# Lectures on Sintering

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Textbook: "Sintering: densification, grain growth and microstructure" Elsevier BH(2005)

Supporting materials: selected papers and book chapters

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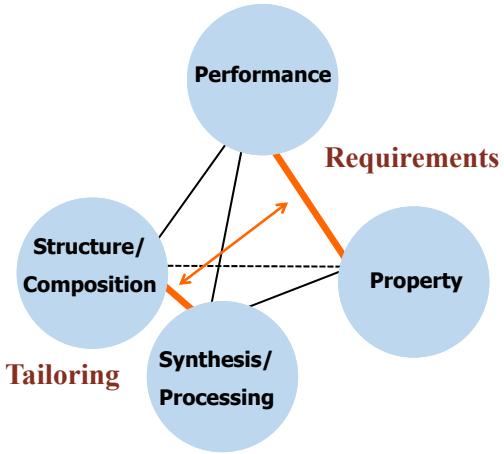
# Introductory Remarks

## Four Basic Elements of MSE




**Materials Design and Tailoring**

Sheppard, Am. Ceram. Soc. Bull., 68 2038 (1989)

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# PI: Basis of Sintering Science

## Outline:

- Brief description of sintering processes and their parameters
- Interfacial energy and driving force of sintering
- Sintering and polycrystalline microstructure

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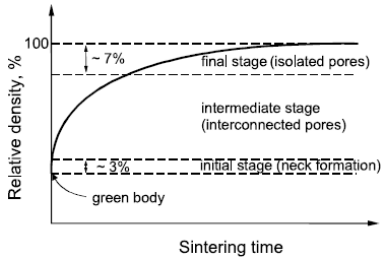
# PII: Bonding and Densification

## Outline:

- Solid state sintering (SSS) Models and Densification




- Models and kinetics
- Effects of processing variables:

  particle size, temperature, external pressure, atmosphere (entrapped gases)

- Liquid phase sintering (LPS) Models and Densification
  - Validity of three stage models
  - Role of liquid in densification
  - Densification kinetics (effects of processing variables)

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# PIII: GG and Microst. Evolution

## Outline:

Types of grain growth: Stationary vs. Nonstationary

- Liquid phase sintering (LPS)
  - Grain growth in a matrix (Ostwald ripening)
  - Effect of pores on microstructure development
  - Effect of interfacial energy anisotropy
- Solid state sintering (SSS)
  - Grain growth in a pure dense system
  - Effect of 2nd phase particles on grain growth
  - Effect of pores on microstructure development
  - Effect of solute segregation on boundary migration
  - Effect of boundary energy anisotropy

Mixed Mechanism Principle of Microstructural Evolution

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# PIV: Supplementary Subjects

## Defect Chemistry and Sintering

- Formation of point defects by additives
- Diffusion (ambipolar) in ionic compounds
- Boundary segregation in pure and impure compound

Electrostatic potential effect

## Diffusion Induced Interface Migration

- Effect of chemical instability on boundary migration
- Control of boundary migration and physical properties

## Discussion on Potential Strategies for Full Densification

Kang, *Materials,* **13**, 3578 (2020).

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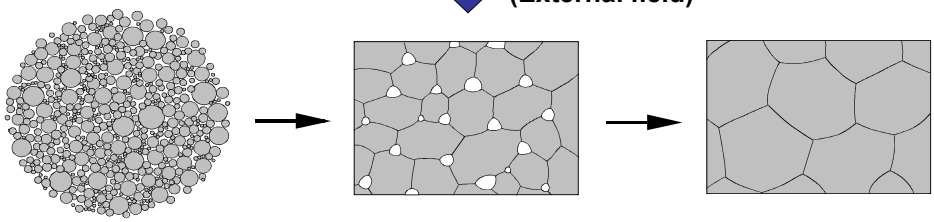
# What is Sintering?

**Thermal Energy**

**( External Pressure )**
**(External field)**



- Densification
- Grain Growth

} **Microstructural Design**

A processing technique of materials to produce density and microstructure controlled materials and components from metallic or ceramic powders by applying, in general, thermal energy.

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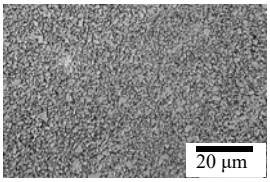
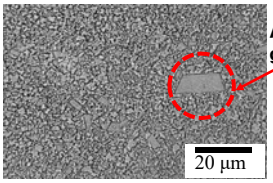
# Effect of Microstructure on Physical Properties

***Mechanical Property***

**WC-Co (die)**



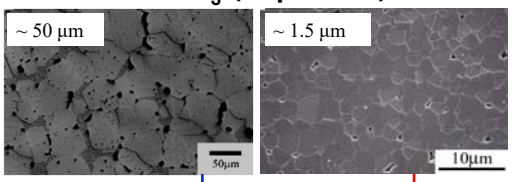

2242 times of use

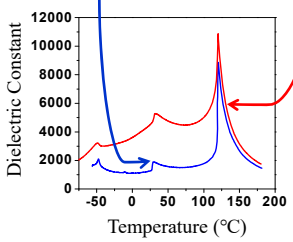



539 times of use

***Electrical Property***

**$BaTiO_3$ (capacitor)**

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# Sintering:

**the oldest, but probably an everlasting technique in materials and components fabrication**

**Prehistoric era**

**Firing of pottery**

**21st century**


**Fabrication of MLCC**

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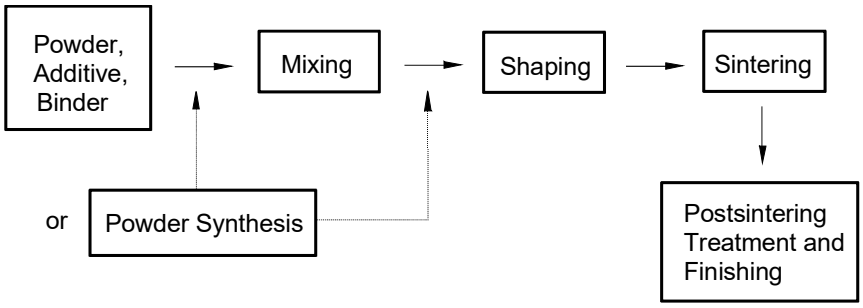
## *General fabrication pattern of sintered parts*




S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

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# What to Learn?

- Fundamentals of sintering.

  (Bonding,) Densification, grain growth and microstructure.

  Sit and Think!

## Contents of the Course:

Rearranged contents of the text book

"Sintering: densification, grain growth and microstructure" Elsevier (2005)

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# PI: Basis of Sintering Science

## Outline:

- Brief description of sintering processes and their parameters
- Interfacial energy and driving force of sintering
- Characteristics of polycrystalline microstructure

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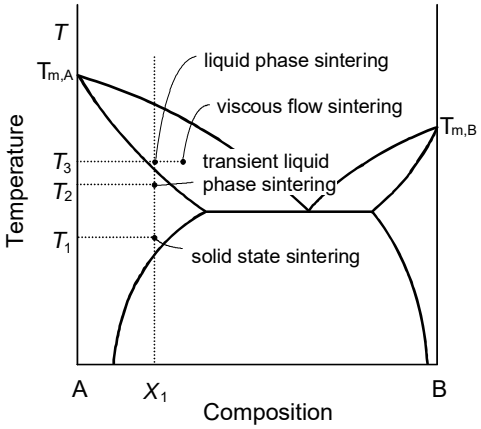
# Chap. Sintering Processes

## Categories of sintering:

SSS; LPS; TLPS; VFS




S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

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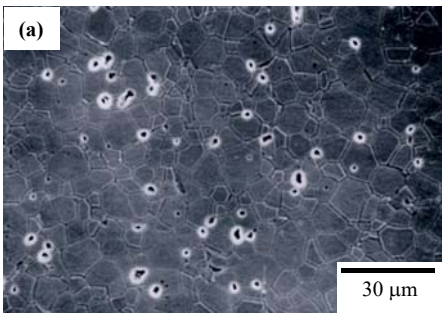
# Typical microstructures observed during SSS and LPS

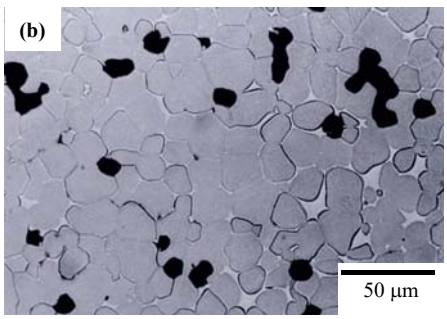
SSS

$Al_2O_3$




LPS

98W-1Ni-1Fe(wt%)




S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

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- SSS
  - No liquid phase
  - Densification is achieved by changing grain shape
  - Equilibrium grain shape (microstructure)?
- LPS
  - Presence of a liquid phase
  - Insufficient volume of liquid ($0 < f^l \leq 30$ vol%)
  - Equilibrium grain shape (microstructure)?
  - Wettability and solubility
- TLPS -Formation of a transient liquid
- VFS - Formation of a sufficient volume of liquid

Difficulties for densification: SSS > LPS > VFS
Physical properties?

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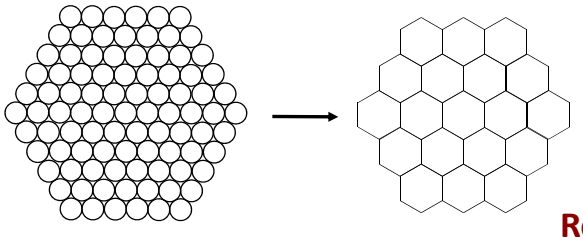
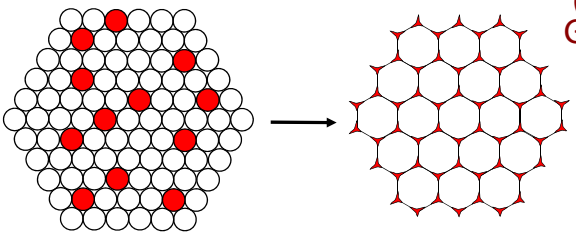
# Densification and Grain Growth

**Solid-state sintering (SSS)**



**Liquid-phase sintering (LPS)**



**Role of Liquid** in Densification (shape accommodation) & Grain growth

"Liquid phase sintering: Fundamentals" in "*Encyclopedia of Materials: Technical Ceramics and Glasses,*" A. Leriche and F. Cambier (eds), Elsevier (2020).

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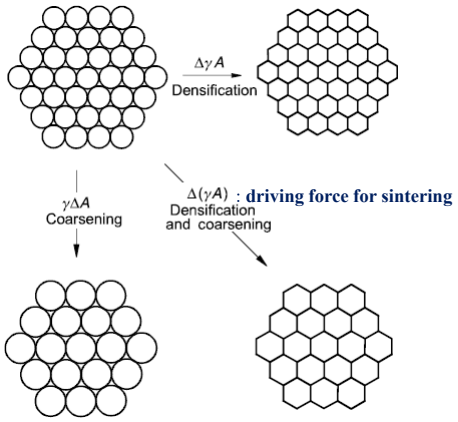
# Driving Force for Sintering

## Reduction of the total surface energy

0.5 ~ 500J/mole (100μm ~ submicron size)
(cf. chemical free energy of compound formation)




Note: the meaning of sintering

S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

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# Exercise:

- Energy change with the sintering of cube-shaped powder with an edge of *l* with no grain growth

$$6L^2\gamma_s \frac{1}{L^3} \rightarrow \frac{6}{2}L^2\gamma_b \frac{1}{L^3}$$

$$\Delta E = \frac{6}{L}\left(\frac{\gamma_b}{2} - \gamma_s\right)$$

- Meaning of $\gamma_s$ and $\gamma_b$
- Sintering of SiC (addition of C and B)

# Qn:

Total surface energy = f(particle size)

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# Densification and Coarsening

- The two processes are themselves complex.
- Multiple mechanisms can be operative for each process (parallel processes) cf. serial processes
- Simultaneous and mutually interactive processes (The choice of processing condition is important)
- We usually want to prepare materials with high density and fine grain size by increasing the densification rate relative to coarsening rate.

$$(\dot{\rho}/\dot{G})\uparrow$$

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# Directions for attaining $(\dot{\rho}/\dot{G})\uparrow$

- Modification of powder characteristic (shape, size and size distribution, etc.)
- Modification of chemistry
  - Use of additives in solid solution Why?
    eg) $Al_2O_3$ + MgO, WC-Co + VC
  - Use of a second phase, commonly liquid
  - Atmosphere control (Po2 control) Why?
    eg) BaTiO3, SrTiO3, Ni, Cu
- Modification of the sintering process
  Unconventional sintering processes
  eg) HP, HIP, Fast Firing, Two-step sintering, SPS, Flash sintering, Cold sintering

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# Sintering Variables

i) Variables inherent to raw powders (material variables)

- Powder : shape, size, size dist, agglomeration (hard and soft), mixedness
- Chemistry : composition, impurity, nonstoichiometry-atomosphere, homogeneity

i) Variables related to sintering condition (process variables)

- T, t, P, atmosphere, heating and cooling rate, E, B (magnetic field)

  eg) P: HP, GPS, HIP and SPS(with E)

  eg) E: SPS and Flash sintering

  eg) Atmosphere : Po2 (oxidizing or reducing), inert

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# Chap. Thermodynamics of the Interface

- Qn: Why does bonding occurs between particles?

  (i) Two particle model, (ii)Surface and Geometry

  (iii) Driving force (difference in chemical potential)

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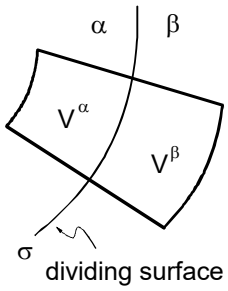
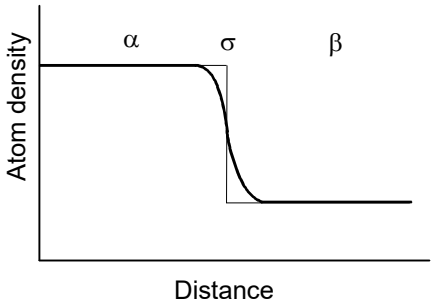
# Definition of the Interface

- Phenomenological treatment of Gibbs
- Any extensive thermodynamic property ø

  $ø = ø^{\alpha} + ø^{\beta} + ø^{\sigma}$ (2.1)

  $ø^{\sigma}$ is characterized by the area and curvature of the dividing surface

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# *Specific surface energy*

- $\gamma = \left(\frac{\partial E}{\partial A}\right)_{S,ni,V^{\alpha}V^{\beta}}$ (2.4) (∂(total energy)/∂A)

  Reversible work required to create a unit area of the surface

- For a planar interface

  $\gamma = \left(\frac{\partial E}{\partial A}\right)_{s,ni,V}$ : the position of the geometrical surface

  σ no longer affects the definition of γ

- Note : $V^{\alpha}$, $V^{\beta} = f$(curvature)

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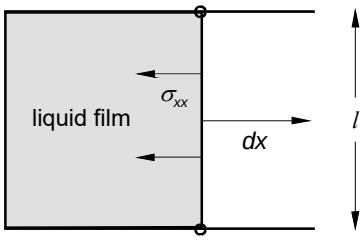
# Surface Tension (stress) and Surface Energy

Qn: How do we know that there is a tension force on a surface?




Work : $W = 2\sigma_{xx} l dx$

Energy : $\Delta E = \Delta A \cdot \gamma = 2\gamma l dx$

$\sigma_{xx} = \gamma$

$\sigma = (\sigma_{xx} + \sigma_{yy})/2 = \gamma$

$\sigma$ // to the surface

$\gamma \perp$ to surface

Nature of surface tension:

surface configuration of atoms

Qn: Cases of liquid and solid

Qn: Case of a thin film or 2-D material



# *Relation btw. $\gamma$ and $\sigma$*

- $\sigma_{ij} = \delta_{ij}\gamma + d\gamma/d\varepsilon_{ij}$

  $\delta_{ij}$ : Kronecker's delta

  for $i = j$, $\delta_{ij} = 1$

  for $i \neq j$, $\delta_{ij} = 0$

  - The equality of $\sigma$ and $\gamma$ ← mobility of atoms
  - Driving force of sintering

    Thermodynamics: $\Delta(\gamma A)$

    Kinetics: $\sigma$ and geometry
  - Case of sintering

    $T_{sinter}$ is usually ~2/3 $T_m$. $T_{sinter} \downarrow$ as a $\downarrow$.

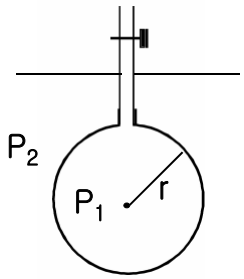
    At usual sintering temperatures, $\gamma \approx \sigma$.

# Thermodynamics of curved interface

Qn: Pressure difference btw two adjacent phases with a curved interface

- Blow of a soap bubble
- Inflate a balloon
- Water droplet and Gas bubble

**Curved interface**




$$P\mathrm{d}V = \gamma \mathrm{d}A$$

$$P_1 - P_2 = \frac{2\gamma}{r}$$

**Young-LaPlace Eq.**

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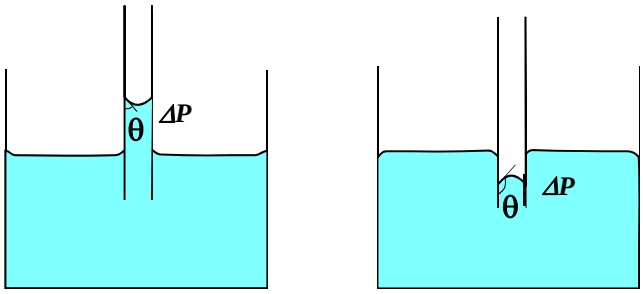
# *Capillary Pressure*

**Capillary action of a glass tube**




$\theta < 90^o$ $\theta > 90^o$

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# Capillrity and Chemical Potential

System with two incompressible phases that are separated by a curved interface

$$d\Omega = 0 = d\Omega^{\alpha} + d\Omega^{\beta} + d\Omega^{\sigma}$$
$$= -P^{\alpha}dV^{\alpha} - P^{\beta}dV^{\beta} + \gamma dA$$
$$P^{\alpha} - P^{\beta} = \gamma \frac{dA}{dV^{\alpha}}$$
$$= \gamma K \qquad K = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$
$$P^{\alpha} - P^{\beta} = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma$$

Cf: Energy change of compressible fluid due to a curved interface

Deformation energy

$$W = -\int_0^P P dV = -\int_0^P P\left(\frac{\partial V_m}{\partial P}\right)_T dP = V_m \kappa \int_0^P P dP$$
$$= \frac{1}{2} V_m \kappa P^2$$

$$\mu_r^{\alpha} = \mu_{\infty}^{\alpha} + \gamma K V_m^{\alpha}$$
$$\mu_r^{\beta} = \mu_{\infty}^{\beta}$$

**Gibbs-Thompson Eq.** Only to phase α

Freezing point of liq. ↓ Melting point of fine powder ↓

For r <$10^{-8}$m, the size effect becomes significant (~0.1).

For r > 0.1μm, the size effect is insignificant.

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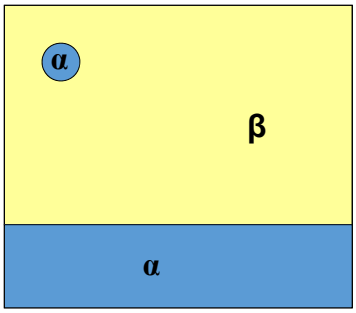
# Capillarity and Atom Activity

## Curved Interface and Solubility




$$a_r = a_{\infty} \exp\left(\frac{2\gamma V_m}{RTr}\right)$$
$$a_r = a_{\infty}\left(1 + \frac{2\gamma V_m}{RTr}\right)$$

**Gibbs -Thompson Eq.**

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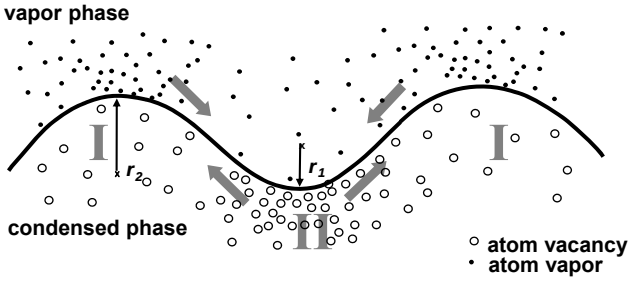
## *Condensed and Dispersed Phase*

α : a condensed phase
β : a dispersed phase

$P^{\alpha} - P_{\infty} = (2\gamma/r)\cdot V^{\beta}_m/(V^{\beta}_m - V^{\alpha}_m) = 2\gamma/r$ for the condensed phase

$p^{\beta} - p_{\infty} = (2\gamma/r)\cdot V^{\alpha}_m/(V^{\beta}_m - V^{\alpha}_m) = p_{\infty}(1+2\gamma V^{\alpha}_m/RTr)$ for the dispersed phase

*As P increases, p increases.* (equality of μ)




Differences in i) Pressure, ii) Vacancy concentration, and iii) Vapor pressure (solubility).

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# Chap. Polycrystalline Microstructure

A few Questions:

Qn: What are the factors that affect microstructure and microstructural evolution?

Qn: What are the characteristics of a polycrystalline microstructure?

Representative (equilibrium) shape of grains?
A stationary microstructure?

- Polycrystal: an Aggregate of Single Crystals

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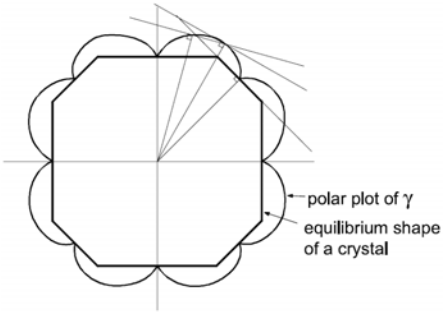
# Equilibrium Shape of a Single Crystal

**Equilibrium Shape:** $\sum (\gamma_i A_i)_{\min}$

Polar plot of surface energy γ (γ-plot)




Wulff construction

(γ of a plane ∝ the distance from the center to the corresponding γ point )

Herring, Phys. Review, 82, 87 (1951)

Kang, in *Sintering: Densification, Grain Growth and Microstructure*, Elsevier, Oxford (2005)

**Wulff Theorem**

Under equilibrium

$$dF = \sum_i \gamma_i dA_i + \left(\frac{\partial F}{\partial n^c}\right)_{T,V} dn^c + \left(\frac{\partial F}{\partial V^c}\right)_{T,V} dV^c + \left(\frac{\partial F}{\partial n^s}\right)_{T,V} dn^s + \left(\frac{\partial F}{\partial V^s}\right)_{T,V} dV^s = 0$$

$$\sum \gamma_i dA_i + (\mu^c - \mu^s) dn^c - (P^c - P^s) dV^c = 0$$

$$\sum_i \left[\gamma_i - \frac{h_i}{2}(P^c - P^s)\right] dA_i + (\mu^c - \mu^s) dn^c = 0$$

$$P^c - P^s = \frac{2\gamma_i}{h_i} \equiv K_w$$

$K_w$:Wulff constant

$$\mu = \mu^o + \frac{2\gamma_i V_m}{h_i}$$

cf. Gibbs-Thompson eq.

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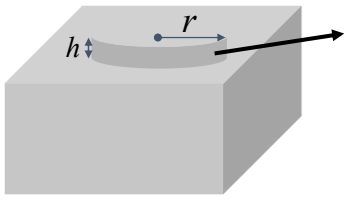
# Step Free Energy and Faceting

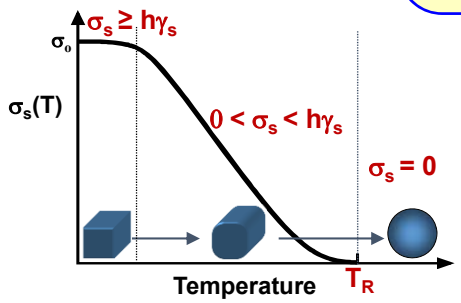



$\sigma_s(T)$ = step free energy

$$\sigma_s(T) = \text{step free energy}$$

$$\Delta g = \pi r^2 h \Delta g_v + 2\pi r \sigma_s$$

$$\Delta g^* = -\frac{\pi \sigma_s^2}{h \Delta g_v}$$ : Critical Driving Force for Nucleation




$$\sigma_s(T) = \alpha \exp\left[-A/\sqrt{T_R - T}\right]$$

**Infinite order transition**

H. V. Beijeren, *Phys. Rev. Lett.*, 38, 993 (1977).
J. M. Kosterlitz and D. J. Thouless, *J. Phys.*, C6, 1181 (1973).
H. J. Leamy and G. H. Gilmer, *J. Cryst. Growth*, 24/25, 499 (1974).

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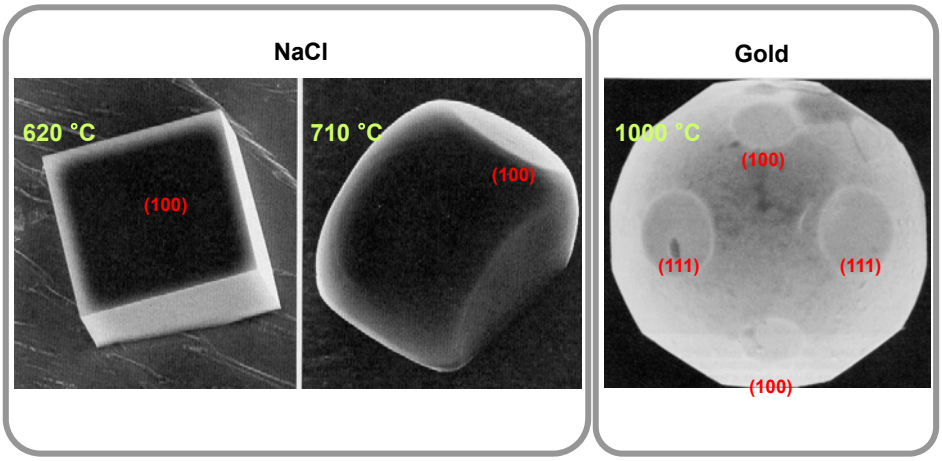
# Equilibrium Shape of Single Crystals

Examples




Simple calculation of surface energy using the broken bond model

$$\gamma_\theta = \frac{U_b}{2a}(\cos\theta + \sin\theta) = \frac{U_b}{a\sqrt{2}}\cos(\theta - \frac{\pi}{4})$$

Heyraud and Métois, *J. Crystal Growth*, **84,** 503 (1987).
Heyraud and Métois, *J. Crystal Growth*, **50,** 571 (1980).

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# Growth of Single Crystals

Equilibrium Shapes of Ice

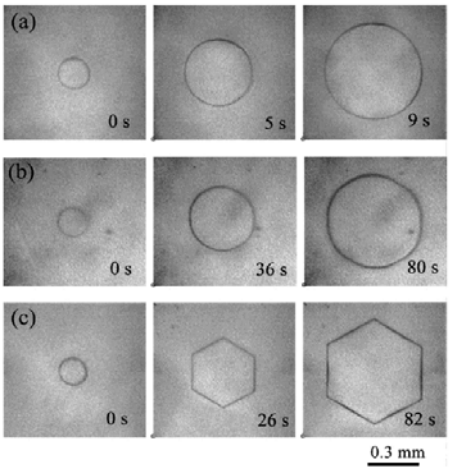


*Figure 1.* Growth sequences of ice above, just above and below the roughening temperature of the prism facet which is −16°C. Water is contained in a Bridgman apparatus and held at fixed temperature while pressure is used to control growth which is observed parallel to the *c*-axis using an optical microscope as described in refs. [18, 51]. By this method a crystal can be "walked" along solid-liquid coexistence and small growth drives can be imposed. The equilibrium temperature and pressure are measured at 0 seconds. The normalized growth drive, $\Delta\mu/kT$, is applied after zero seconds. (a) $T = -5.68$°C, $P = 666$ bars, $\Delta\mu/kT = 3.3 \times 10^{-4}$ (b) $T = -14.45$°C, $P = 1513$ bars, $\Delta\mu/kT = 3.5 \times 10^{-4}$ (c) $T = -20.24$°C, $P = 2029$ bars, $\Delta\mu/kT = 4.0 \times 10^{-4}$. Data kindly provided by Y. Kishimoto and M. Maruyama.

Maruyama, et al., *J. Crystal Growth*, 172, 521 (1997);
J. S. Wettlaufer, *Interface Sci.*, **9**,117-129 (2001)

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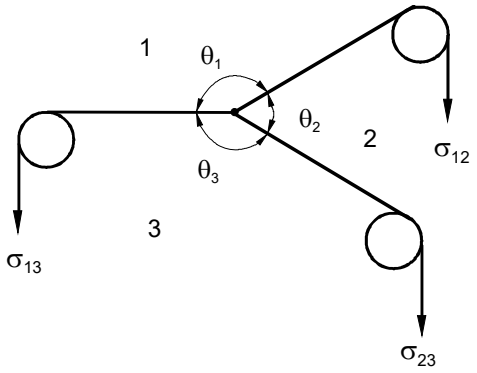
# Interfacial Tension and Microstructure

Equilibrium state btw three interfacial tensions




The sine law is satisfied. $\frac{\sigma_{12}}{\sin\theta_3} = \frac{\sigma_{23}}{\sin\theta_1} = \frac{\sigma_{31}}{\sin\theta_2}$

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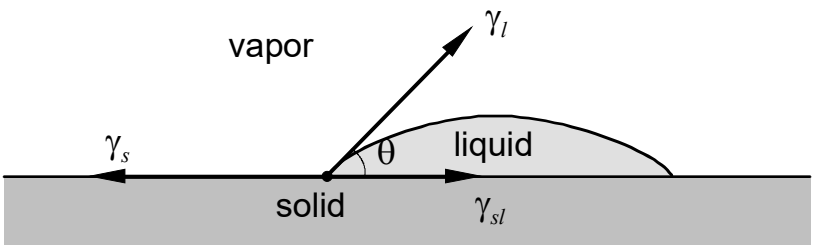
# *Wetting Angle*

3-phase system, s/l/v




$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$

Complete wetting at $\theta = 0$

$\gamma_s \geq \gamma_{sl} + \gamma_l$

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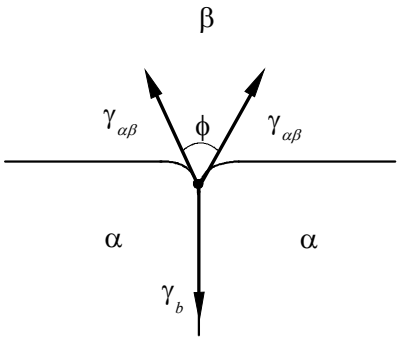
# Dihedral Angle

2-phase system, s/v or s/l




$$\gamma_b = 2\gamma_{\alpha\beta}\cos\frac{\phi}{2}$$

grain boundary

Usually, $\gamma_s > \gamma_b$ $\varnothing > 120°$

$\gamma_s \approx 3\gamma_b$ $\varnothing \sim 160°$

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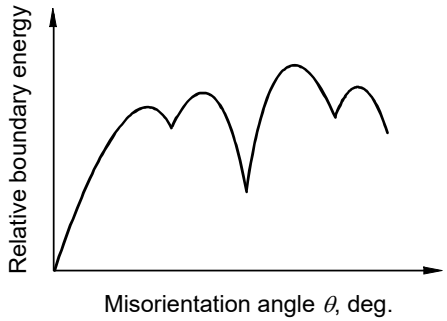
# Single Phase Microstructure

$\gamma_b = f(\text{orientation})$




Density of atoms at the boundary

Simplification : $\gamma_b$ = const. (a foam structure)

Grain shape is determined by

i) Local geometrical requirement
(minimization of the total interface energy and the equilibrium condition of surface tensions)

ii) Overall requirement of space filling

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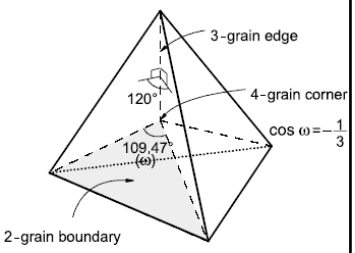
# *Equilibrium Grain Shape*

2-dim: hexagon  consider triangle and square

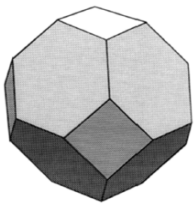
3-dim:

Soap film equilibrium in a tetrahedral frame

C = 22.794 vertices




- Pentagonal dodecahedron (12 pentagons)
  with 20 corners  (close-packing of spheres)
- Tetrakaidecahedron (Regularly truncated octahedron)
  with 24 corners (bcc packing)
  (8 hexagons and 6 squares)



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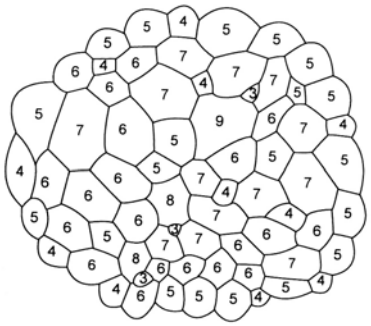
# *Topological Relationship*

Euler's Law describes the relationship btw. features of different dimensionality

$n_0-n_1+n_2-n_3=1$ ( C-E+P-B=1)  eg.

- 2-dim:
  av. number of sides of polygons = 6



Case of NGG
AGG

- 3-dim:
  av. number of sides of polygons < 6

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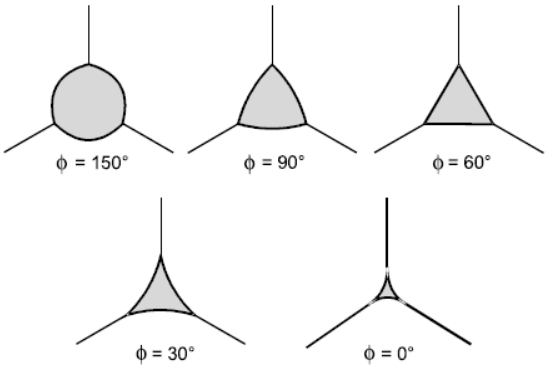
# 2-Phase Microstructure

## Shape of a second phase = f(ϕ)

In 2-dim




ex. Dihedral angle and physical properties

Qn: Distribution?

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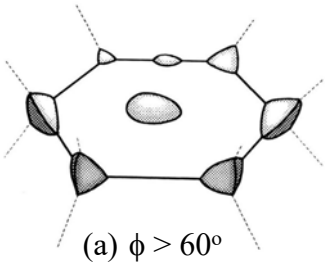
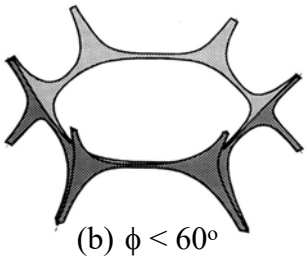
# 2-Phase Microstructure

## Shape of a second phase = f(ϕ)

In 3-dim



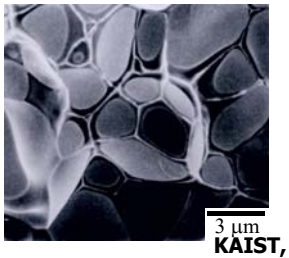
(a) $\phi > 60^o$



(b) $\phi < 60^o$

Qn: Measurement of dihedral angle?

Qn: Thickness of liquid film?

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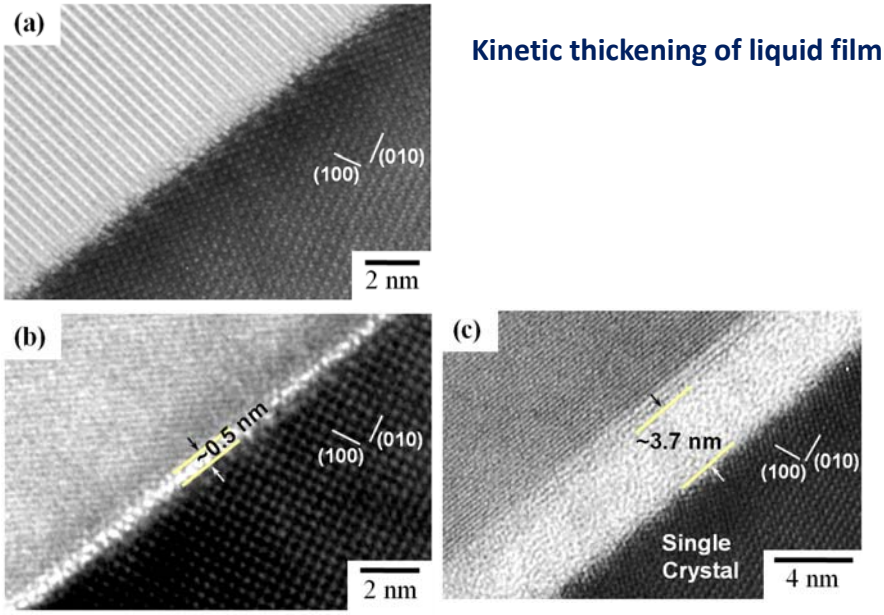


**Figure 3-12.** HREM images of the boundaries between a single crystal and a fine matrix grain. (100) single crystal/polycrystal bi-layer samples with 0.4-mol%-$TiO_2$ addition annealed at 1350°C for (a) 5, (b) 20, and (c) 50 h in air after $H_2$-treatment at 1250°C for 10 h.[22]

Choi, et al., *Acta Mater.*, **52**, 3721 (2004)

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# 2-Phase Microstructure

## *Equilibrium Microstructure*

Qn: Conditions that govern the equilibrium microstructure of mono-size grains?

Qn: Effective pressure of a powder compact?

eg) Elimination of pores during sintering

Redistribution of liquid between two samples in contact with different amounts of liquid

Minimum Interfacial Energy Configuration = f(ϕ, amt of matrix)

For an infinitesimal change under equilibrium,

work done = $P_e \cdot dV_m$

= total interfacial energy change ($\Delta(\gamma A)$)

$$P_e = -\frac{(1-f_m)^2}{V_g}\left[\frac{\partial E}{\partial f_m}\right]_{V_g}$$

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## Calculated variation of total interfacial energy

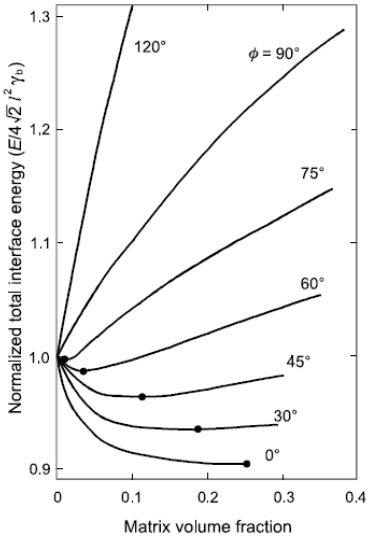


**Figure 3.13.** Calculated variation of total interfacial energy, $E$, with the matrix volume fraction (at constant grain volume) for various dihedral angles.[24] The minimum $E$ values are shown by filled circles.

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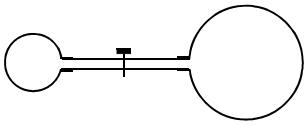
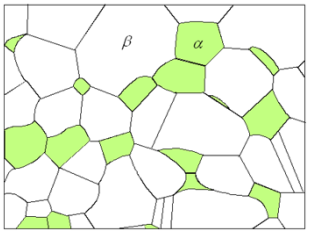
## Exercises:

- Elastic balloons



- Equilibrium shape of an entrapped pore
- Measurement of $\gamma_{\alpha/\alpha}/\gamma_{\beta/\beta}$

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