



# Sintering theory

Peter M Derlet  
Condensed Matter Theory  
Paul Scherrer Institut

[peter.derlet@psi.ch](mailto:peter.derlet@psi.ch)

## Semestre d'hiver 2018

Week- DATE	File. no.		Powder Technology – Wednesday 10.15-13.00 – MXG 110
1- sept 19	1&2	PB	Introduction – example rheology – Yodel - Powder packing and compaction – 1 (i) – (3hrs)
2 – sept 26	2&3	PB MS	Powder packing and compaction – 1(ii), 2- Examples and DEM guest lecturer – (3hrs)
3 – oct 3	4	PD	Powder packing and compaction -3 & 4(i) – (3hrs)
4 – oct 10	4&5	PD	Powder packing and compaction - 4 (ii) – (1hr)
		PB	Particle – Particle Interactions 1 - 2hrs
5 – oct 17	6&7	PB	Particle – Particle Interactions 2 & 3(i) – (3hrs) – Download Hamaker
6 – oct 24	7	PB	Particle – Particle Interactions – 3(ii) YODEL-PB (1hr) <b><u>Exercices</u></b> – Intro to Hamaker & YODEL software & groups project (2hrs)
7 – Oct 30		AK M	<b><u>Exercices</u></b> - Hamaker and Yodel Modelling – group projects
8 – nov 7	8	PB	<b><u>Exercices</u></b> –presentation of interparticle project results (1 hr)
		PD	Introduction to atomistic scale simulations – (2hrs)
9 – nov -14	9&	PD	Compaction, Sintering & Defects in metals at atomistic scale (2hrs)
	11		Sintering Mechanisms – 1(i) (1 hr)
10 – nov 21	11	PD	Sintering Mechanisms - 1 (ii) & 2 (3hrs)
11 -nov-28		PD	<b><u>Exercices</u></b> -Introduction to Molecular Dynamics Modelling using LAMMPS (3hrs) .
12 - dec 5		PD	<b><u>Exercices</u></b> - MD- DEM modelling exercise using LAMMPS –particle packing - Effect of parameters (3 hrs)
13 – dec 12	10	PB	New Technologies -1 Processing – Forming – Shaping (2hrs) <b><u>Exercices or invited lecture or visit of AM lab (1hr)</u></b>
14 – dec 19	10	PB	New Technologies-2 – Sintering Methods <b><u>Exercices or invited lecture or visit of AM lab</u></b> (1 hr) & Exam method

# References

- German, R.M. (1994) Powder metallurgy science, in Metal Powder Industries Federation, 2nd edn, Princeton, New York.
- Coble, R. L., A model for boundary diffusion controlled creep in polycrystalline materials, J. Appl. Phys., 34, 1679-82, 1963.

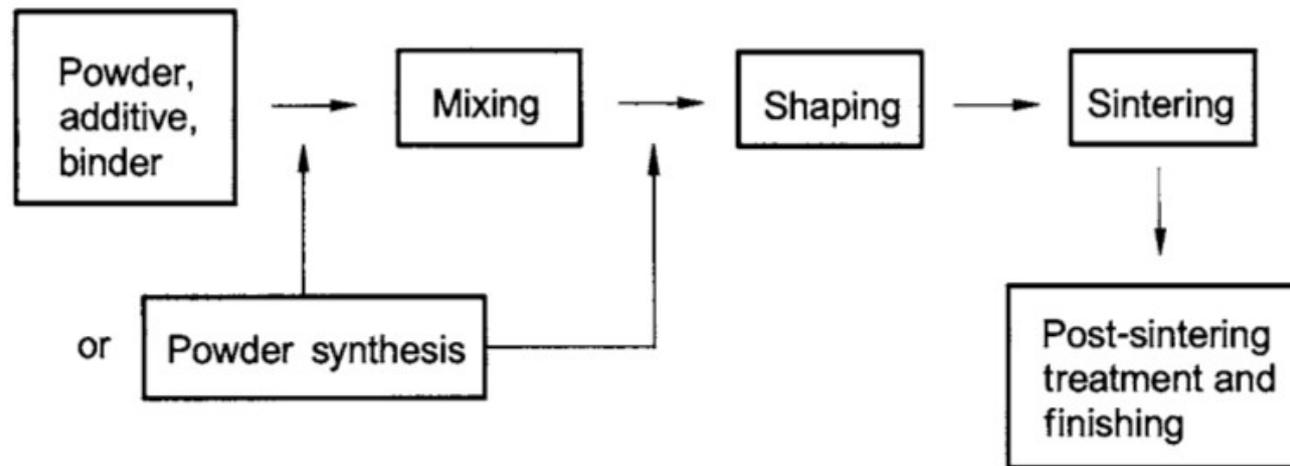
# Lecture outline

- 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
  - 1<sup>st</sup> law of thermodynamics
  - Thermodynamic Potentials
  - The chemical potential
  - 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
  - The important equation in sintering physics
- 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.



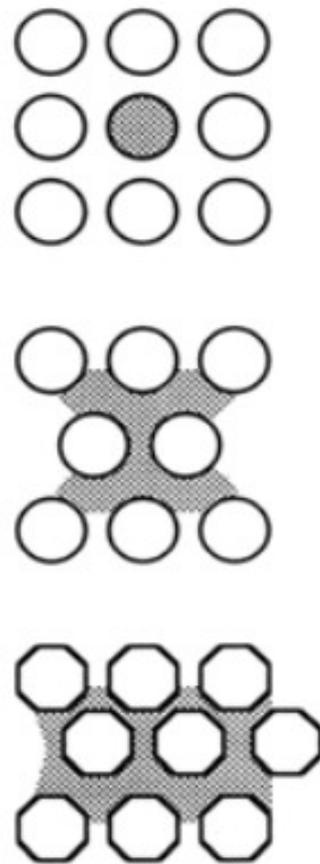
**Figure I.2.** General fabrication pattern of sintered parts.

# Sintering – types

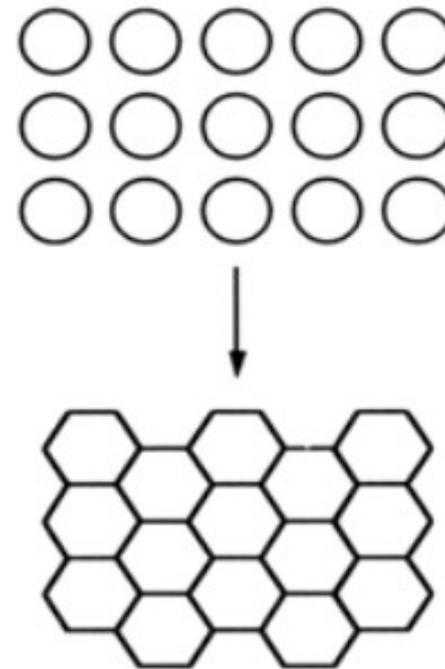
- **Solid phase** sintering – only solid phases are present
- **Liquid phase** sintering – liquid phases are also present
- **Reactive phase** sintering – different phases are present which react to produce new phases

# 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).'

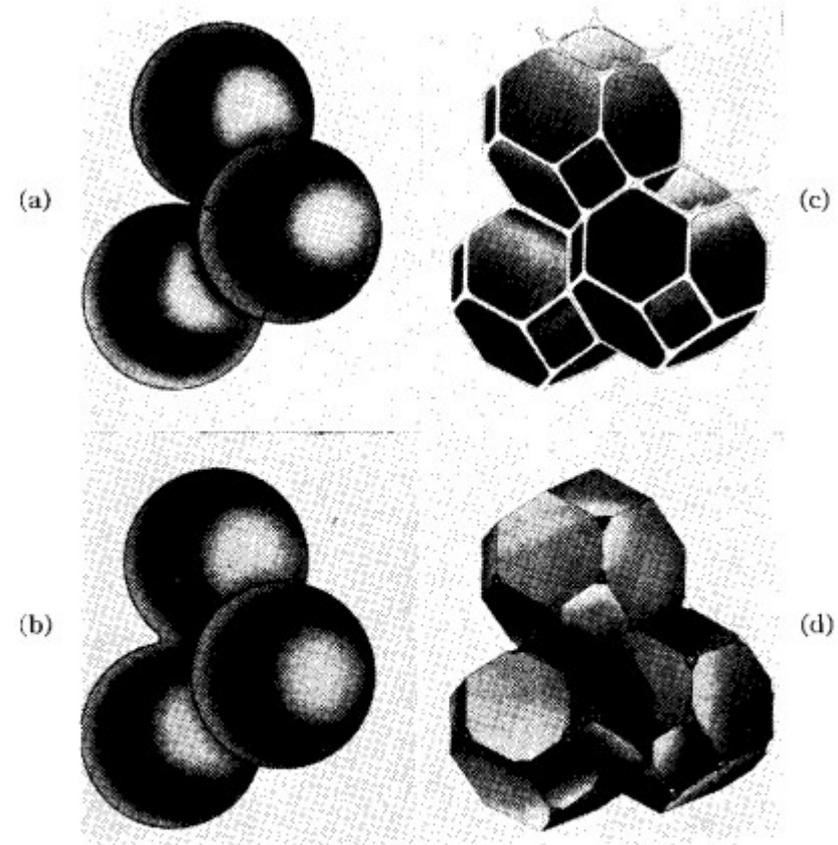


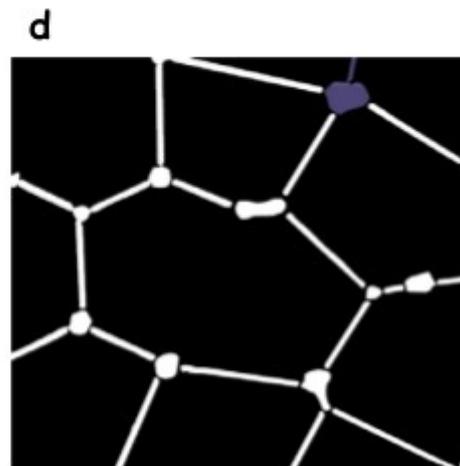
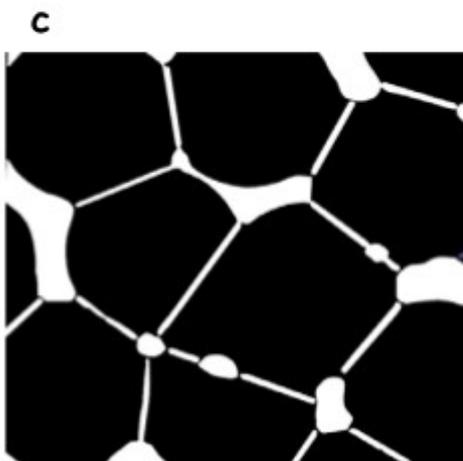
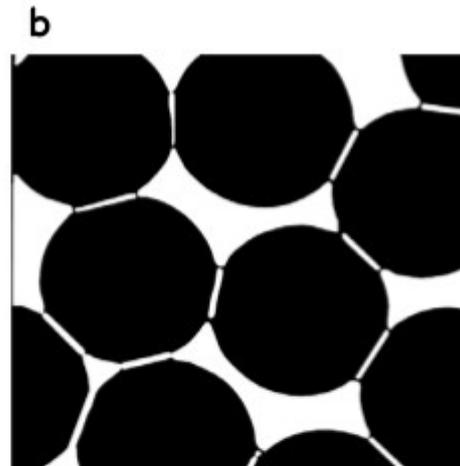
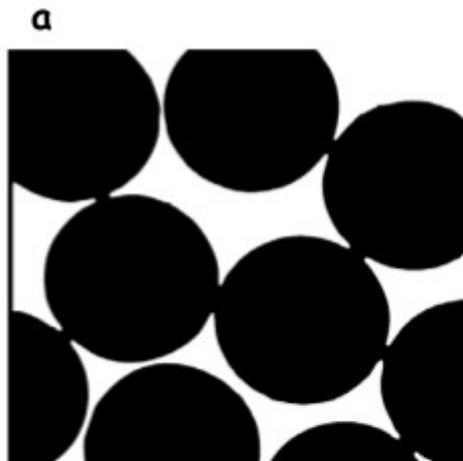
FIG. 1. (a) Initial stage of sintering; model structure represented by spheres in tangential contact. (b) Near end of initial stage. Spheres have begun to coalesce. The neck growth illustrated is for center-center shrinkage of 4%. (c) Intermediate stage; dark grains have adopted shape of tetrakaidecahedron, 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

# Sintering – stages



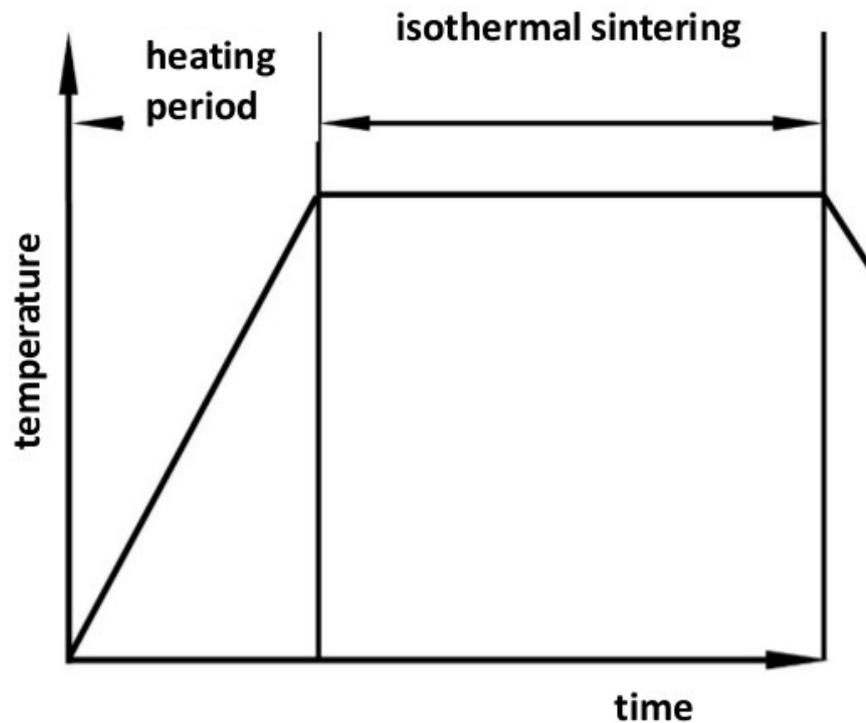
a) Green body, loose powder

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

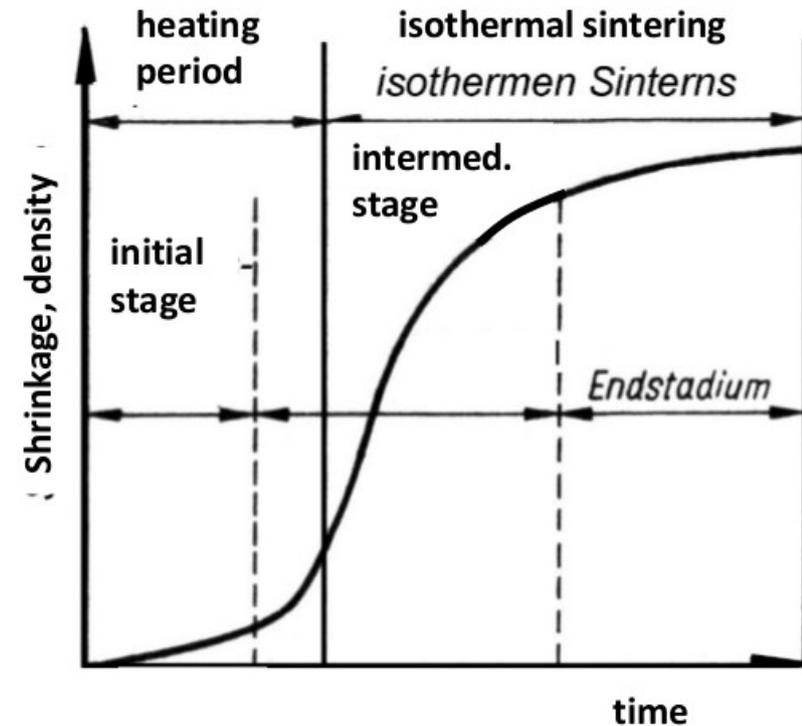
c) Intermediate stage: further increase of the contact area, stage characterized by continuous pore channels along three grain edges, increase of the density from 65 to 90%.

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

# The simplest temperature protocol



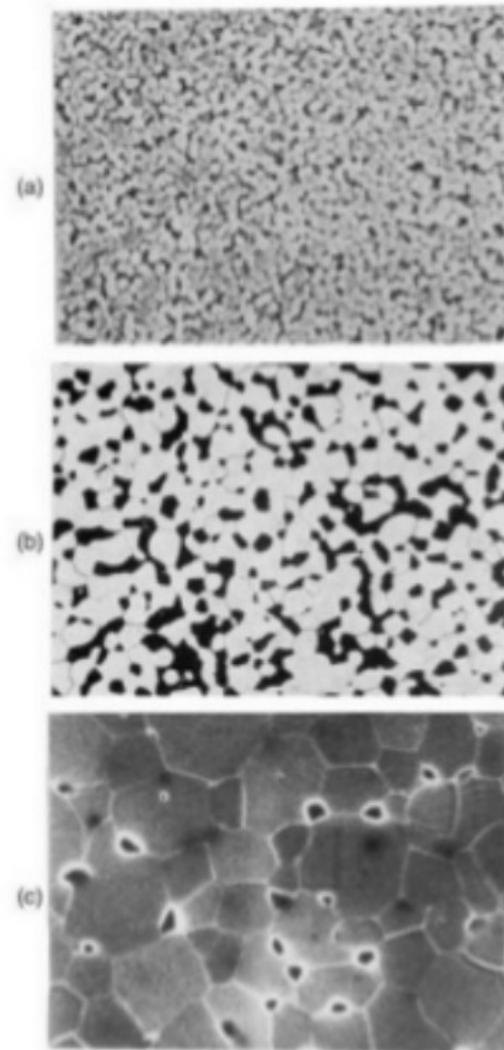
Temperature evolution during a simple sintering cycle



Development of density and shrinkage during a simple sintering cycle

# 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



# Driving force for sintering – the general framework

# Sintering – driving force

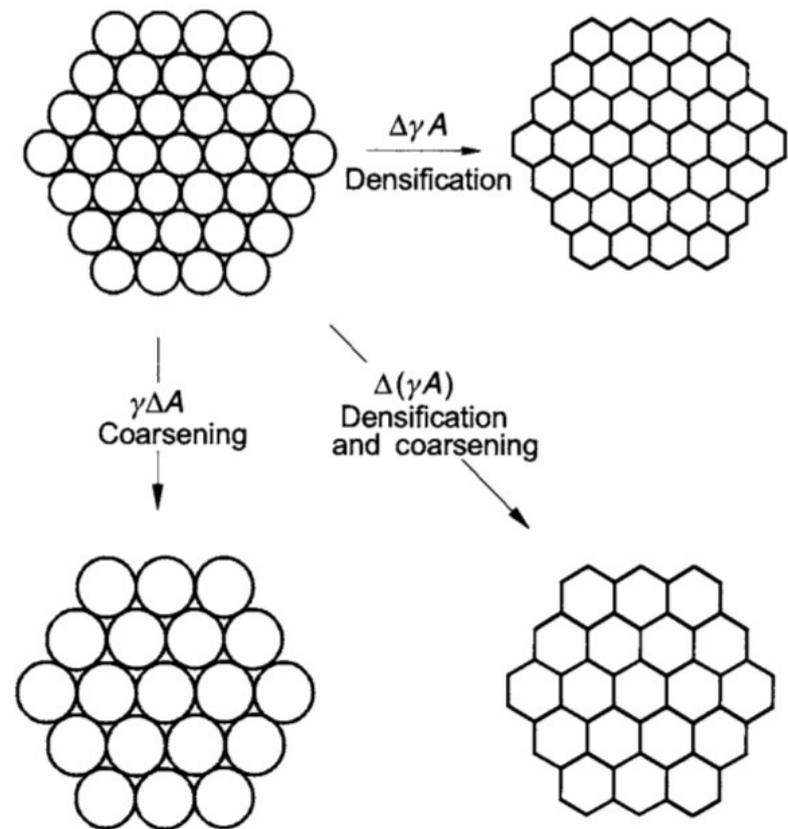
- The fundamental driving force for sintering is the reduction of internal interface/surface energy

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

$\gamma$  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.

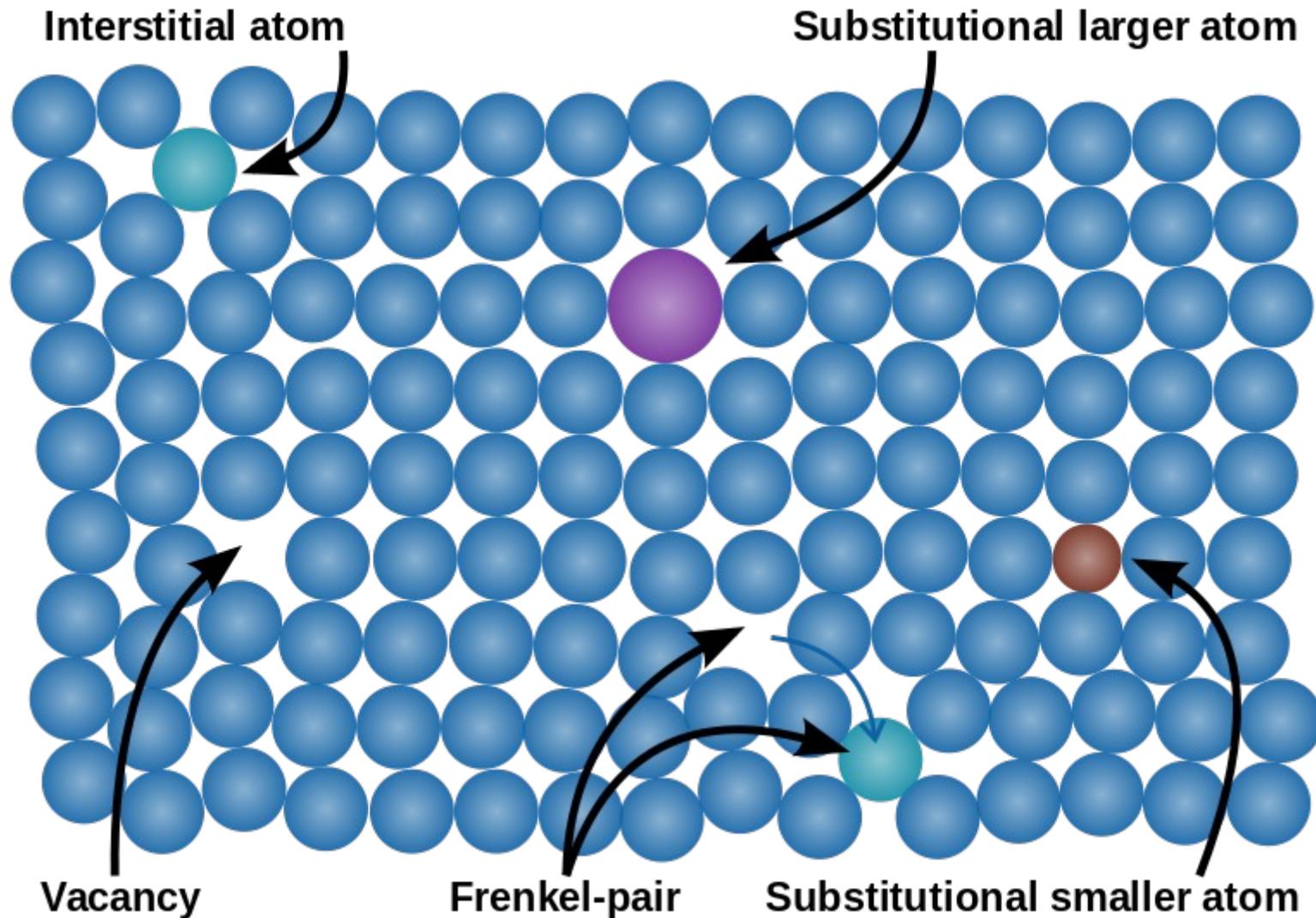
Mass transport is driven by the desire of the system to reduce the total interface energy and the energy of the particles/grains ...

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

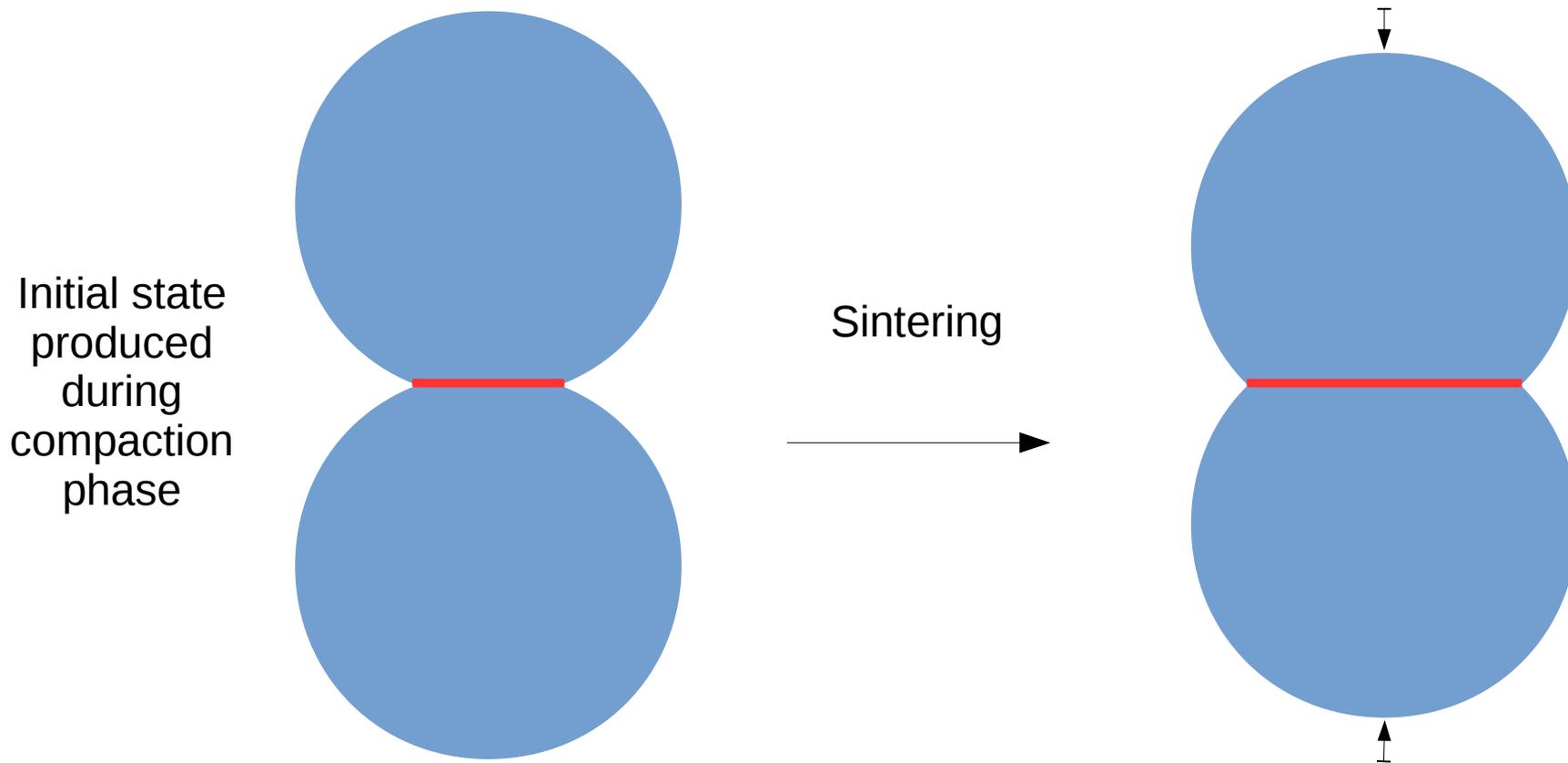
Mass transport can be facilitated by diffusion and plasticity (creep)

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

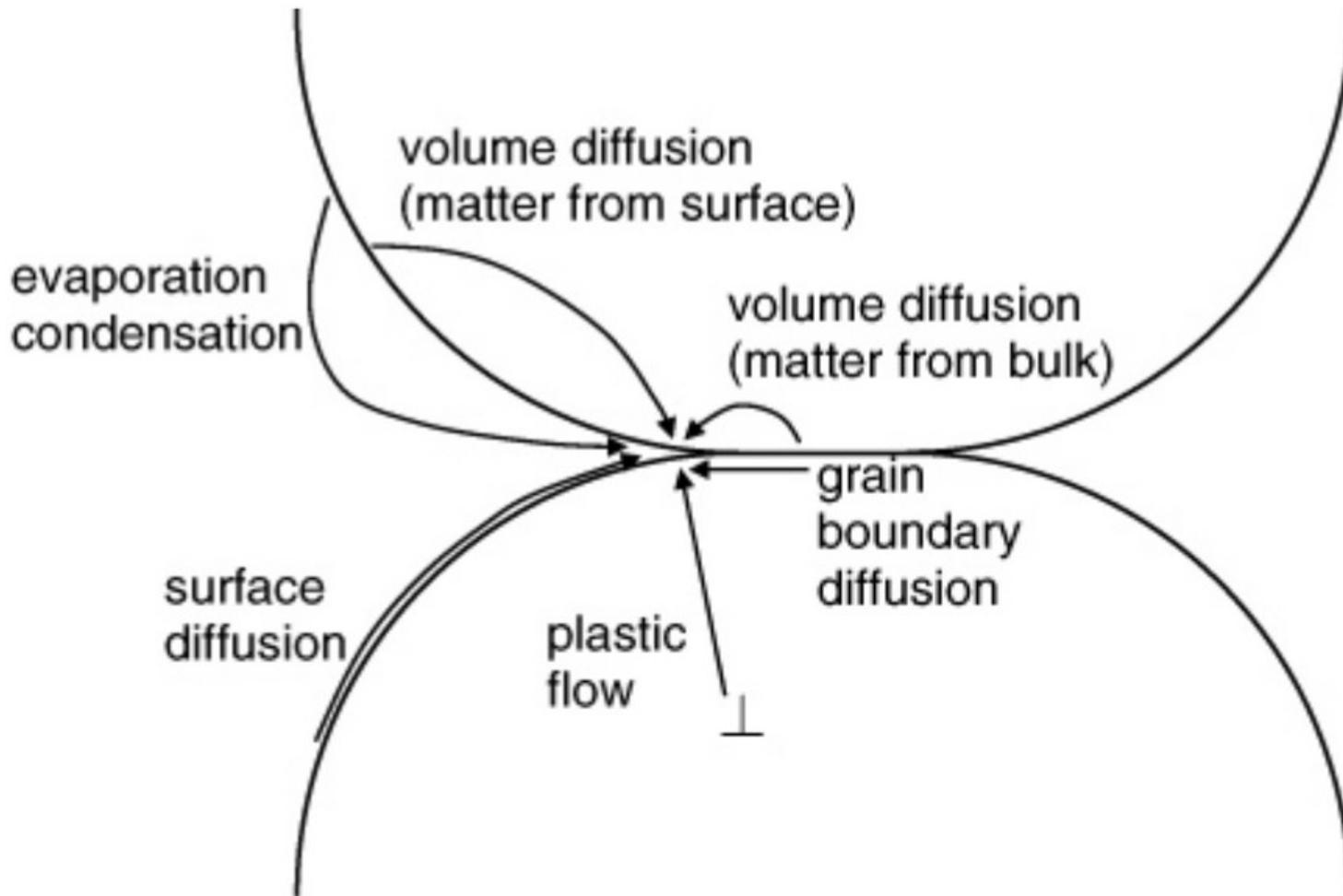
# Mass transport via point defects



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



# Mass transport at green compact contact area



# Theory of diffusion

# The diffusion equation

$C(\mathbf{r}, t)$  Particle concentration at position  $\mathbf{r}$  and time  $t$ : number of particles per unit volume  $[m^{-3}]$

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

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

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

$C(\mathbf{r}, t)$  Particle concentration at position  $\mathbf{r}$  and time  $t$ : number of particles per unit volume  $[m^{-3}]$

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

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

Fick's first law  $\rightarrow$  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

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

$$\mathbf{J}(\mathbf{r}, t) = -D\nabla C(\mathbf{r}, t) \quad \text{Fick's first law}$$

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

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

# The diffusion equation (in 1D)

$$\frac{\partial C(x, t)}{\partial t} = -\frac{\partial J(x, t)}{\partial x} \quad \text{continuity equation}$$

$$J_x(x, t) = -D \frac{\partial C(x, t)}{\partial x} \quad \text{Fick's first law}$$

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

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

# The diffusion equation

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

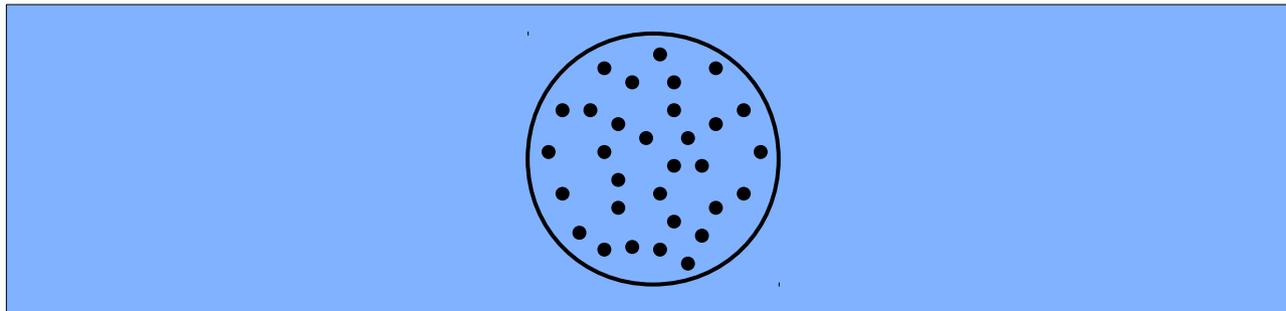
$$C(L, t = 0) = 0$$



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

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

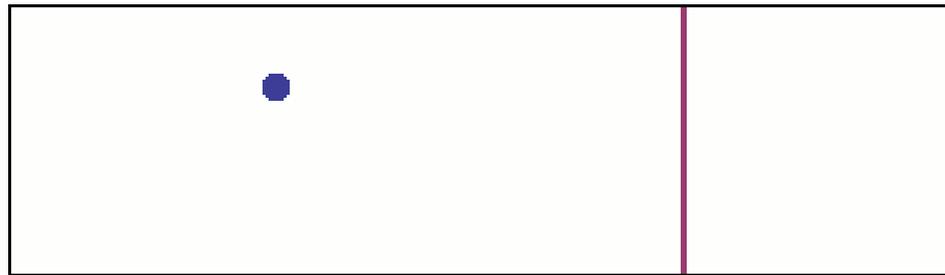
$$C(x, t \rightarrow \infty) = C_{\text{uniform}}$$



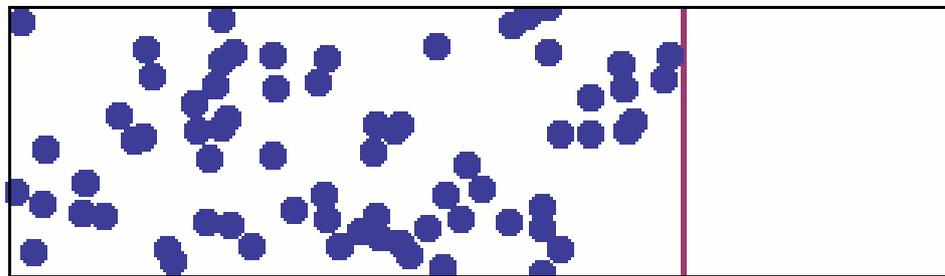
Final state is an equilibrium uniform concentration → no concentration gradient.

But there is still microscopic diffusion

# The diffusion equation – an average of microscopic processes



Individual particle



Ensemble of particles



Continuum concentration  
limit  $\rightarrow$  the diffusion equation

# 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

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

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

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

In equilibrium at fixed T and P,  
 $dG = -SdT + VdP + \mu dN = \mu dN$   
 $\rightarrow G = \mu N$

When out-of-equilibrium

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

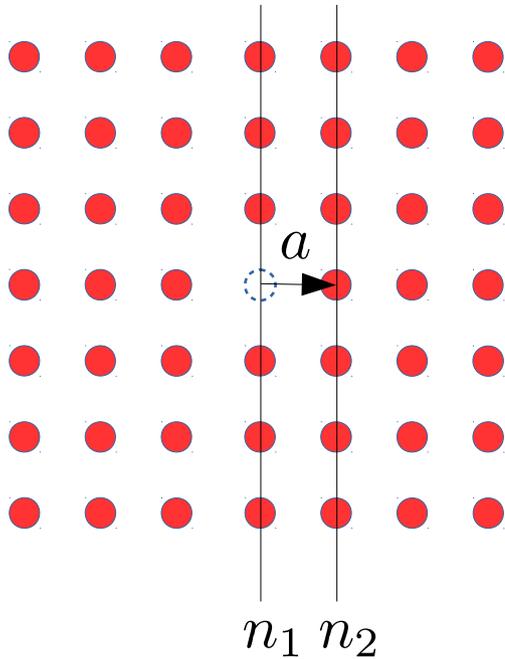
Pressure gradients

# 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)  $p_V \approx p_{V, r \rightarrow \infty} + \frac{p_{V, r \rightarrow \infty} 2\gamma M}{r \rho R T}$  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:

$\Gamma_{\text{vacancy}}$  - 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

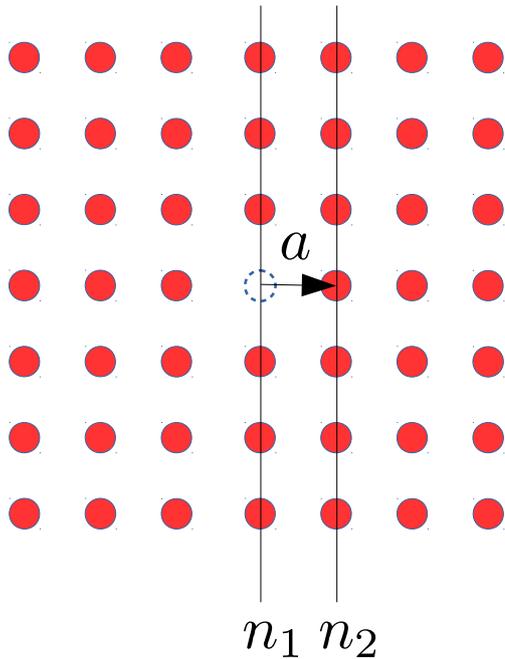
$a$  - lattice constant

Vacancy fluxes

$$J_{x,1} = \frac{1}{z} \Gamma_{\text{vacancy}} n_1$$

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

# The vacancy defect



Define:

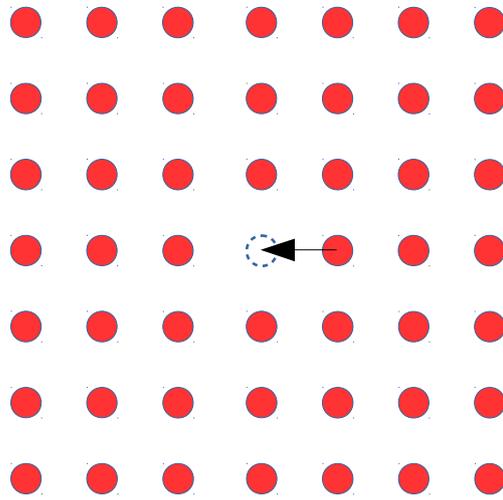
- $\Gamma_{\text{vacancy}}$  - the rate of vacancy hopping per site
- $n_i = C(x_i)a$  - the number of vacancies in the  $i$ th plane per unit area
- $z$  - atomic coordination
- $a$  - lattice constant

$$J_{x,\text{net}} = J_{x,1} - J_{x,2} = \frac{1}{z} \Gamma_{\text{vacancy}} (n_1 - n_2)$$

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

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

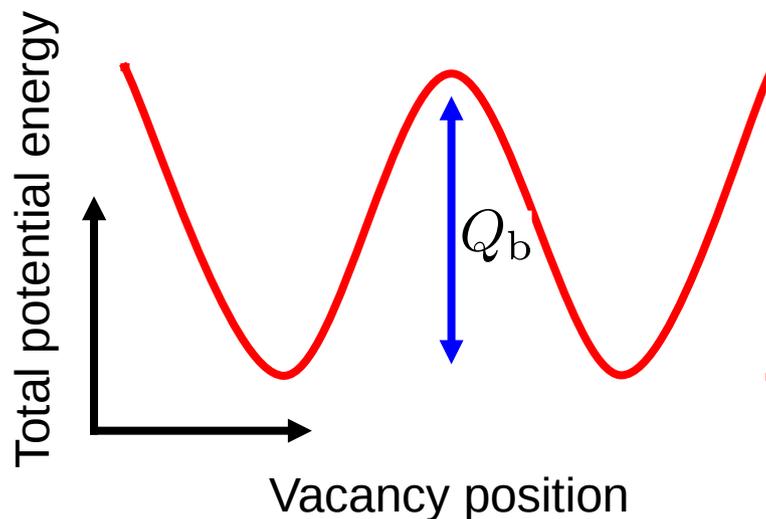
# Microscopic diffusion: the vacancy hopping rate



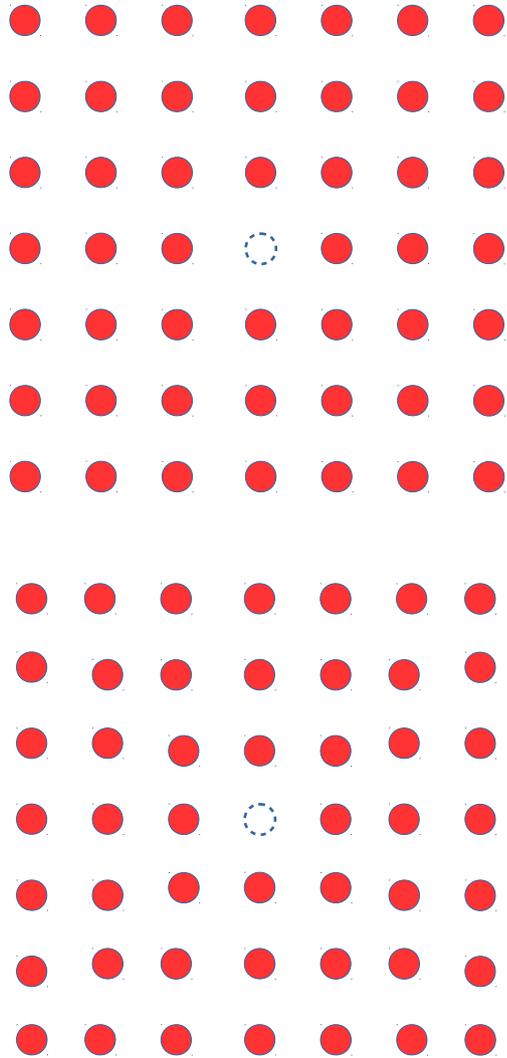
$$\Gamma_{\text{vacancy}} = \nu \exp\left(-\frac{Q_b}{k_B T}\right)$$

Activation energy

Attempt rate



# Microscopic diffusion: the equilibrium vacancy concentration



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

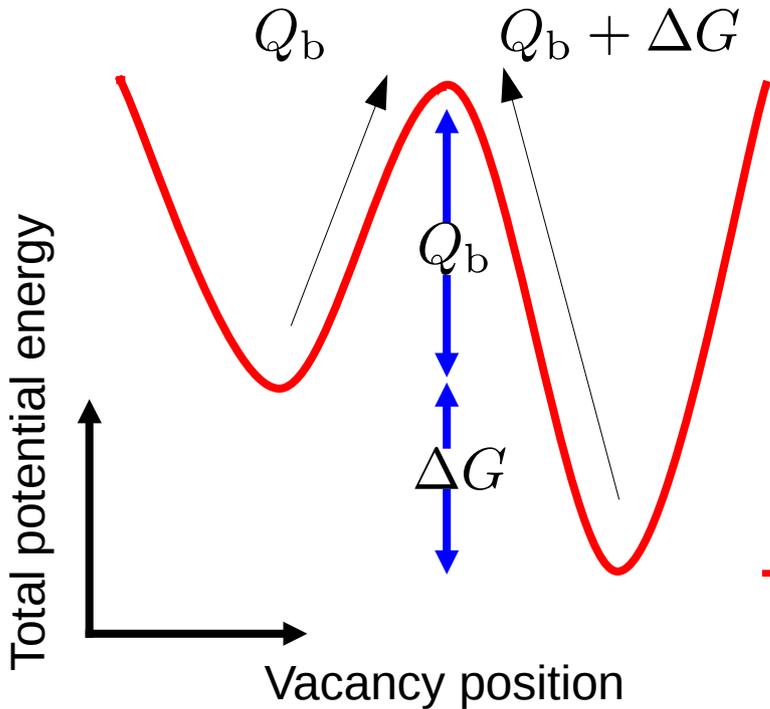
$$C_{\text{vacancy}} = \frac{1}{a^3} \exp\left(-\frac{E_{\text{vacancy}}}{k_B T}\right)$$

↓  
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



$$\Gamma_{1 \rightarrow 2} = \nu \exp\left(-\frac{Q_b}{k_B T}\right)$$

$$\Gamma_{2 \rightarrow 1} = \nu \exp\left(-\frac{Q_b + \Delta G_{12}}{k_B T}\right)$$

$$J_{x, \text{net}} = n_1 \nu \exp\left(-\frac{Q_b}{k_B T}\right) - n_2 \nu \exp\left(-\frac{Q_b + \Delta G_{12}}{k_B T}\right)$$

$$\approx n_1 \nu \exp\left(-\frac{Q_b}{k_B T}\right) \left(1 - \exp\left(-\frac{\Delta G_{12}}{k_B T}\right)\right)$$

$$\approx n_1 \nu \exp\left(-\frac{Q_b}{k_B T}\right) \frac{\Delta G_{12}}{k_B T}$$

$$= \nu \exp\left(-\frac{Q_b}{k_B T}\right) \frac{C_1 a^2}{k_B T} \frac{d\mu}{da}$$

$$= C_1 \frac{D}{k_B T} \frac{d\mu}{da} = C_1 M \frac{d\mu}{da}$$

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

# Additional content: thermodynamics primer

# Thermodynamics primer

$$dU = dQ - dW$$

First law of thermodynamics

$dQ \rightarrow$  Heat transferred to the system

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

$$\sum_i \frac{Q_i}{T_i} \leq 0 \quad \int \frac{dQ}{T} \leq 0$$

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

Clausius' theorem

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

Define:  $dS = \frac{dQ_{\text{rev}}}{T} \quad dS \geq \frac{dQ}{T}$

$$\frac{Q_2}{Q_1} \leq \frac{Q_{r2}}{Q_{r1}} = \frac{T_2}{T_1}$$

For a thermally isolated system there is no transfer of heat

Thermodynamic temperature definition

$dS \geq 0$  The entropy of an isolated system cannot decrease

$$dQ = TdS$$

# Thermodynamics primer

$$dU = dQ - dW \quad \text{First law of thermodynamics}$$

$$dW \longrightarrow \text{Work done by the system} \quad dW = PdV$$

$$V(T, P) \rightarrow dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

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

$$\beta_P = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{Isobaric cubic expansivity}$$

# Thermodynamics primer

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

$$\left. \begin{aligned} dU &= \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \\ &= TdS - PdV \end{aligned} \right\} T = \left( \frac{\partial U}{\partial S} \right)_V \quad P = - \left( \frac{\partial U}{\partial V} \right)_S$$

$$C_V = \left( \frac{dQ}{dT} \right)_V = \left( \frac{dU + PdV}{dT} \right)_V = \left( \frac{dU}{dT} \right)_V$$

$H(S, P) = U(S, V) + PV$  → Enthalpy

$$\left. \begin{aligned} dH &= dU(S, V) + PdV + VdP \\ &= TdS + VdP \end{aligned} \right\} T = \left( \frac{\partial H}{\partial S} \right)_P \quad V = \left( \frac{\partial H}{\partial P} \right)_S$$

$$C_P = \left( \frac{dQ}{dT} \right)_P = \left( \frac{dH - VdP}{dT} \right)_P = \left( \frac{dH}{dT} \right)_P$$

# Thermodynamics primer

$$A(T, V) = U(S, V) - TS \quad \rightarrow \text{Helmholtz free energy}$$

$$\left. \begin{aligned} dA &= dU(S, V) - TdS - SdT \\ &= -SdT - PdV \end{aligned} \right\} S = - \left( \frac{\partial A}{\partial T} \right)_V \quad P = - \left( \frac{\partial A}{\partial V} \right)_T$$

$$G(T, P) = H(S, P) - TS \quad \rightarrow \text{Gibbs free energy}$$

$$\left. \begin{aligned} dG &= dH(T, V) - TdS - SdT \\ &= -SdT + VdP \end{aligned} \right\} S = - \left( \frac{\partial G}{\partial T} \right)_P \quad V = \left( \frac{\partial G}{\partial P} \right)_T$$

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

$$d\Phi \rightarrow d\Phi + \sum_i \mu_i dN_i$$

$dN_i$  - change in number of particles of type  $i$   
 $\mu_i$  - chemical potential of type  $i$

$$U(S, V) \rightarrow U(S, V, \{N_i\})$$

$$A(T, V) \rightarrow A(T, V, \{N_i\})$$

$$H(S, P) \rightarrow H(S, P, \{N_i\})$$

$$G(T, P) \rightarrow G(T, P, \{N_i\})$$

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

$$dG = \sum_i \mu_i dN_i \quad \longrightarrow \quad G = \sum_i \mu_i N_i$$

# Thermodynamics primer

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

$$d\Phi \rightarrow d\Phi + \sum_i \mu_i dN_i$$

$dN_i$  - change in number of particles of type  $i$   
 $\mu_i$  - chemical potential of type  $i$

$$U(S, V) \rightarrow U(S, V, \{N_i\})$$

$$A(T, V) \rightarrow A(T, V, \{N_i\})$$

$$H(S, P) \rightarrow H(S, P, \{N_i\})$$

$$G(T, P) \rightarrow G(T, P, \{N_i\})$$

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

$$dG = \sum_i \mu_i dN_i \quad \longrightarrow \quad G = \sum_i \mu_i N_i$$

# 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:

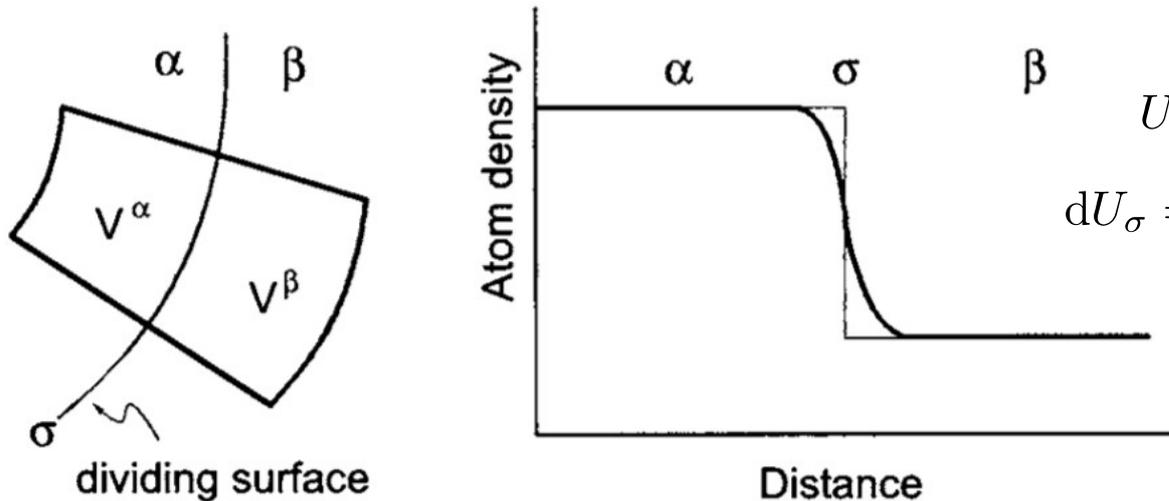
- Two systems are in thermal equilibrium when their temperatures are the same.
- Two systems are in mechanical equilibrium when their pressures are the same.
- Two systems are in diffusive equilibrium when their chemical potentials are the same.
- All forces are balanced and there is no significant external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



$$U_\sigma = TS_\sigma + \mu_\alpha n_\alpha^\sigma + \mu_\beta n_\beta^\sigma + \gamma A$$

$$dU_\sigma = TdS_\sigma + \mu_\alpha dn_\alpha^\sigma + \mu_\beta dn_\beta^\sigma + \gamma dA$$

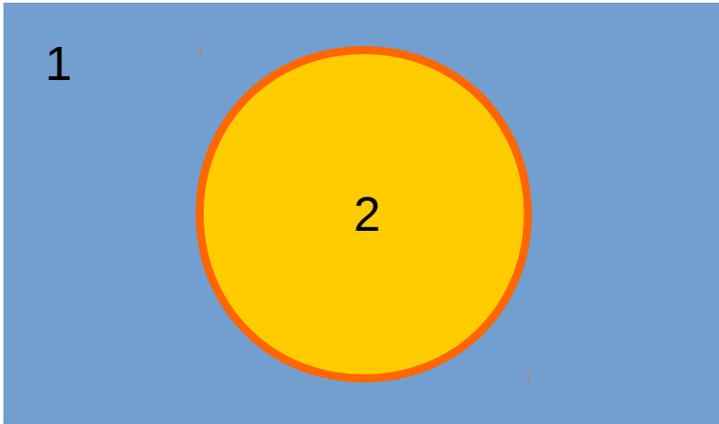
$$\left. \begin{aligned} dU &= dU_\alpha + dU_\alpha + dU_\sigma \\ &= TdS + \mu_\alpha dn_\alpha + \mu_\beta dn_\beta + P_\alpha dV_\alpha + P_\beta dV_\beta + \gamma dA \end{aligned} \right\} \gamma \equiv \left( \frac{\partial U}{\partial A} \right)_{S, \mu_\alpha, \mu_\beta, V_\alpha, V_\beta}$$

$$d\gamma = -\frac{S_\sigma}{A} dT + \frac{n_\alpha^\sigma}{A} d\mu_\alpha + \frac{n_\beta^\sigma}{A} d\mu_\beta$$

# 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)  $p_V \approx p_{V, r \rightarrow \infty} + \frac{p_{V, r \rightarrow \infty} 2\gamma M}{r \rho R T}$  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

$$A = TdS - PdV - \mu dN$$

When in equilibrium  $dA = dA_1 + dA_2 + dA_i = 0$  and  $\mu_1 = \mu_2$

$$dA_1 = -P_1dV_1 + \mu_1dN_1$$

$$dA_2 = -P_2dV_2 + \mu_2dN_2$$

$$dA_i = \gamma dS$$

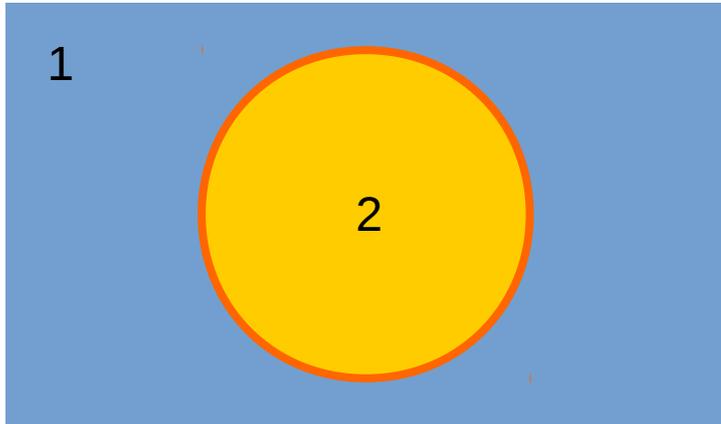
$$P_1 - P_2 = \gamma \frac{dA}{dV_1} = \gamma K$$

Young–Laplace equation

$$\frac{dA}{dV_1} = K$$

Average curvature of interface

# Thermodynamics of interfaces



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

$$N_1 + N_2 = N \rightarrow dN_1 + dN_2 = 0$$

$$V_1 + V_2 = V \rightarrow dV_1 + dV_2 = 0$$

When in equilibrium  $dA = dA_1 + dA_2 + dA_i = 0$  and  $\mu_1 = \mu_2$

$$dA_1 = -P_1 dV_1 + \mu_1 dN_1$$

$$dA_2 = -P_2 dV_2 + \mu_2 dN_2$$

$$dA_i = \gamma dS$$

$$P_1 - P_2 = \gamma \frac{dA}{dV_1} = \gamma K$$

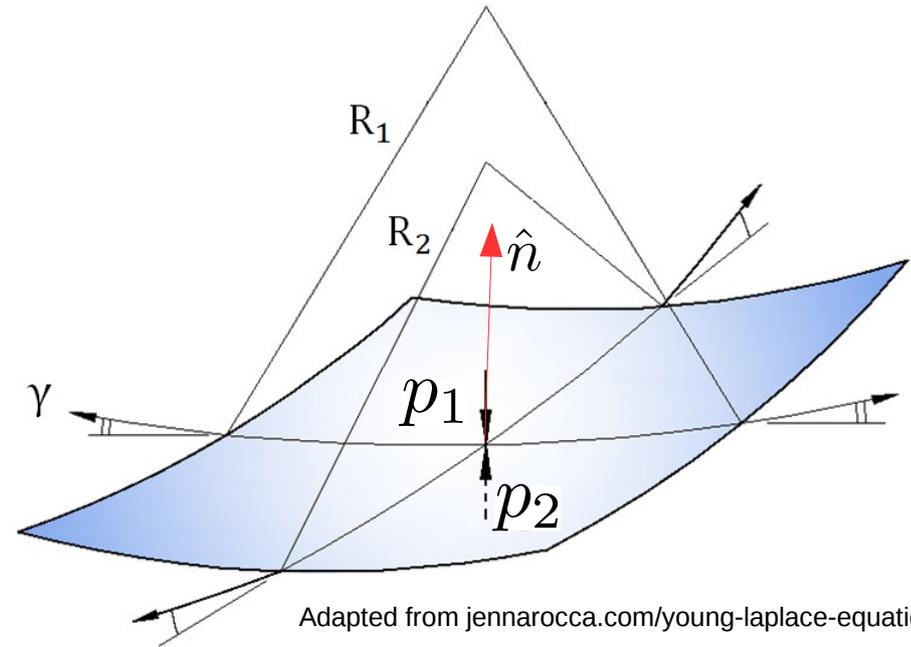
Young–Laplace equation

$$\frac{dA}{dV_1} = K$$

Average curvature of interface

# Young–Laplace equation

$$\begin{aligned}\Delta p &= -\gamma \nabla \cdot \hat{n} \\ &= 2 \gamma H = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)\end{aligned}$$



$\gamma$  : surface energy density

$H$  : average curvature

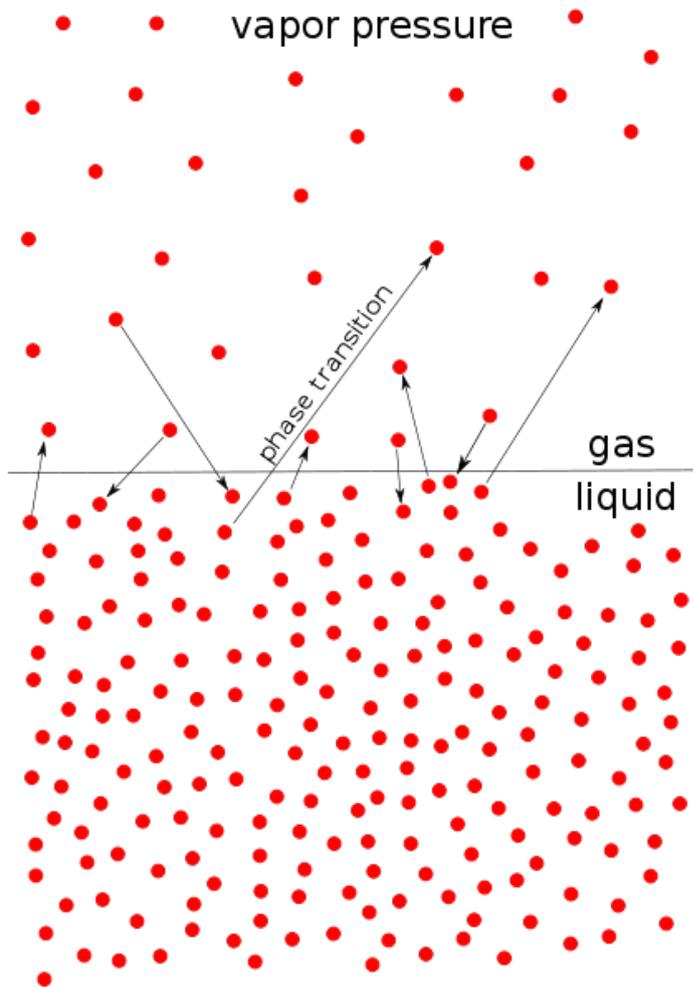
$R_1/R_2$  : max/min curvature

$\Delta p = p_1 - p_2$  : 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
- 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)  $p_V \approx p_{V, r \rightarrow \infty} + \frac{p_{V, r \rightarrow \infty} 2\gamma M}{r \rho R T}$  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

# Vapor pressure – surface effects



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

$$dG = dm_L (u_L + p_0 v_L - T_0 s_L) + dm_V (u_V + p_0 v_V - T_0 s_V) + dG_S$$

$$dG_S = \gamma dA = \gamma \frac{2v_L}{r} dm_L$$

$$dG = dm_L \left( u_L + v_L \left( p_0 + \gamma \frac{2v_L}{r} \right) - T_0 s_L \right) + dm_V (u_V + p_0 v_V - T_0 s_V)$$

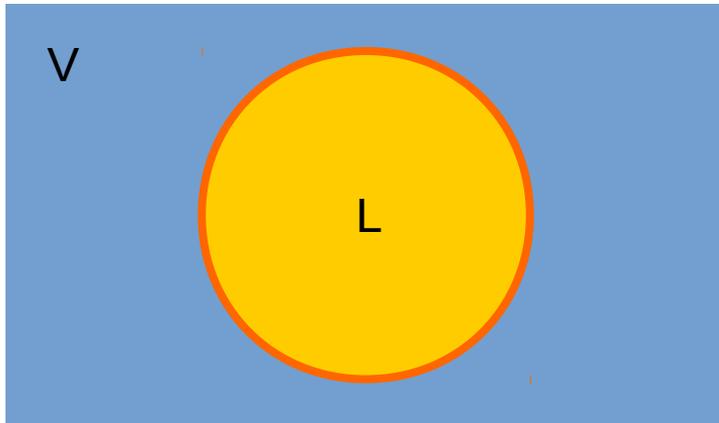
[en.wikipedia.org/wiki/Vapor\\_pressure](http://en.wikipedia.org/wiki/Vapor_pressure)

$$p_L = p_0 + \gamma \frac{2v_L}{r} \longrightarrow dG = g_L(p_L, T) dm_L + g_V(p_V = p_0, T) dm_V$$

$$^{51} dm_L + dm_V = 0 \longrightarrow g_L(p_L, T) = g_V(p_V, T)$$

# Vapor pressure – surface effects

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



$$dG = dm_L (u_L + p_0 v_L - T_0 s_L) + dm_V (u_V + p_0 v_V - T_0 s_V) + dG_S$$

$$dG_S = \gamma dA = \gamma \frac{2v_L}{r} dm_L$$

$$dG = dm_L \left( u_L + v_L \left( p_0 + \gamma \frac{2v_L}{r} \right) - T_0 s_L \right) + dm_V (u_V + p_0 v_V - T_0 s_V)$$

$$p_L = p_0 + \gamma \frac{2v_L}{r} \longrightarrow dG = g_L(p_L, T) dm_L + g_V(p_V = p_0, T) dm_V$$

$$^{52} dm_L + dm_V = 0 \longrightarrow g_L(p_L, T) = g_V(p_V, T)$$

# Vapor pressure – surface effects

$$g_L(p_L, T) = g_V(p_V, T)$$



When changing the volume of the drop, equilibrium requires:

$$\left(\frac{\partial g_L}{\partial p_L}\right)_T dp_L = \left(\frac{\partial g_V}{\partial p_V}\right)_T dp_V$$

$$v_L \left( dp_V - \frac{2\gamma}{r^2} dr \right) = v_V dp_V$$

$$(v_V - v_L) dp_V = -\frac{2\gamma}{r^2} v_L dr$$

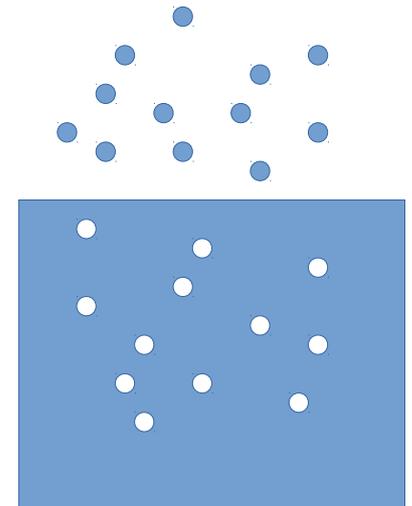
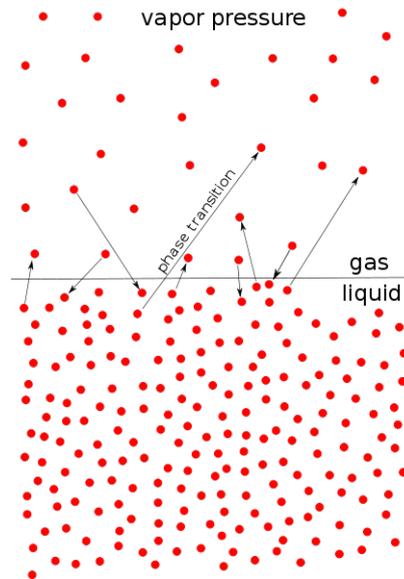
$$v_V \gg v_L \quad v_V dp_V = -\frac{2\gamma}{r^2} v_L dr$$

$$\frac{RT}{p_V} dp_V = -\frac{2\gamma}{r^2} v_L dr$$

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

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

53



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
- 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)  $p_V \approx p_{V, r \rightarrow \infty} + \frac{p_{V, r \rightarrow \infty} 2\gamma M}{r \rho R T}$  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

# ... in terms of the chemical potential

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

$$\begin{aligned} \mu_1(T, P_{1,r}) &= \mu_1(T, P_{2,r} + \gamma K) \approx \mu_1(T, P_{2,r}) + \gamma K \left( \frac{\partial \mu_1}{\partial P} \right)_{T, P_{1,r}} \\ &= \mu_1(T, P_{2,r}) + \gamma K \Omega_1 \end{aligned}$$

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

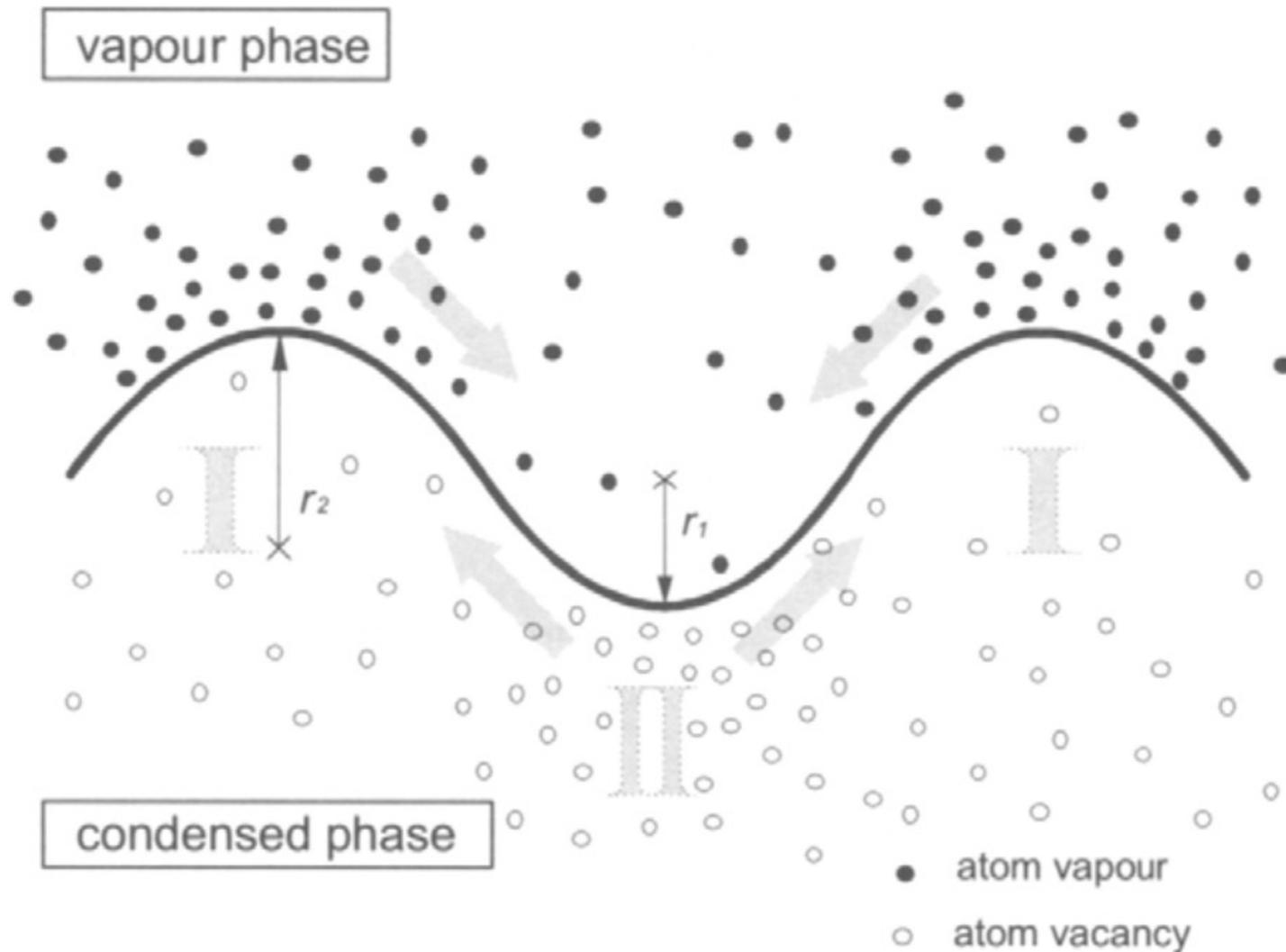
$$\mu_2(T, P_2) \approx \mu_2(T, P_{2,\infty}) \equiv \mu_{2,\infty} \quad (= \mu_1(T, P_{2,\infty}) \equiv \mu_{1,\infty})$$

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

# 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
- 3)  $P_1 - P_2 = \gamma \frac{2}{r}$  Pressure difference across a curved interface
- 4)  $p_V \approx p_{V, r \rightarrow \infty} + \frac{p_{V, r \rightarrow \infty} 2\gamma M}{r \rho R T}$  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

# Atomic transport kinetics effected by capillary pressure differences



# ... in terms of the chemical activity

$$a = \exp\left(-\frac{\mu_0 - \mu}{RT}\right)$$

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

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

$$\mu_1 = \mu_{\text{ref}} + RT \ln \left( \gamma_{\text{activity}} \frac{C_0}{C_{\text{ref}}} \right)$$

$$\mu_2 = \mu_{\text{ref}} + RT \ln \left( \gamma_{\text{activity}} \frac{C_0 + \Delta C}{C_{\text{ref}}} \right)$$

$$\mu_2 - \mu_1 = RT \ln \left( \frac{C_0 + \Delta C}{C_0} \right) \approx RT \frac{\Delta C}{C_0}$$

At local  
equilibrium

$$\frac{\partial \mu}{\partial P} = \Omega_0 \longrightarrow \mu_2 - \mu_1 \approx (P_2 - P_1) \Omega_0 \approx \frac{\gamma}{r} \Omega_0$$

$$RT \frac{\Delta C}{C_0} \approx \frac{\gamma}{r} \Omega_0$$

$$\Delta C \approx \frac{\gamma}{RT r} C_0 \Omega_0$$

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

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