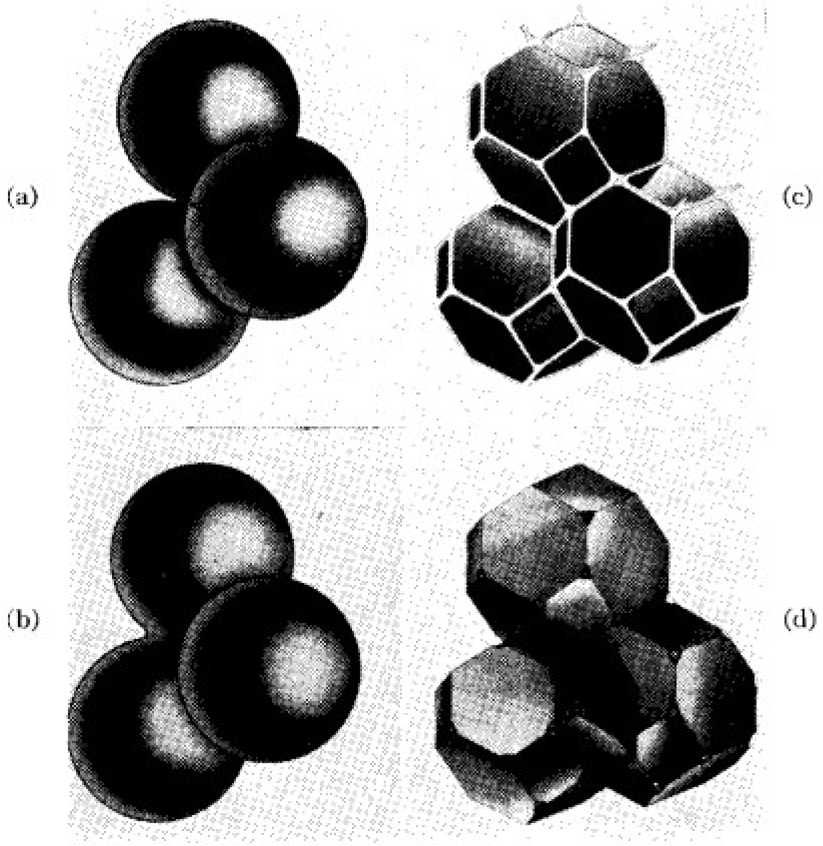
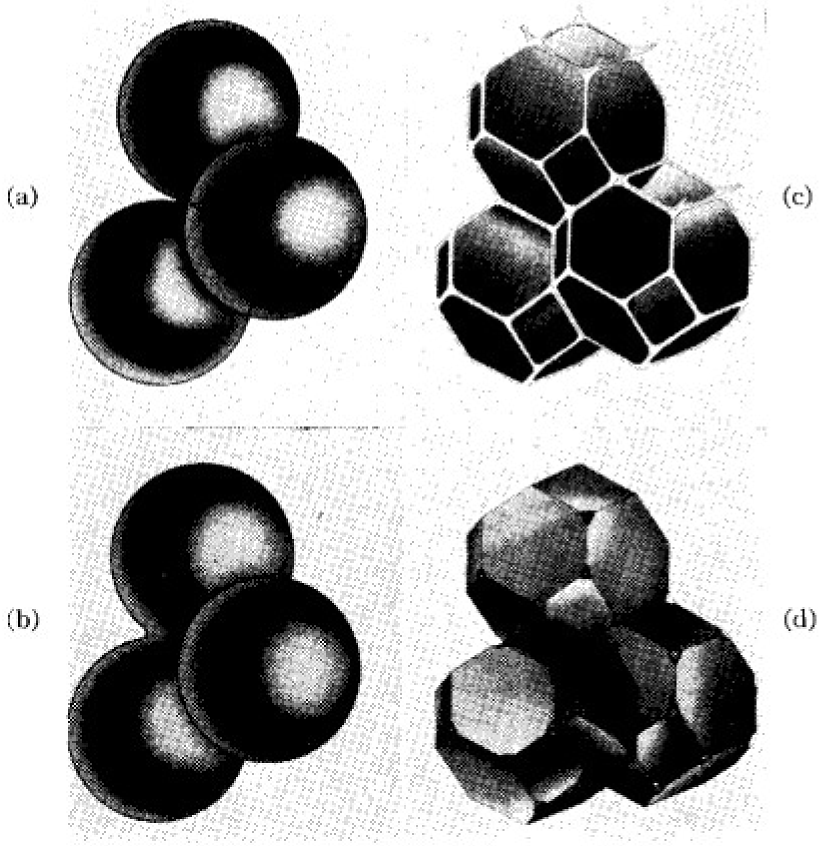


FIG. 1. (a) Initial stage of sintering; model structure represented by spheres in tangential contact. (b) Near end of initial stage. Spheres have begun to coalesce. The neck growth illustrated is for center-center shrinkage of 4%. (c) Intermediate stage; dark grains have adopted shape of tetrakaidecahedron, enclosing white pore channels at grain edges. (d) Final stage; pores are tetrahedral inclusions at corners where four tetrakaidecahedra meet.

Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Sintering – stages

- Initial stage
  - Neck and grain boundary formation
  - Surface smoothing
- Intermediate stage
  - Creation of isolated pore structures
  - Grain growth
  - Densification
- Final stage
  - Pore shrinkage and closure
  - Grain growth



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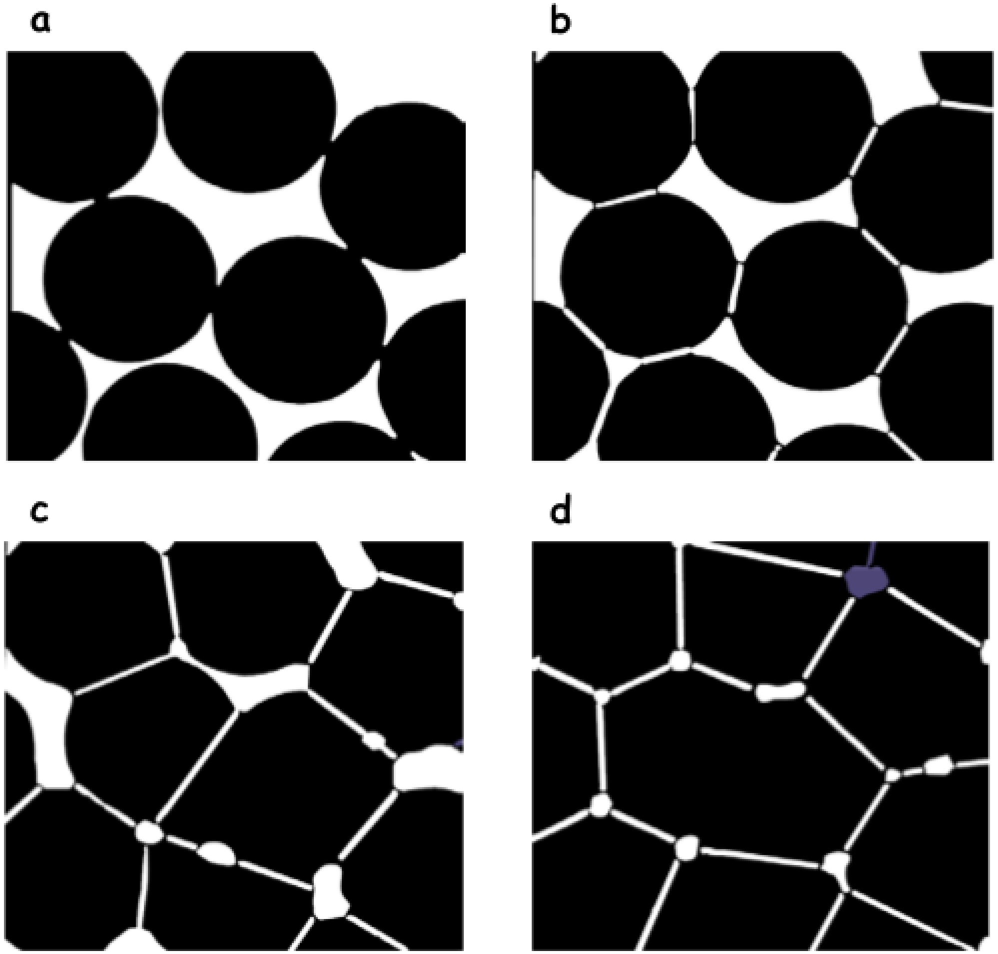
Sintering – stages



a) Green body, loose powder

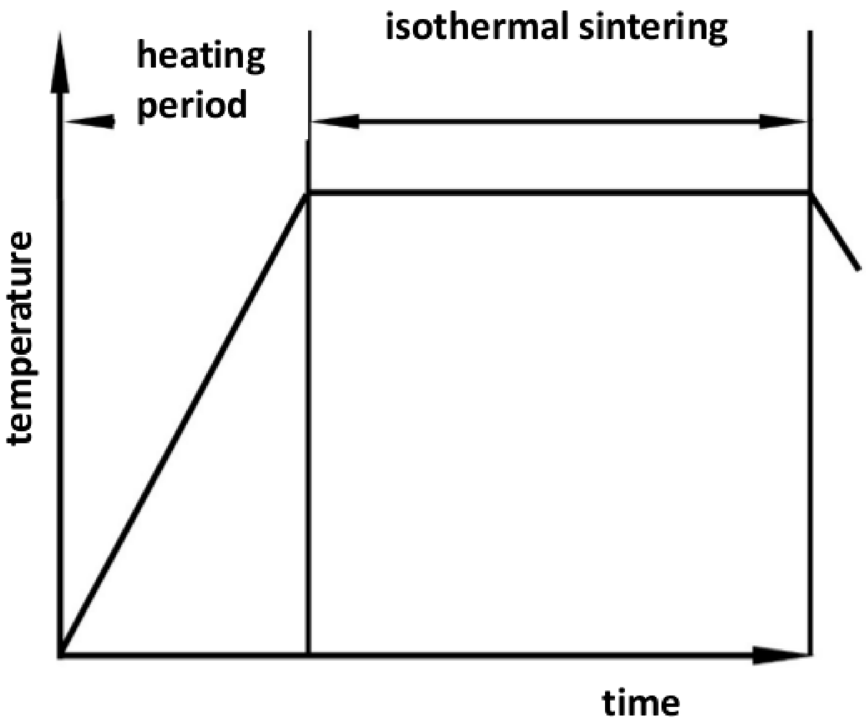
b) Initial stage: increase of the interparticle contact area from 0 to 0.2 grain diameter, increase of the density from 60 to 65%

c) Intermediate stage: further increase of the contact area, stage characterized by continuous pore channels along three grain edges, increase of the density from 65 to 90%.

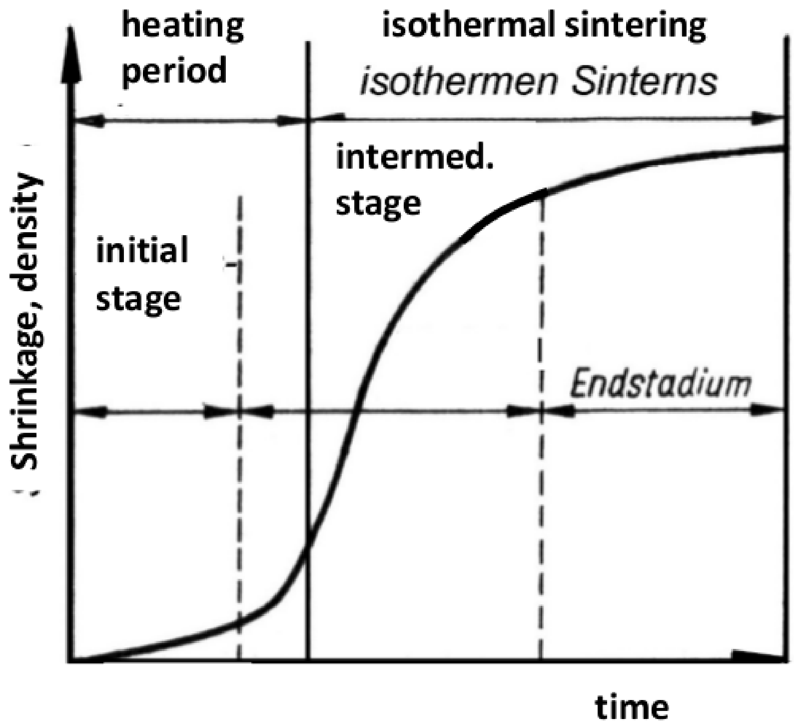
d) Elimination of the pore channel along three grain edges, increase of the density to 95 - 99%

https://www.slideshare.net/ashking235/lecturesolid-state-sintering

The simplest temperature protocol



Temperature evolution during a simple sintering cycle



Development of density and shrinkage during a simple sintering cycle

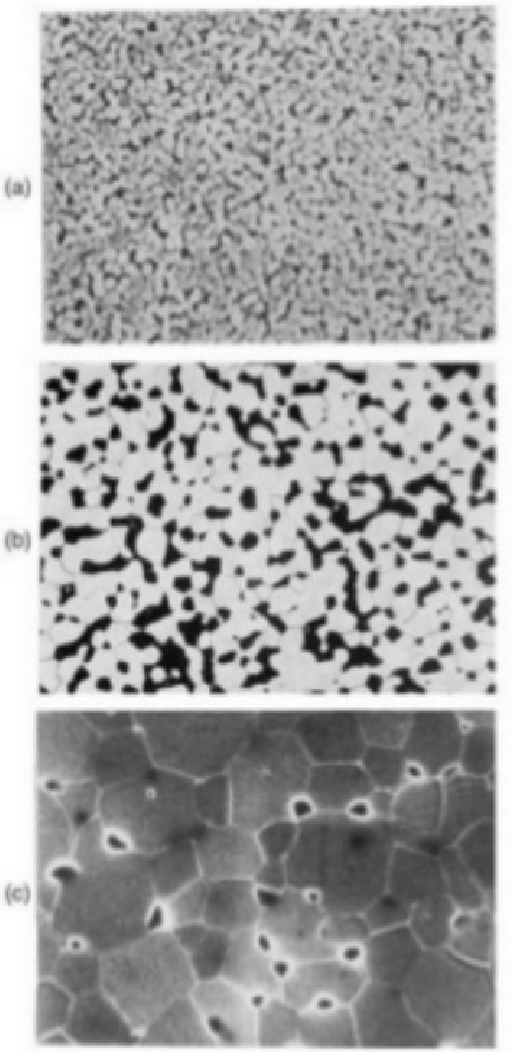
Adapted from: https://www.slideshare.net/ashking235/lecturesolid-state-sintering

The simplest temperature protocol

a) Initial stage – rapid interparticle growth (various mechanisms), neck formation, linear shrinkage of 3-5 %

b) Intermediate stage – continuous pores, porosity is along grain edges, pore cross section reduces, finally pores pinch off. Up to 0.9 of TD

c) Final stage – isolated pores at grain corners, pores gradually shrink and disappear. From 0.9 to TD



Adapted from: https://www.slideshare.net/ashking235/lecturesolid-state-sintering

Driving force for sintering – the general framework

Sintering – driving force

- The fundamental driving force for sintering is the reduction of internal interface/surface energy

$$\Delta(\gamma A) = (\Delta\gamma)A + \gamma(\Delta A)$$

γ interface energy density

A interface area

The interface can be a grain boundary or a surface (matter/atmosphere interface)

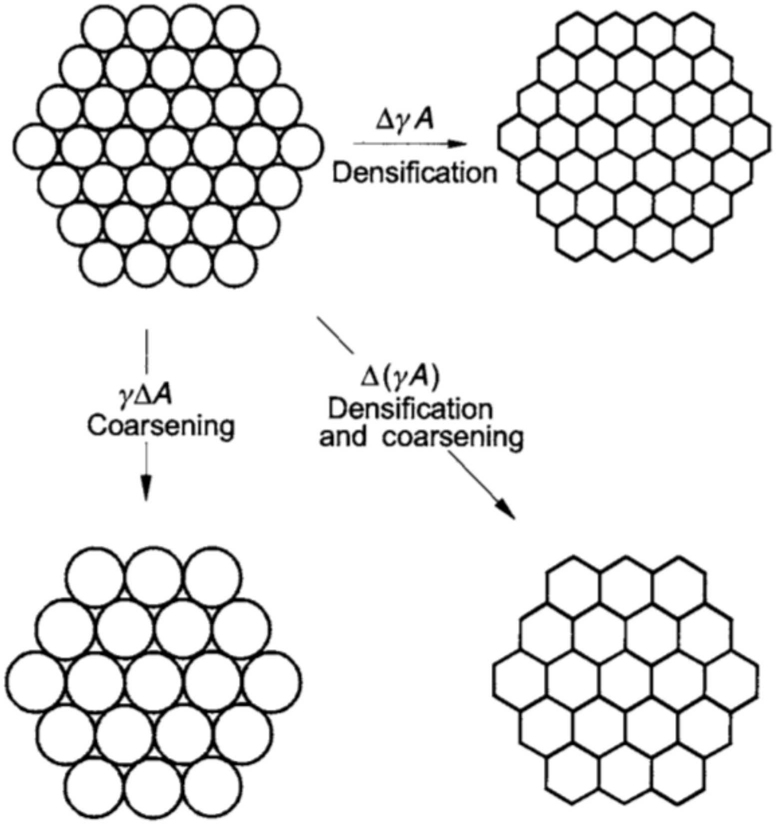


Figure I.5. Basic phenomena occurring during sintering under the driving force for sintering, $\Delta(\gamma A)$.

How can such micro-structural evolution occur?

Mass transport is the underlying mechanism of sintering.

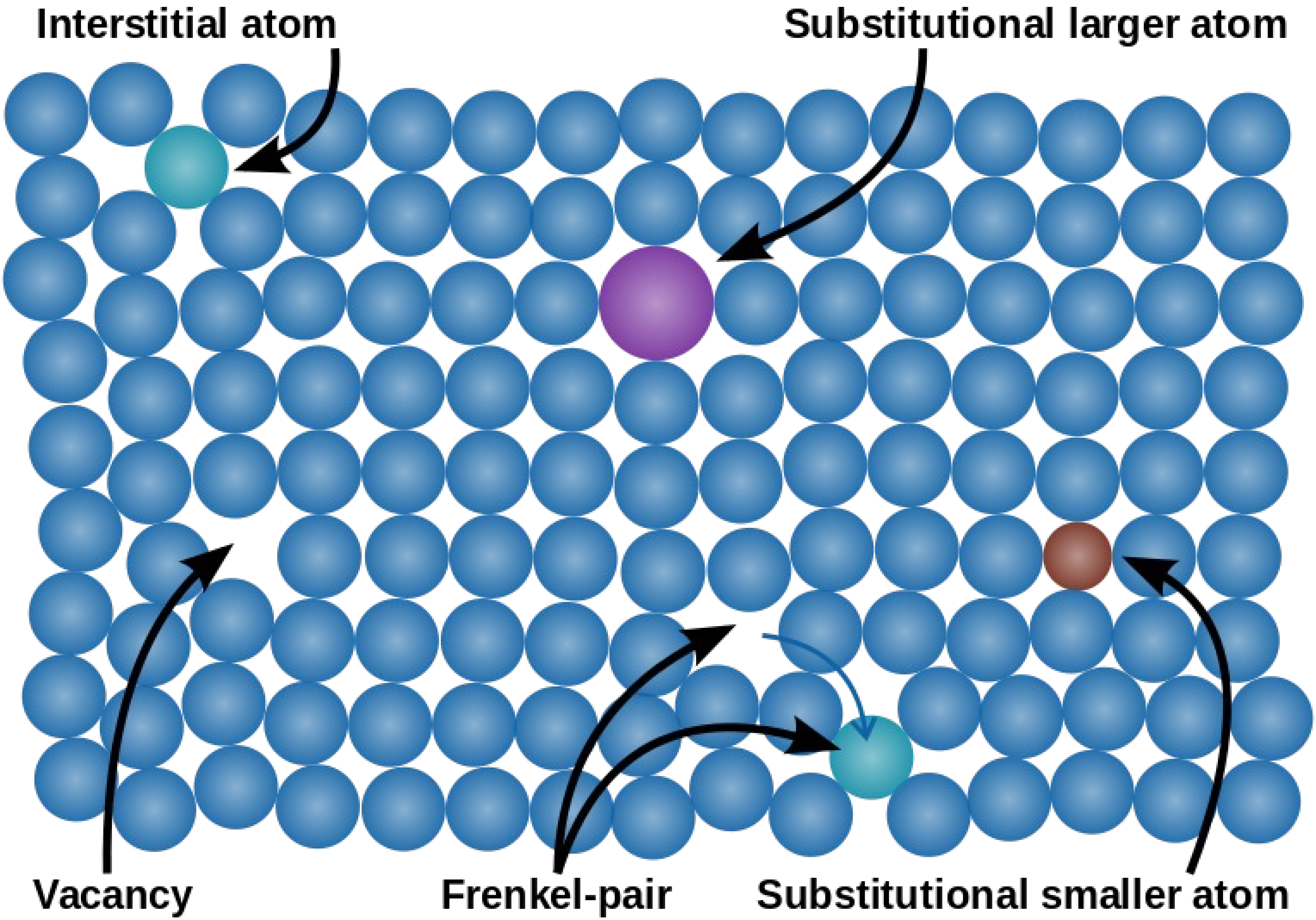
Mass transport is driven by the desire of the system to reduce the total interface energy and the energy of the particles/grains ...

… actually the free energy → the system wants to achieve thermal equilibrium.

Mass transport can be facilitated by diffusion and plasticity (creep)

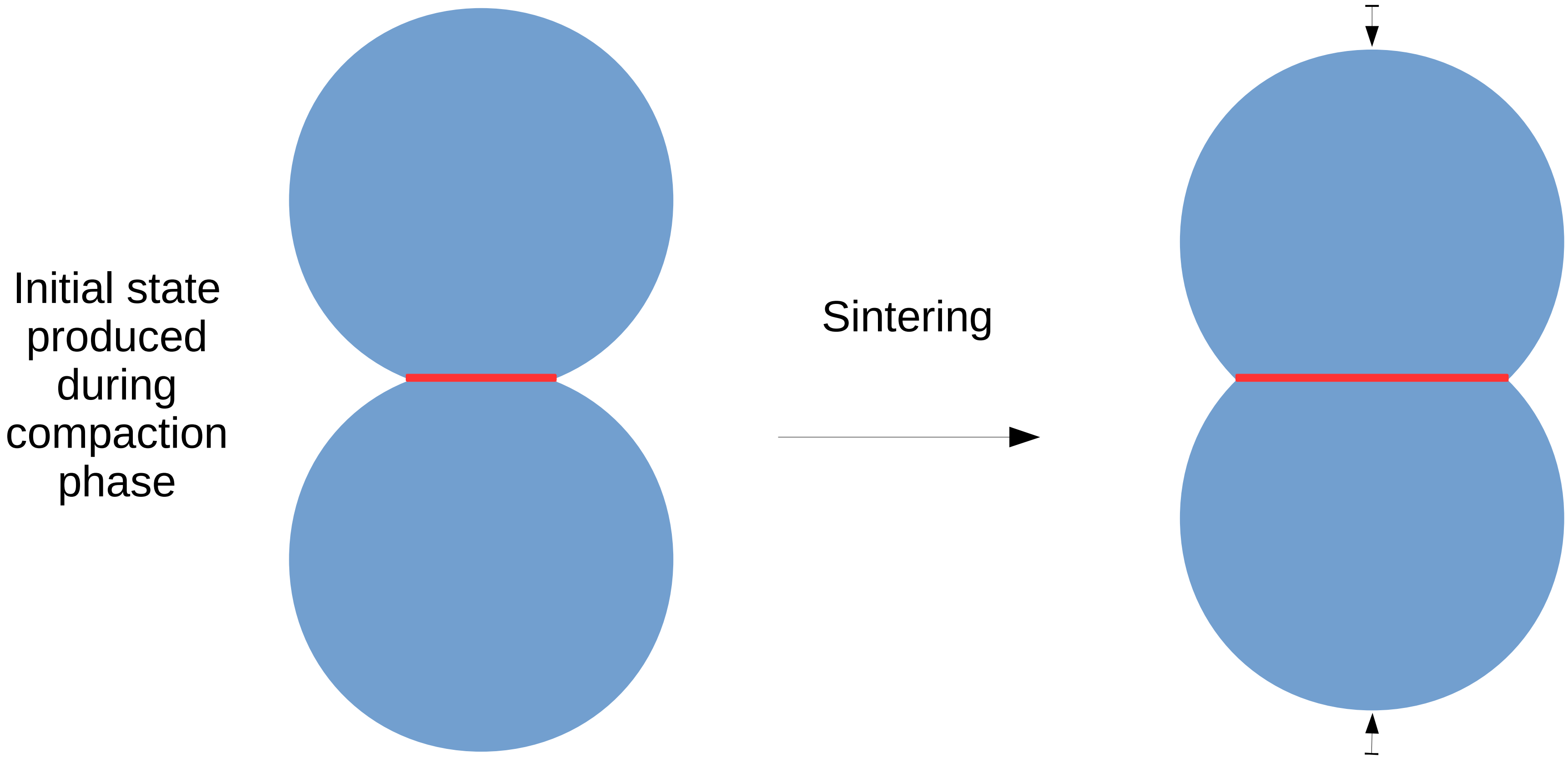
How does diffusion lead to a reduction of the (free) energy?

Mass transport via point defects



source: commons.wikimedia.org

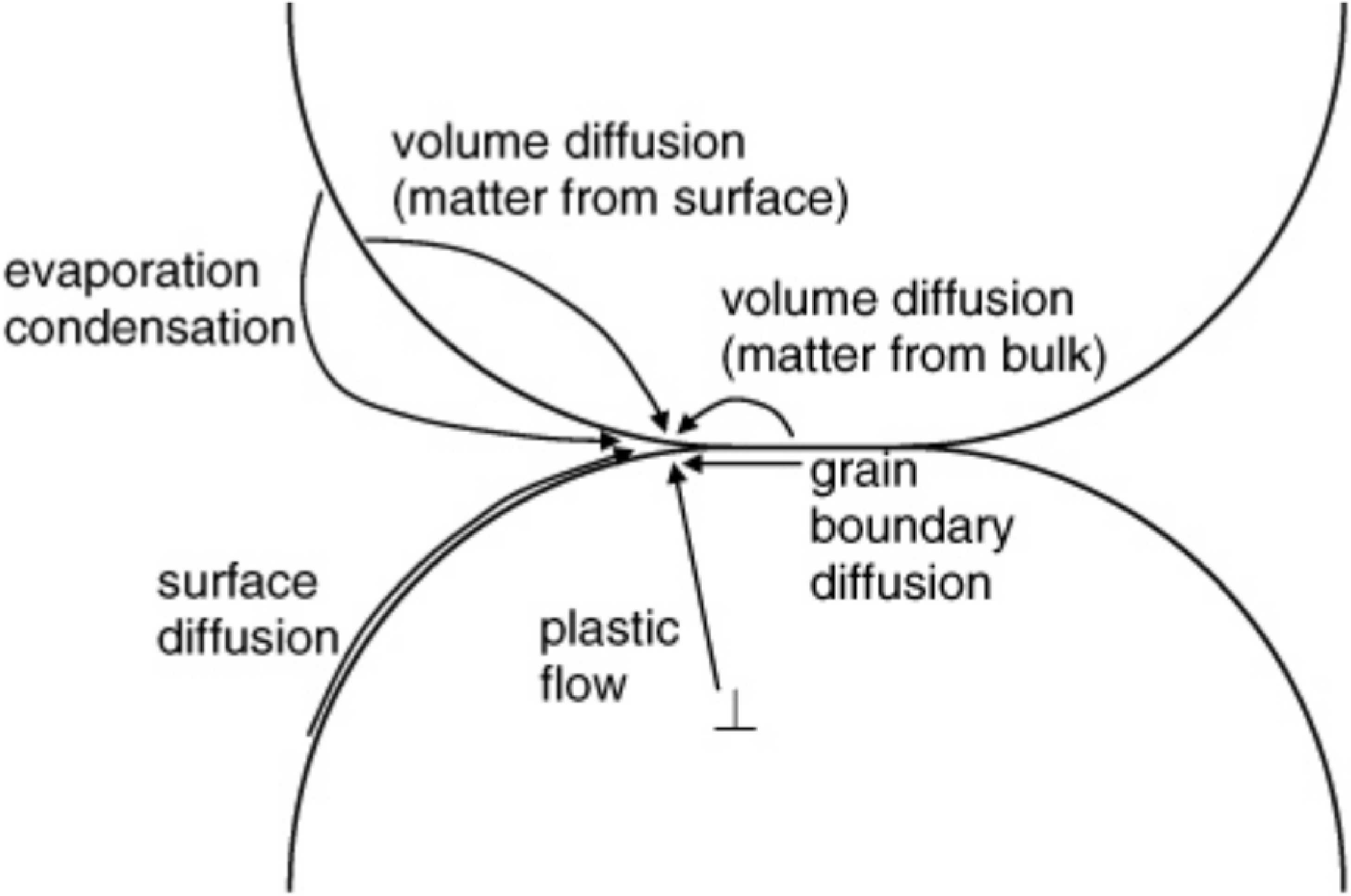
To develop analytical models for sintering the two particle approximation is used



Initial state produced during compaction phase

Sintering

Mass transport at green compact contact area



Theory of diffusion

The diffusion equation

$C(\mathrm{r},t)$	Particle concentration at position r and time t : number of particles per unit volume	$[m^{-3}]$
$\mathbf{J}(\mathrm{r},t)$	Particle flux at position r and time t : the number of particles passing per unit area per unit time	$[s^{-1}m^{-2}]$

continuity equation →

$$\frac{\partial C(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r},t)$$

Can be derived by starting from the integral form – the change of the number of particles within a volume is equal to the net flux through the surface bounding the volume. The above differential form is obtained by Gauss's (divergence) theorem

The diffusion equation

$C(\mathrm{r},t)$	Particle concentration at position r and time t : number of particles per unit volume	$[m^{-3}]$
$\mathbf{J}(\mathrm{r},t)$	Particle flux at position r and time t : the number of particles passing per unit area per unit time	$[s^{-1}m^{-2}]$

continuity equation →

$$\frac{\partial C(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r},t)$$

Fick's first law → flux goes from regions of high concentration to low concentration with a magnitude that is proportional to the concentration gradient

$$\mathbf{J}(\mathbf{r},t) = -D\nabla C(\mathbf{r},t)$$

D	Diffusion constant	$[s^{-1}m^{2}]$

The diffusion equation

$$\frac{\partial C(\mathbf{r},t)}{\partial t} = -\nabla \cdot \mathbf{J}(\mathbf{r},t)$$

continuity equation

$$\mathbf{J}(\mathbf{r},t) = -D\nabla C(\mathbf{r},t)$$

Fick’s first law

$$\frac{\partial C(\mathbf{r},t)}{\partial t} = \nabla \cdot (D\nabla C(\mathbf{r},t)) = D\nabla^2 C(\mathbf{r},t)$$

The diffusion equation (**Fick's second law**) when the diffusion constant does not depend on position

The diffusion equation (in 1D)

$$\frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x}$$

continuity equation

$$J_x(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

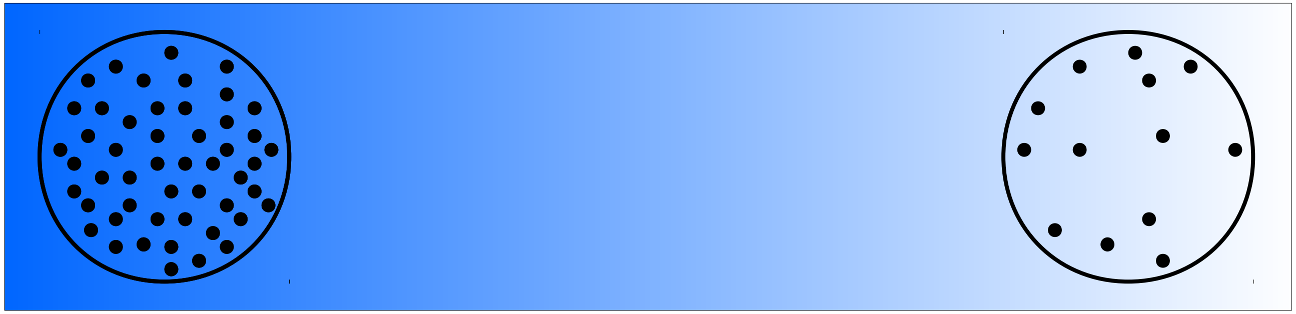
Fick’s first law

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

The diffusion equation (**Fick's second law**) when the diffusion constant does not depend on position

The diffusion equation

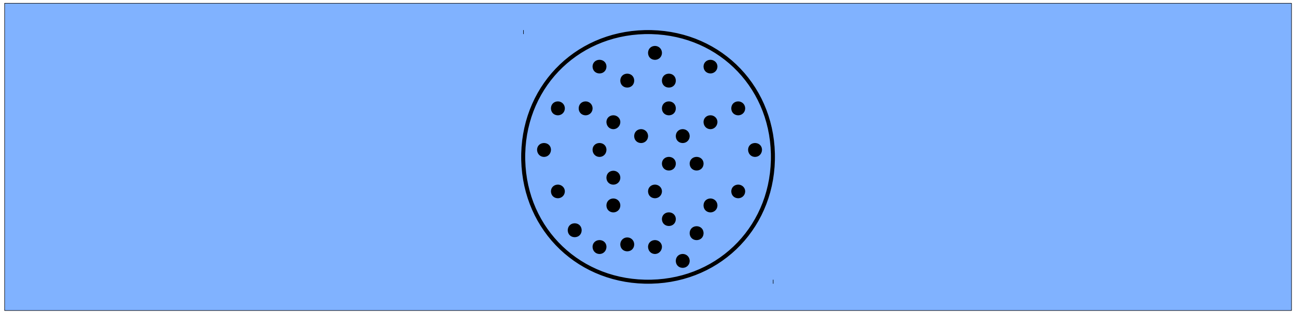
$$C(0, t=0) = C_{\text{initial}} \qquad C(L, t=0) = 0$$



Initial state has a concentration gradient, and is out-of-equilibrium

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2}$$

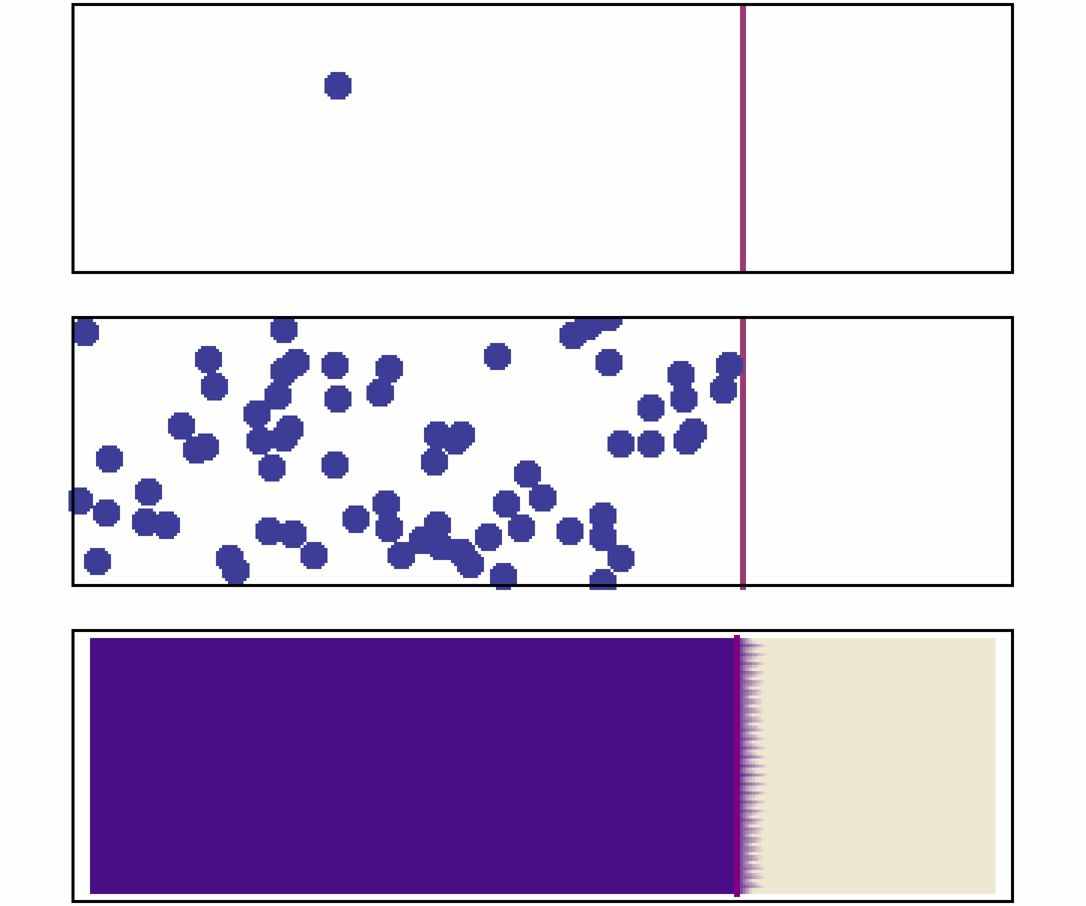
$$C(x, t \to \infty) = C_{\text{uniform}}$$



Final state is an equilibrium uniform concentration → no concentration gradient.

But there is still microscopic diffusion

The diffusion equation – an average of microscopic processes



Individual particle

Ensemble of particles

Continuum concentration limit → the diffusion equation

https://en.wikipedia.org/wiki/Diffusion

The diffusion equation (in 1D)

$$J_x(x,t) = -D\frac{\partial C(x,t)}{\partial x}$$

Fick's first law

This form is purely empirical and only valid for an ideal solution (no interactions between the particles and translational invariance)

Diffusion occurs to minimise the free energy and therefore should be driven by spatial gradients in the free energy

mobility

$$J_x(x,t) = -C(x,t)M\frac{\partial \mu(x,t)}{\partial x} = -D_{\text{eff}}(x,t)\frac{\partial C(x,t)}{\partial x}$$

$$C(x,t)M\left(\frac{\partial \mu(x,t)}{\partial x}\Big/\frac{\partial C(x,t)}{\partial x}\right) = C(x,t)M\left.\frac{\partial \mu}{\partial C}\right|_{x,t}$$

The (effective) diffusion coefficient depends on concentration, chemical potential gradients, and can be negative

In equilibrium at fixed T and P,

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N = \mu\mathrm{d}N$$

$$\rightarrow G = \mu N$$

When out-of-equilibrium

$$G = \sum_{i=1}^{N}\mu(x_i) = \sum_{i=1}^{N}\mu(P(x_i))$$

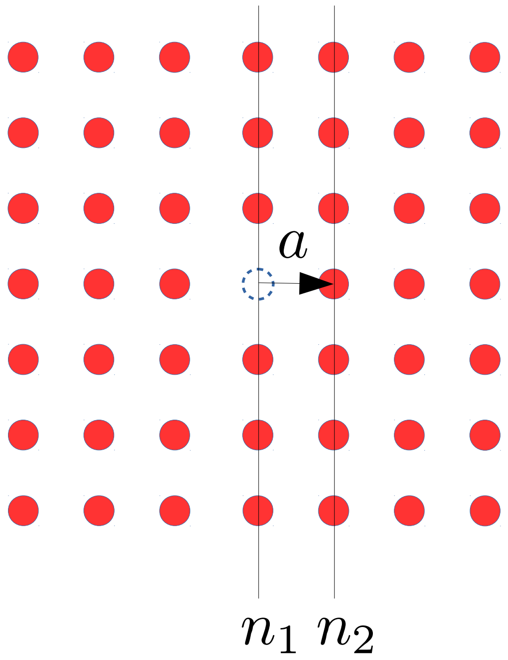
Pressure gradients

The important equations for sintering physics

1)	$J_x(x,t) = -C(x,t)M\frac{\partial \mu(x,t)}{\partial x}$	Diffusion equation in a chemical potential gradient
2)	$\Delta(\gamma A) = (\Delta\gamma)A + \gamma(\Delta A) \approx \gamma\Delta A$	Minimization of interface energy
3)	$P_1 - P_2 = \gamma\frac{2}{r}$	Pressure difference across a curved interface
4)	$p_V \approx p_{V,r\to\infty} + \frac{p_{V,r\to\infty}2\gamma M}{r\rho RT}$	Vapor pressure of an ideal gas at a curved surface
5)	$\mu_{1,r} = \mu_{1,\infty} + \gamma K\Omega_1$	Chemical potential gradient at a curved surface

Microscopic diffusion: the vacancy defect

The vacancy defect



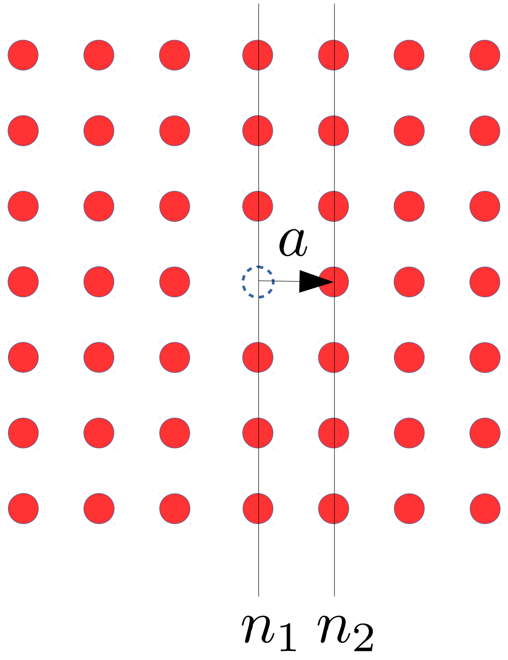
Define:

Γ_{vacancy}	- the rate of vacancy hopping per site
$n_i = C(x_i)a$	- the number of vacancies in the *i*th plane per unit area
z	- atomic coordination
a	- lattice constant

Vacancy fluxes

$$\begin{cases} J_{x,1} = \frac{1}{z}\Gamma_{\text{vacancy}} n_1 \\ J_{x,2} = \frac{1}{z}\Gamma_{\text{vacancy}} n_2 \end{cases}$$

The vacancy defect



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Γ_{vacancy}	- the rate of vacancy hopping per site
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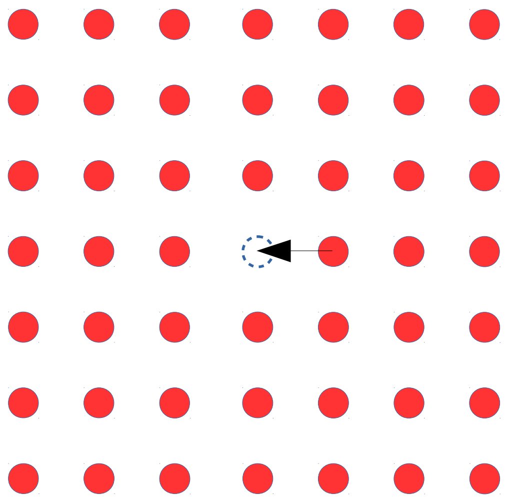
$$J_{x,\text{net}} = J_{x,1} - J_{x,2} = \frac{1}{z}\Gamma_{\text{vacancy}}\left(n_1 - n_2\right)$$

$$= \frac{1}{z}\Gamma_{\text{vacancy}}a\left(C(x_1) - C(x_2)\right) = -\frac{1}{z}\Gamma_{\text{vacancy}}a^2\frac{\partial C(x)}{\partial x} = -D_{\text{vacancy}}\frac{\partial C(x)}{\partial x}$$

$$\boxed{D_{\text{vacancy}} = \frac{1}{z}\Gamma_{\text{vacancy}}a^2}$$

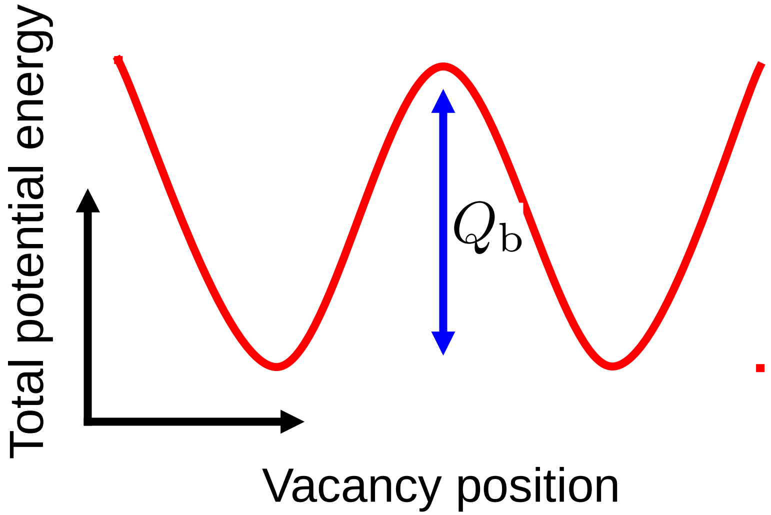
Microscopic diffusion: the vacancy hopping rate



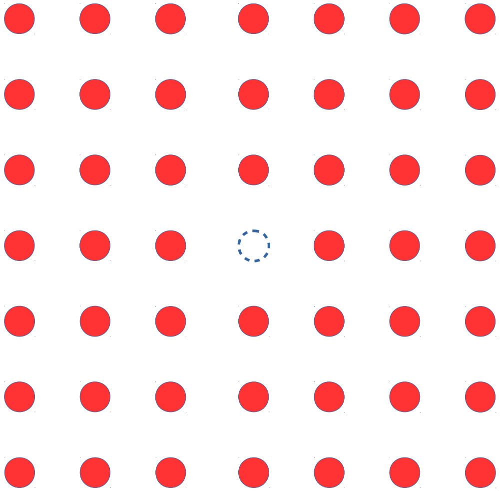
Activation energy

$$\Gamma_{\text{vacancy}} = \nu \exp\left(-\frac{Q_{\text{b}}}{k_{\text{B}}T}\right)$$

Attempt rate



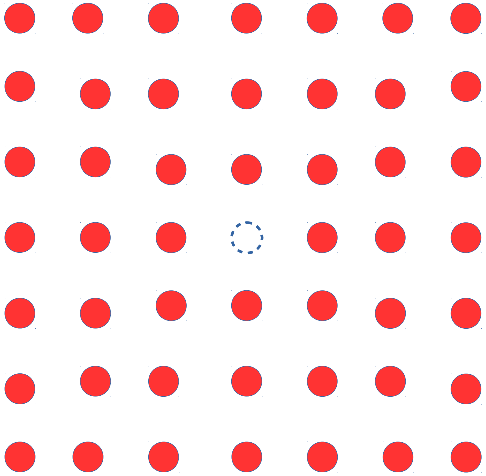
Microscopic diffusion: the equilibrium vacancy concentration



$$E_{\text{vacancy}} = E_{N-1} - (N-1)E_0$$

$$C_{\text{vacancy}} = \frac{1}{a^3} \exp\left(-\frac{E_{\text{vacancy}}}{k_{\text{B}}T}\right)$$

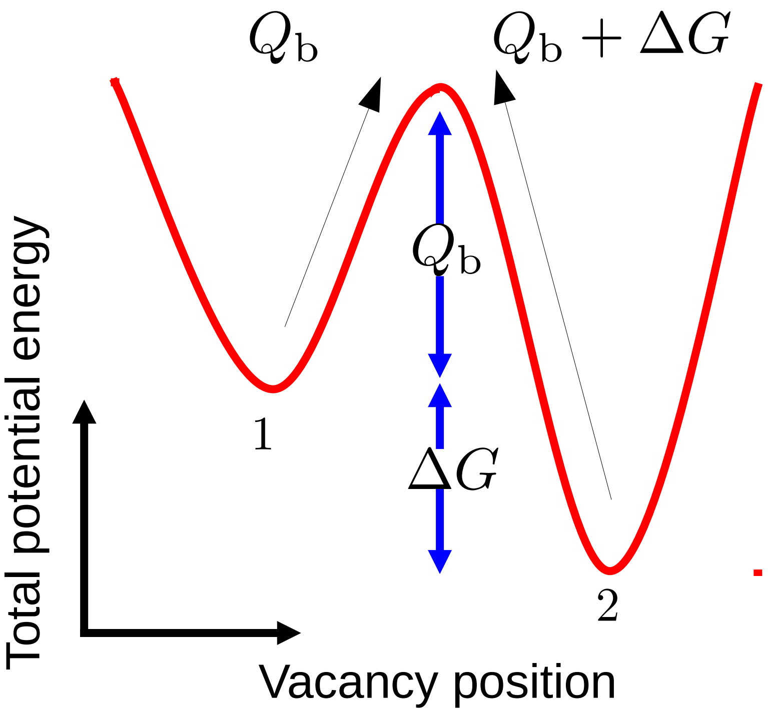
Lattice constant



Under compression the vacancy formation energy decreases, and so regions under a positive pressure will tend to have a higher equilibrium vacancy concentration

If there is a pressure gradient the equilibrium concentration will vary with position

The vacancy defect in a chemical potential gradient



$$\Gamma_{1\to 2} = \nu \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right)$$

$$\Gamma_{2\to 1} = \nu \exp\left(-\frac{Q_\mathrm{b} + \Delta G_{12}}{k_\mathrm{B}T}\right)$$

$$\begin{aligned} J_{x,\mathrm{net}} &= n_1 \nu \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right) - n_2 \nu \exp\left(-\frac{Q_\mathrm{b} + \Delta G_{12}}{k_\mathrm{B}T}\right) \\ &\approx n_1 \nu \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right)\left(1 - \exp\left(-\frac{\Delta G_{12}}{k_\mathrm{B}T}\right)\right) \\ &\approx n_1 \nu \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right)\frac{\Delta G_{12}}{k_\mathrm{B}T} \\ &\approx \nu \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right)\frac{C_1 a^2}{k_\mathrm{B}T}\frac{\mathrm{d}\mu}{\mathrm{d}a} \\ &= C_1 \frac{D}{k_\mathrm{B}T}\frac{\mathrm{d}\mu}{\mathrm{d}a} = C_1 M \frac{\mathrm{d}\mu}{\mathrm{d}a} \end{aligned}$$

$$n_1 \approx n_2 = C_1 a$$

$$\Delta G_{12} = \mu_1 - \mu_2 = \Delta a \frac{\Delta\mu}{\Delta a} \approx a \frac{\mathrm{d}\mu}{\mathrm{d}a}$$

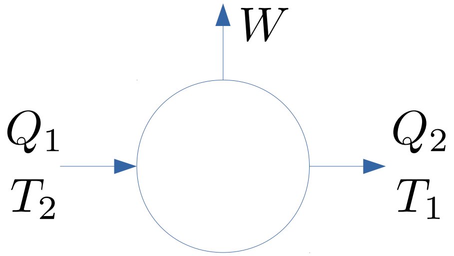
Additional content: thermodynamics primer

The first law

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$$

First law of thermodynamics
equivalence of heat and work

$\mathrm{d}Q \longrightarrow$ Heat transferred to the system



$$\eta = \frac{\text{Work out}}{\text{Heat in}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$\eta \leq \eta_{\mathrm{rev}}$ Carnot's theorem

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{Q_{r2}}{Q_{r1}}$$

$$\frac{Q_2}{Q_1} \leq \underbrace{\frac{Q_{r2}}{Q_{r1}} = \frac{T_2}{T_1}}_{\text{Thermodynamic temperature definition}}$$

$$\sum_i \frac{Q_i}{T_i} \leq 0 \qquad \int \frac{\mathrm{d}Q}{T} \leq 0$$

Clausius' theorem

Define: $\mathrm{d}S = \dfrac{\mathrm{d}Q_{\mathrm{rev}}}{T} \qquad \mathrm{d}S \geq \dfrac{\mathrm{d}Q}{T}$

For a thermally isolated system there is no transfer of heat

$\mathrm{d}S \geq 0$ The entropy of an isolated system cannot decrease

$$\mathrm{d}Q = T\mathrm{d}S$$

The first law

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W$$

First law of thermodynamics
equivalence of heat and work

$\mathrm{d}W \longrightarrow$ Work done by the system $\qquad \mathrm{d}W = P\mathrm{d}V$

$$V(T,P) \to \mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial V}{\partial P}\right)_T \mathrm{d}P$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Isothermal compressibility

$$\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Isobaric cubic expansivity

$$V(T,P) \to PV = nRT$$

Equation of state for
an ideal gas

Thermodynamic potentials

$U(S,V)$ → Internal energy (potential + kinetic energy) at a fixed entropy and volume

$$\left.\begin{aligned} \mathrm{d}U &= \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V \\ &= T\mathrm{d}S - P\mathrm{d}V \end{aligned}\right\} \quad T = \left(\frac{\partial U}{\partial S}\right)_V \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$C_V = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_V = \left(\frac{\mathrm{d}U + P\mathrm{d}V}{\mathrm{d}T}\right)_V = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V$$

$H(S,P) = U(S,V) + PV$ → Enthalpy

$$\left.\begin{aligned} \mathrm{d}H &= \mathrm{d}U(S,V) + P\mathrm{d}V + V\mathrm{d}P \\ &= T\mathrm{d}S + V\mathrm{d}P \end{aligned}\right\} \quad T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$C_P = \left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_P = \left(\frac{\mathrm{d}H - V\mathrm{d}P}{\mathrm{d}T}\right)_P = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_P$$

Thermodynamics potentials

$A(T,V) = U(S,V) - TS$ → Helmholtz free energy

$$\left.\begin{aligned} \mathrm{d}A &= \mathrm{d}U(S,V) - T\mathrm{d}S - S\mathrm{d}T \\ &= -S\mathrm{d}T - P\mathrm{d}V \end{aligned}\right\} \quad S = -\left(\frac{\partial A}{\partial T}\right)_V \qquad P = -\left(\frac{\partial A}{\partial V}\right)_T$$

$G(T,P) = H(S,P) - TS$ → Gibbs free energy

$$\left.\begin{aligned} \mathrm{d}G &= \mathrm{d}H(T,V) - T\mathrm{d}S - S\mathrm{d}T \\ &= -S\mathrm{d}T + V\mathrm{d}P \end{aligned}\right\} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

Gibbs free energy is the most commonly used since most experiments are done at fixed temperature and pressure

Thermodynamics primer

If the number of particles is allowed to vary, need to modify the differentials of all thermodynamic potentials

$$\mathrm{d}\Phi \to \mathrm{d}\Phi + \sum_i \mu_i \mathrm{d}N_i$$

$\mathrm{d}N_i$ - change in number of particles of type i

μ_i - chemical potential of type i

$$\begin{aligned} U(S,V) &\to U(S,V,\{N_i\}) \\ A(T,V) &\to A(T,V,\{N_i\}) \\ H(S,P) &\to H(S,P,\{N_i\}) \\ G(T,P) &\to G(T,P,\{N_i\}) \end{aligned}$$

Again, the Gibbs free energy is the most commonly used, since changing the number of particles under fixed pressure and temperature gives

$$\mathrm{d}G = \sum_i \mu_i \mathrm{d}N_i \longrightarrow G = \sum_i \mu_i N_i$$

Thermodynamics primer

Conditions for thermodynamic equilibrium:

- For a completely isolated system, S is maximum at thermodynamic equilibrium.
- For a system with controlled constant temperature and volume, A is minimum at thermodynamic equilibrium.
- For a system with controlled constant temperature and pressure, G is minimum at thermodynamic equilibrium.

The various types of equilibriums are achieved as follows:

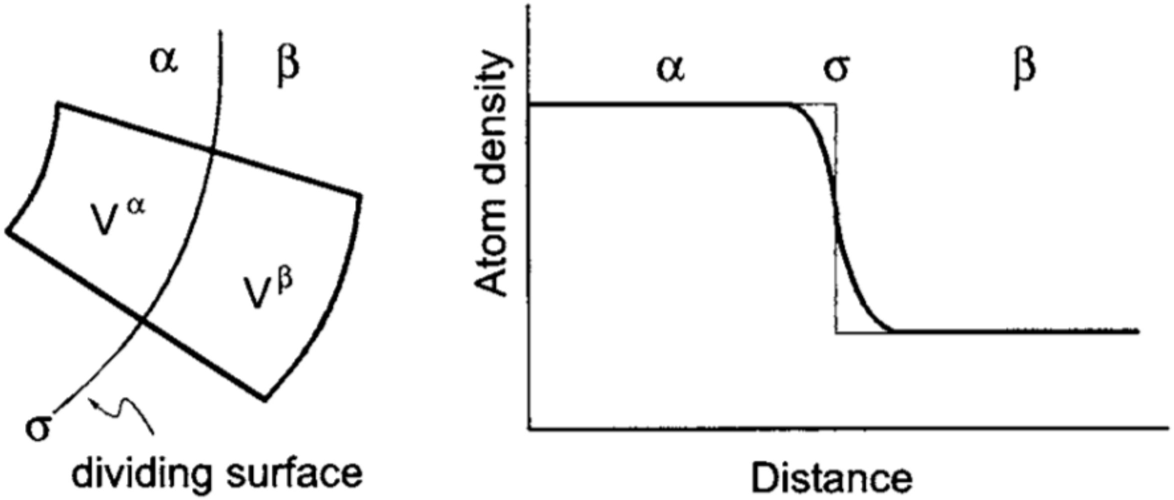
- Two systems are in thermal equilibrium when their temperatures are the same.
- Two systems are in mechanical equilibrium when their pressures are the same.
- Two systems are in diffusive equilibrium when their chemical potentials are the same.
- All forces are balanced and there is no significant external driving force.

No internal macroscopic motion is possible in a state of equilibrium

Interface thermodynamics

Interface (free) energy

The surface/interface is defined as the plane between condensed matter and a vapour phase or vacuum, such as solid/vapour and liquid/vapour interfaces – the term 'interface' is used for the dividing plane between any two different phases.



$$\left.\begin{aligned} \mathrm{d}U &= \mathrm{d}U_\alpha + \mathrm{d}U_\beta + \mathrm{d}U_\sigma \\ &= T\mathrm{d}S + \mu_\alpha \mathrm{d}n_\alpha + \mu_\beta \mathrm{d}n_\beta + P_\alpha \mathrm{d}V_\alpha + P_\beta \mathrm{d}V_\beta + \gamma \mathrm{d}A \end{aligned}\right\} \quad \gamma \equiv \left(\frac{\partial U}{\partial A}\right)_{S,\mu_\alpha,\mu_\beta,V_\alpha,V_\beta}$$

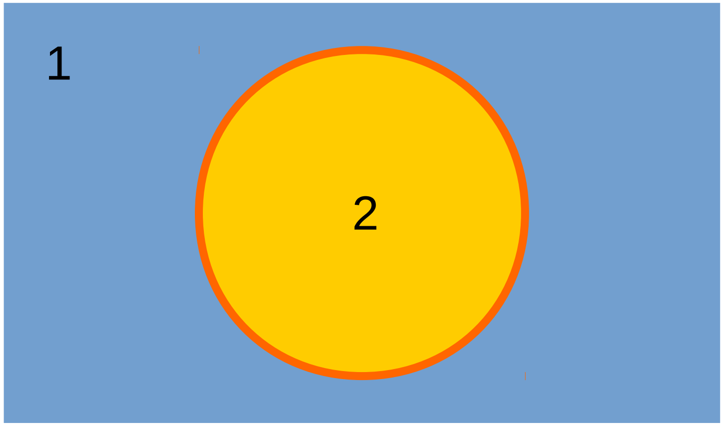
$$\mathrm{d}U_\sigma = T\mathrm{d}S_\sigma + \mu_\alpha \mathrm{d}n_\alpha^\sigma + \mu_\beta \mathrm{d}n_\beta^\sigma + \gamma \mathrm{d}A$$

Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

The important equations for sintering physics

1)	$J_x(x,t) = -C(x,t)M\frac{\partial \mu(x,t)}{\partial x}$	Diffusion equation in a chemical potential gradient
2)	$\Delta(\gamma A) = (\Delta\gamma)A + \gamma(\Delta A) \approx \gamma\Delta A$	Minimization of interface energy
3)	$P_1 - P_2 = \gamma\frac{2}{r}$	Pressure difference across a curved interface
4)	$p_V \approx p_{V,r\to\infty} + \frac{p_{V,r\to\infty}2\gamma M}{r\rho RT}$	Vapor pressure of an ideal gas at a curved surface
5)	$\mu_{1,r} = \mu_{1,\infty} + \gamma K\Omega_1$	Chemical potential gradient at a curved surface

Thermodynamics of interfaces



Consider an equilibrium two phase system at constant temperature, volume and component number

$$A = S\mathrm{d}T - P\mathrm{d}V - \mu\mathrm{d}N$$

Helmholtz free energy

When in equilibrium $\mathrm{d}A = \mathrm{d}A_1 + \mathrm{d}A_2 + \mathrm{d}A_i = 0$ and $\mu_1 = \mu_2$

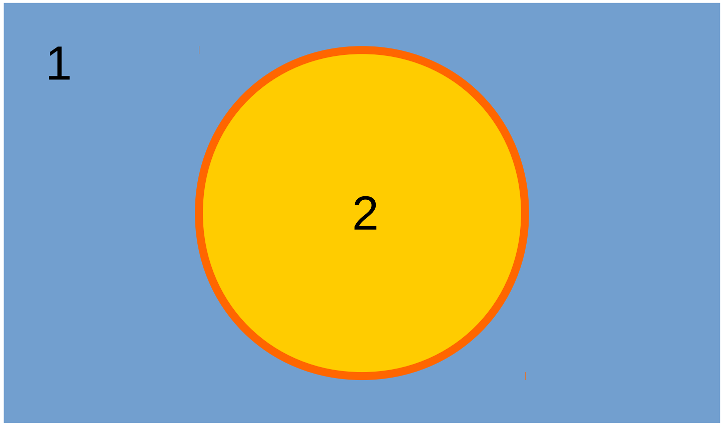
$$\left.\begin{aligned} \mathrm{d}A_1 &= -P_1\mathrm{d}V_1 + \mu_1\mathrm{d}N_1 \\ \mathrm{d}A_2 &= -P_2\mathrm{d}V_2 + \mu_2\mathrm{d}N_2 \\ \mathrm{d}A_i &= \gamma\mathrm{d}\,(\mathrm{Surface\ Area}) \end{aligned}\right\} \quad P_1 - P_2 = \gamma\frac{\mathrm{d}\,(\mathrm{Surface\ Area})}{\mathrm{d}V_1} = \gamma K$$

Young–Laplace equation

$$\frac{\mathrm{d}\,(\mathrm{Surface\ Area})}{\mathrm{d}V_1} = K \longleftarrow$$

Average curvature of interface

Thermodynamics of interfaces



Consider an equilibrium two phase system at constant temperature, volume and component number

$$\mathrm{d}T = 0$$

$$N_1 + N_2 = N \rightarrow \mathrm{d}N_1 + \mathrm{d}N_2 = \mathrm{d}N = 0$$

$$V_1 + V_2 = V \rightarrow \mathrm{d}V_1 + \mathrm{d}V_2 = \mathrm{d}V = 0$$

When in equilibrium $\mathrm{d}A = \mathrm{d}A_1 + \mathrm{d}A_2 + \mathrm{d}A_i = 0$ and $\mu_1 = \mu_2$

$$\left.\begin{aligned} \mathrm{d}A_1 &= -P_1\mathrm{d}V_1 + \mu_1\mathrm{d}N_1 \\ \mathrm{d}A_2 &= -P_2\mathrm{d}V_2 + \mu_2\mathrm{d}N_2 \\ \mathrm{d}A_i &= \gamma\mathrm{d}\,(\mathrm{Surface\ Area}) \end{aligned}\right\} \quad P_1 - P_2 = \gamma\frac{\mathrm{d}\,(\mathrm{Surface\ Area})}{\mathrm{d}V_1} = \gamma K$$

Young–Laplace equation

$$\frac{\mathrm{d}\,(\mathrm{Surface\ Area})}{\mathrm{d}V_1} = K \longleftarrow$$

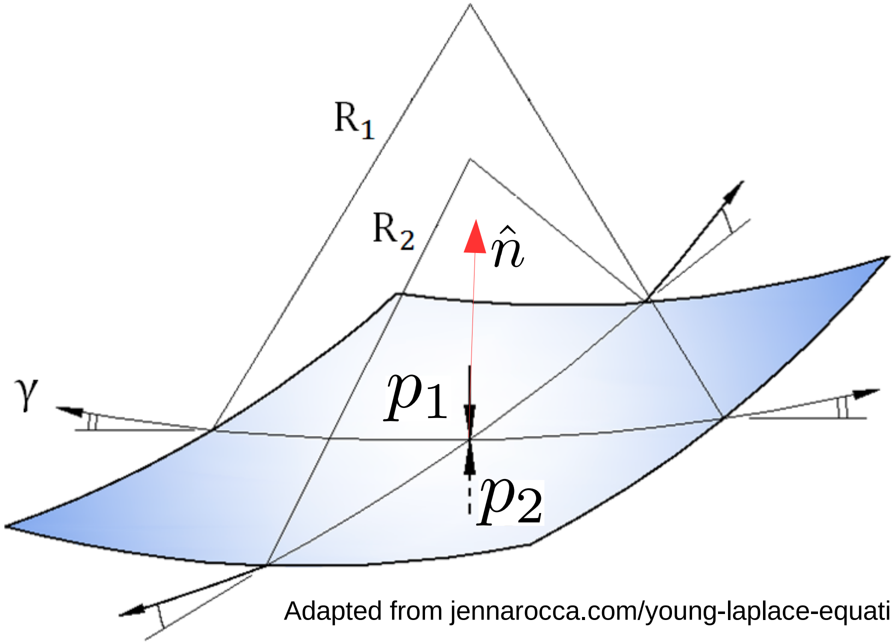
Average curvature
of interface

Young–Laplace equation

$$\Delta p = -\gamma \nabla \cdot \hat{n}$$

$$= \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = 2\gamma H = \frac{2\gamma}{r}$$

$(= \gamma H$ in 2d)



Adapted from jennarocca.com/young-laplace-equation/

γ : surface energy density

H : average curvature

R_1/R_2 : max/min curvature

$\Delta p = p_1 - p_2$: pressure difference across interface

The important equations for sintering physics

1)	$J_x(x,t) = -C(x,t)M\frac{\partial\mu(x,t)}{\partial x}$	Diffusion equation in a chemical potential gradient
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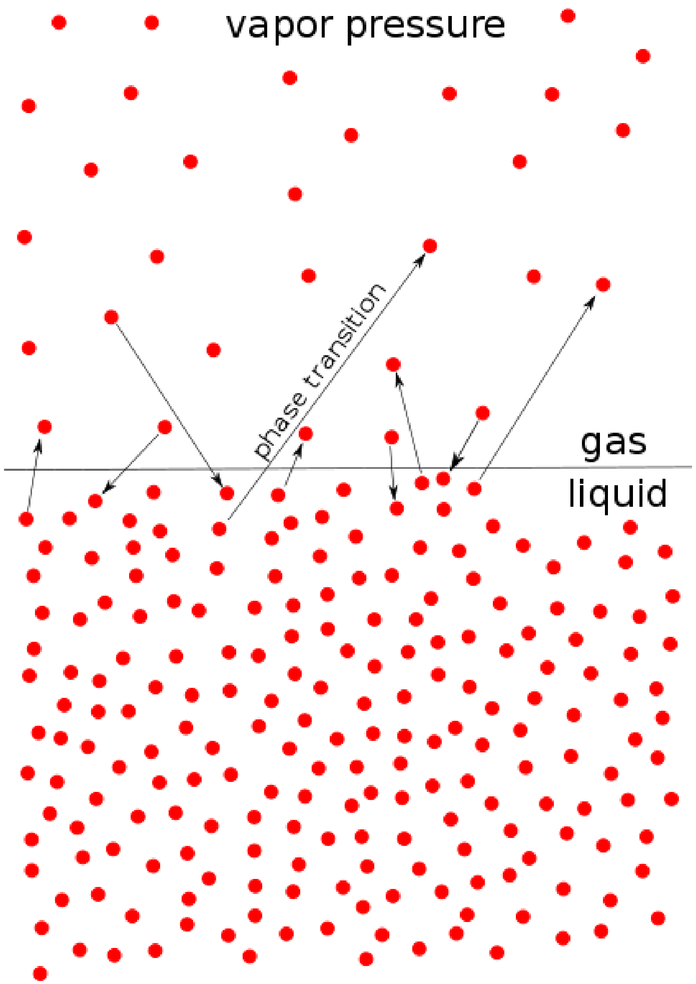
5)	$\mu_{1,r} = \mu_{1,\infty} + \gamma K\Omega_1$	Chemical potential gradient at a curved surface

Vapor pressure – surface effects



en.wikipedia.org/wiki/Vapor_pressure

Consider a spherical liquid drop immersed in its vapor at temperature T_0 and pressure p_0

$$\mathrm{d}G = \mathrm{d}m_\mathrm{L}\left(u_\mathrm{L} + p_0 v_\mathrm{L} - T_0 s_\mathrm{L}\right) + \mathrm{d}m_\mathrm{V}\left(u_\mathrm{V} + p_0 v_\mathrm{V} - T_0 s_\mathrm{V}\right) + \mathrm{d}G_\mathrm{S}$$

$$\mathrm{d}G_\mathrm{S} = \gamma \mathrm{d}A = \gamma \frac{2 v_\mathrm{L}}{r} \mathrm{d}m_\mathrm{L}$$

$$\mathrm{d}G = \mathrm{d}m_\mathrm{L}\left(u_\mathrm{L} + v_\mathrm{L}\left(p_0 + \gamma \frac{2}{r}\right) - T_0 s_\mathrm{L}\right) + \mathrm{d}m_\mathrm{V}\left(u_\mathrm{V} + p_0 v_\mathrm{V} - T_0 s_\mathrm{V}\right)$$

$$p_\mathrm{L} = p_0 + \gamma \frac{2}{r} \longrightarrow \mathrm{d}G = g_\mathrm{L}\left(p_\mathrm{L}, T\right) \mathrm{d}m_\mathrm{L} + g_\mathrm{V}\left(p_\mathrm{V} = p_0, T\right) \mathrm{d}m_\mathrm{V}$$

$$\mathrm{d}m_\mathrm{L} + \mathrm{d}m_\mathrm{V} = 0 \longrightarrow g_\mathrm{L}\left(p_\mathrm{L}, T\right) = g_\mathrm{V}\left(p_\mathrm{V}, T\right)$$

Vapor pressure – surface effects

$$g_{\mathrm{L}}\left(p_{\mathrm{L}},T\right)=g_{\mathrm{V}}\left(p_{\mathrm{V}},T\right) \quad \longrightarrow$$

When changing the volume of the drop, equilibrium requires:

$$\left(\frac{\partial g_{\mathrm{L}}}{\partial p_{\mathrm{L}}}\right)_T \mathrm{d}p_{\mathrm{L}}=\left(\frac{\partial g_{\mathrm{V}}}{\partial p_{\mathrm{V}}}\right)_T \mathrm{d}p_{\mathrm{V}}$$

$$v_{\mathrm{L}}\mathrm{d}p_{\mathrm{L}}=v_{\mathrm{L}}\left(\mathrm{d}p_{\mathrm{V}}-\frac{2\gamma}{r^2}\mathrm{d}r\right)=v_{\mathrm{V}}\mathrm{d}p_{\mathrm{V}}$$

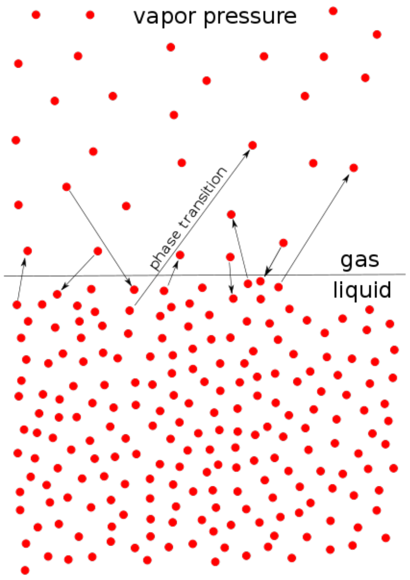
$$\left(v_{\mathrm{V}}-v_{\mathrm{L}}\right)\mathrm{d}p_{\mathrm{V}}=-\frac{2\gamma}{r^2}v_{\mathrm{L}}\mathrm{d}r$$

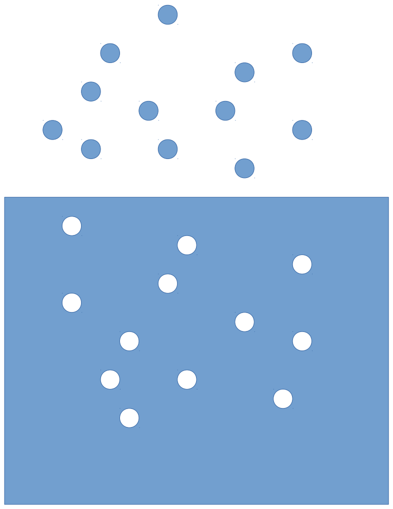
$$v_{\mathrm{V}}>>v_{\mathrm{L}} \qquad v_{\mathrm{V}}\mathrm{d}p_{\mathrm{V}}=-\frac{2\gamma}{r^2}v_{\mathrm{L}}\mathrm{d}r$$

$$\frac{RT}{M}\frac{\mathrm{d}p_{\mathrm{V}}}{p_{\mathrm{v}}}=-\frac{2\gamma}{r^2}v_{\mathrm{L}}\mathrm{d}r$$

$$p_{\mathrm{V}}=p_{V,r\to\infty}\exp\left(\frac{2\gamma M}{r\rho RT}\right)$$

$$\approx p_{V,r\to\infty}+\frac{p_{V,r\to\infty}2\gamma M}{r\rho RT}$$





Solid-vacuum/gas regime with vacancies

The important equations for sintering physics

1)	$J_x(x,t) = -C(x,t)M\frac{\partial\mu(x,t)}{\partial x}$	Diffusion equation in a chemical potential gradient
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5)	$\mu_{1,r} = \mu_{1,\infty} + \gamma K\Omega_1$	Chemical potential gradient at a curved surface

… in terms of the chemical potential

At equilibrium: $\mu_1 = \mu_2 \quad \longrightarrow \quad \mu_1(T, P_{1,r}) = \mu_2(T, P_{2,r})$

$$\mu_1(T, P_{1,r}) = \mu_1(T, P_{2,r} + \gamma K) \approx \mu_1(T, P_{2,r}) + \gamma K \left(\frac{\partial \mu_1}{\partial P}\right)_{T, P_{1,r}}$$

$$= \mu_1(T, P_{2,r}) + \gamma K \Omega_1$$

Assume that the chemical potential for phase 2 remains constant for the range of pressure changes due to curvature

$$\mu_2(T, P_2) \approx \mu_2(T, P_{2,\infty}) \equiv \mu_{2,\infty} \qquad (= \mu_1(T, P_{2,\infty}) \equiv \mu_{1,\infty})$$

$$\mu_1(T, P_{1,r}) = \mu_1(T, P_{2,\infty}) + \gamma K \Omega_1 \quad \longrightarrow \quad \mu_{1,r} = \mu_{1,\infty} + \gamma K \Omega_1$$

The important equations for sintering physics

1)	$J_x(x,t) = -C(x,t)M\frac{\partial \mu(x,t)}{\partial x}$	Diffusion equation in a chemical potential gradient
2)	$\Delta(\gamma A) = (\Delta\gamma)A + \gamma(\Delta A) \approx \gamma \Delta A$	Minimization of interface energy
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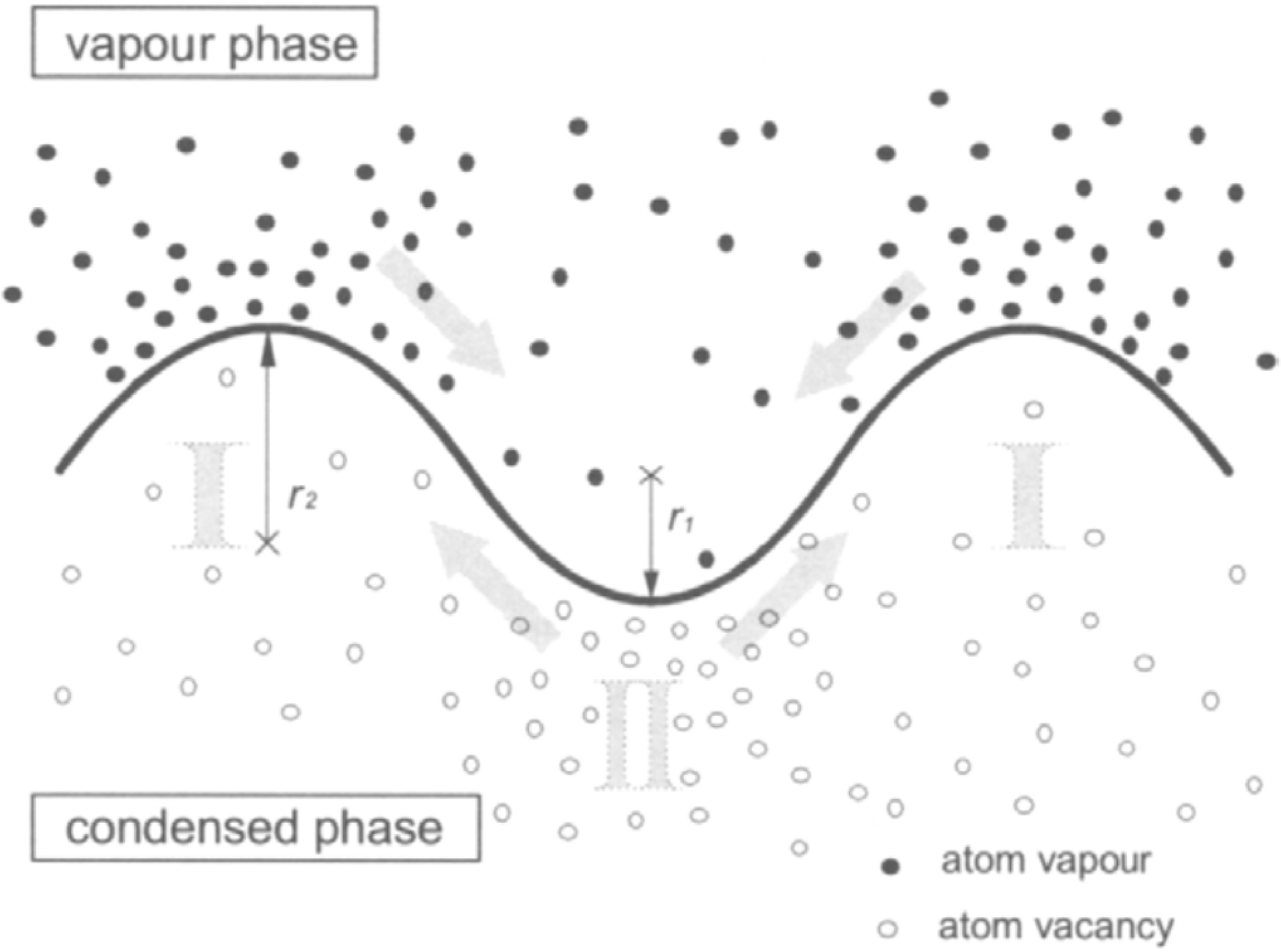
Atomic transport kinetics effected by capillary pressure differences



… in terms of the chemical activity

$$a = \exp\left(-\frac{\mu_{\mathrm{ref}} - \mu}{RT}\right)$$

$$\mu = \mu_{\mathrm{ref}} + RT\ln a$$

$$a = \gamma_{\mathrm{activity}}\frac{C}{C_{\mathrm{ref}}}$$

$$\frac{\partial\mu}{\partial x} = \frac{RT}{C}\frac{\partial C}{\partial x}$$

$$J = -D\frac{\partial C}{\partial x} = -C\frac{D}{RT}\frac{\partial\mu}{\partial x} = -CM\frac{\partial\mu}{\partial x}$$

$$\underbrace{\mu_1 = \mu_{\mathrm{ref}} + RT\ln\left(\gamma_{\mathrm{activity}}\frac{C_0}{C_{\mathrm{ref}}}\right) \qquad \mu_2 = \mu_{\mathrm{ref}} + RT\ln\left(\gamma_{\mathrm{activity}}\frac{C_0 + \Delta C}{C_{\mathrm{ref}}}\right)}_{\mu_2 - \mu_1 = RT\ln\left(\frac{C_0 + \Delta C}{C_0}\right) \approx RT\frac{\Delta C}{C_0}}$$

At local equilibrium

$$\frac{\partial\mu}{\partial P} = \Omega_0 \quad \longrightarrow \quad \mu_2 - \mu_1 \approx (P_2 - P_1)\,\Omega_0 \approx \frac{2\gamma}{r}\Omega_0 \left\{ \begin{aligned} & RT\frac{\Delta C}{C_0} \approx \frac{2\gamma}{r}\Omega_0 \\ & \Delta C \approx \frac{2\gamma}{RTr}C_0\Omega_0 \end{aligned} \right.$$

Initial stage sintering: two particle sintering models

Initial stage sintering

'During the initial stage of sintering, single-crystal particles in contact cannot undergo grain growth because the solid-vapor surfaces diverge at an acute angle from the particle-particle contact area. Migration of the grain boundary away from the minimum area position would require it to increase significantly in area and energy. Therefore the boundary is initially confined to the neck area. After the "neck" surface has become blunted by neck growth, the inhibition to boundary motion decreases until grain growth becomes possible. The point at which grain growth first occurs is considered to terminate the initial stage of sintering.'

Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Two particle model useful for initial stage sintering

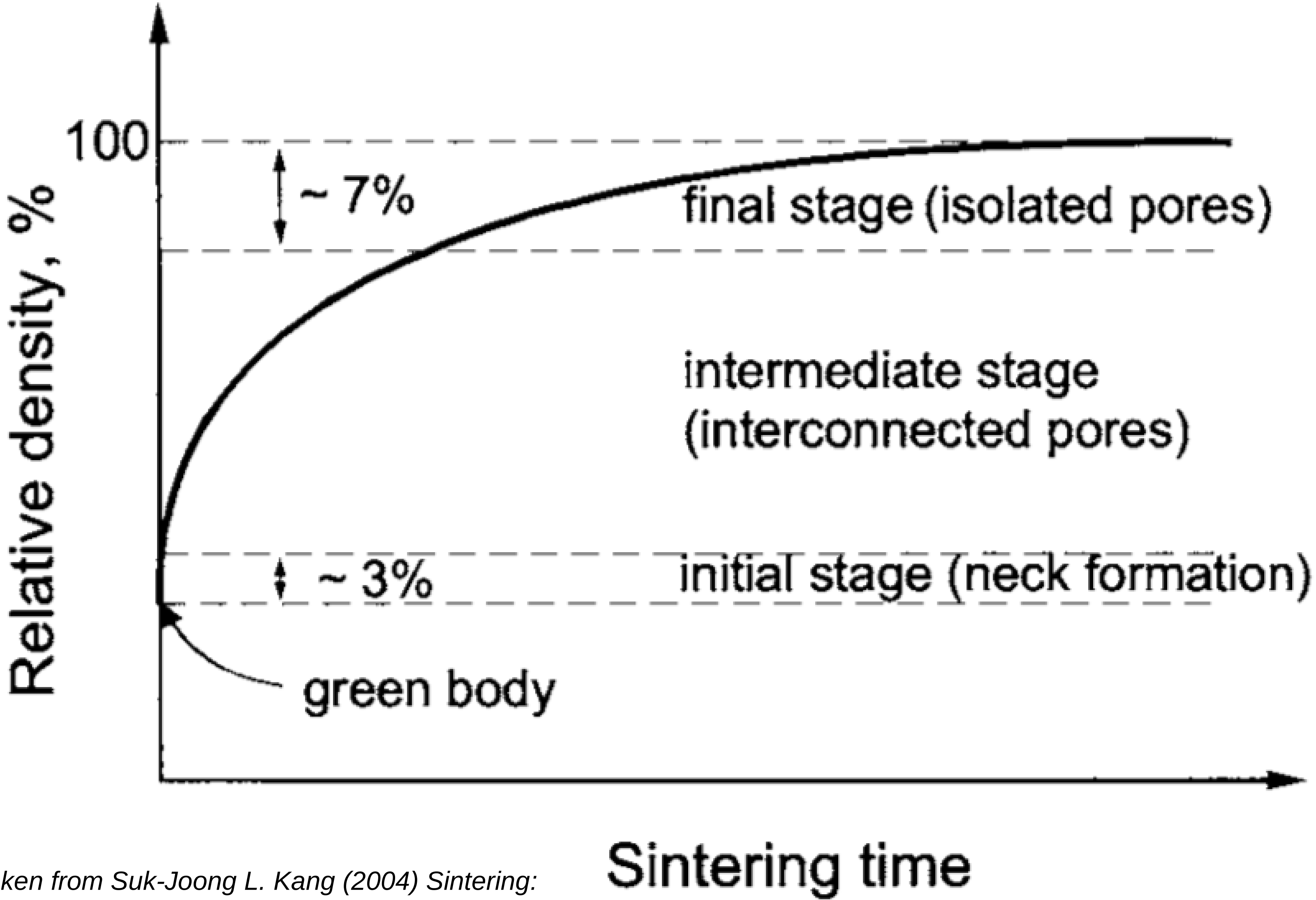
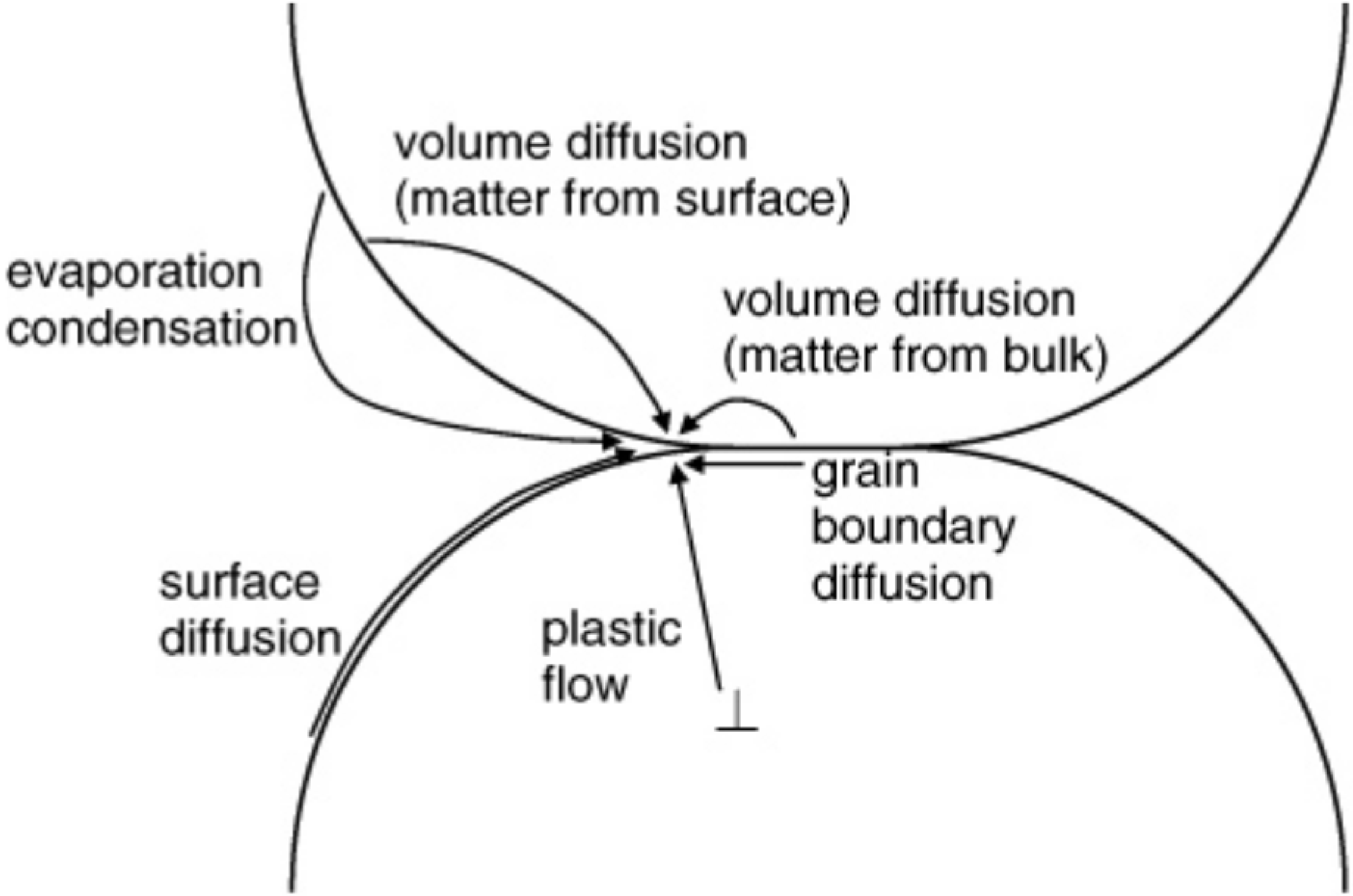


Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Mass transport at green compact contact area



Consider general atomic diffusion

$$J_{x,\mathrm{net}} = C\frac{D}{k_{\mathrm{B}}T} \times \frac{\mathrm{d}\mu}{\mathrm{d}a} = C\frac{D}{k_{\mathrm{B}}T} \times \frac{\mathrm{d}\mu}{\mathrm{d}P} \times \frac{\mathrm{d}P}{\mathrm{d}a}$$

$$= C\frac{D}{k_{\mathrm{B}}T} \times \Omega_0 \times \frac{\Delta P}{\Delta a}$$

$$= \frac{1}{\Omega_0}\frac{D}{k_{\mathrm{B}}T} \times \Omega_0 \times \frac{\gamma K}{L} = \frac{D}{k_{\mathrm{B}}T} \times \frac{\gamma K}{L}$$

Volume of
diffusing species

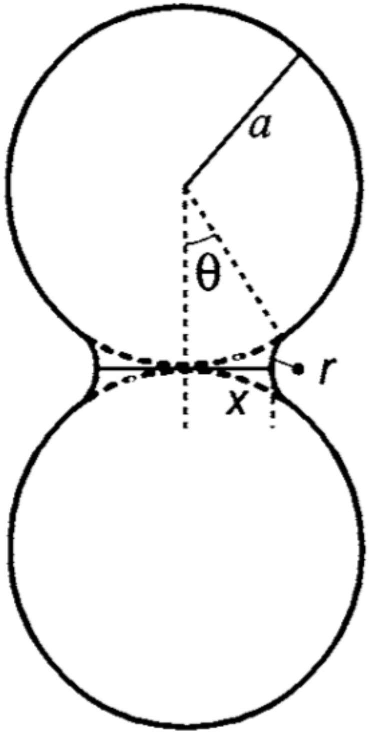
Volume change due
to diffusion through
an area A

$$\frac{\mathrm{d}V}{dt} = J \times A \times \Omega_0$$

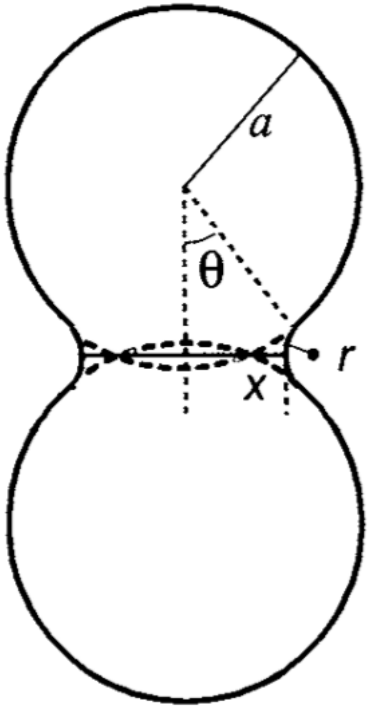
Species flux

The important geometries

Without shrinkage



With shrinkage



$$a^2 + x^2 = (a+r)^2 = a^2 + 2ar + r^2$$

$$x^2 = 2ar + r^2 = 2ar\left(1 + \frac{r}{2a}\right) \approx 2ar$$

$$r \approx \frac{x^2}{2a}$$

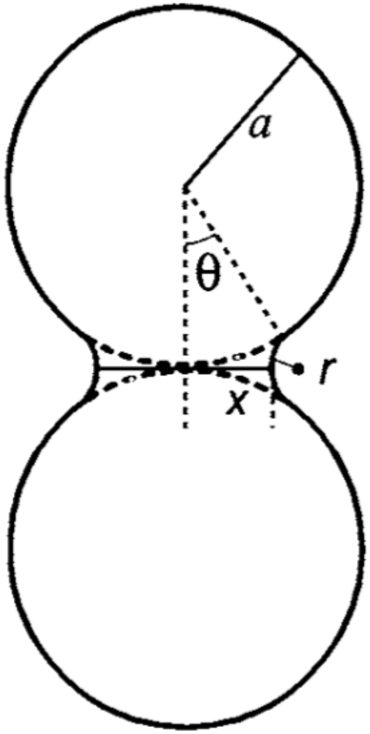
$$(a-h)^2 + x^2 = (a+r)^2 = a^2 + 2ar + r^2$$

$$h \approx r \rightarrow r \approx \frac{x^2}{4a}$$

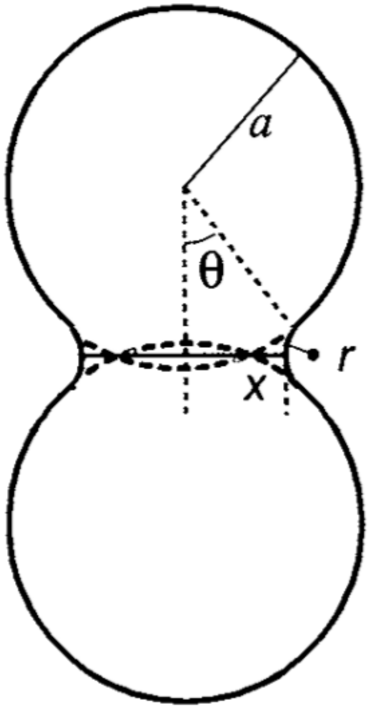
Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

The important geometries

Without shrinkage



With shrinkage



$$a^2 + x^2 = (a+r)^2 = a^2 + 2ar + r^2$$

$$x^2 = 2ar + r^2 = 2ar\left(1 + \frac{r}{2a}\right) \approx 2ar$$

$$r \approx \frac{x^2}{2a}$$

$$(a-h)^2 + x^2 = (a+r)^2 = a^2 + 2ar + r^2$$

$$h \approx r \rightarrow r \approx \frac{x^2}{4a}$$

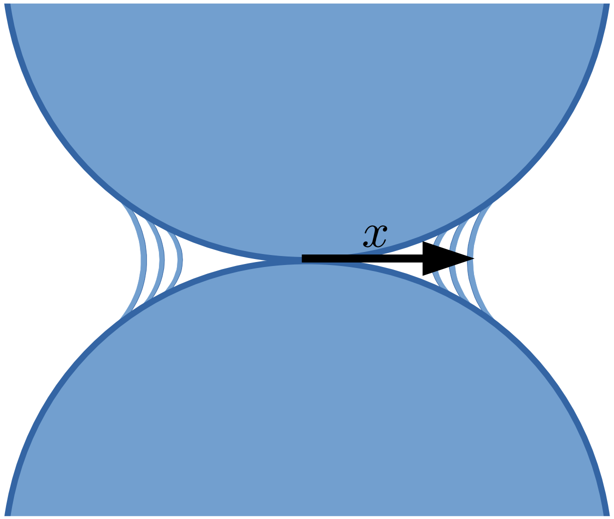
Shrinkage measure ➞ $$\frac{\Delta l}{l} \approx \frac{h}{a} \approx \frac{r}{a} = \frac{x^2}{4a^2}$$

Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

The important geometries

$$r \approx \frac{x^2}{2a}$$ With shrinkage

$$r \approx \frac{x^2}{4a}$$ Without shrinkage



Area of neck surface

$$A \approx 2\pi x \times 2r \approx 2\pi \frac{x^3}{a}$$

$$\left[\pi \frac{x^3}{a} \right]$$

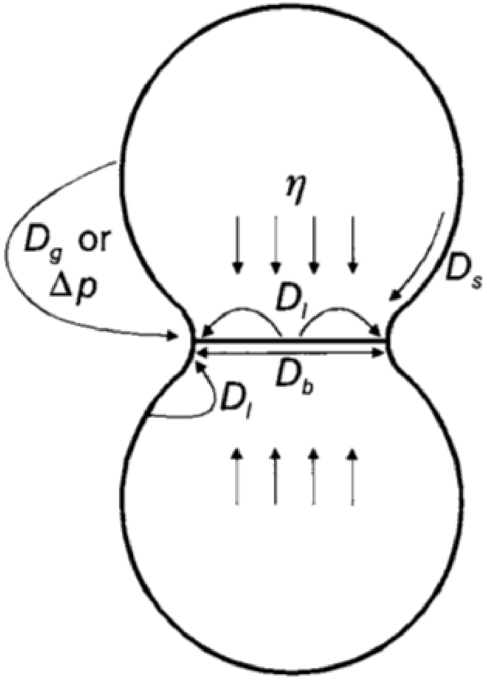
Volume of neck region

with shrinkage

$$V = \int_0^x A \mathrm{d}x \approx \pi \frac{x^4}{2a}$$

$$\left[\pi \frac{x^4}{4a} \right]$$

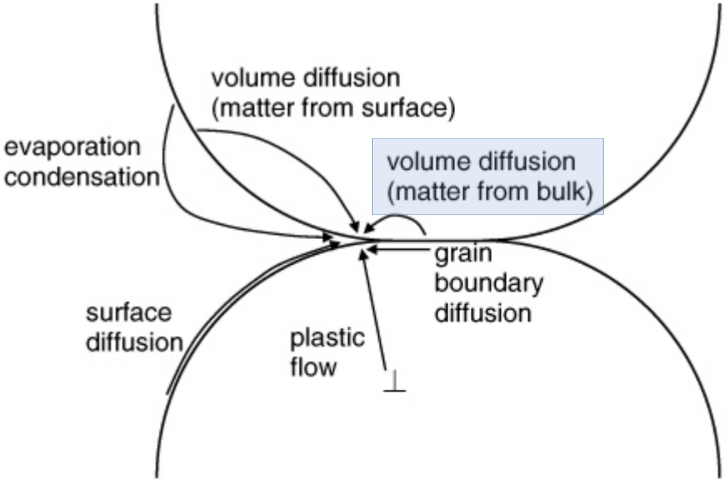
The important processes

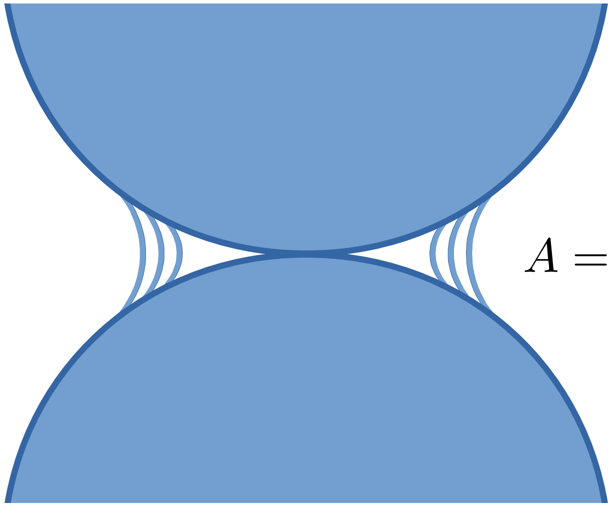


Material transport mechanism	Material source	Material sink	Related parameter
1. Lattice diffusion	Grain boundary	Neck	Lattice diffusivity, D_l
2. Grain boundary diffusion	Grain boundary	Neck	Grain boundary diffusivity, D_b
3. Viscous flow	Bulk grain	Neck	Viscosity, η
4. Surface diffusion	Grain surface	Neck	Surface diffusivity, D_s
5. Lattice diffusion	Grain surface	Neck	Lattice diffusivity, D_l
6. Gas phase transport			
6.1. Evaporation/ condensation	Grain surface	Neck	Vapour pressure difference, Δp
6.2. Gas diffusion	Grain surface	Neck	Gas diffusivity, D_g

Figure and table taken from Suk-Joong L. Kang (2004)
Sintering: Densification, Grain Growth, and Microstructure.

Lattice diffusion from the bulk to neck surface





$$A = \pi \frac{x^3}{a}$$

shrinkage

shrinkage

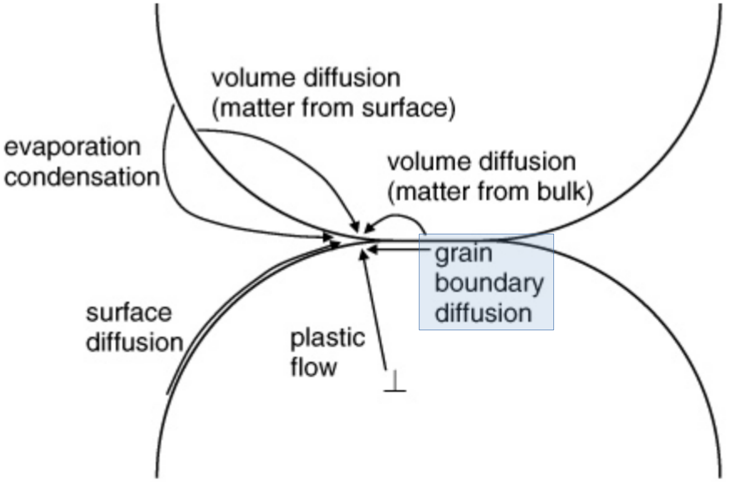
$$\frac{\mathrm{d}V}{dt} = J \times A \times \Omega_0$$

$$\frac{\mathrm{d}}{dt}\left[\pi \frac{x^4}{4a}\right] = \frac{D_\mathrm{l}}{RT} \times \frac{\gamma K}{L} \times \pi \frac{x^3}{a} \times \Omega_0$$

$$\pi \frac{x^3}{a} \frac{\mathrm{d}x}{dt} = \frac{D_\mathrm{l}}{RT} \times \frac{\gamma_\mathrm{s}}{r} \frac{1}{x} \times \pi \frac{x^3}{a} \times \Omega_0 \quad (L \simeq x)$$

$$x^4 = \frac{16 D_\mathrm{l} \gamma_\mathrm{s} a \Omega_0}{RT} t \qquad \left(r \approx \frac{x^2}{2a}\right)$$

Grain boundary diffusion to neck surface



shrinkage

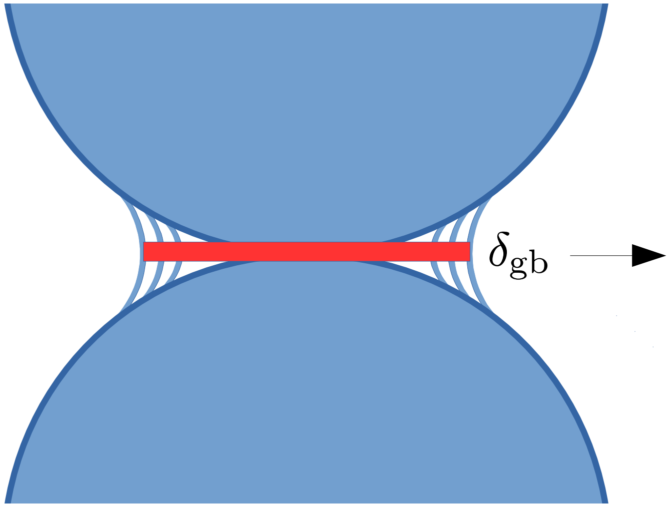
$$\frac{\mathrm{d}V}{dt} = J \times A \times \Omega_0$$

$$\frac{\mathrm{d}}{dt}\left[\pi\frac{x^4}{4a}\right] = \frac{D_{\mathrm{gb}}}{RT} \times \frac{\gamma K}{L} \times 2\pi x \delta_{\mathrm{gb}} \times \Omega_0$$

$$\pi\frac{x^3}{a}\frac{\mathrm{d}x}{dt} = \frac{D_{\mathrm{gb}}}{RT} \times \frac{\gamma_{\mathrm{s}}}{r}\frac{1}{x} \times 2\pi x \delta_{\mathrm{gb}} \times \Omega_0$$

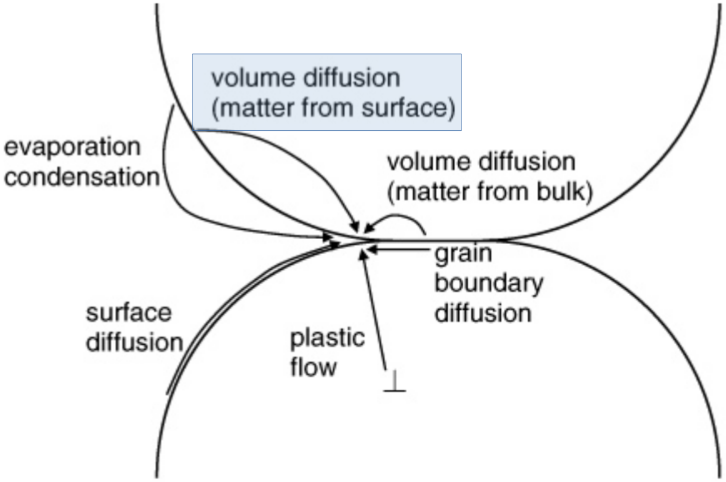
$$(L \simeq x)$$

$$x^6 = \frac{48 D_{\mathrm{gb}} \gamma_{\mathrm{s}} \delta_{\mathrm{gb}} a^2 \Omega_0}{RT} t$$



GB thickness
$A = 2\pi x \delta_{\mathrm{gb}}$

Lattice diffusion from surface to neck surface



no shrinkage

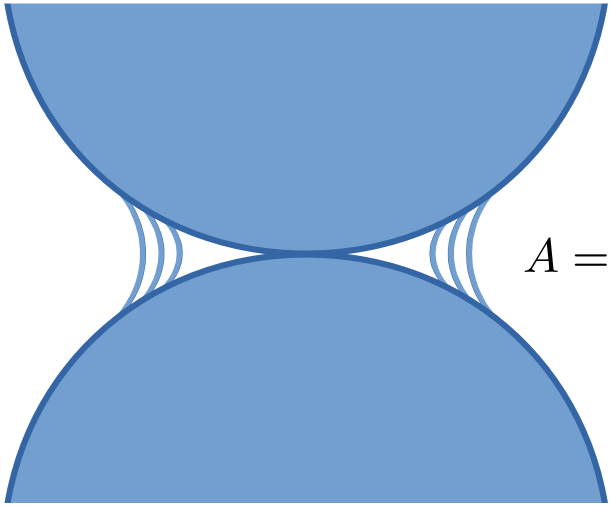
no shrinkage

$$\frac{\mathrm{d}V}{dt} = J \times A \times \Omega_0$$

$$\frac{\mathrm{d}}{dt}\left[\pi\frac{x^4}{2a}\right] = \frac{D_\mathrm{l}}{RT} \times \frac{\gamma K}{L} \times 2\pi\frac{x^3}{a} \times \Omega_0$$

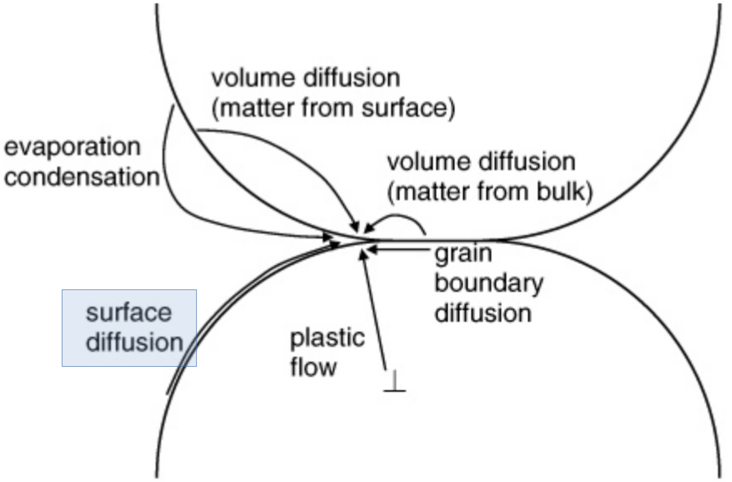
$$\pi\frac{x^3}{a}\frac{\mathrm{d}x}{dt} = \frac{D_\mathrm{l}}{RT} \times \frac{\gamma_\mathrm{s}}{r}\frac{1}{r} \times 2\pi\frac{x^3}{a} \times \Omega_0 \quad (L \simeq r)$$

$$x^5 = \frac{20 D_\mathrm{l}\gamma_\mathrm{s} a^2 \Omega_0}{RT} t$$



$$A = 2\pi\frac{x^3}{a}$$

Surface diffusion to neck surface



no shrinkage

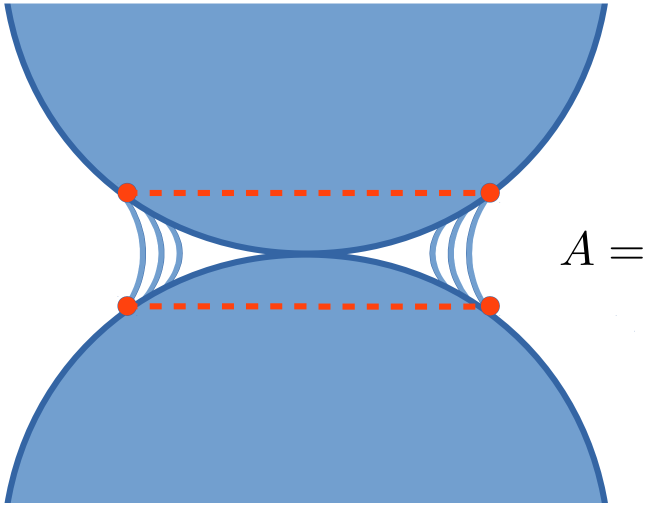
$$\frac{\mathrm{d}V}{dt} = J \times A \times \Omega_0$$

$$\frac{\mathrm{d}}{dt}\left[\pi \frac{x^4}{2a}\right] = \frac{D_\mathrm{s}}{RT} \times \frac{\gamma K}{L} \times 2\pi x 2\delta_\mathrm{s} \times \Omega_0$$

$$\pi \frac{x^3}{a}\frac{\mathrm{d}x}{dt} = \frac{D_\mathrm{s}}{RT} \times \frac{\gamma_\mathrm{s}}{r}\frac{1}{r} \times 2\pi x 2\delta_\mathrm{s} \times \Omega_0$$

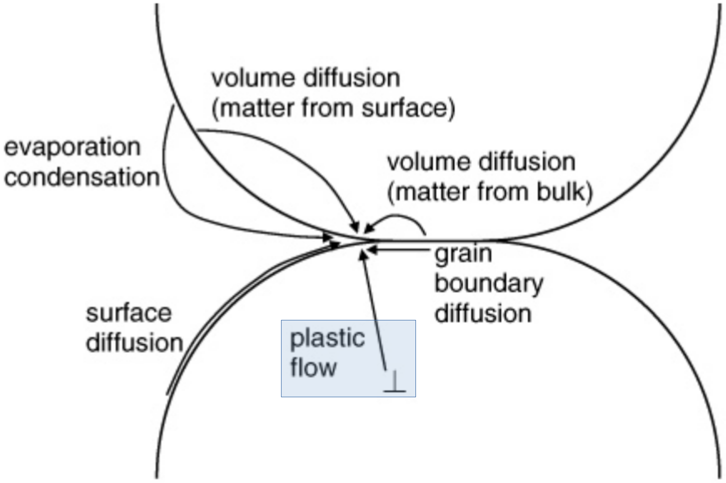
$$(L \simeq r)$$

$$x^7 = \frac{56 D_\mathrm{s} \gamma_\mathrm{s} \delta_\mathrm{s} a^3 \Omega_0}{RT} t$$



$$A = 2 \times 2\pi x \delta_\mathrm{s}$$

Plasticity – the case of Newtonian viscous flow



$$\dot{\varepsilon} = \frac{1}{\eta}\Delta\sigma$$

Newtonian viscosity

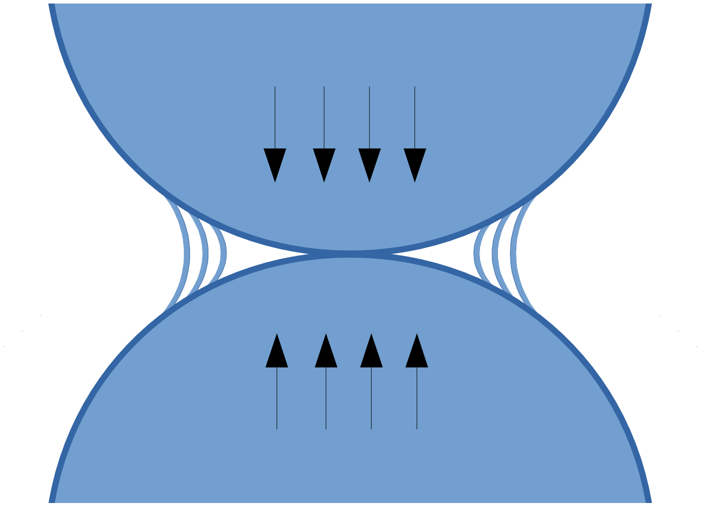
$$\dot{\varepsilon} = \frac{1}{h}\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{1}{\eta}\frac{\gamma_\mathrm{s}}{r}$$

h

Penetration depth of one particle into another: $h \approx r$

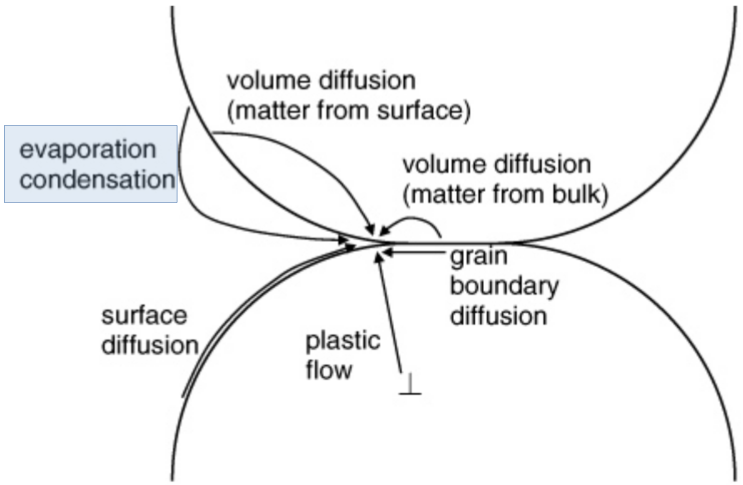
$$\mathrm{d}h = \frac{1}{\eta}\frac{h}{r}\gamma_\mathrm{s}\mathrm{d}t \approx \frac{1}{\eta}\gamma_\mathrm{s}\mathrm{d}t$$

$$h \approx \frac{x^2}{4a} \approx \frac{1}{\eta}\gamma_\mathrm{s}t$$



Such a description of plasticity is generally suited to amorphous solids at high temperature (below the glass transition temperature)

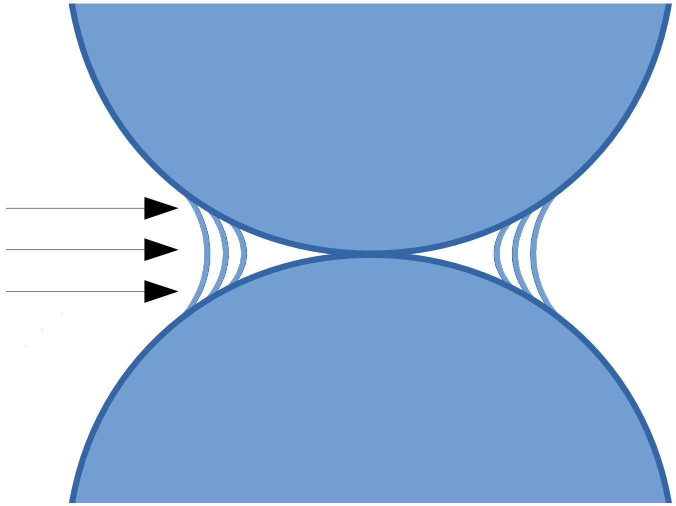
Evaporation/condensation



According to the Langmuir adsorption equation, the amount (weight) of material deposited per unit area and per unit time is expressed as

$$m = \alpha \left(p_{\mathrm{V}} - p_{\mathrm{V},r\to\infty}\right)\sqrt{\frac{M}{2\pi RT}} = \alpha\frac{p_{\mathrm{V},r\to\infty}\gamma M}{r\rho RT}\sqrt{2\frac{M}{\pi RT}}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = 2\pi\frac{x^3}{a}\frac{\mathrm{d}x}{dt} = \frac{m}{\rho}A = \frac{m}{\rho}2\pi\frac{x^3}{a} \longrightarrow \frac{\mathrm{d}x}{dt} = \frac{m}{\rho}$$

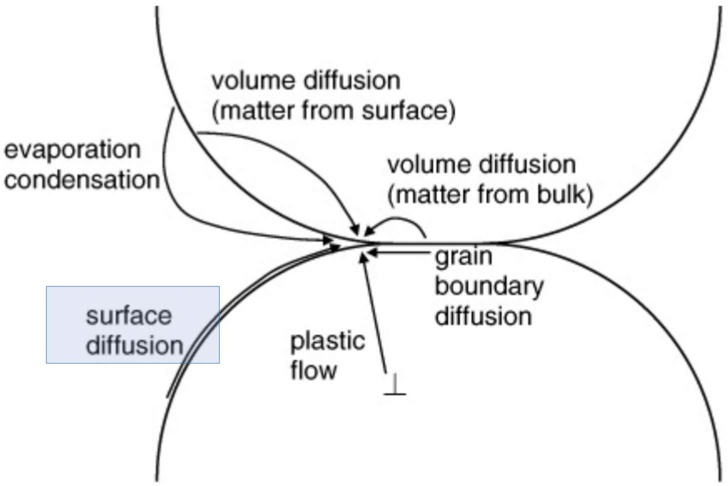


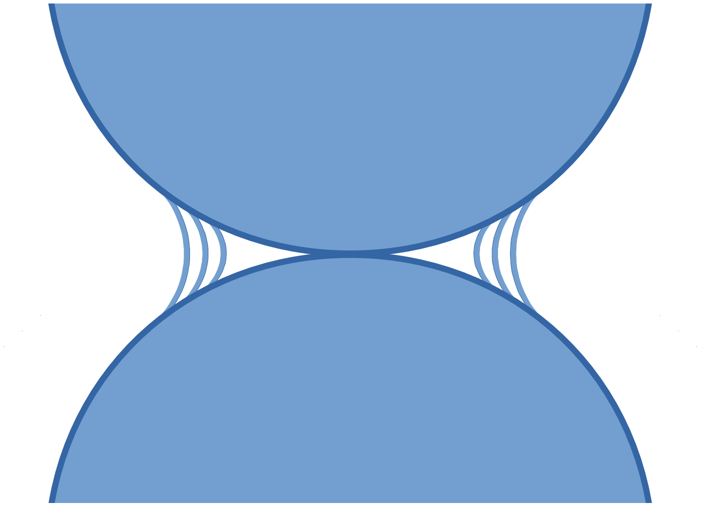
$$\frac{\mathrm{d}x}{dt} = \alpha\frac{p_{\mathrm{V},r\to\infty}\gamma M}{r\rho^2 RT}\sqrt{\frac{M}{2\pi RT}} = \alpha\frac{p_{\mathrm{V},r\to\infty}2a\gamma M}{x^2\rho^2 RT}\sqrt{\frac{M}{2\pi RT}}$$

$$r \to \frac{x^2}{2a}$$

$$x^3 = \alpha\sqrt{\frac{18}{\pi}}\frac{p_{\mathrm{V},r\to\infty}\gamma}{\rho^2}\left(\frac{M}{RT}\right)^{\frac{3}{2}} at$$

Gas diffusion at the surface





$$\frac{\mathrm{d}V}{\mathrm{d}t} = 2\pi \frac{x^3}{a}\frac{\mathrm{d}x}{dt} = J\Omega_0 A = J\Omega_0 2\pi \frac{x^3}{a}$$

$$\frac{\mathrm{d}x}{dt} = J\Omega_0 = D_\mathrm{g}\nabla \underbrace{C\Omega_0 = D_\mathrm{g}\frac{\nabla p}{RT}}_{PV = nRT}\Omega_0 \approx D_\mathrm{g}\frac{\Delta p}{rRT}\Omega_0$$

$$= D_\mathrm{g}\frac{p_{V,r\to\infty}\gamma M}{r^2\rho(RT)^2}\Omega_0 = D_\mathrm{g}\frac{p_{V,r\to\infty}\gamma}{r^2(RT)^2}\Omega_0^2$$

$$= D_\mathrm{g}\frac{p_{V,r\to\infty}4\gamma}{x^4(RT)^2}\Omega_0^2 a^2 \qquad r \to \frac{x^2}{2a}$$

$$x^5 = D_\mathrm{g}\frac{p_{V,r\to\infty}20\gamma}{(RT)^2}\Omega_0^2 a^2 t$$

The effect of particle size

The effect of particle size on sintering is described by Herring's scaling law. When powders with similar shapes but different sizes are sintered under the same experimental conditions and by the same sintering mechanism, the scaling law predicts the relative periods of sintering time required to get the same degree of sintering (defined by x / a).

For the sintering of two kinds of powders with radii a_1 and a_2, where

$$a_2 = \lambda a_1$$

the required sintering times, t_1 and t_2 are interrelated as

$$t_2 = \lambda^\alpha t_1$$

Generally, one has

$$\left(\frac{x}{a}\right)^n = f(T)a^{m-n}t \longrightarrow \left(\frac{x}{a_1}\right)^n = f(T)a_1^{m-n}t_1 = \left(\frac{x}{a_2}\right)^n = f(T)a_2^{m-n}t_2$$

$$\boxed{\alpha = m - n}$$

The effect of temperature

$$\left(\frac{x}{a}\right)^n = f(T)a^{m-n}t \longrightarrow \left(\frac{x}{a}\right)^n \propto \frac{D(T)}{T}t$$

For a fixed level of evolution, the time taken follows: $\log\left(\frac{t}{T}\right) \propto const - \log D(T)$

$$D(T) \propto \exp\left(-\frac{Q_\mathrm{b}}{k_\mathrm{B}T}\right) \longrightarrow \log\left(\frac{t}{T}\right) \propto const' - \frac{Q_\mathrm{b}}{k_\mathrm{B}T}$$

The effect of pressure and composition

Thus far, the driving force of sintering is the capillary pressure difference due to curvature difference. When an external pressure $P_{\text{appl.}}$ is applied, the total sintering pressure is the sum of the capillary and external pressures,

$$P = \frac{\gamma}{r} + f(\rho, \text{geometry})P_{\text{appl.}}$$

In the studied diffusion-controlled sintering, atom diffusivity (mobility) increases with increased vacancy concentration. Sintering kinetics can therefore be enhanced by increasing the vacancy concentration via alloying or dopant addition (for the case of ionic compounds).

Effect of sintering parameters on densification

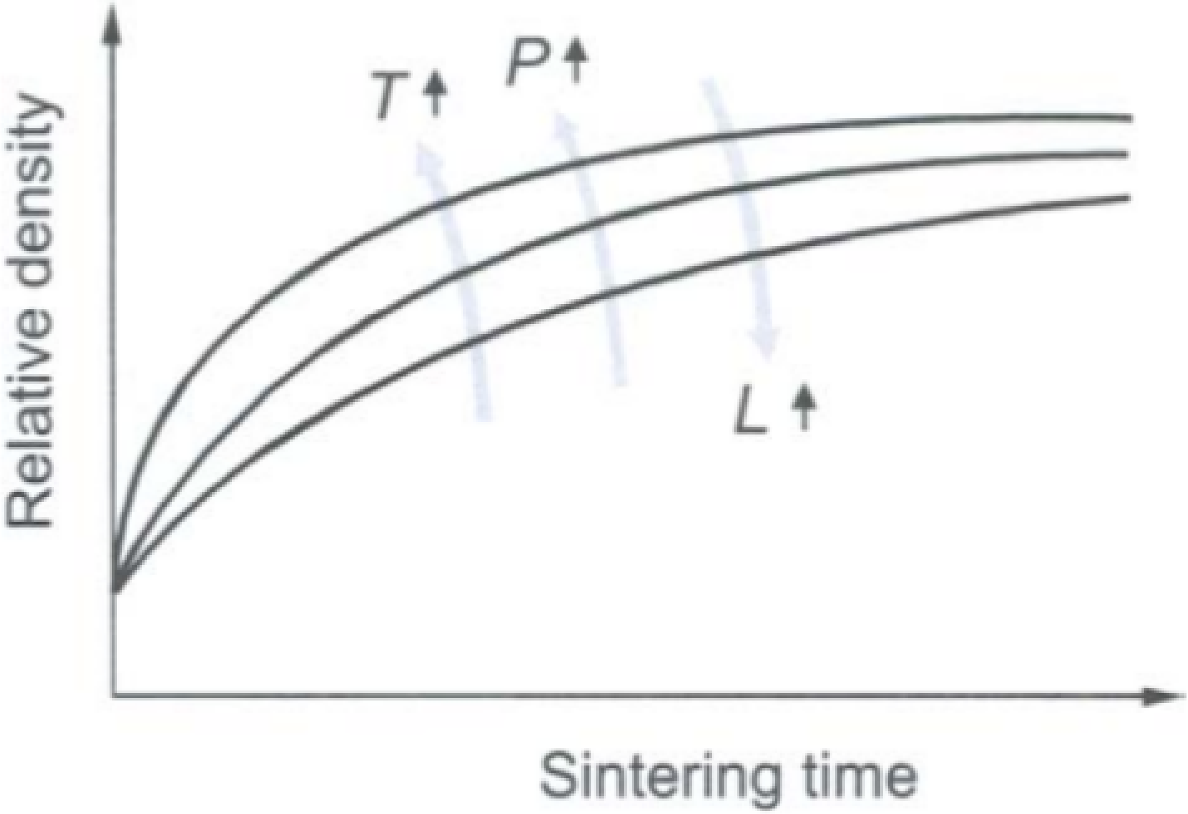
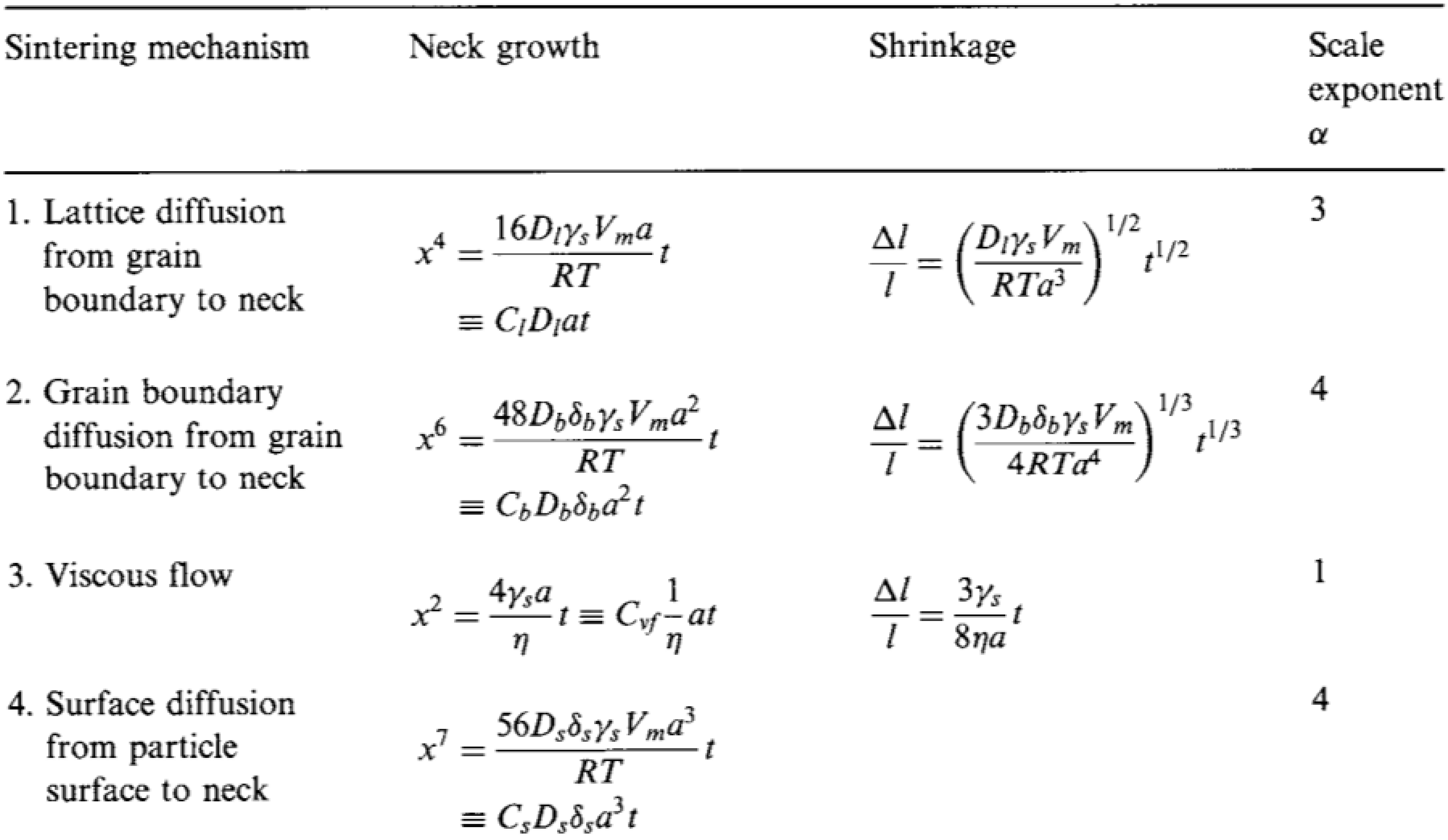


Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

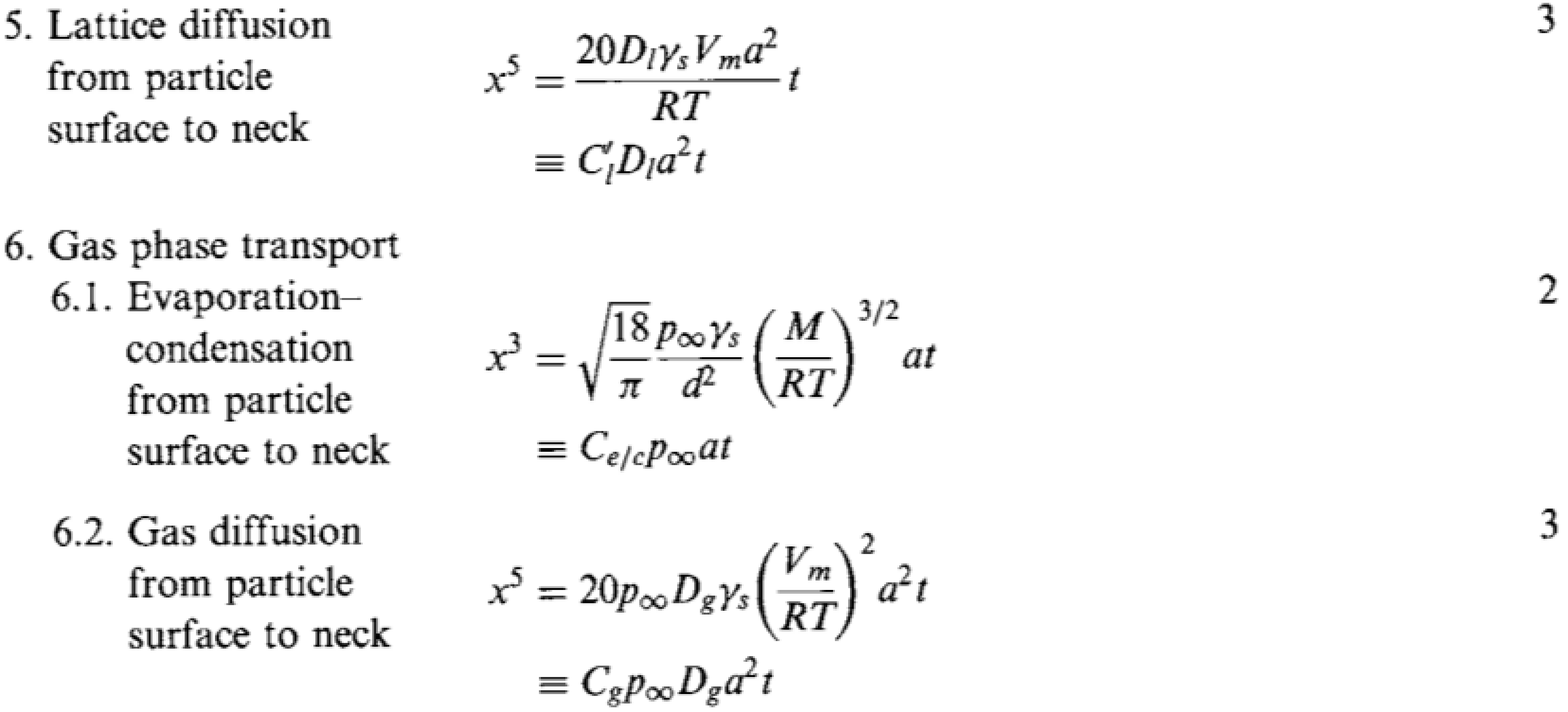
Summary of kinetic equations for various mechanisms of initial stage sintering



Sintering mechanism	Neck growth	Shrinkage	Scale exponent α
1. Lattice diffusion from grain boundary to neck	$x^4 = \frac{16D_l\gamma_s V_m a}{RT}t \equiv C_l D_l a t$	$\frac{\Delta l}{l} = \left(\frac{D_l\gamma_s V_m}{RTa^3}\right)^{1/2} t^{1/2}$	3
2. Grain boundary diffusion from grain boundary to neck	$x^6 = \frac{48D_b\delta_b\gamma_s V_m a^2}{RT}t \equiv C_b D_b \delta_b a^2 t$	$\frac{\Delta l}{l} = \left(\frac{3D_b\delta_b\gamma_s V_m}{4RTa^4}\right)^{1/3} t^{1/3}$	4
3. Viscous flow	$x^2 = \frac{4\gamma_s a}{\eta}t \equiv C_{vf}\frac{1}{\eta}at$	$\frac{\Delta l}{l} = \frac{3\gamma_s}{8\eta a}t$	1
4. Surface diffusion from particle surface to neck	$x^7 = \frac{56D_s\delta_s\gamma_s V_m a^3}{RT}t \equiv C_s D_s \delta_s a^3 t$		4

Table taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Summary of kinetic equations for various mechanisms of initial stage sintering



5. Lattice diffusion from particle surface to neck	$x^5 = \frac{20 D_l \gamma_s V_m a^2}{RT} t$ $\equiv C_l' D_l a^2 t$	3
6. Gas phase transport		
6.1. Evaporation–condensation from particle surface to neck	$x^3 = \sqrt{\frac{18}{\pi}} \frac{p_\infty \gamma_s}{d^2} \left(\frac{M}{RT}\right)^{3/2} at$ $\equiv C_{e/c} p_\infty at$	2
6.2. Gas diffusion from particle surface to neck	$x^5 = 20 p_\infty D_g \gamma_s \left(\frac{V_m}{RT}\right)^2 a^2 t$ $\equiv C_g p_\infty D_g a^2 t$	3

Table taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Sintering diagrams

Sintering diagram of an aggregate of pure silver spheres of 38 micron radius

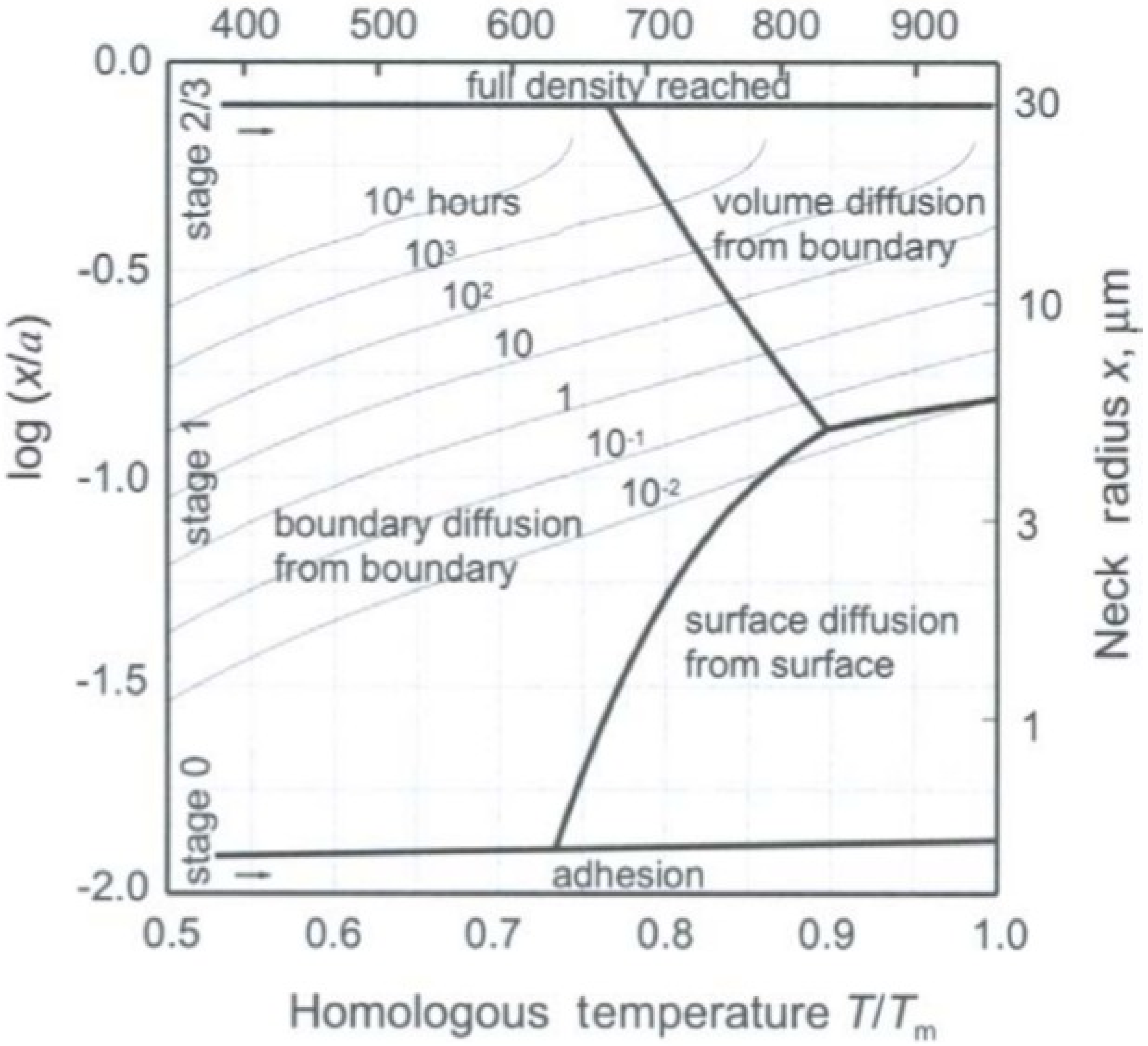


Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Intermediate and final stage sintering

Intermediate and final stage sintering

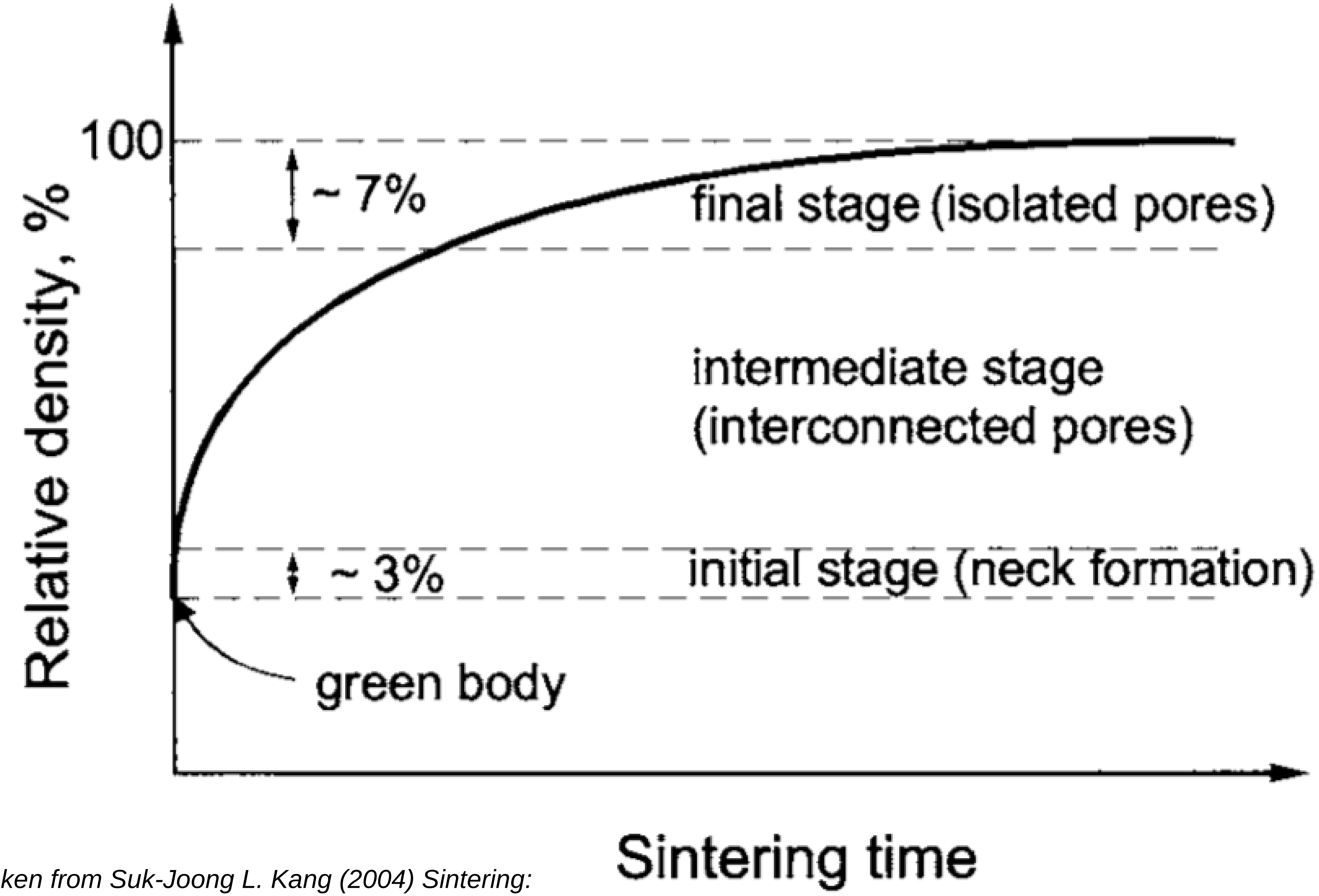
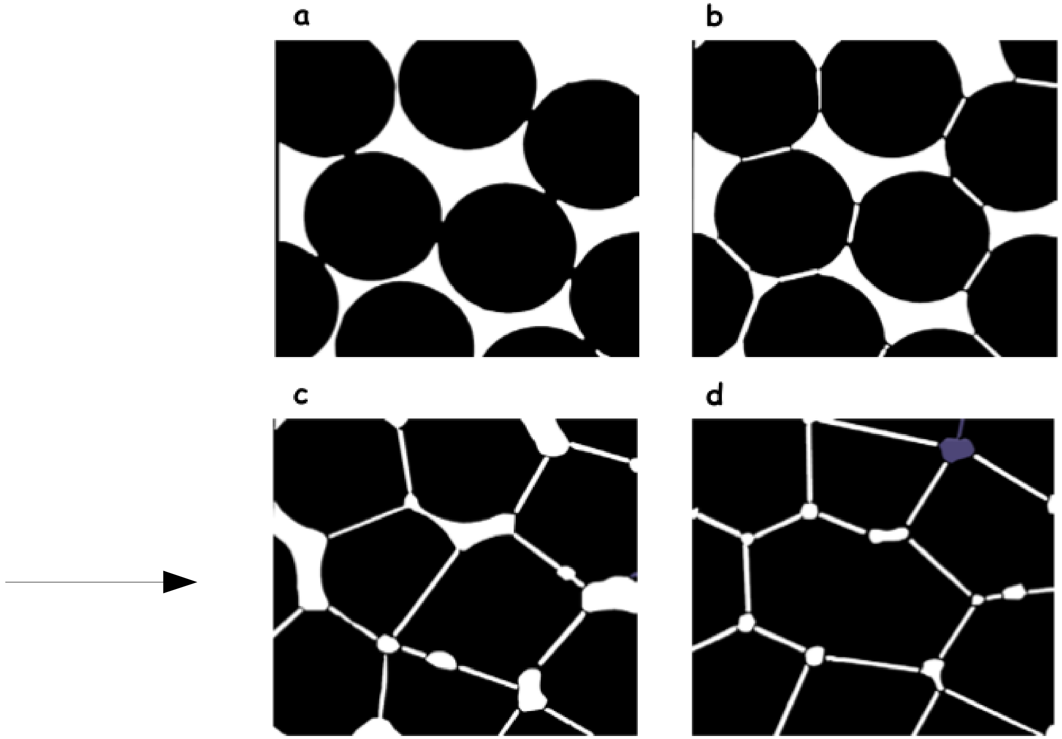


Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Intermediate and final stage sintering

When necks form between particles in real powder compacts, pores form interconnected channels along 3-grain edges (triple junctions). As the sintering proceeds, the pore channels are disconnected and isolated pores form.

At the same time, the grains grow.



a) Green body, loose powder

b) Initial stage: increase of the interparticle contact area from 0 to 0.2 grain diameter, increase of the density from 60 to 65%

c) Intermediate stage: further increase of the contact area, stage characterized by continuous pore channels along three grain edges, increase of the density from 65 to 90%.

d) Elimination of the pore channel along three grain edges, increase of the density to 95 - 99%

https://www.slideshare.net/ashking235/lecturesolid-state-sintering

Intermediate stage sintering

The intermediate stage begins after grain growth and pore shape change causes transition to a pore and grain boundary matrix consisting of equilibrium dihedral angles formed on the solid-vapor (pore) surface at the locus of intersections with the solid-solid (grain boundary) surfaces with singly curved surfaces between Intersections … the features of the structure which make this sample appropriate for representation of the intermediate stage of sintering are that the pore phase is continuous, and that the pores arc all intersected by grain boundaries. The complex shape of the pore may be approximated by a continuous cylinder.

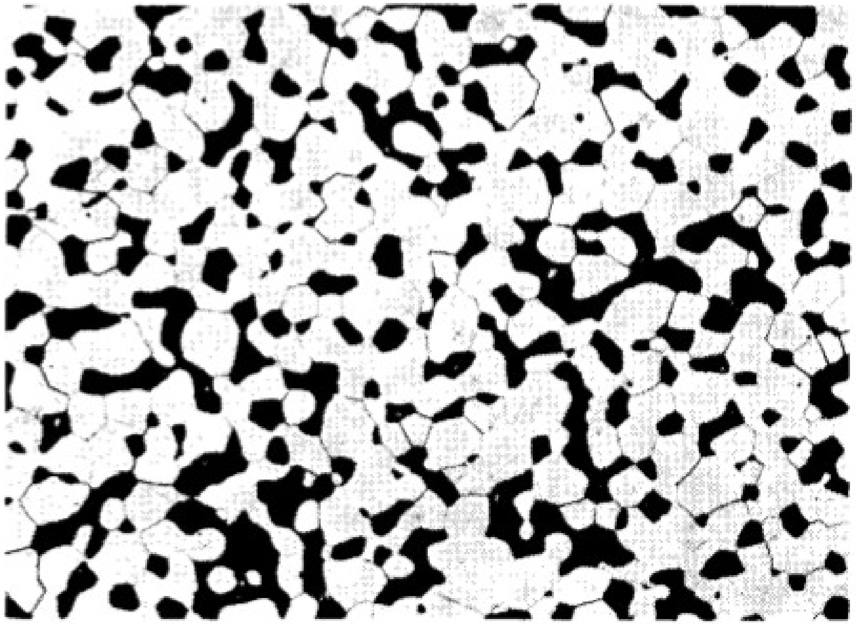
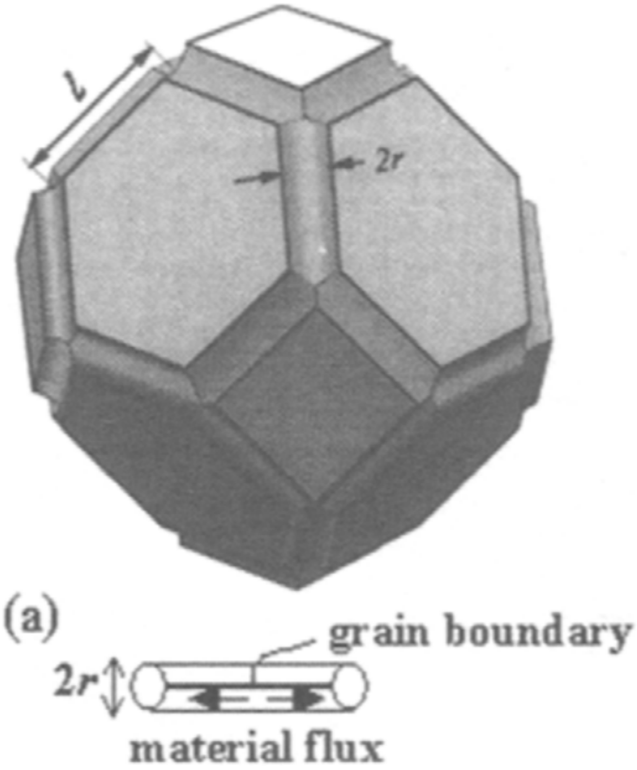


FIG. 2. Typical intermediate stage structure: photomicrograph at 250× of alumina gel pressed 10 tsi sintered 1750° for 12 hr, polished, etched $\simeq$5 min in boiling phosphoric acid.

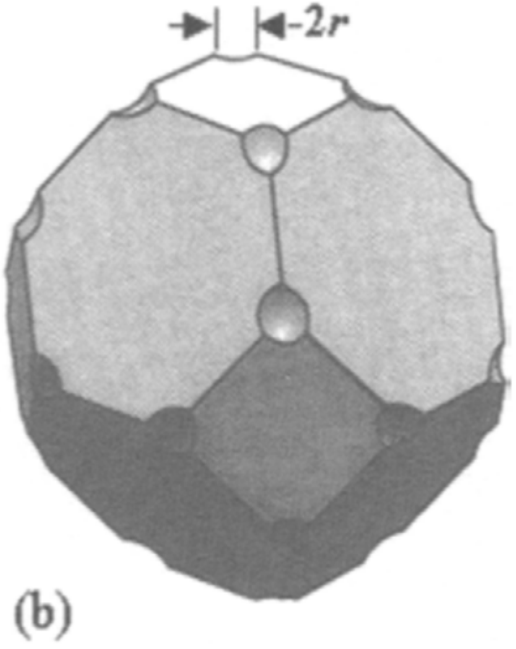
Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Coble’s model

Coble proposed two geometrically simple models for the shape changes of pores during intermediate and final stage sintering → the channel pore model and the isolated pore model



Intermediate stage model



Final stage model

Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Coble’s model

Coble proposed two geometrically simple models for the shape changes of pores during intermediate and final stage sintering:

→ the channel pore model and the isolated pore model

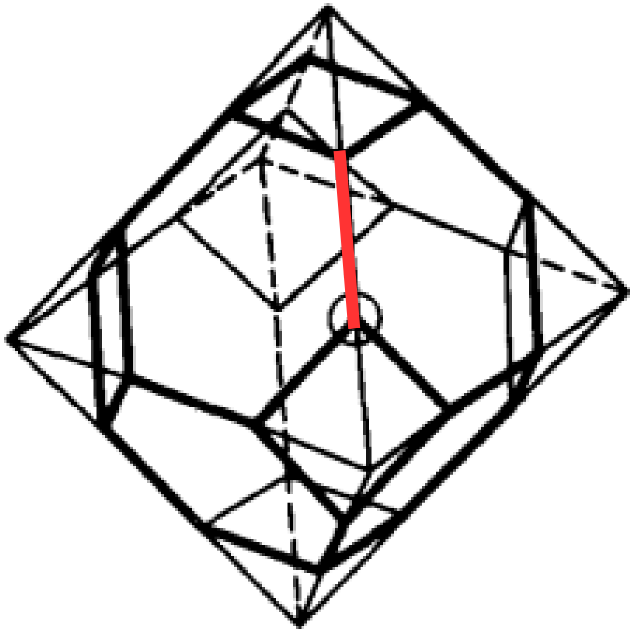
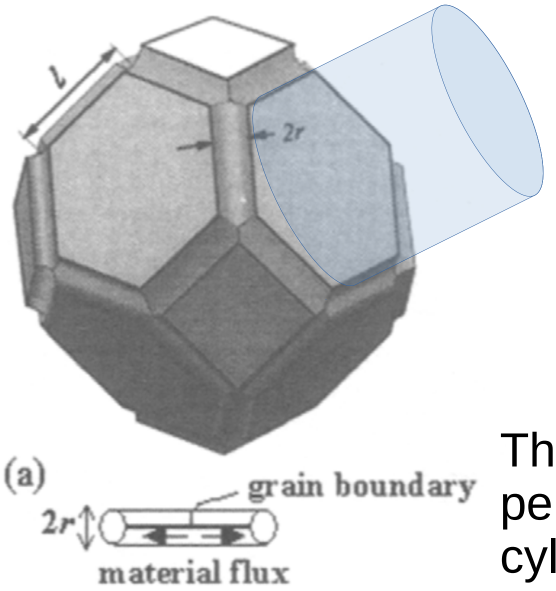


FIG. 7. Tetrakaidecahedron, dark lines shown as formed from truncated octahedron.

$$V = 8\sqrt{2}l^3$$

Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Coble's model: intermediate stage model



$$V = 8\sqrt{2}l^3$$

$$V_\mathrm{P} = \frac{1}{3}\left(36 l \pi r^2\right)$$

$$P = \frac{V_\mathrm{P}}{V} = \frac{\frac{1}{3}\left(36 l \pi r^2\right)}{8\sqrt{2}l^3} = 1.06\left(\frac{r}{l}\right)^2$$

The volume flux per unit length of cylinder

$$4\pi D \Delta C \Omega_0 \longrightarrow J = 4\pi D \Delta C \Omega_0 \times 2r$$

$$\frac{\mathrm{d}V_\mathrm{P}}{\mathrm{d}t} = -\frac{14}{2}J = -7 \times 2 \times 4\pi D \Omega_0 \Delta C r \longrightarrow \Delta C = C_0 \frac{\gamma \Omega_0}{RTr} \longrightarrow \frac{\mathrm{d}V_\mathrm{P}}{\mathrm{d}t} = -7 \times 2 \times 4\pi D \Omega_0^2 C_0 \frac{\gamma}{RT}$$

$$\int \mathrm{d}V_\mathrm{P} = \frac{36}{3} l \pi r^2 \bigg|_0^r = -7 \times 2 \times 4\pi D \Omega_0^2 C_0 \frac{\gamma}{RT}(t - t_0)$$

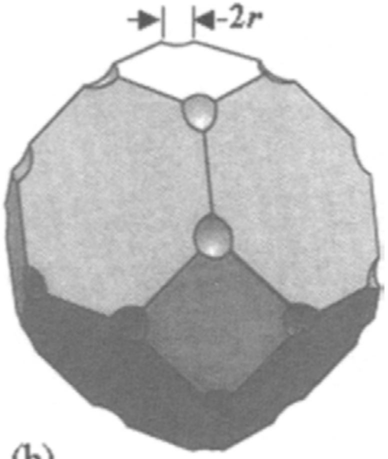
$$\boxed{P \approx \left(\frac{r}{l}\right)^2 \propto t_0 - t}$$

When via grain boundary diffusion

$$\frac{\mathrm{d}V_\mathrm{P}}{\mathrm{d}t} = -\frac{14}{2} 4\pi \frac{D_\mathrm{gb}}{RT} \frac{\gamma}{r} \delta_\mathrm{gb} \Omega_0$$

$$P \approx \left(\frac{r}{l}\right)^2 \propto (t_0 - t)^{\frac{2}{3}}$$

Coble’s model: final stage model



(b)

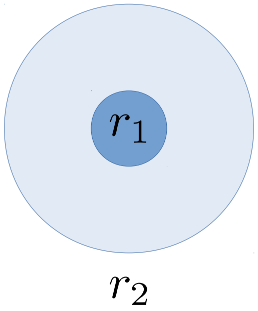
$$V = 8\sqrt{2}l^3 \qquad V_\mathrm{P} = \frac{24}{4}\frac{4}{3}\pi r^3$$

$$P = \frac{V_\mathrm{P}}{V} = \frac{8\pi r^3}{8\sqrt{2}l^3} = \frac{\pi}{\sqrt{2}}\left(\frac{r}{l}\right)^3$$

The volume flux into a pore

$$J = 4\pi D\Delta C\Omega_0\frac{r_2 r_1}{r_2 - r_1} \simeq 4\pi D\Delta C\Omega_0 r_1$$

$$r_2 >> r_1$$



$$\frac{\mathrm{d}V_\mathrm{P}}{\mathrm{d}t} = -6J = -24\pi D\Delta C\Omega_0 r_1 \longrightarrow \Delta C = C_0\frac{2\gamma\Omega_0}{RTr_1} \longrightarrow \frac{\mathrm{d}V_\mathrm{P}}{\mathrm{d}t} = -48\pi DC_0\frac{\gamma\Omega_0}{RT}\Omega_0$$

$$\int \mathrm{d}V_\mathrm{P} = 6\frac{4}{3}l\pi r^3\Big|_0^r \propto -(t - t_0)$$

$$\boxed{P \approx \left(\frac{r}{l}\right)^3 \propto \frac{1}{l^3}\times(t_0 - t)}$$

This form is appropriate for a porosity change from approximately two volume percent to zero. If the transition to the discontinuous pore phase takes place at larger porosity, for example, at 5% rather than at 2% porosity then $r_2 \sim r_1$

Then the prefactor will decrease with time

An example

Calculated densification curves at final stage sintering at a temperature of 1727C of an alumina powder compact with (a) 0.8 and (b) 4.0 microngrain size at 90% relative density.

$$P \propto \frac{1}{(l(t'-t))^3} \times (t'-t) \qquad \rho_{\mathrm{r}} = 1 - P$$

Length-scale changes due to grain growth – derived from another model

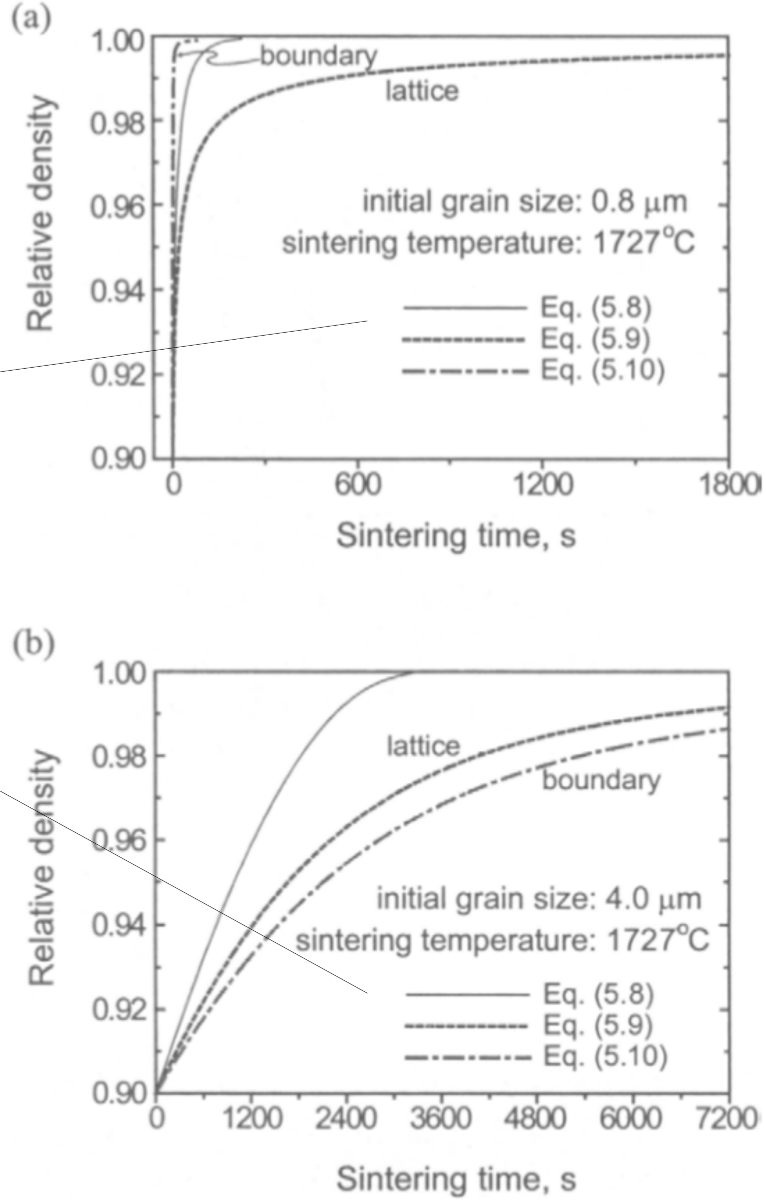


Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Final stage sintering

Final stage begins when the pore phase is eventually pinched off. The energetically favored structure is that in which the closed (nearly spherical) pores occupy four-grain corners.

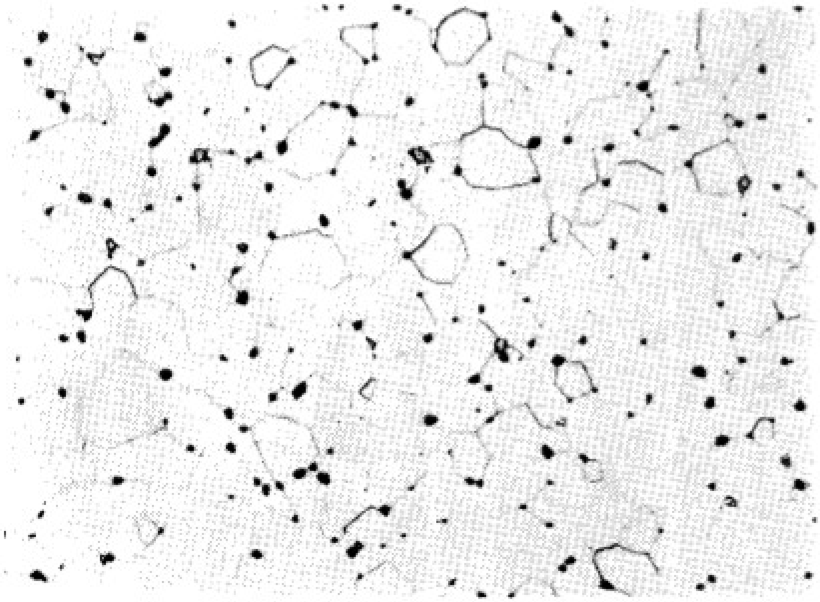


FIG. 3. Typical final stage structure: photomicrograph of α alumina with MgO pressed at 10 tsi, sintered 1800°C for 12 hr, polished, etched.

Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Final stage sintering

'An alternate final stage of sintering results when discontinuous grain growth occurs before all porosity is removed … called discontinuous or exaggerated growth, or secondary recrystallization … the majority of the pores arc closed and spherical because they are not intersected by grain boundaries … continued heating at the sintering temperature leads to pore elimination at grain boundaries … the fact that pores are observed adjacent to one side of many boundaries and arc absent from the other side is attributed to the migration of boundaries in a direction toward their centers of curvature. The areas through which the boundaries have passed are those from which the pores have been eliminated.'

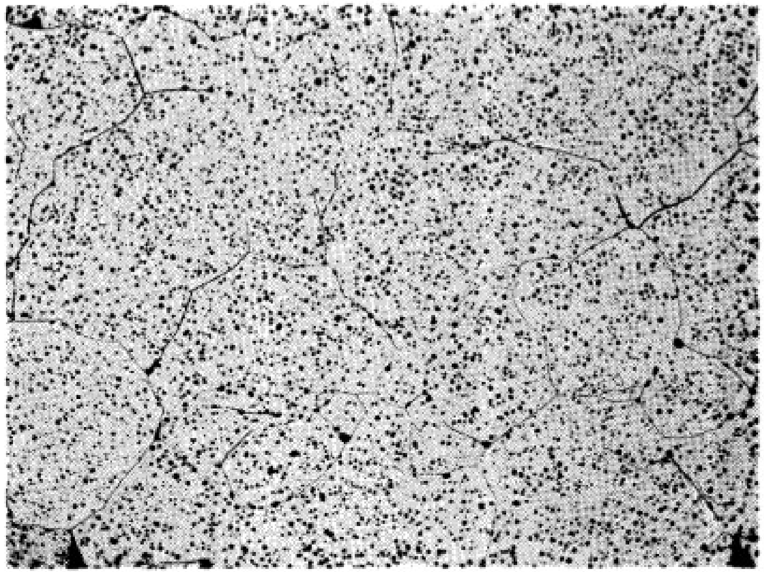


FIG. 5. Final stage after discontinuous grain growth. Photomicrograph at 50×; α alumina sintered 1900°C, 1 hr.

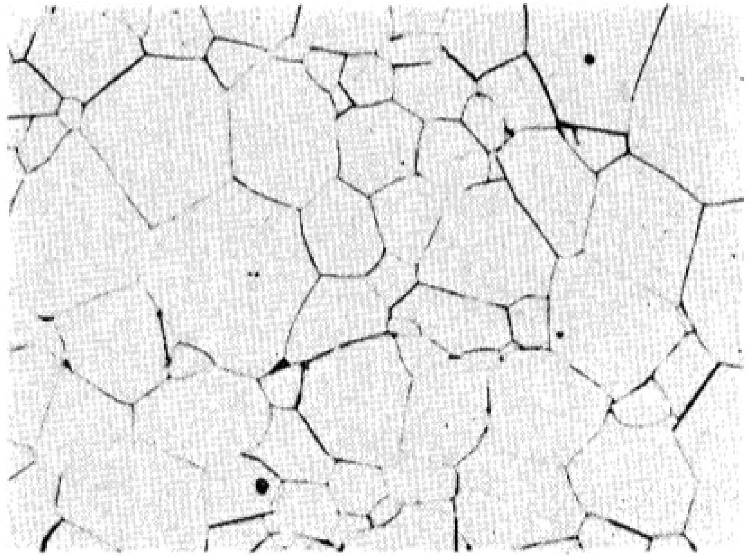
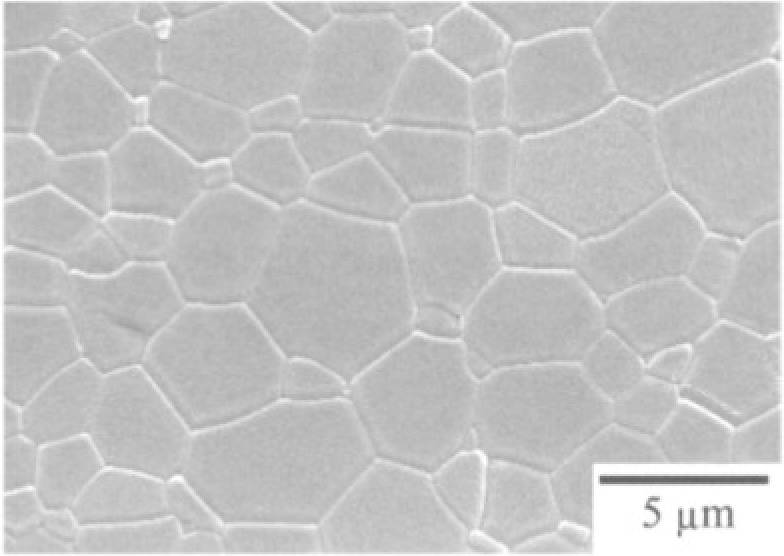


FIG. 4. End state at theoretical density: photomicrograph at 250×; α alumina with MgO, pressed, sintered 1900°C for 24 hr, polished, etched.

Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

Modelling normal grain growth



$$\frac{\mathrm{d}\langle R\rangle}{\mathrm{d}t} = \alpha\langle v\rangle = \alpha J_{\mathrm{to-gb}}\Omega_0 = \alpha\frac{D_{\mathrm{to-gb}}}{RT}\nabla P\Omega_0$$

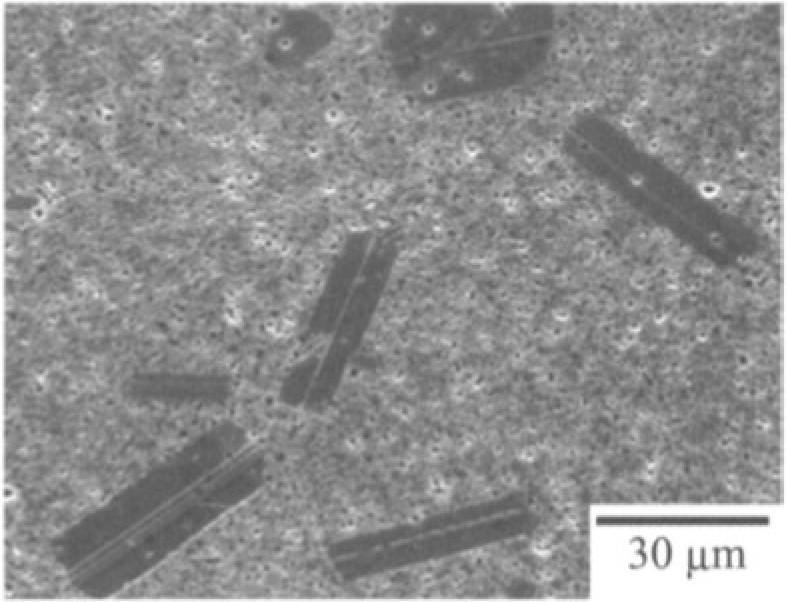
$$= \alpha\frac{D_{\mathrm{to-gb}}}{RT}\frac{2\gamma_{\mathrm{gb}}}{\langle R\rangle}\Omega_0$$

$$\langle R\rangle_{t'}^2 - \langle R\rangle_t^2 = \alpha\frac{D_{\mathrm{to-gb}}}{RT}4\gamma_{\mathrm{gb}}\Omega_0(t'-t)$$

Here it is assumed that the driving force is determined by the radius of curvature of the grain boundary and that the average grain growth rate is proportional to the average rate of grain boundary movement. These conditions appear to be satisfied in real microstructures that are free of abnormal grain growth.

Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Modelling simple abnormal grain growth



$$\frac{\mathrm{d}\langle R\rangle}{\mathrm{d}t} = \alpha\langle v\rangle = \alpha J_{\mathrm{to-gb}}\Omega_0 = \alpha\frac{D_{\mathrm{to-gb}}}{RT}\nabla P\Omega_0$$

$$= \alpha\frac{D_{\mathrm{to-gb}}}{RT}\frac{2\gamma_{\mathrm{gb}}}{R_0}\Omega_0$$

$$\langle R\rangle_{t'} - \langle R\rangle_t = \alpha\frac{D_{\mathrm{to-gb}}}{RT}\frac{\gamma_{\mathrm{gb}}}{R_0}\Omega_0(t'-t)$$

Abnormal grain growth is when some large grains grow unusually quickly in a matrix of fine grains with a very slow growth rate.

Figure taken from Suk-Joong L. Kang (2004) Sintering: Densification, Grain Growth, and Microstructure.

Plasticity in metals

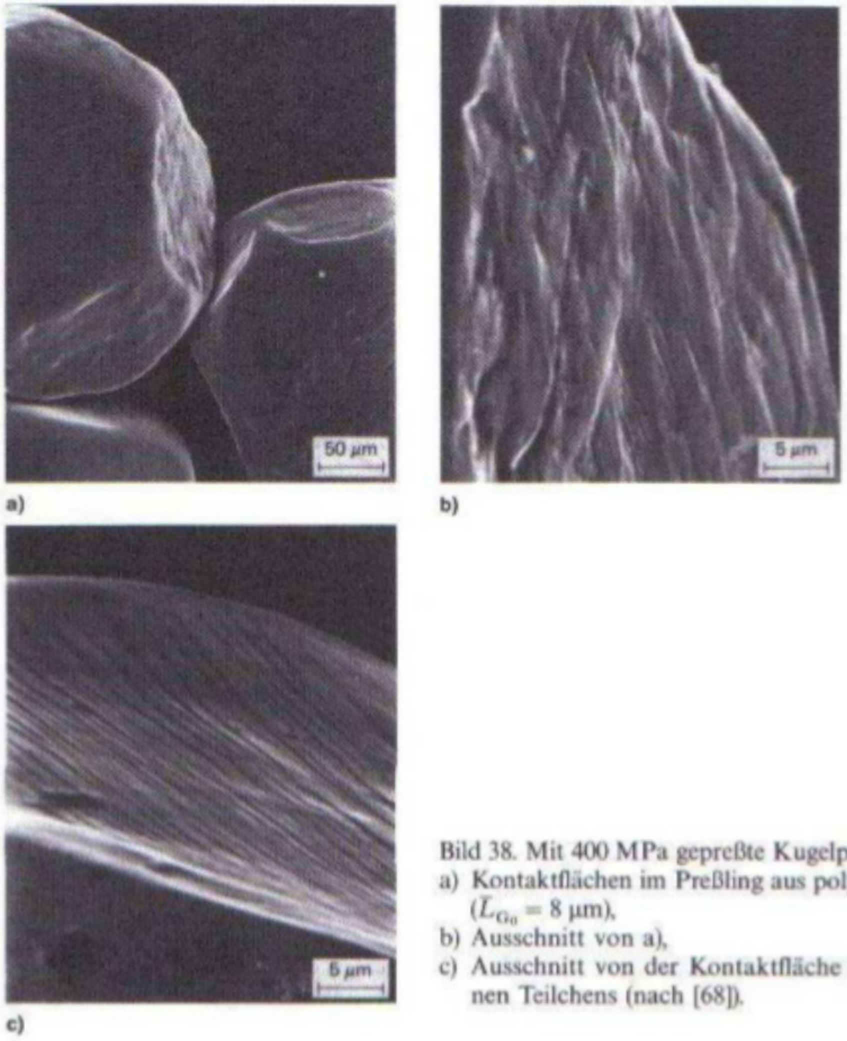


Bild 38. Mit 400 MPa gepreßte Kugelpackung, $a = 125$ µm;
a) Kontaktflächen im Preßling aus polykristallinen Pulvern ($\bar{L}_{G_0} = 8$ µm),
b) Ausschnitt von a),
c) Ausschnitt von der Kontaktfläche eines monokristallinen Teilchens (nach [68]).

The shown theories may be applied to both metals and ceramics. However, metals are ductile (compared to ceramics) and significant plasticity can occur during cold compaction.

Plasticity in metals

The very high local internal stresses associated with large interface curvatures can also cause local plasticity in metals

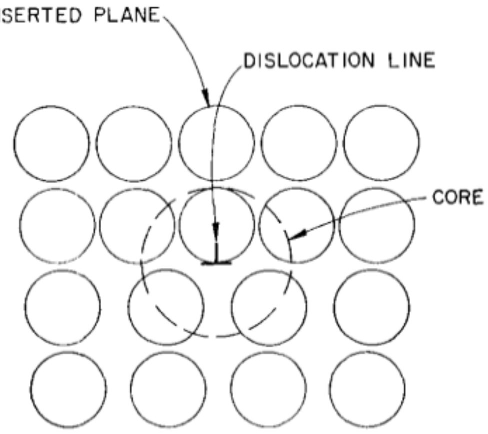
Local internal
stress scale

$$\sim \frac{\gamma}{r} \simeq \frac{Jm^{-2}}{10^{-6}m} \simeq 1MPa$$

Such large stresses can cause local plastic deformation.

Together, such plasticity will result in a dense population of dislocations within the metallic crystallites – this can result in significantly enhanced material transport.

Pipe
diffusion



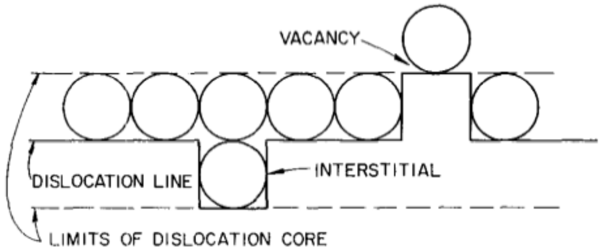


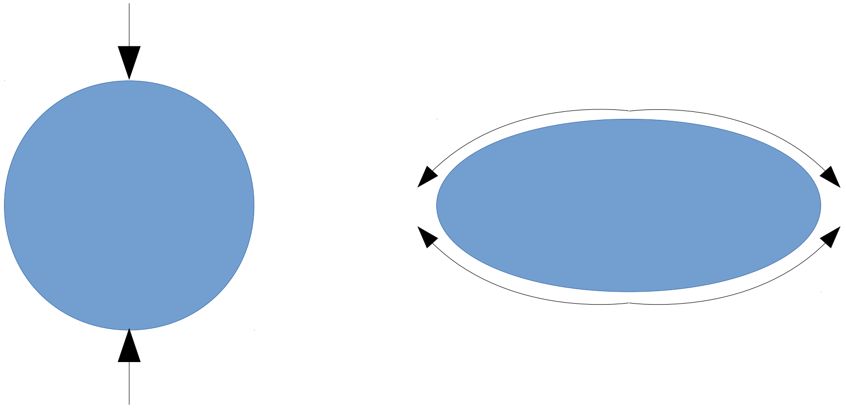
FIG. 2. Illustrating "interstitial" and "vacancy" in pure edge dislocation (simple cubic lattice).

Results in:
- Dislocation creep
- Enhanced diffusion

Plasticity in metals

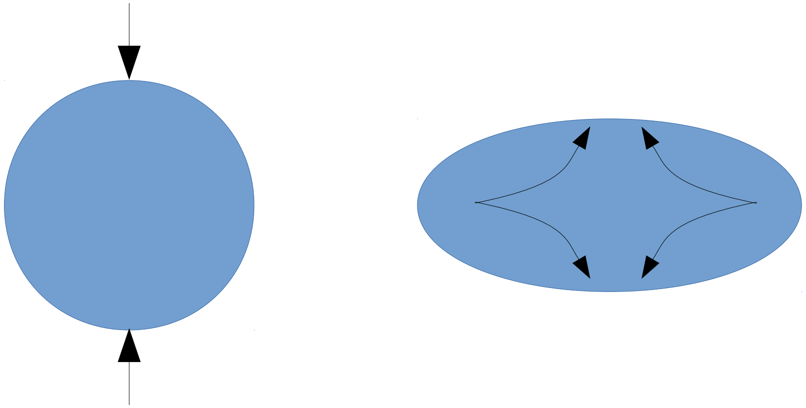
The metallic crystallites may also undergo creep to relieve local stress gradients – and becomes very important in pressure assisted sintering – crystallites can change shape.

Coble creep



Diffusion in the grain boundary

Nabarro-Herring creep



Vacancy diffusion in the crystal and pipe diffusion due to a dislocation network

Questions

- Why does sintering need to occur at an elevated temperature?
- Using the picture of a potential energy landscape, describe the origin of the terms in the equation for thermal activation.
- Describe the three stages of sintering and their corresponding pore geometries.
- Discuss the origin of particle flux, in terms of gradients in terms of concentration gradient and chemical potential. Which is the more relevant for sintering?
- What is the central thermodynamic driving force for sintering?
- In the initial sintering phase, where the two particle model may be applied, what length scale dominates the degree of material transport? Why?
- List the seven main diffusion mechanisms associated with the initial sintering phase.
- In very general terms, how are these mechanisms affected by particle size, temperature and pressure?
- What additional phenomenon occurs in metals and not in ceramics?
- Describe how a vacancy might diffuse in a perfect crystal or at a dislocation? Which can result in a significantly higher diffusion constant? Why?
- What is the essential difference between Coble creep and Nabarro-Herring creep.
- What can be a source of discontinuous grain growth?
- What is general anomolous grain growth?