

2021 Fall

“Phase Transformation *in* Materials”

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Contents for previous class

3.4 Interphase Interfaces in Solids

Interphase boundary - different two phases : **different crystal structure**
different composition

coherent,

Perfect atomic matching at interface

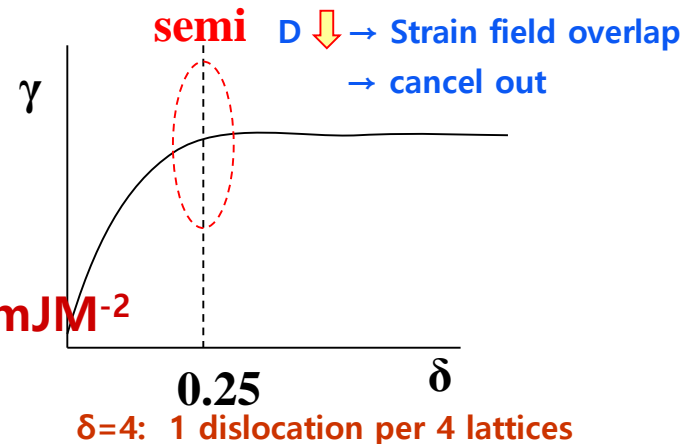
$$\gamma(\text{coherent}) = \gamma_{ch} \quad \gamma(\text{coherent}) \sim 200 \text{ mJM}^{-2}$$

semicoherent

$$\gamma(\text{semicoherent}) = \gamma_{ch} + \gamma_{st}$$

$\gamma_{st} \rightarrow$ due to structural distortions
caused by the misfit dislocations

$$\gamma(\text{semicoherent}) \sim 200 \sim 500 \text{ mJM}^{-2}$$



incoherent

1) $\delta > 0.25$ No possibility of good matching across the interface

2) different crystal structure (in general)

$$\gamma(\text{incoherent}) \sim 500 \sim 1000 \text{ mJM}^{-2}$$

Complex Semicoherent Interfaces

Nishiyama-Wasserman (N-W) Relationship

Kurdjumov-Sachs (K-S) Relationships

(The only difference between these two is a rotation in the closest-packed planes of 5.26° .)

The degree of coherency can, however, be greatly increased if a macroscopically irrational interface is formed.

3.4 Interphase Interfaces in Solids

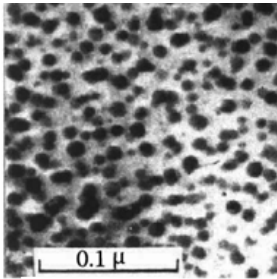
$$\sum A_i \gamma_i + \Delta G_s = \text{minimum}$$

Lowest total interfacial free energy
by optimizing the shape of the precipitate and its orientation relationship

Fully coherent precipitates

γ_{ch}

different composition



$\gamma_{ch} + \text{Lattice misfit}$

Coherency strain energy

$$\Delta G_s = 4\mu\delta^2 \cdot V \quad (\text{If } \nu=1/3)$$

Fully coherent precipitates



$\gamma_{ch} + \text{Volume Misfit } \Delta = \frac{\Delta V}{V}$

Chemical and structural interfacial E

$$\Delta G_s = \frac{2}{3}\mu\Delta^2 \cdot V \cdot f(c/a)$$

Incoherent inclusions

$$\Delta G(\text{coherent}) = 4\mu\delta^2 \cdot \frac{4}{3}\pi r^3 + 4\pi r^2 \cdot \gamma_{ch}$$

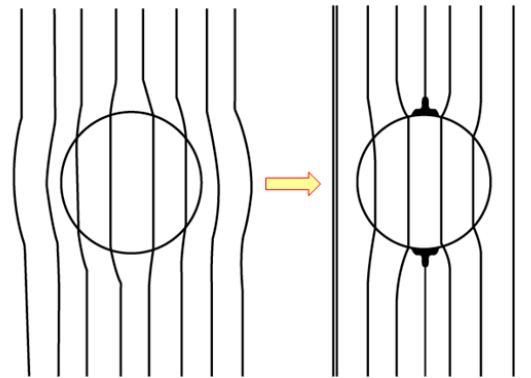
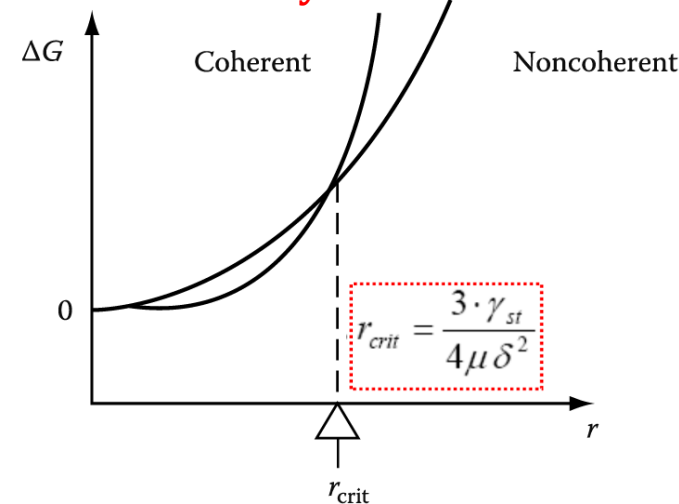


$$\Delta G(\text{non-coherent}) = 4\pi r^2 \cdot (\gamma_{ch} + \gamma_{st})$$

"Coherency loss"



Incoherent inclusions

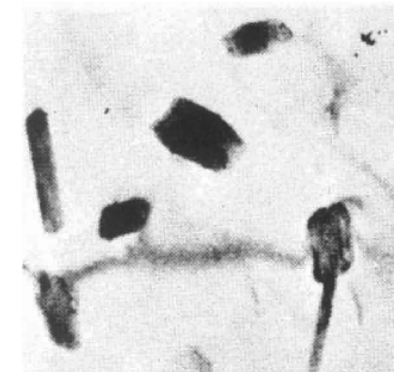


(a) Coherent with strain E

(b) Coherency strain replace by dislocation loop.



(c) Precipitate with dislocation



Contents for today's class

- Interphase Interfaces in Solid (α/β)

- Types of interphase interfaces in solid (α/β)

- Second-Phase Shape $\left\{ \begin{array}{l} \text{Interface Energy Effects} \\ \text{Coherent / Semi-coherent / incoherent} \\ \text{Misfit Strain Effects} \end{array} \right.$

$$\sum A_i \gamma_i + \Delta G_s = \text{minimum}$$

- Coherency Loss

- Glissil Interfaces \longleftrightarrow Non-Glissil Interfaces
e.g. Solid/Liquid Interfaces

- Interface migration

- Interface controlled growth \longleftrightarrow Diffusion controlled growth

\Rightarrow Classification of Heterogeneous (Nucleation and Growth) Transformation

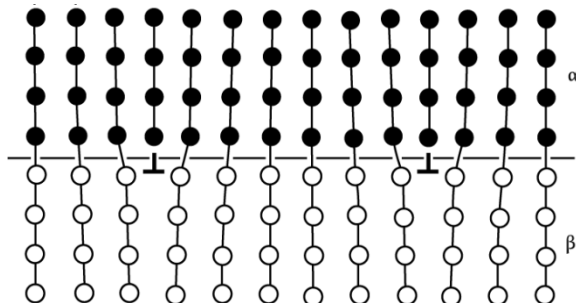
Glissil Interfaces  **Non-Glissil Interfaces**

Q: What is Glissile interface?

Glissile interface → coordinated glide of the interfacial disl. → ($\alpha \rightarrow \beta$) phase transformation

Interphase Interfaces in Solid (α/β)

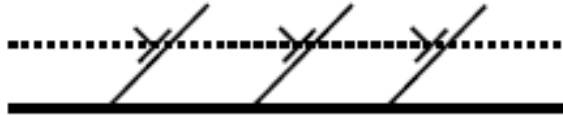
1) Glissile Interfaces (평활 이동 계면)



: epitaxial; Can't move forward or backward

(interface//burgers vector) \longrightarrow **Non-glissile interface**

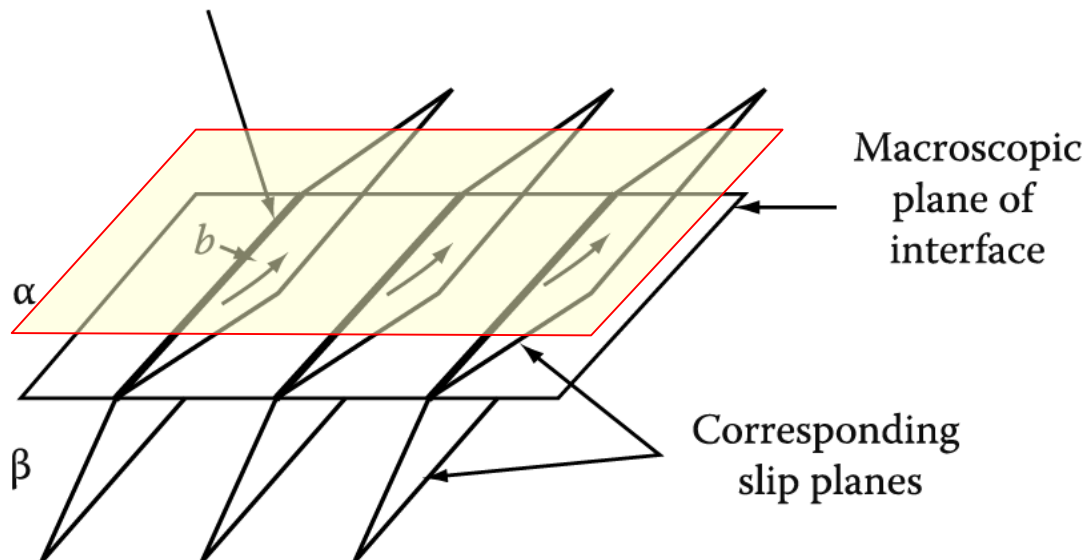
: Glide of the interfacial disl. cannot cause the interface to advance



: Glissile; Boundary moves toward α or β

: semi-coherent interfaces which can advance by the coordinated glide of the interfacial disl.

Interfacial dislocations



Macroscopic plane of interface

Corresponding slip planes

The dislocations have a Burgers vector that can glide on matching planes in the adjacent lattices.

Slip planes : continuous across the interface

Gliding of the dislocation : α is sheared into the β structure.

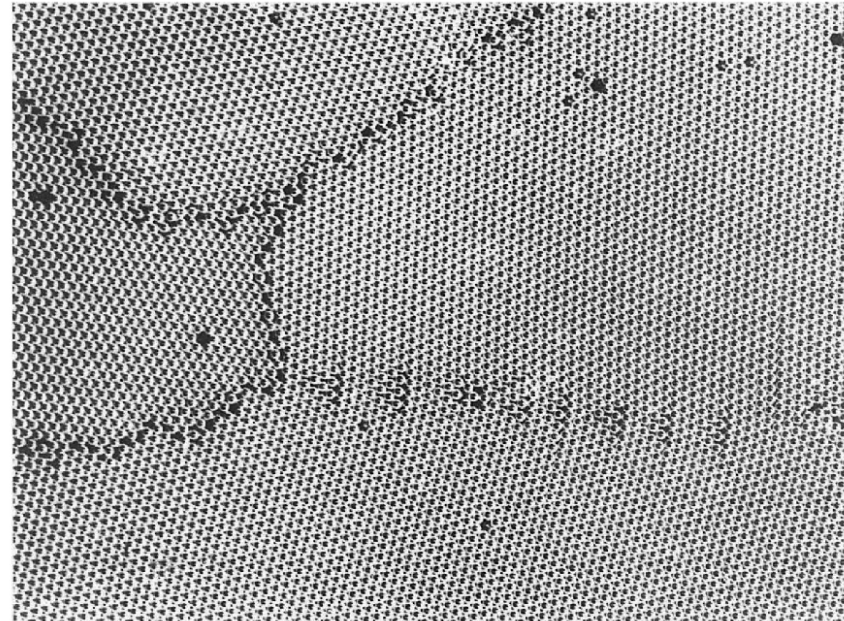
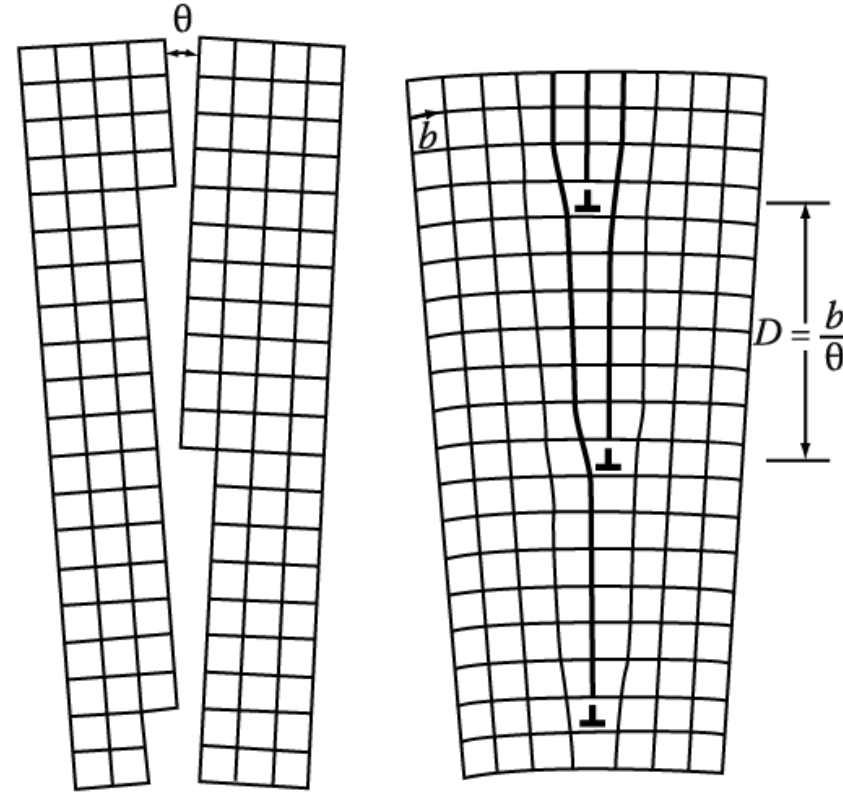
Fig. 3. 55 The nature of a glissile interface.

Low-Angle tilt Boundaries

Burgers vector = edge dislocation

But, this is not interphase interface.

∴ crystal structure is same,
only lattice rotation



- * As disl. glide at low-angle grain boundary
- : no change in crystal structure,
- just rotation of the lattice into the other grain

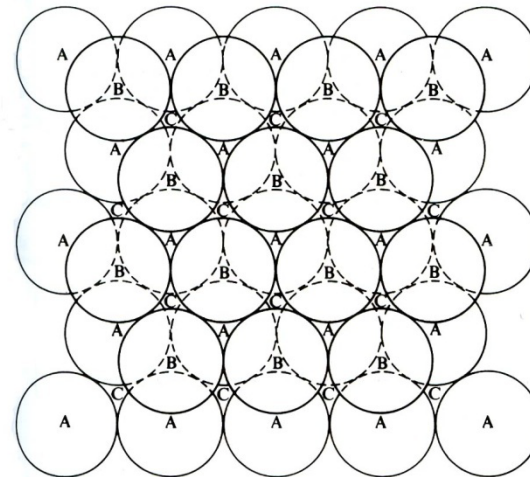
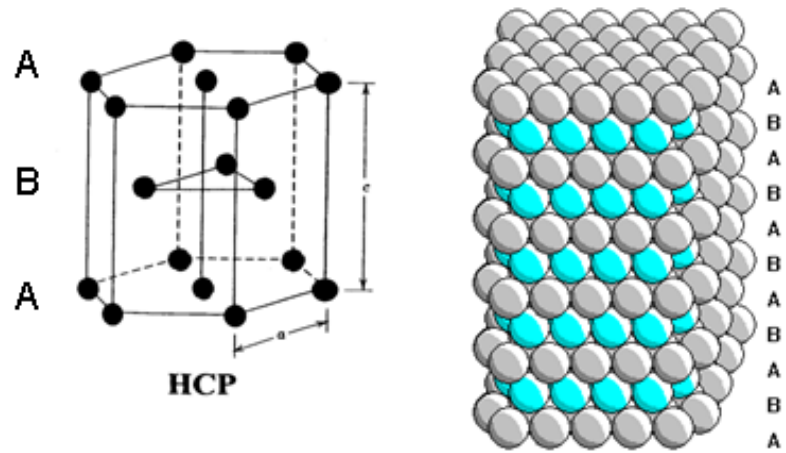
Glissile Interfaces between two lattices

Shockley partial dislocation

HCP: ABABABAB...

close packed plane: (0001)

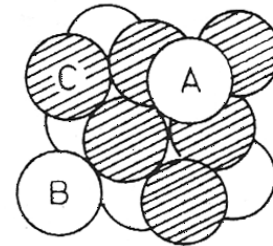
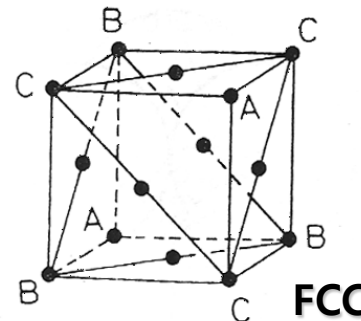
close packed directions: $\langle 11\bar{2}0 \rangle$



FCC: ABCABCAB...

close packed planes: {111}

close packed directions: $\langle 110 \rangle$



1) Perfect dislocation

$$\vec{b} = \frac{a}{2}[10\bar{1}]$$

In C layer, atoms move

$C' \rightarrow C''$

: remain a cubic close-packed arrangement with a fcc unit cell
 < FCC \rightarrow FCC >

2) Shockley partial dislocation

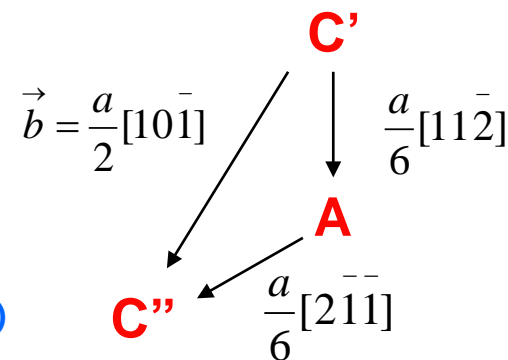
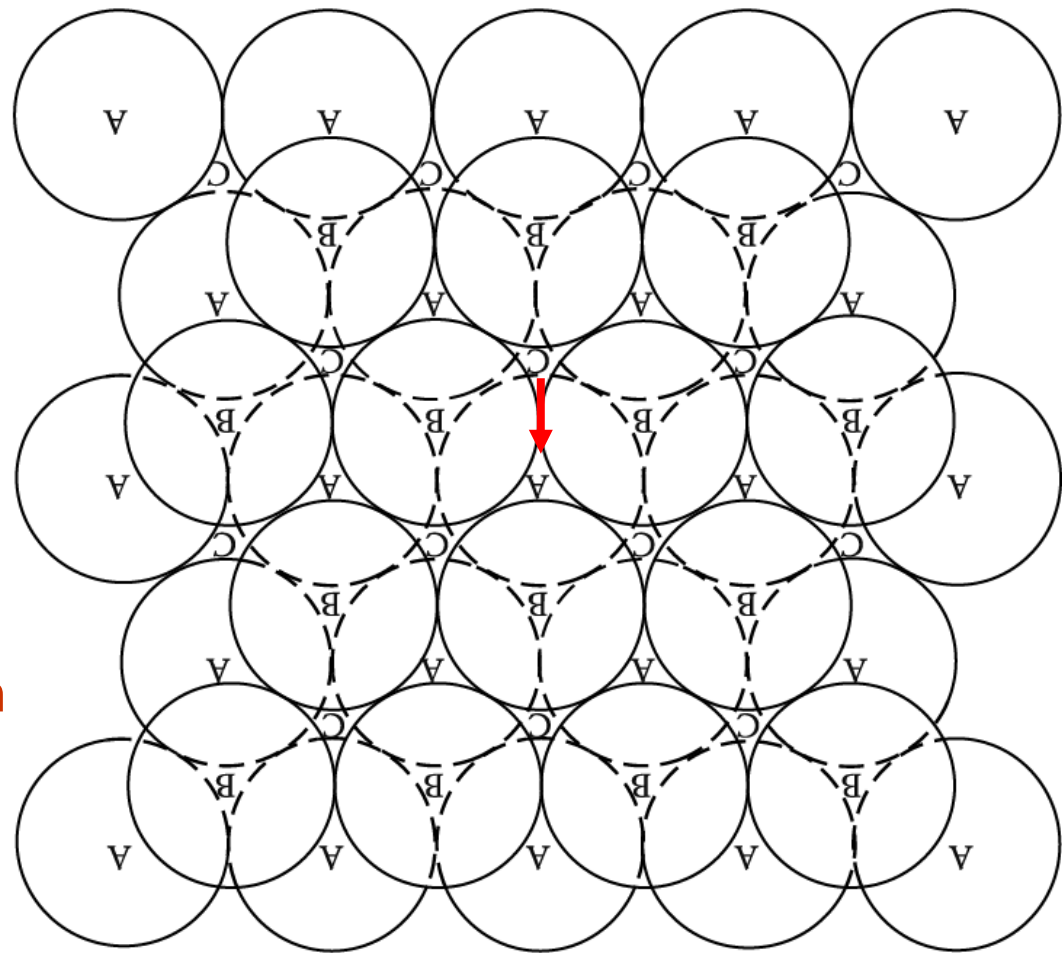
when atoms move: $C' \rightarrow C''$

possible to move $C' \rightarrow A \rightarrow C''$

$$\frac{a}{2}[10\bar{1}] = \boxed{\frac{a}{6}[11\bar{2}]} + \frac{a}{6}[2\bar{1}\bar{1}]$$

This burgers vector of partial disl.
 is not located at lattice point.

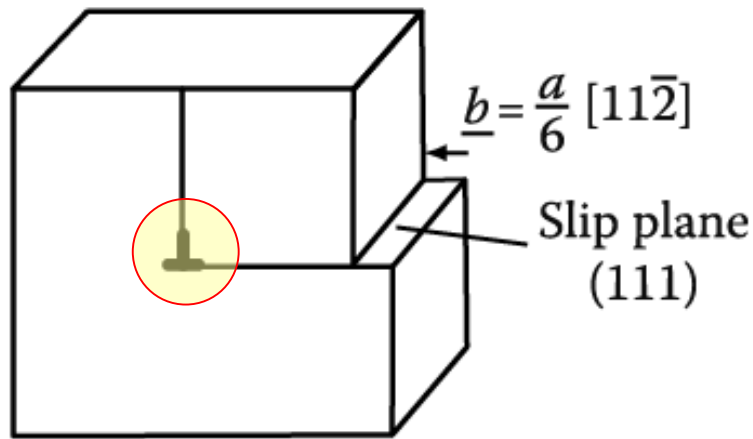
(can't connect lattice points in the FCC structure)



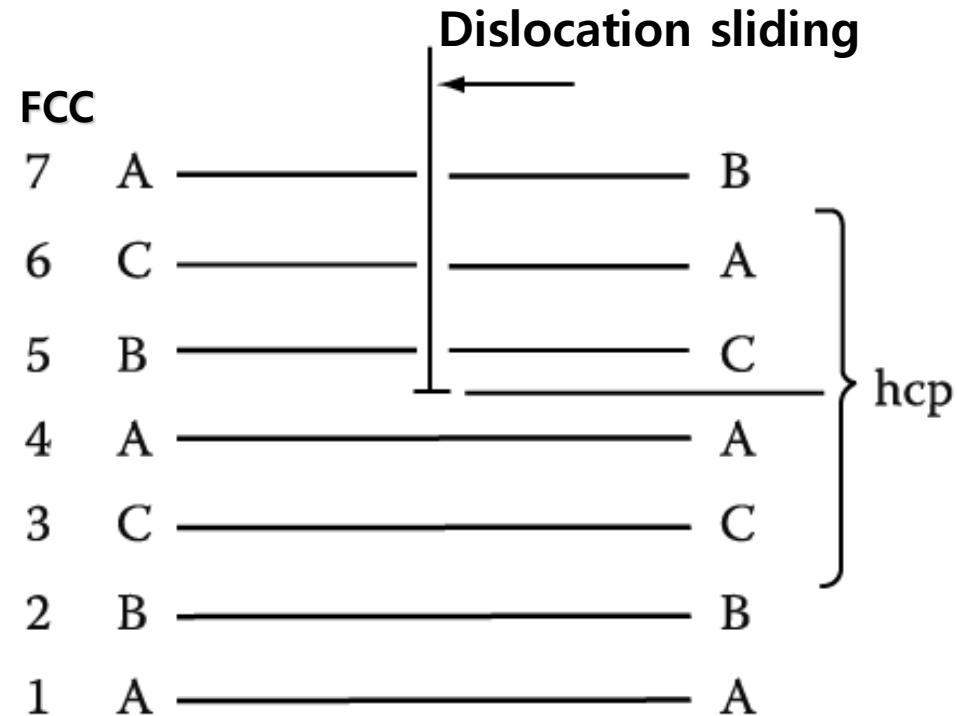
< FCC \rightarrow HCP: phase transformation by stacking fault over the area of glide plane swept by the disl.>

Gliding of Shockley partial dislocations → Stacking fault region 적층결함

In thermodynamically stable FCC lattices, the stacking fault is a region of high free energy.
→ gliding of partial dislocations : **difficult**



(a)



(b)

Fig. 3. 59 (a) An edge dislocation with a Burgers vector $b = \frac{a}{6} [11\bar{2}]$ on $(11\bar{1})$. (shockley partial dislocation.)
(b) The same dislocation locally changes the stacking sequence from fcc to hcp.

If FCC lattice is only metastable with respect to the HCP structure → stacking fault E ~ effectively negative → gliding of partial dislocation: easy due to decrease the free energy of system

Glissile Interfaces between two lattices

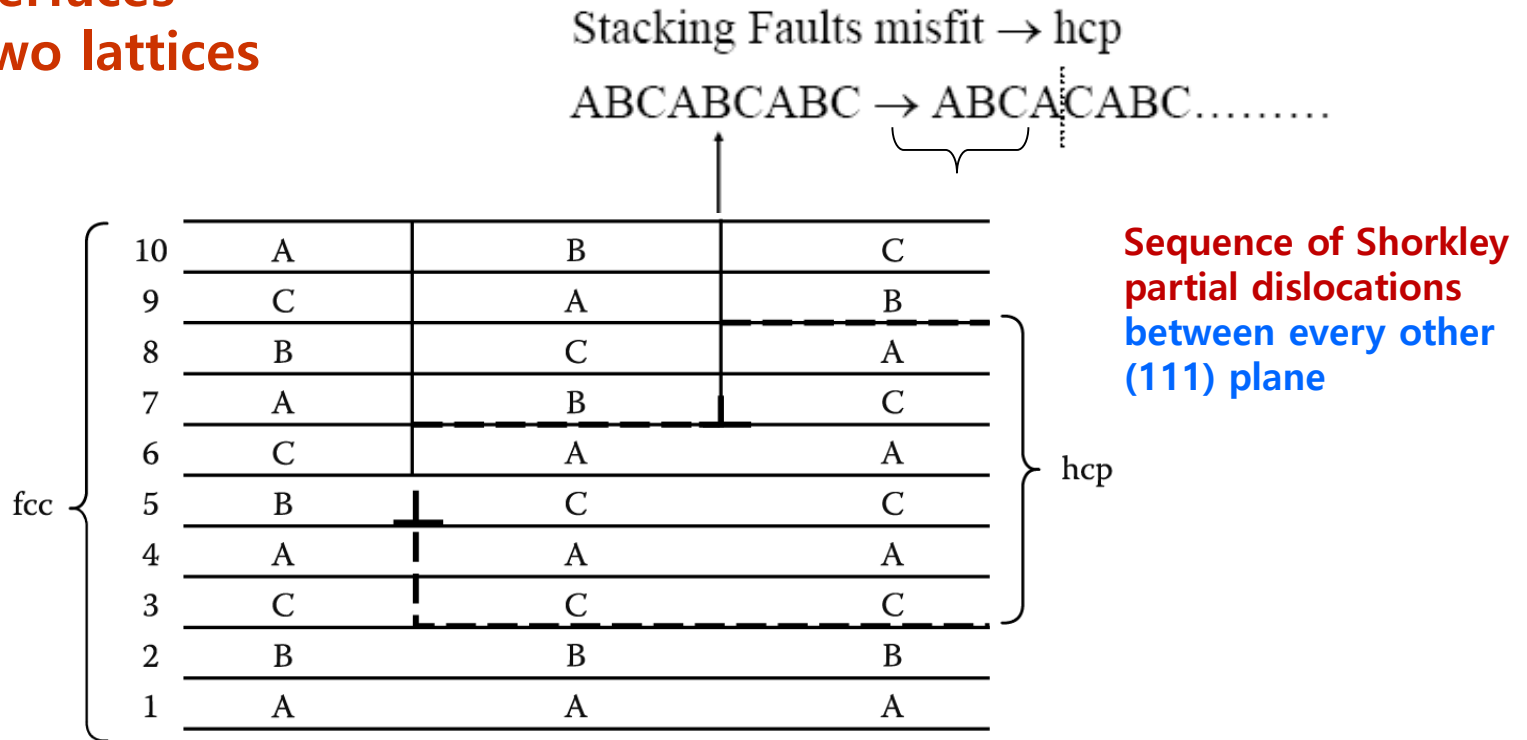


Fig. 3. 60 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

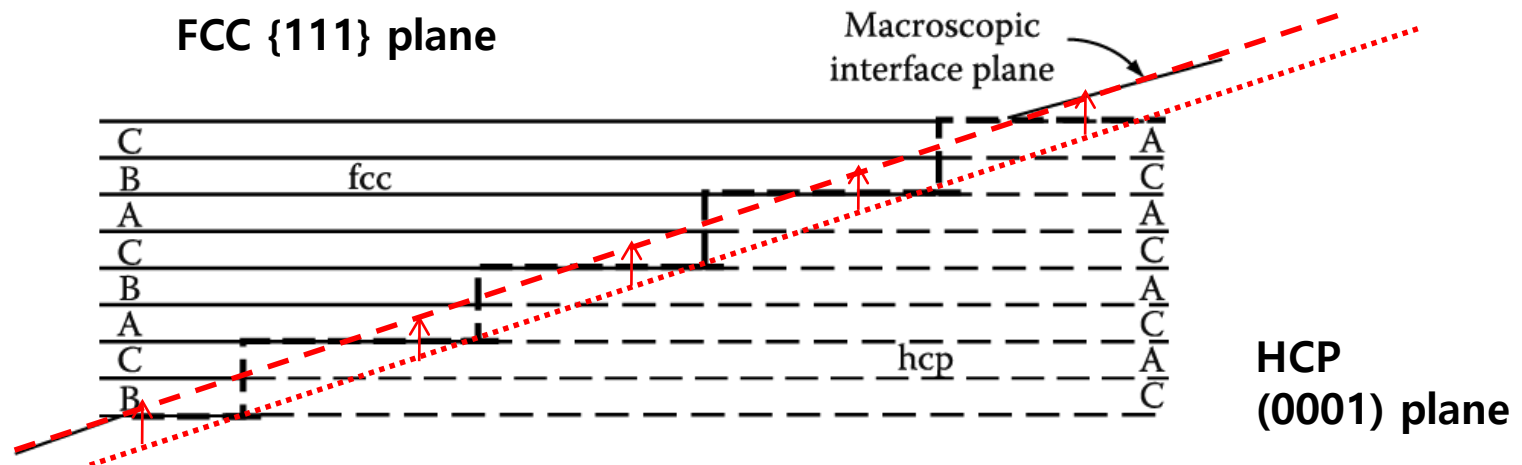


Fig. 3. 61 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

An important characteristic of **glissile dislocation interfaces**

→ they can produce **a macroscopic shape change in the crystal.**

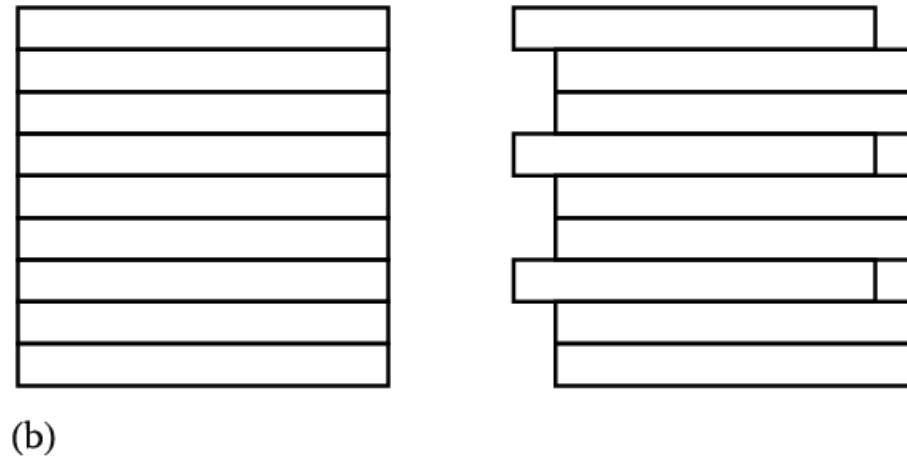
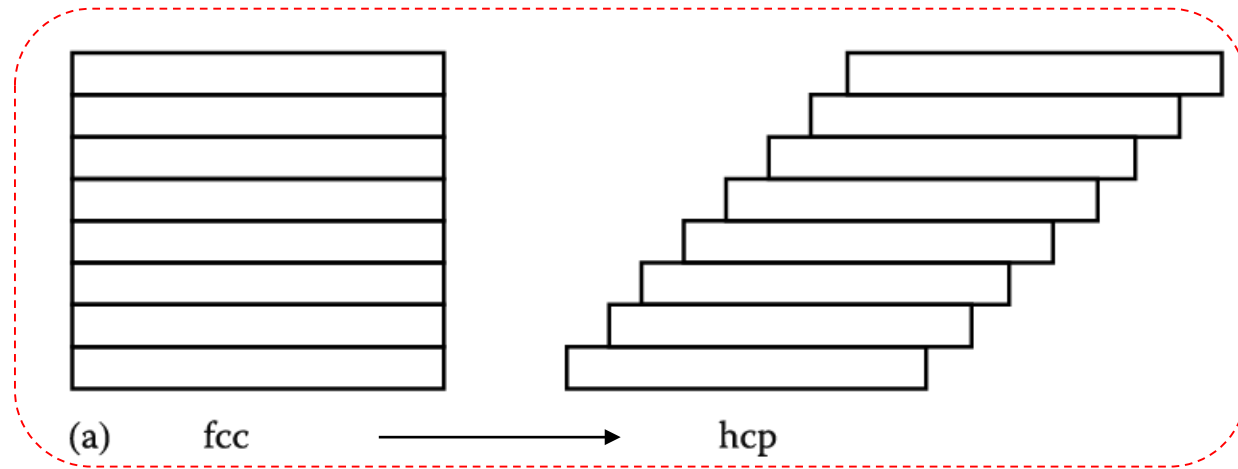
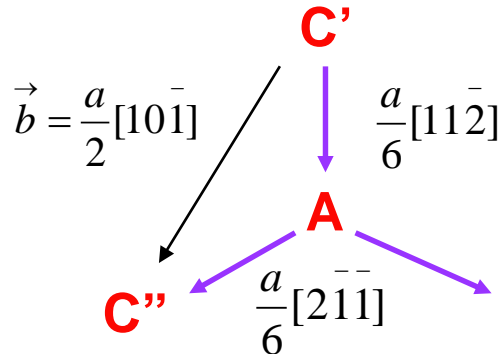
1) Sequence of same Shockley partial dislocations between every other (111) plane

→ **Pure shear deformation**

→ **Fcc → Hcp**

→ **shape change**

2) If transformation is achieved using all three partials in equal #s,



→ **No overall shape change**

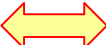
Fig. 3. 62 Schematic representation of the different ways of shearing cubic close-packed planes into hexagonal close-packed
(a) Using only one Shockley partial, (b) using equal numbers of all three Shockley partials.

* **Formation of martensite in steel and other alloys:** Motion of Glissile-dislocation interface

: **macroscopic shape change & no change in composition**

→ **more complex interface but same principles** (chapter 6)

**Q: What is the role of interface migration
on phase transformation ?**

Interface controlled growth  Diffusion controlled growth

3.5. Interface Migration

Phase transformation = Interface creation & Migration

Heterogeneous Transformation (general): parent and product phases during trans.

Nucleation (interface creation) + **Growth** (interface migration)

Nucleation barrier Ex. Precipitation

- at certain sites within metastable alpha phase → new beta phase = Nucleation
- most of transformation product is formed during the growth stage by the transfer of atoms across the moving parent/product interface.

Homogeneous Transformation: PT occurs homogeneously throughout the parent phase.

Growth-interface control

No Nucleation barrier Ex. Spinodal decomposition (Chapter 5)

Order-disorder transformation

* **Types of Interface**

→ **Types of transformation**

- **Glissile Interface:** **Athermal, Shape change**
Dislocation gliding

→ **Military transformation**

- **Non-Glissile Interface:** **Thermal,**

→ **Civilian transformation**

Random jump of individual atoms: extremely sensitive to temp.
~ similar way to the migration of a random high angle GB

Classification of Nucleation and Growth Transformation

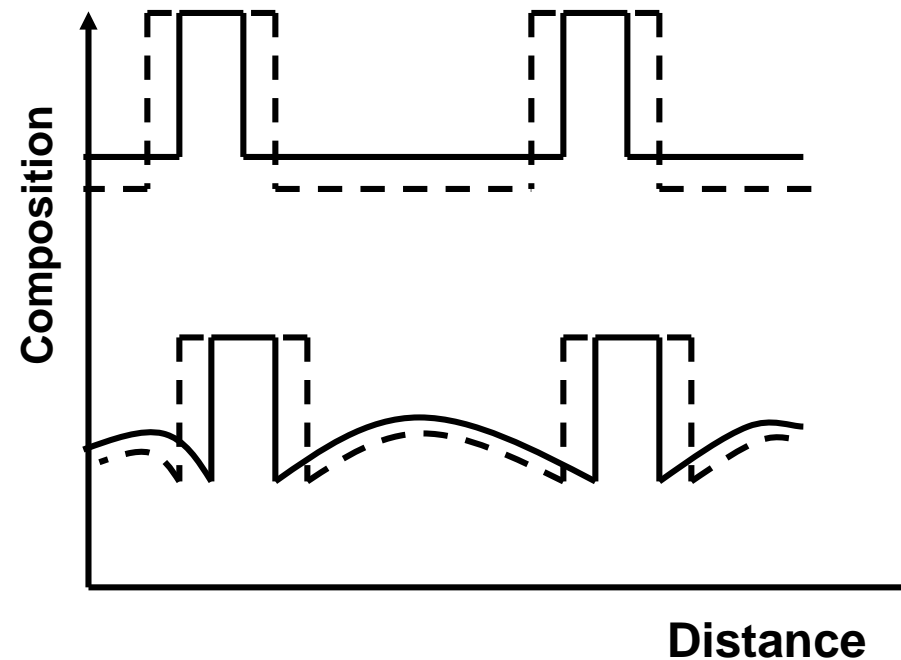
Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent, Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different compositions		
Nature of diffusion process	No diffusion	Short-range diffusion (across interface)	Long-range diffusion (through lattice)		
Interface, diffusion or mixed control?	Interface control	Interface control	Mainly interface control	Mainly diffusion control	Mixed control
Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Solidification and melting	Precipitation dissolution Eutectoid Cellular precipitation

Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface
(need to additional research)

3.5. Interface Migration

* Civilian Transformation



1) Interface control

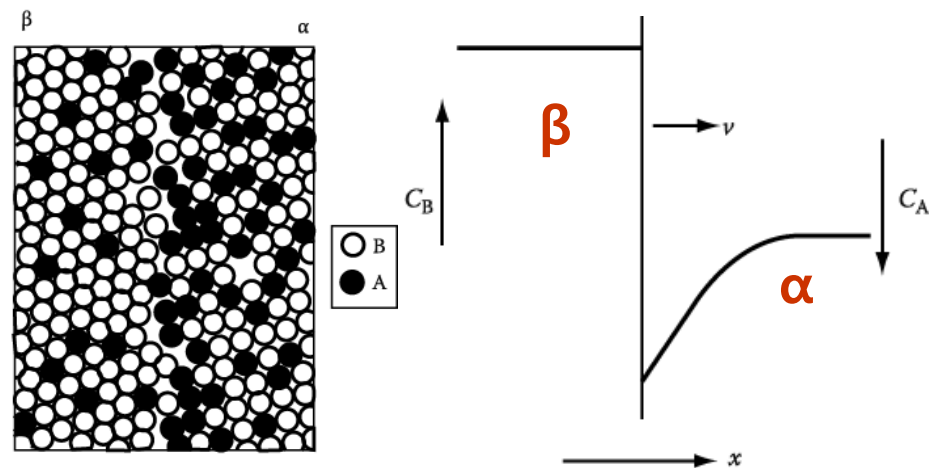
Same composition between parent and product
(Ex. $\alpha \rightarrow \gamma$ transformation in pure iron)

The new phase will be able to grow as fast as the atoms can cross the interface. : interfacial reaction velocity dominant

2) Diffusion control

Different composition between parent and product
(Ex. The growth of the B-rich phase into the A-rich α -phase)

Growth of the new phase will require long-range diffusion
Growth rate: governed by the rate at which lattice diffusion can remove the excess atoms from ahead of the interface.

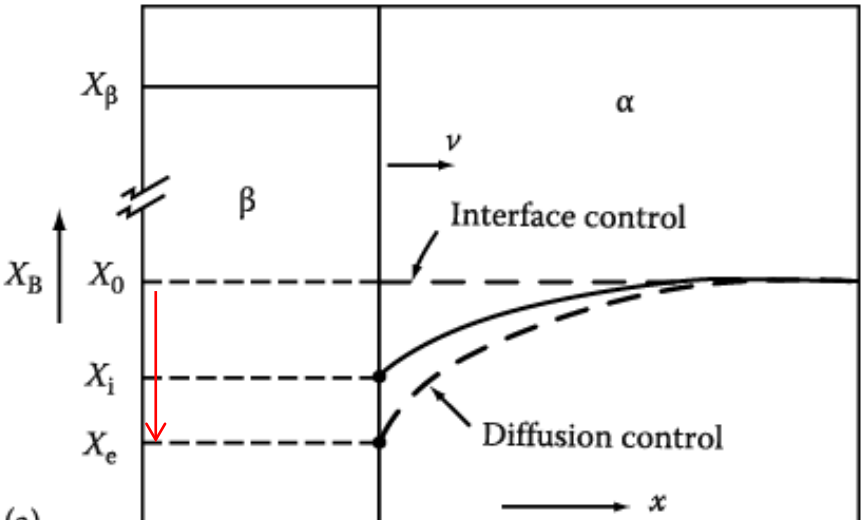


3) Mixed control: interface reaction = diffusion process

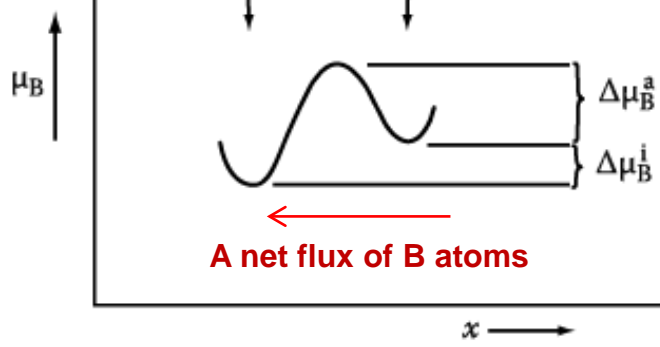
3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion
; the migration of interface separating two phases of different composition

(a) Composition profile across the interface

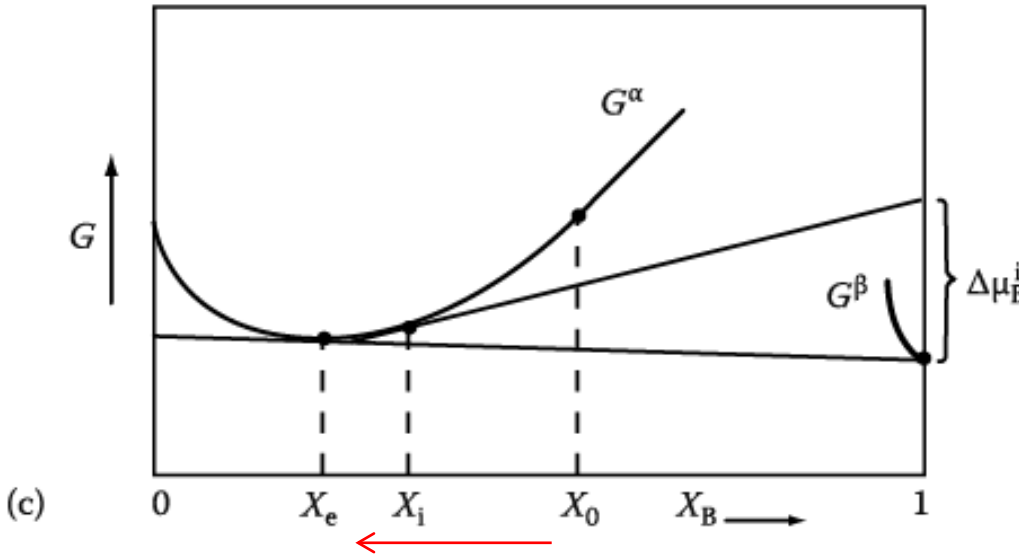


(a)



(b)

(c) A schematic molar free energy diagram showing the relationship between $\Delta\mu_B^i$, X_i , X_0

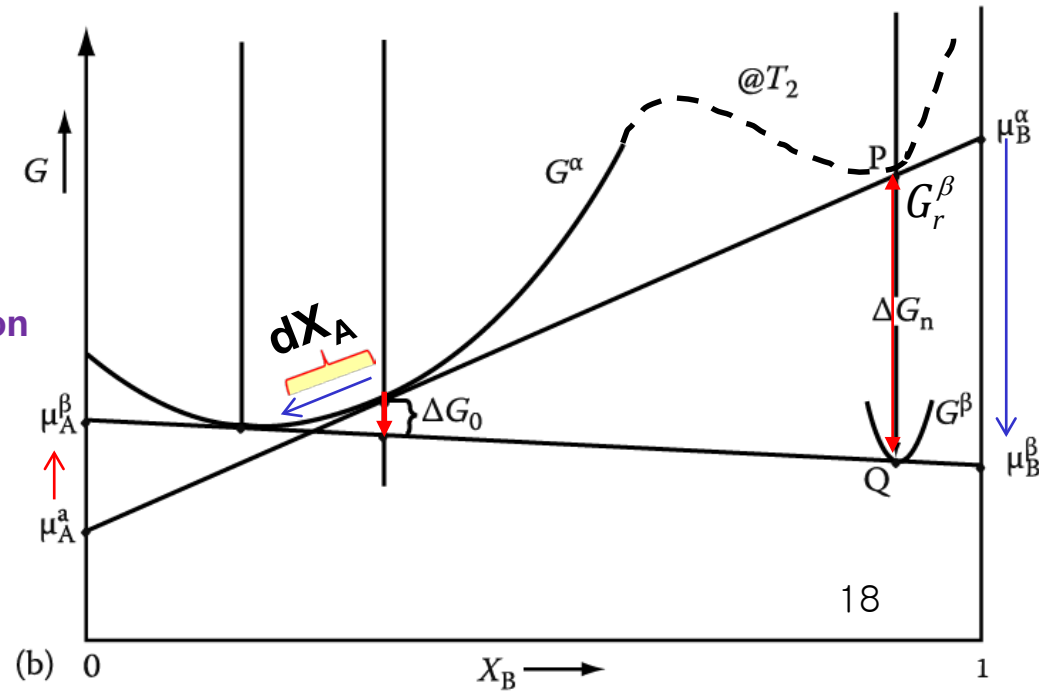
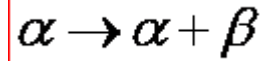


(c)

- 1) Initial composition of A-rich α phase X_0
- 2) Concentration B in the α phase adjacent to the interface X_i
→ B concentration in α : $X_0 \rightarrow X_i$
- 3) For growth to occur the interface, composition must be greater than the equilibrium concentration X_e .

(b) The origin of the driving force for boundary migration into the α -phase $\Delta\mu_B^i$

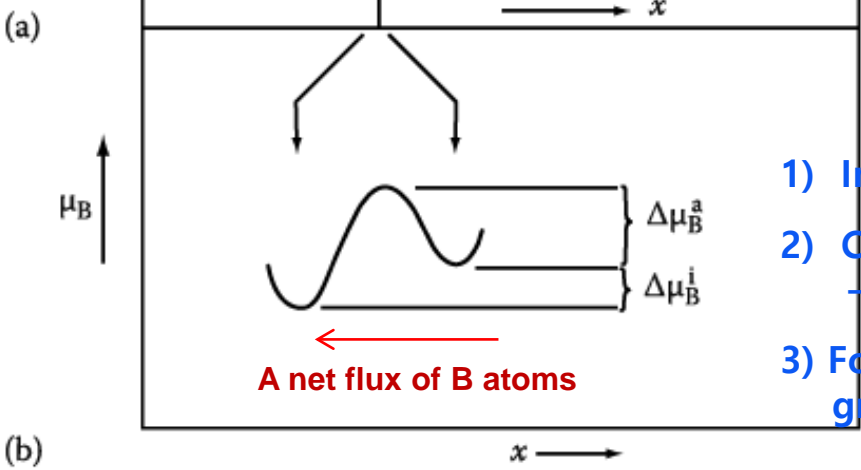
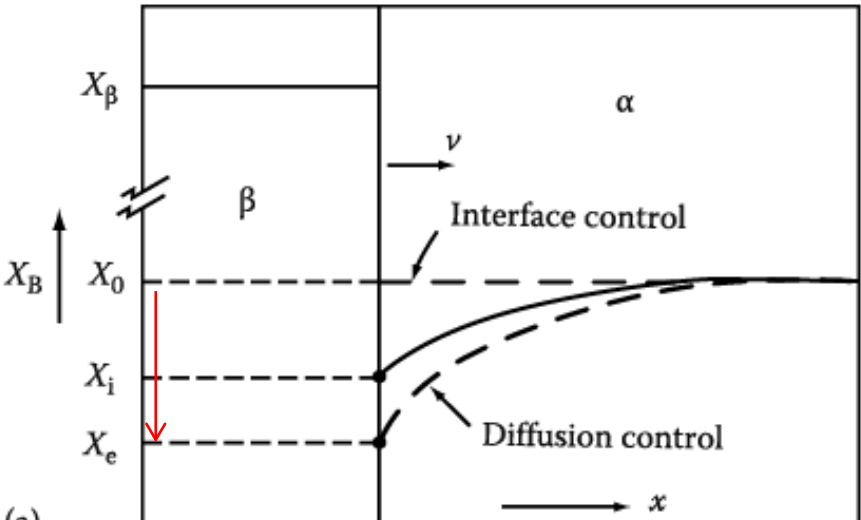
Driving Force for Precipitate Nucleation



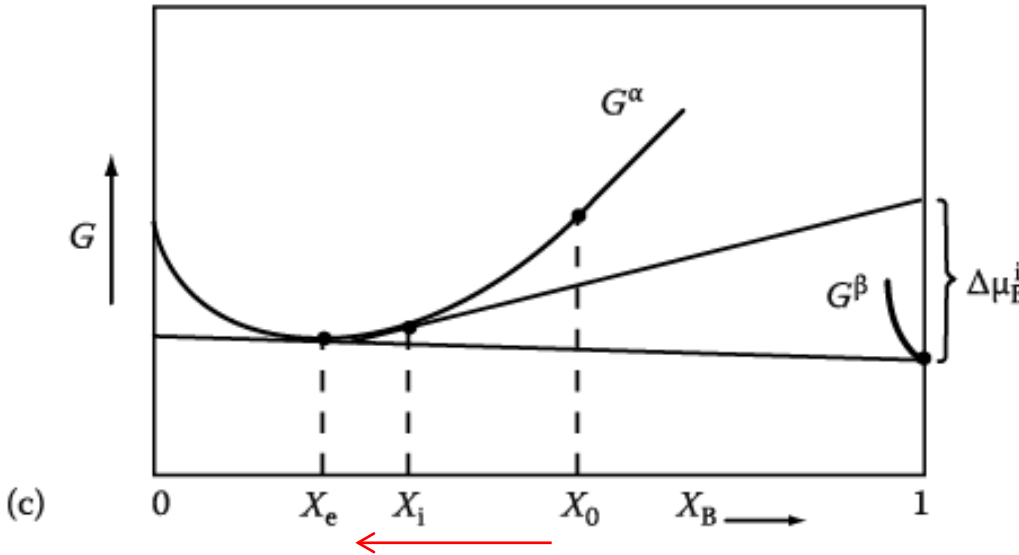
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(c) A schematic molar free energy diagram showing the relationship between $\Delta\mu_B^i$, X_i , X_0



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(b) The origin of the driving force for boundary migration into the α -phase $\Delta\mu_B^i$

By analogy with the migration of a high-angle GB (section 3.3.4), the net flux B across the interface will produce an interface velocity v given by

- (section 3.3.4) Kinetics of grain growth

- Grain boundary migration (v) by thermally activated atomic jump

Boundary velocity $v = \frac{A_2 n_1 v_1 V_m^2}{N_a RT} \exp\left(-\frac{\Delta G^a}{RT}\right) \frac{\Delta G}{V_m}$

$v \sim \Delta G/V_m$ driving force
 $\rightarrow F = \Delta G/V_m$

M : mobility = velocity under unit driving force $\sim \exp(-1/T)$

rate of grain growth $dD/dt \sim 1/D$, exponentially increase with T

- Interface velocity of precipitate

$$v = M \Delta \mu_B^i / V_m$$

M = interface mobility,
 V_m = molar volume of the β phase

- Corresponding flux across the interface (negative sign, negative direction of flux along the x-axis)

$$\begin{aligned} J_B^i &= -C_B^i v_B \\ &= -\frac{1}{V_m} (M \cdot \Delta \mu_B^i \cdot \frac{1}{V_m}) \\ &= J_B^\alpha = -D \left(\frac{\partial C_B}{\partial X} \right)_{\text{interface}} \end{aligned}$$

$\beta \leftarrow \alpha$

$$\Delta \mu_B^i \frac{1}{V_m} = \frac{J_{mol}^{-1}}{m^3 mol^{-1}}$$

Steady state at interface,

$$J_B^i = J_B^\alpha$$

A flux of B atoms toward the interface by the concentration gradient in the α phase

Corresponding flux across the interface (negative sign_negative direction of flux along the x-axis)

$$\begin{aligned}
 J_B^i &= -C_B^i v_B \\
 &= -\frac{1}{V_m} (M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}) \\
 &= J_B^\alpha = -D \left(\frac{\partial C_B}{\partial X} \right)_{\text{interface}}
 \end{aligned}$$

$$\Delta\mu_B^i \frac{1}{V_m} = \frac{J \text{ mol}^{-1}}{m^3 \text{ mol}^{-1}}$$

Steady state at interface,

$$J_B^i = J_B^\alpha$$

A flux of B atoms toward the interface by the concentration gradient in the α phase

1) If the interface mobility is very high, e.g. an incoherent interface,

High Mobility: $\Delta\mu_B^i$ small, $X_i \approx X_e$ Diffusion-Control

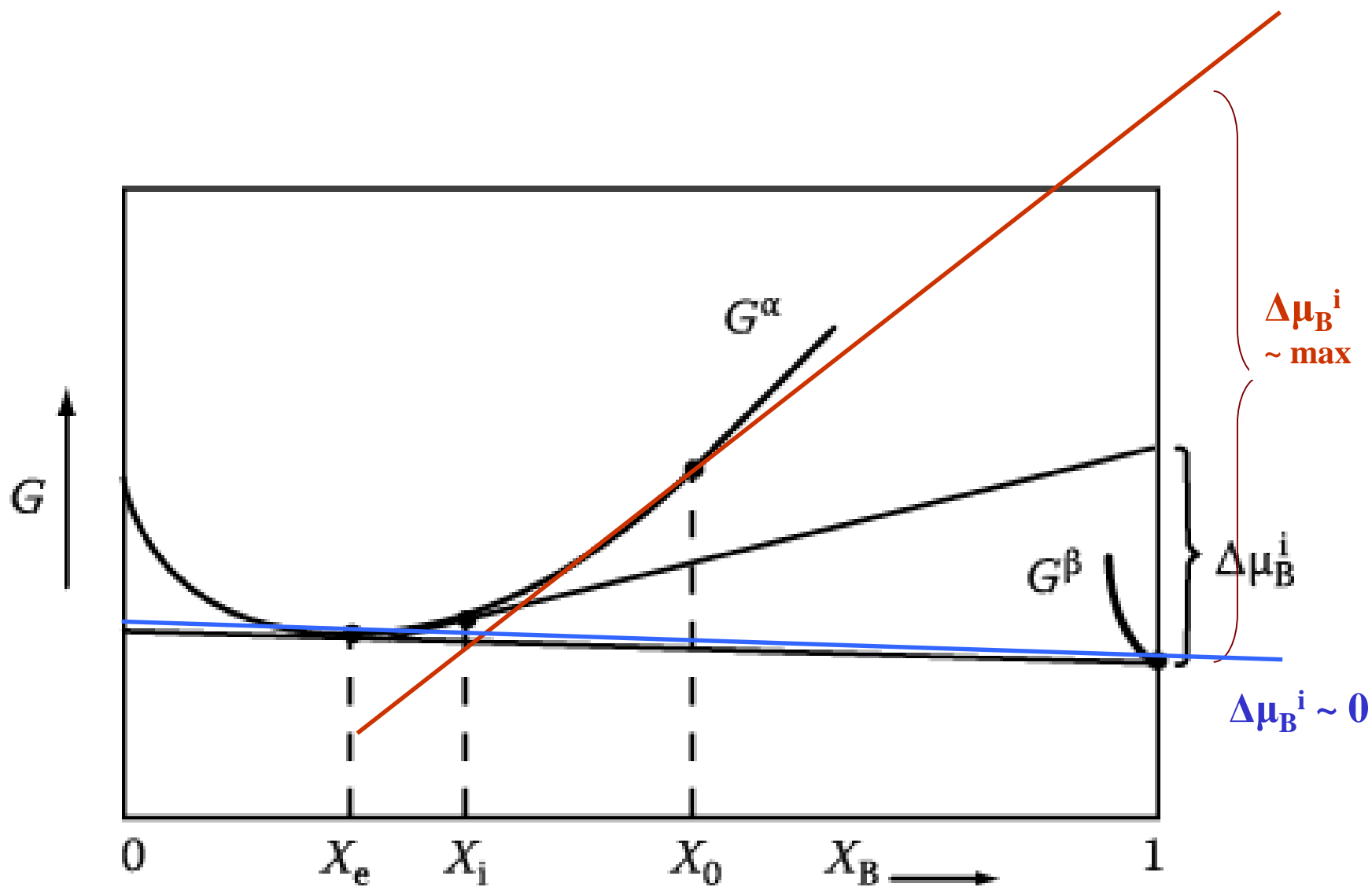
2) When the interface has a low mobility,

Low Mobility: $\Delta\mu_B^i$ must be large Mixed-Control

3) In the limit of a very low mobility,

Very low Mobility: $X_i \approx X_0$, $\left(\frac{\partial C}{\partial X} \right)_{\text{interface}} \approx 0$ Interface-Control

$\Delta\mu_B^i$ 는 최대



When two phases have a different composition,

In general,

the necessary long-range diffusion involves a great many atom jumps
while interface reaction essentially involves only one jump.

All interface reactions should be very rapid in comparison to lattice diffusion, i.e.,
all growth should be diffusion controlled. (next page)

Ex) Diffusion control

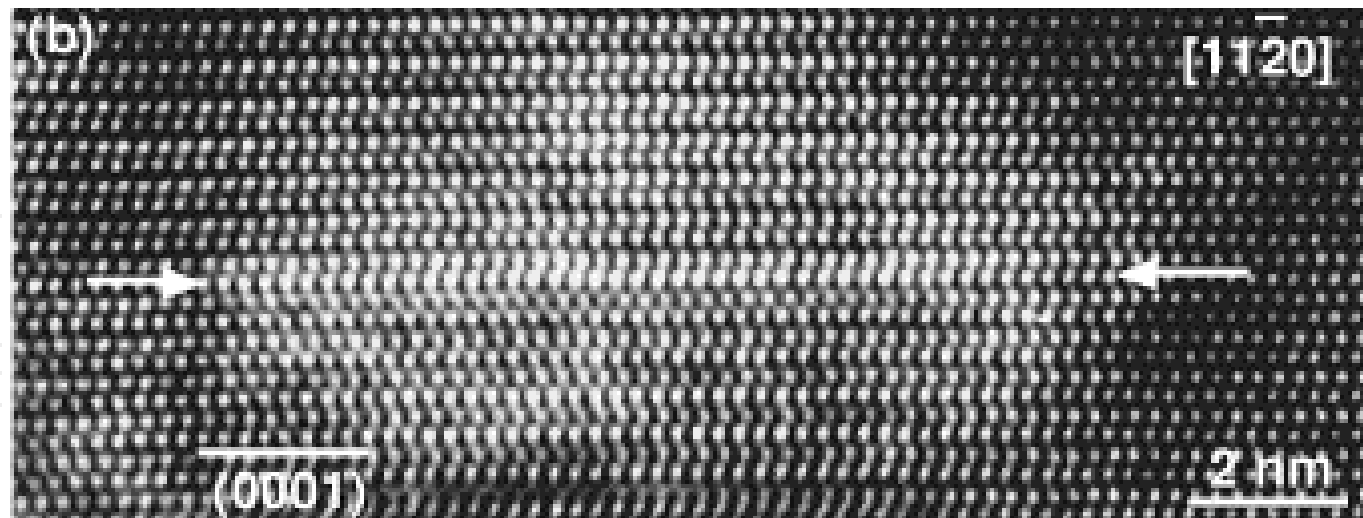
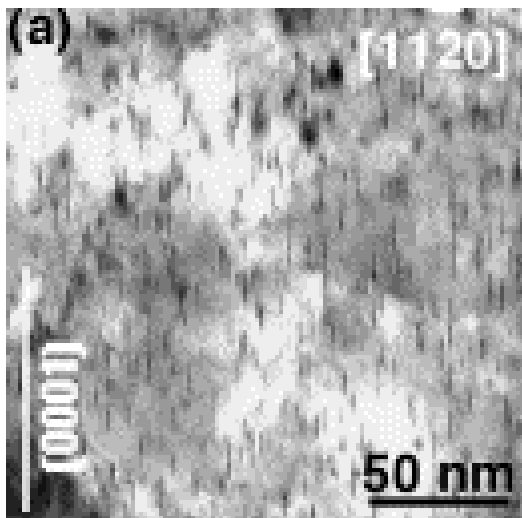
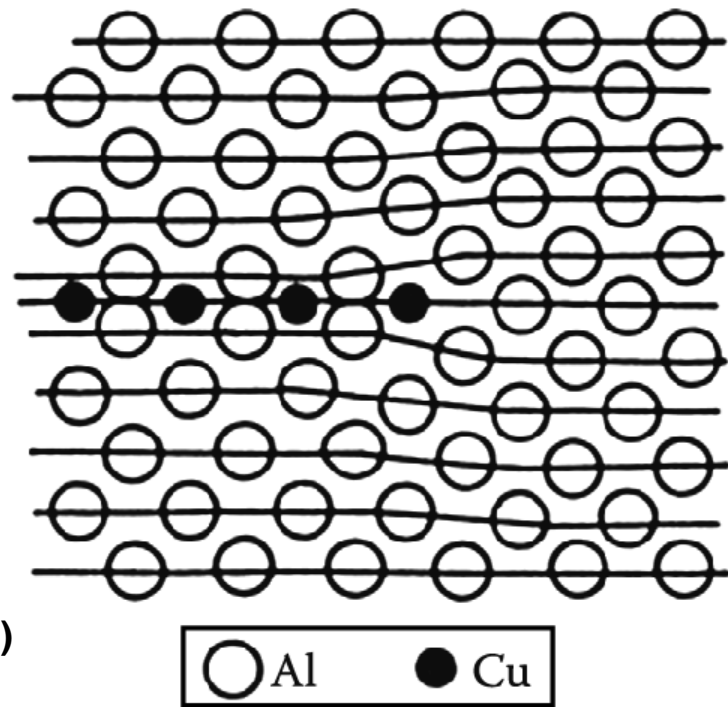
Al-Cu ppt structures

If two phases with different compositions, but the same crystal structure are separated by a coherent interface

Interface can advance by normal lattice diffusion involving vacancies.

No need for a separated interface reaction

Ex) GP zones/ semicoherent interface with misfit dislocation (vacancy creation and annihilation)



(a) Bright-field TEM image showing G.P. zones, and (b) HRTEM image of a G.P. zone formed on a single $(0001)_\alpha$ plane. Electron beam is parallel to in both (a) and (b).

When two phases have a different composition,

In general,

the necessary long-range diffusion involves a great many atom jumps while interface reaction essentially involves only one jump.

All interface reactions should be very rapid in comparison to lattice diffusion, i.e., all growth should be diffusion controlled. (next page)

➡ In many cases ~ valid, but under certain conditions ~ insufficient

Accommodation factor (A _수용인자)

Probability that an atom crossing the boundary will be accommodated on arrival at the new phase

Incoherent interfaces and diffuse interface solid/liquid interfaces,
as high-angle grain boundaries = value of A close to unity ➡ "diffusion control"

Coherent or semicoherent interfaces as well as
smooth solid/liquid interfaces = low values of A ➡ "Some degree of interface control"

Ex) Interface control

1) When two phases forming a coherent or semicoherent interface have different crystal structures.

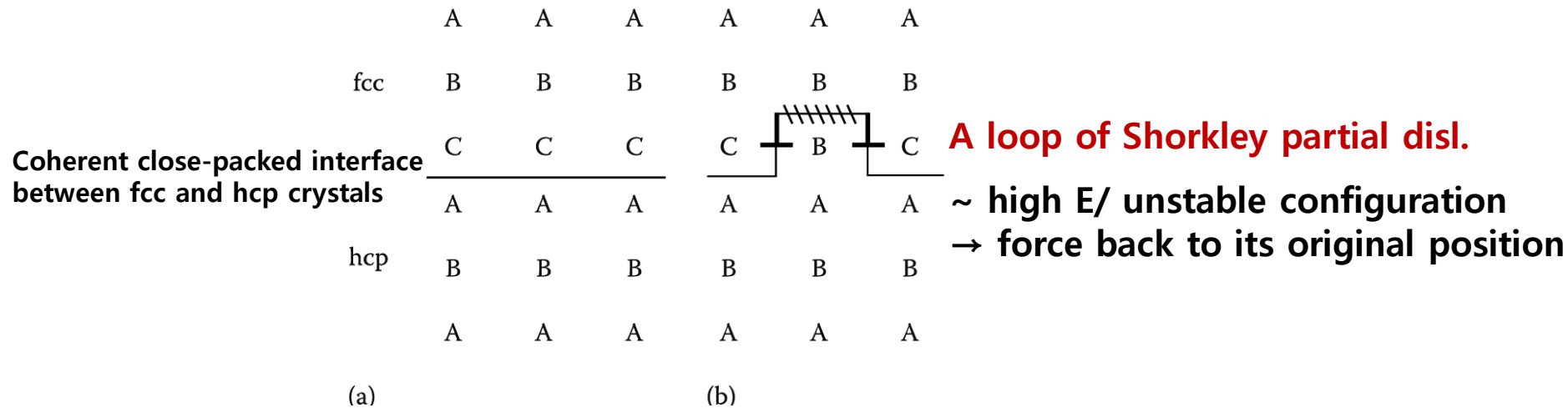


Fig. 3. 68 Problems associated with the continuous growth of coherent interfaces between phases with different crystal structures.

hcp phase growth by individual atomic jumps (i.e., so-called continuous growth) ~ very difficult
 (very low accommodation factors and low mobility)

2) Solid/vapor as well as smooth solid/liquid interfaces ~ similar manner

* A way of avoiding the difficulties of continuous growth

“Growth by ledge mechanism”

Facets: AB, CD, EF

Ledge: BC, DE

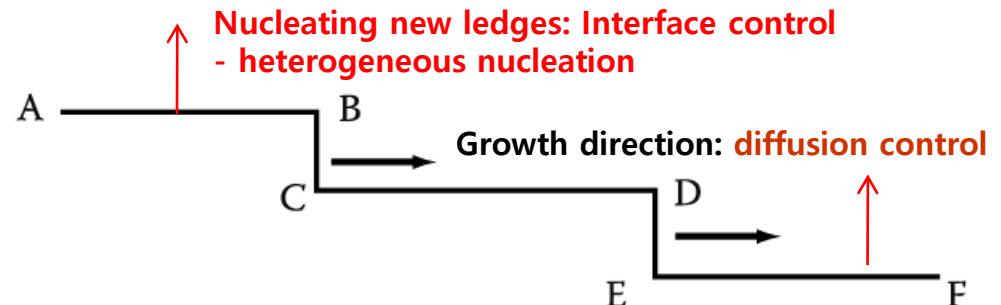
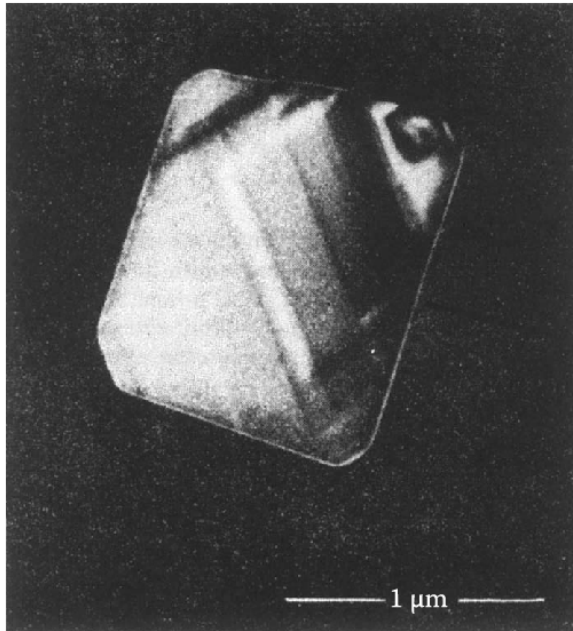


Fig. 3. 69 The ledge mechanism.

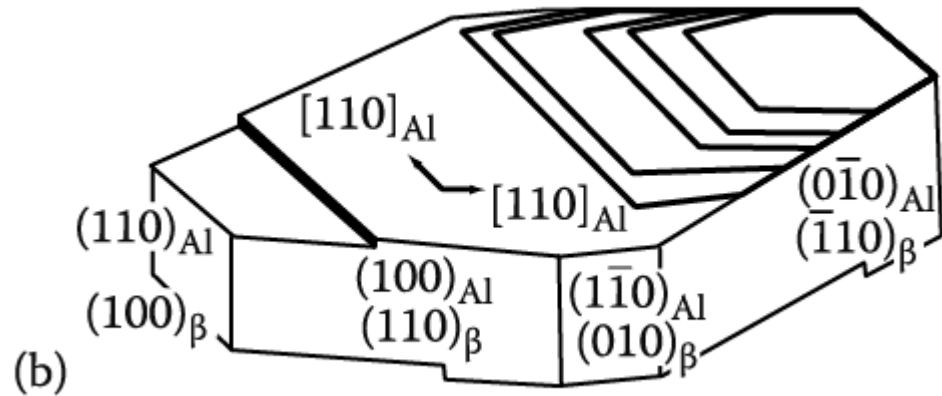
→ Problem of nucleation new ledges may often lead to a degree of interface control on the overall rate.

Fig. 3. 70 (a) Growth ledges at an Mg_2Si plate in $\text{Al-1.5 wt\% Mg}_2\text{Si}$, solution treated and aged 2h at 350 °C. Dark field micrograph.

(b) Schematic diagram of (a) showing ledges on Mg_2Si plate.



(a)



(b)

Note that growth ledges are usually hundreds of atoms layers high.

성장 돌출맥의 층 두께는 보통 수백 원자층 두께

The mechanism of interface migration can have important effects on the shape of second-phase inclusions. (section 3.4.2)

- if absence of strain E effect, equilibrium shape of a precipitate should be determined by
 - a) **the relative energies of the bounding interfaces (dominant)** γ -plot 계면 E의 상대적 비
 - ex) a partially coherent precipitate~disk or plate shape with an aspect ratio of γ_i / γ_c
 - b) **(in practice) "relative rates" at which the coherent and incoherent interface can migrate**

정합/ 부정합 계면의 상대적인 이동속도 차에 의해 형상 변화

Contents for today's class

- Interphase Interfaces in Solid (α/β)

- Types of interphase interfaces in solid (α/β)

- Second-Phase Shape $\left\{ \begin{array}{l} \text{Interface Energy Effects} \\ \text{Coherent / Semi-coherent / incoherent} \\ \text{Misfit Strain Effects} \end{array} \right.$

$$\sum A_i \gamma_i + \Delta G_s = \text{minimum}$$

- Coherency Loss

- Glissil Interfaces \longleftrightarrow Non-Glissil Interfaces
e.g. Solid/Liquid Interfaces

- Interface migration

- Interface controlled growth \longleftrightarrow Diffusion controlled growth

\Rightarrow Classification of Heterogeneous (Nucleation and Growth) Transformation

Classification of Heterogeneous (Nucleation and Growth) Transformation

Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent, Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different compositions		
Nature of diffusion process	No diffusion	Short-range diffusion (across interface)	Long-range diffusion (through lattice)		
Interface, diffusion or mixed control?	Interface control	Interface control	Mainly interface control	Mainly diffusion control	Mixed control
Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Solidification and melting	Precipitation dissolution Eutectoid Cellular precipitation

Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface
(need to additional research)

Contents of this course_Phase transformation

Background
to understand
phase
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative
Phase
transformation

(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

*** Homework 5 : Exercises 3 (pages 186-188)**

until 5th November

Good Luck!!

2021 Fall

“Phase Transformation *in* Materials”

11.01.2021

Eun Soo Park

Office: 33-313

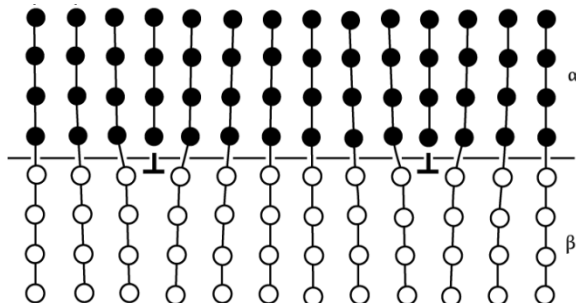
Telephone: 880-7221

Email: espark@snu.ac.kr

Office hours: by an appointment

Interphase Interfaces in Solid (α/β)

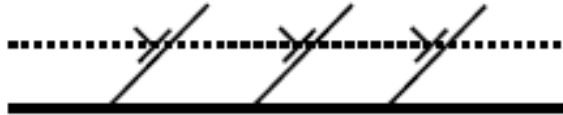
1) Glissile Interfaces (평활 이동 계면)



: epitaxial; Can't move forward or backward

(interface//burgers vector) \longrightarrow **Non-glissile interface**

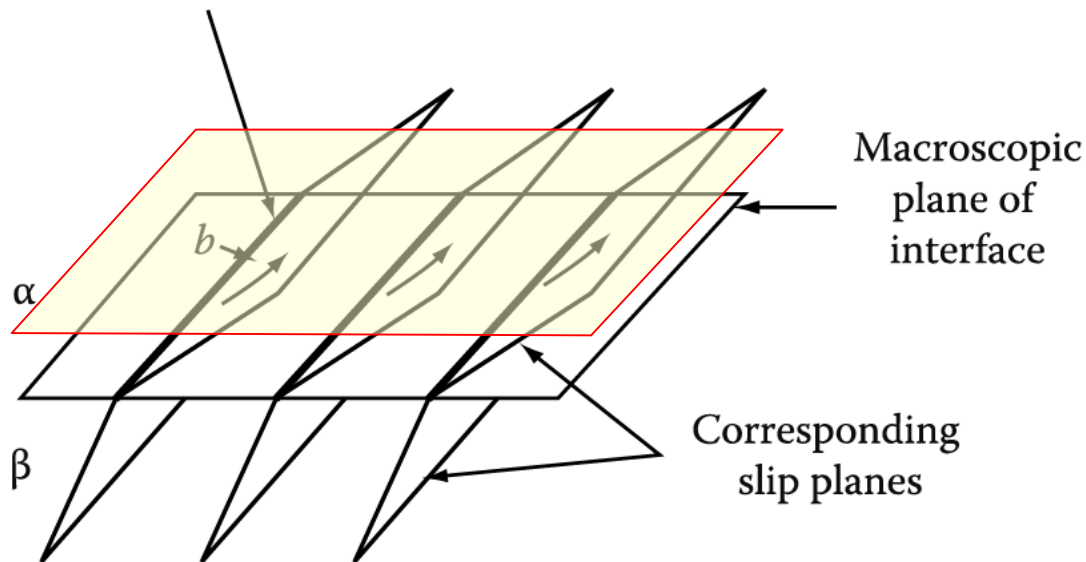
: Glide of the interfacial disl. cannot cause the interface to advance



: Glissile; Boundary moves toward α or β

: semi-coherent interfaces which can advance by the coordinated glide of the interfacial disl.

Interfacial dislocations



Macroscopic plane of interface

Corresponding slip planes

The dislocations have a Burgers vector that can glide on matching planes in the adjacent lattices.

Slip planes : continuous across the interface

Gliding of the dislocation : α is sheared into the β structure.

Fig. 3. 55 The nature of a glissile interface.

Classification of Heterogeneous (Nucleation and Growth) Transformation

Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent. Incoherent, solid/liquid, or solid/vapor)			
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Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

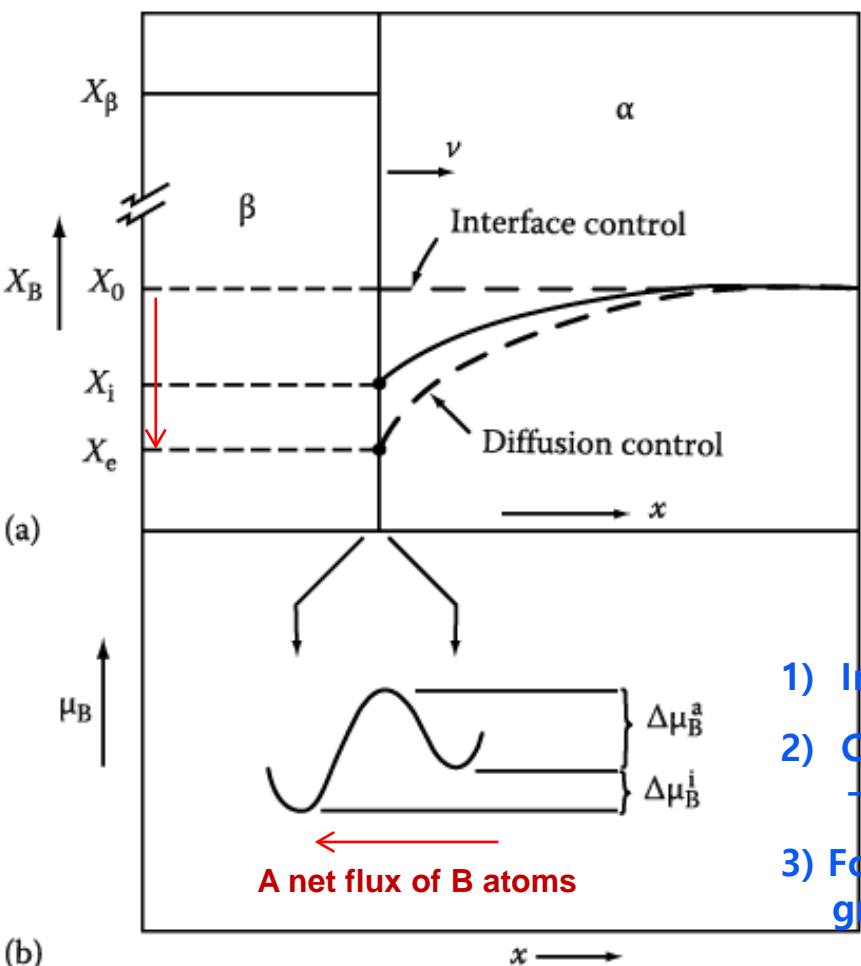
exception) **bainite transformation**: thermally activated growth/ shape change similar to that product by the motion of a glissile interface
(need to additional research)

5) Interface migration

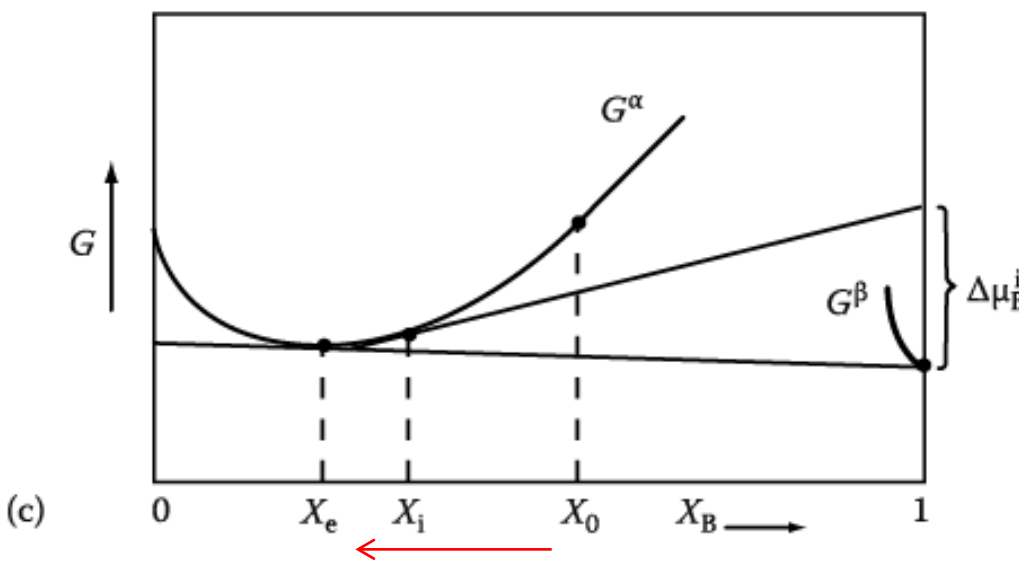
3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion
; the migration of interface separating two phases of different composition

(a) Composition profile across the interface



(c) A schematic molar free energy diagram showing the relationship between $\Delta\mu_B^i$, X_i , X_0



- 1) Initial composition of A-rich α phase X_0
- 2) Concentration B in the α phase adjacent to the interface X_i
→ B concentration in α : $X_0 \rightarrow X_i$
- 3) For growth to occur the interface, composition must be greater than the equilibrium concentration X_e .

(b) The origin of the driving force for boundary migration into the α -phase $\Delta\mu_B^i$

Corresponding flux across the interface (negative sign_negative direction of flux along the x-axis)

$$\begin{aligned}
 J_B^i &= -C_B^i v_B \\
 &= -\frac{1}{V_m} (M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}) \\
 &= J_B^\alpha = -D \left(\frac{\partial C_B}{\partial X} \right)_{\text{interface}}
 \end{aligned}$$

$$\Delta\mu_B^i \frac{1}{V_m} = \frac{J \text{ mol}^{-1}}{m^3 \text{ mol}^{-1}}$$

Steady state at interface,

$$J_B^i = J_B^\alpha$$

A flux of B atoms toward the interface by the concentration gradient in the α phase

1) If the interface mobility is very high, e.g. an incoherent interface,

High Mobility: $\Delta\mu_B^i$ small, $X_i \approx X_e$ Diffusion-Control

2) When the interface has a low mobility,

Low Mobility: $\Delta\mu_B^i$ must be large Mixed-Control

3) In the limit of a very low mobility,

Very low Mobility: $X_i \approx X_0$, $\left(\frac{\partial C}{\partial X} \right)_{\text{interface}} \approx 0$ Interface-Control

$\Delta\mu_B^i$ 는 최대

Contents for previous class

Chapter 3 Crystal Interfaces and Microstructure

- 1) Interfacial Free Energy
- 2) Solid/Vapor Interfaces
- 3) Boundaries in Single-Phase Solids
- 4) Interphase Interfaces in Solid (α/β)
- 5) Interface migration

Contents in Phase Transformation

Background
to understand
phase
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

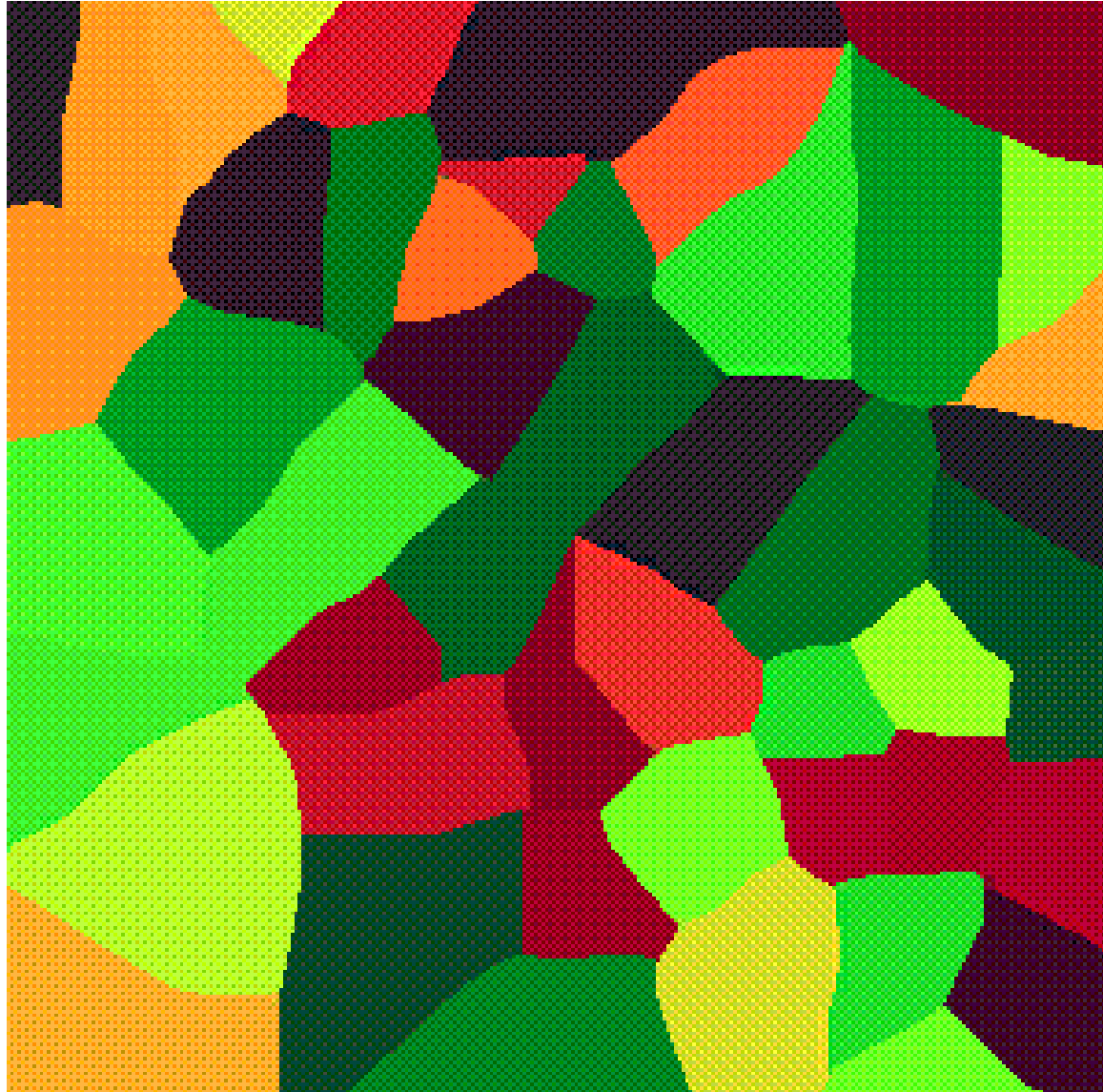
Representative
Phase
transformation

(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

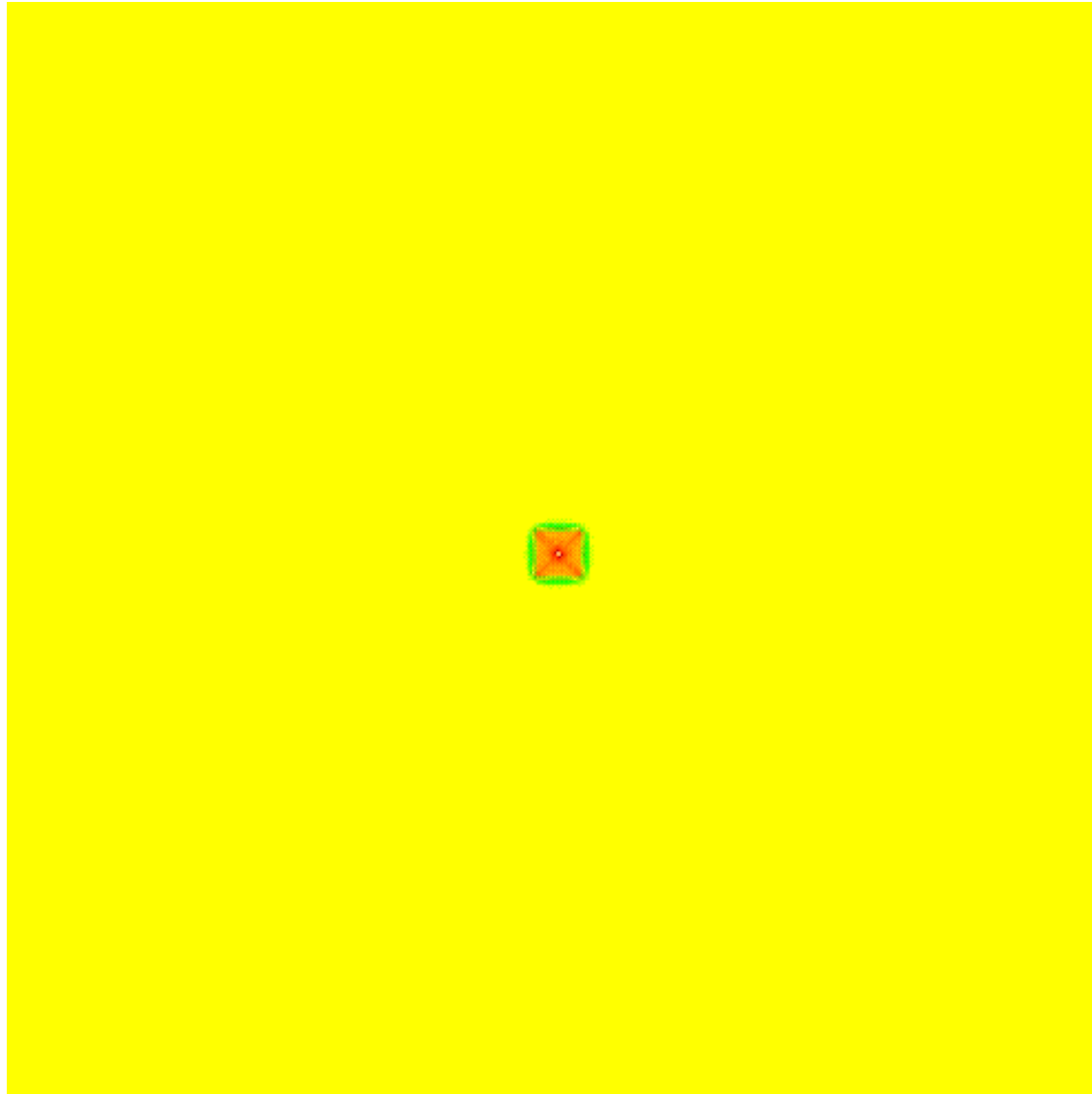
(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

Solidification: Liquid \longrightarrow Solid



4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

Solidification: **Liquid** → **Solid**



4 Fold Symmetric Dendrite Array

Contents for today's class

Solidification: Liquid Solid

< Nucleation >

- Nucleation in Pure Metals
- Homogeneous Nucleation
- Heterogeneous Nucleation
- Nucleation of melting

&

< Growth >

- Equilibrium Shape and Interface Structure on an Atomic Scale
- Growth of a pure solid
 - 1) Continuous growth
 - : Atomically rough or diffuse interface
 - 2) Lateral growth
 - : Atomically flat or sharply defined interface
- Heat Flow and Interface Stability

**Q: Undercooling of
homogenous vs heterogenous nucleation ?**

Solidification: Liquid \longrightarrow Solid

- casting & welding/additive manufacturing
- single crystal growth
- directional solidification
- rapid solidification

4.1. Nucleation in Pure Metals

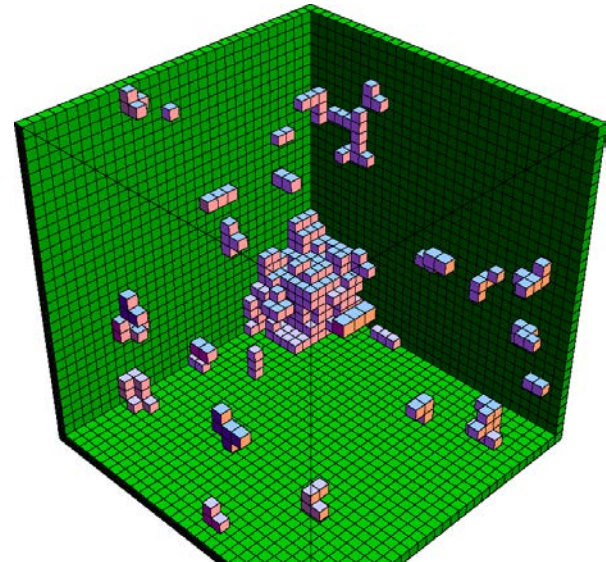
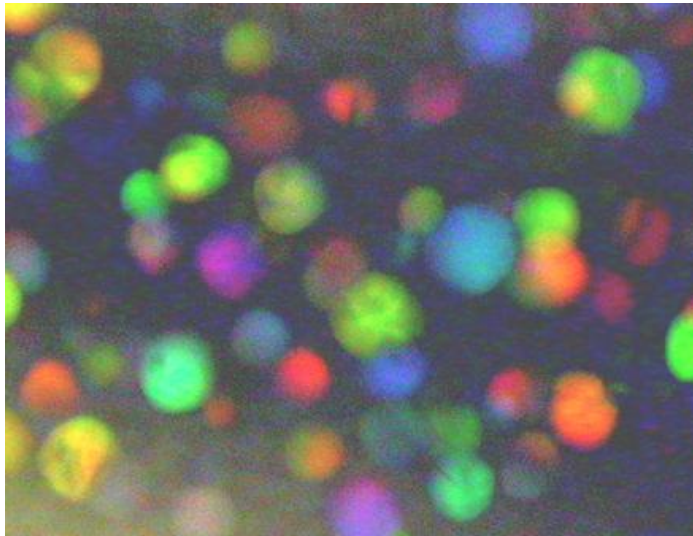
$$T_m : G_L = G_S$$

- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

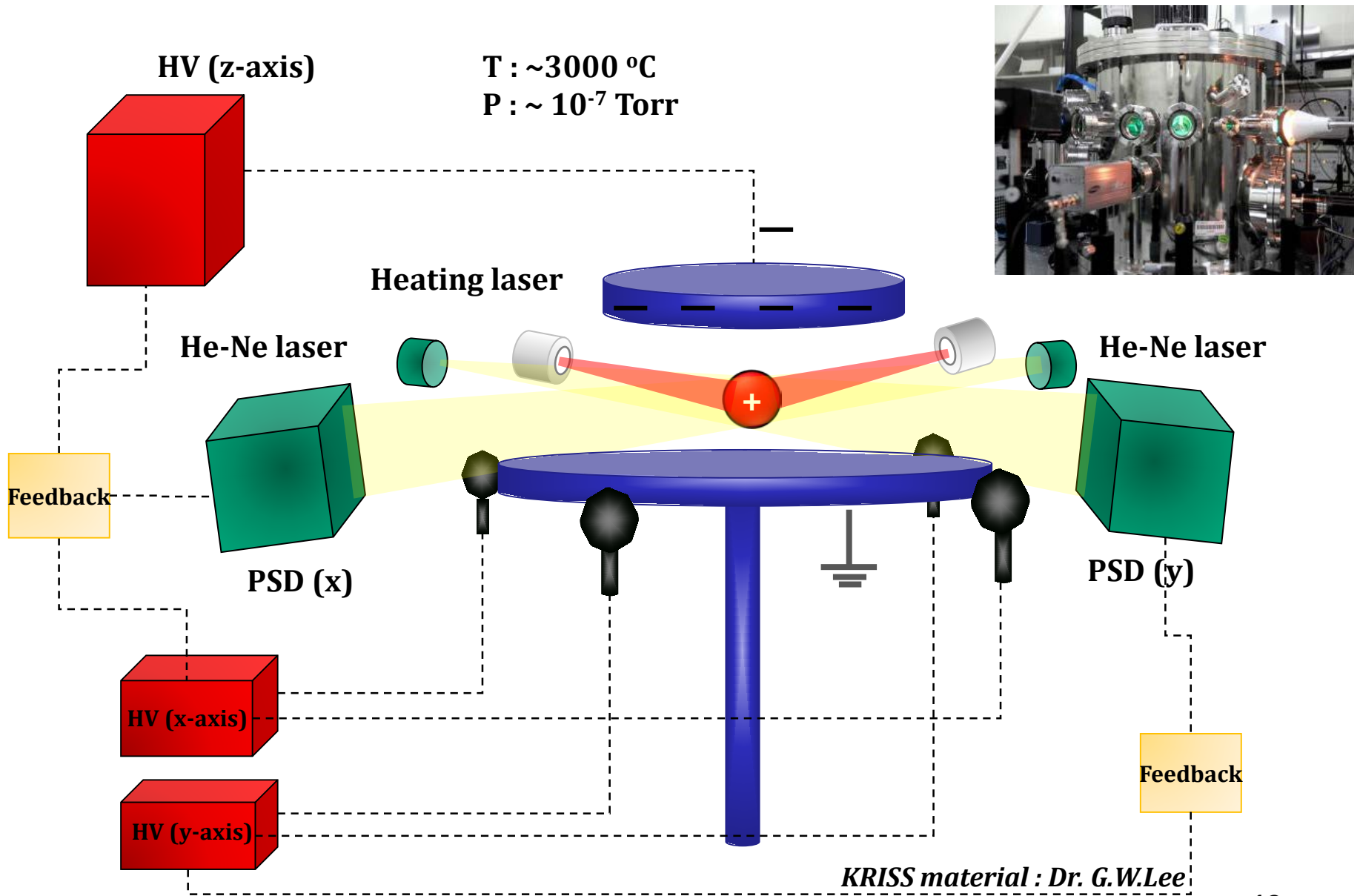
<Types of nucleation>

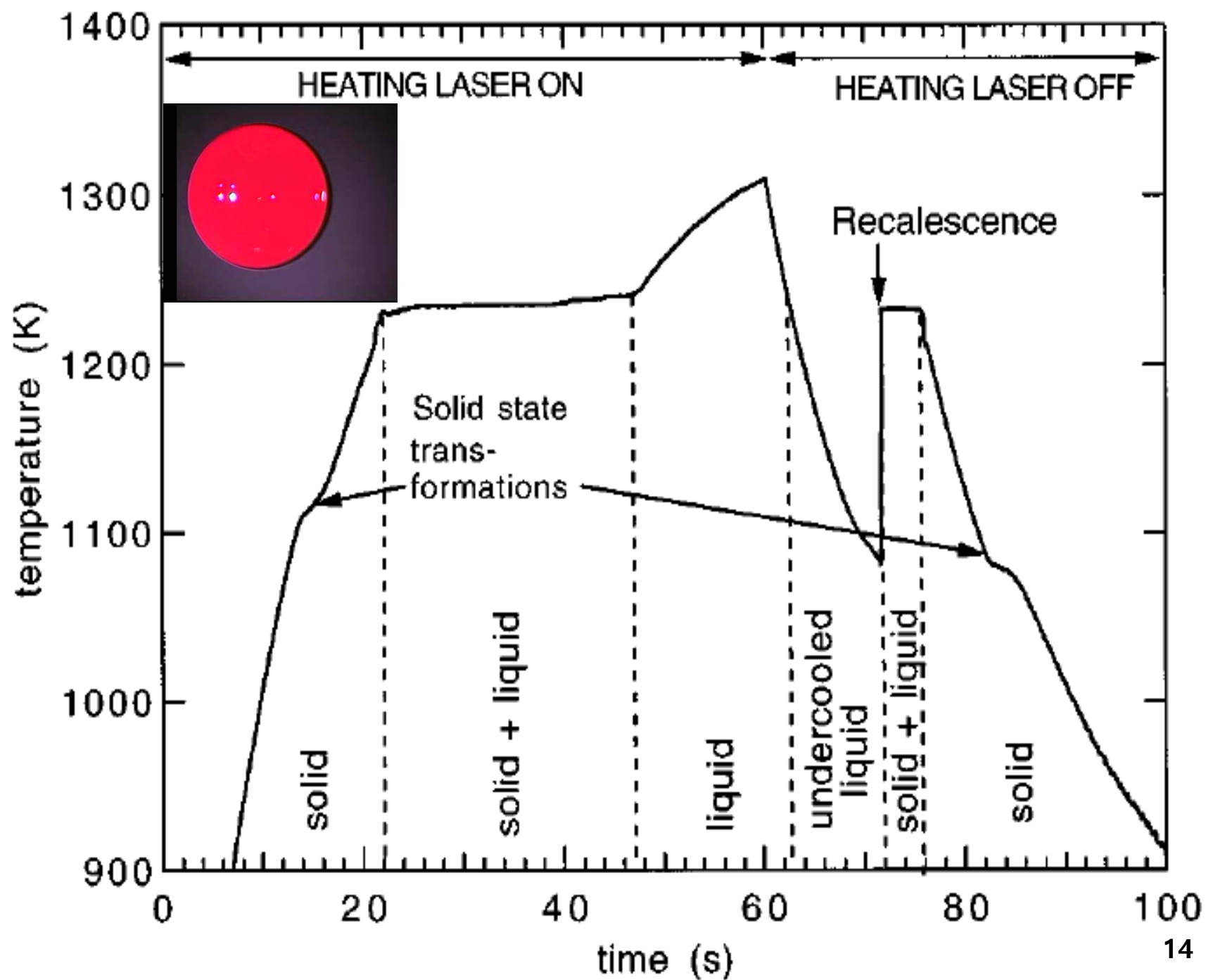
- Homogeneous nucleation

- Heterogeneous nucleation

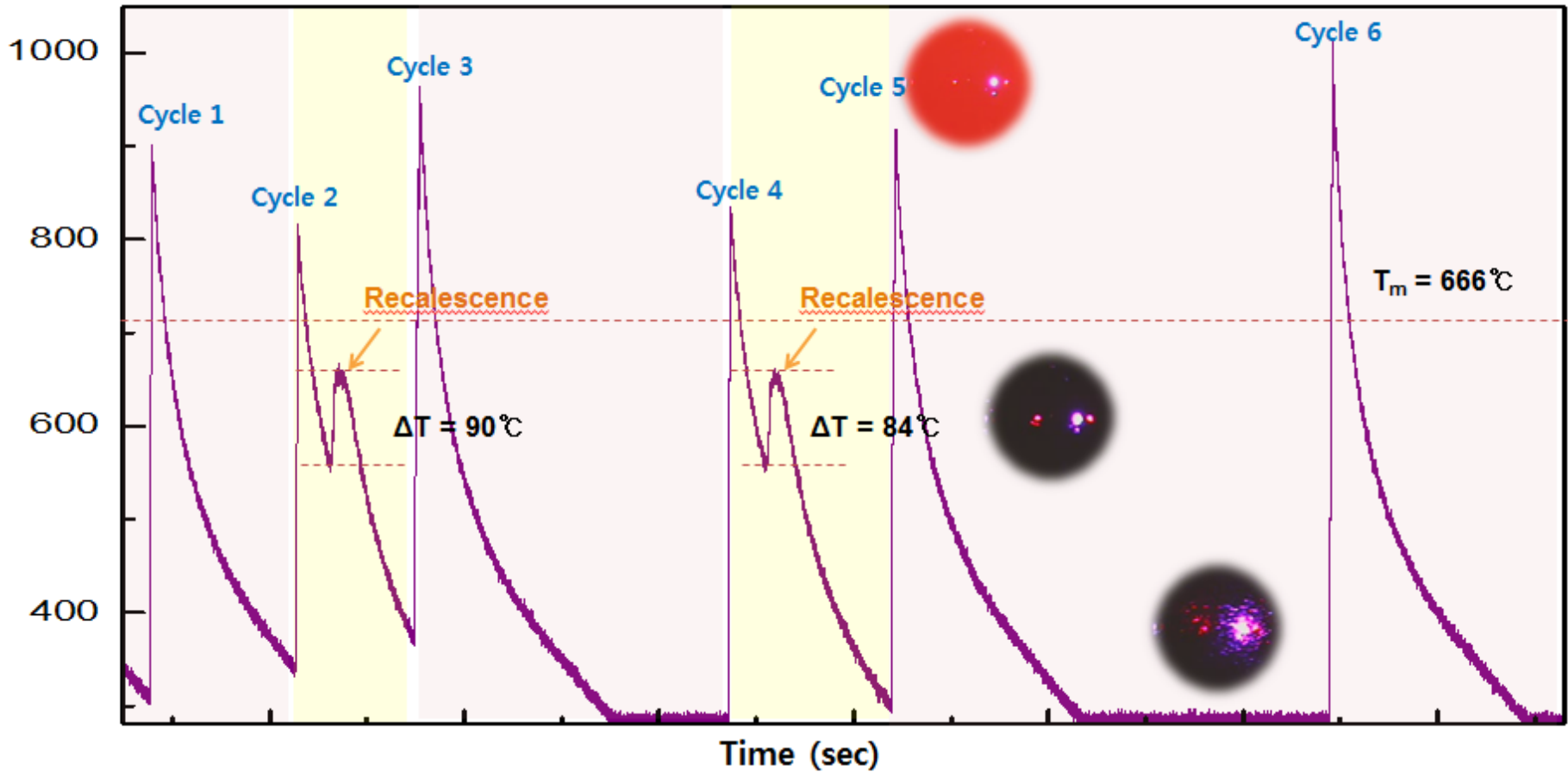


Electrostatic levitation in KRISS





Electrostatic Levitation: cooling curve of Vitreloy 1 system



Q: Homogenous nucleation

(a) Driving force for solidification, ΔG_v

(b) Calculation of ΔG_r , r^* , ΔG^*

4.1.1. Homogeneous Nucleation

Driving force for solidification

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$

$$\Delta G = \Delta H - T \Delta S$$

$$\underline{L : \Delta H = H^L - H^S}$$

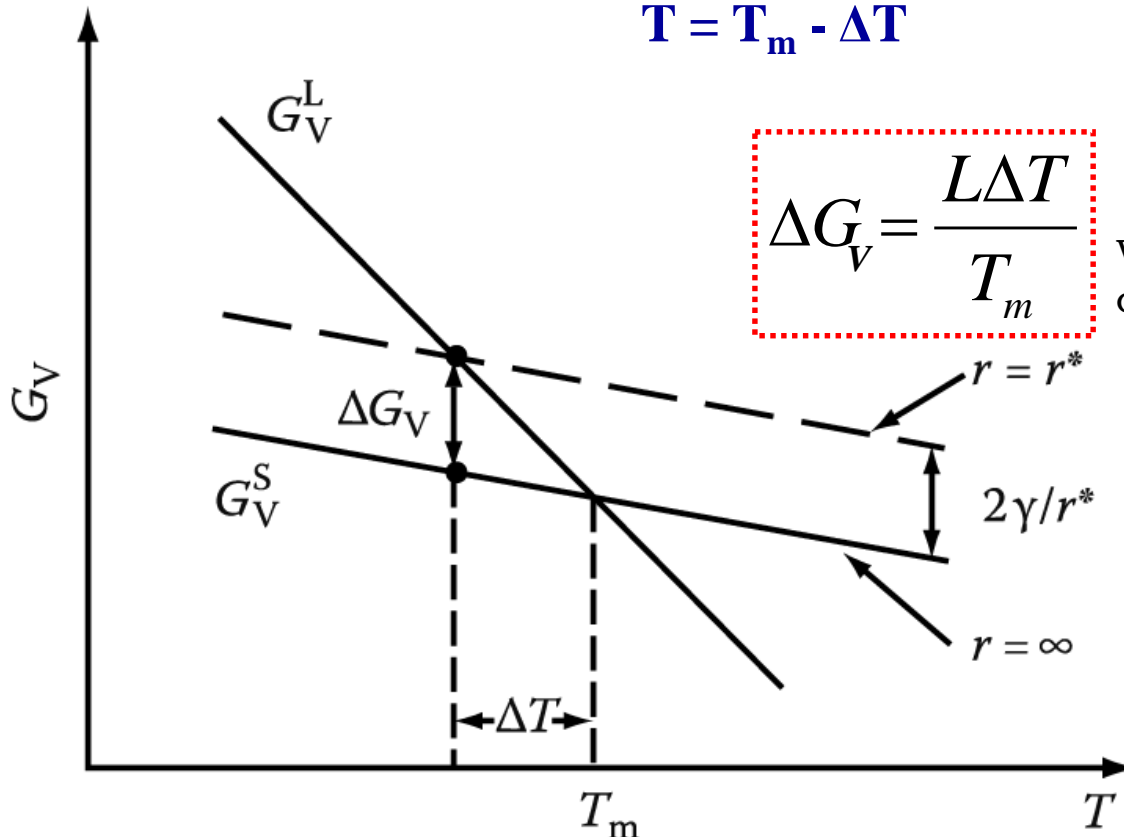
(Latent heat)

$$T = T_m - \Delta T$$

$$\Delta G = 0 = \Delta H - T_m \Delta S$$

$$\underline{\Delta S = \Delta H / T_m = L / T_m}$$

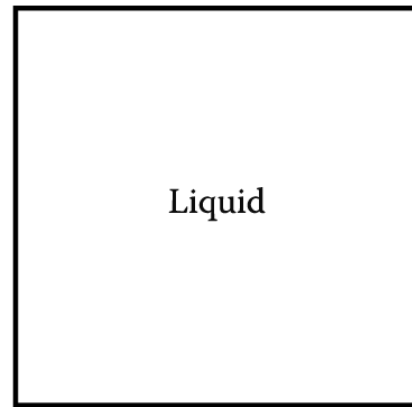
$$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$$



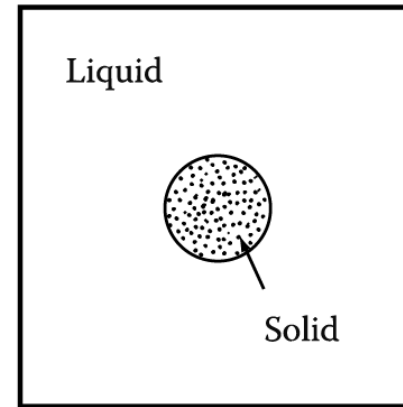
$$\Delta G_V = \frac{L\Delta T}{T_m}$$

Variation of free energy per unit volume obtained from undercooling (ΔT)

4.1.1. Homogeneous Nucleation



(a) G_1



(b) $G_2 = G_1 + \Delta G$

$$G_1 = (V_S + V_L)G_V^L$$

$$G_2 = V_S G_V^S + V_L G_V^L + A_{SL} \gamma_{SL}$$

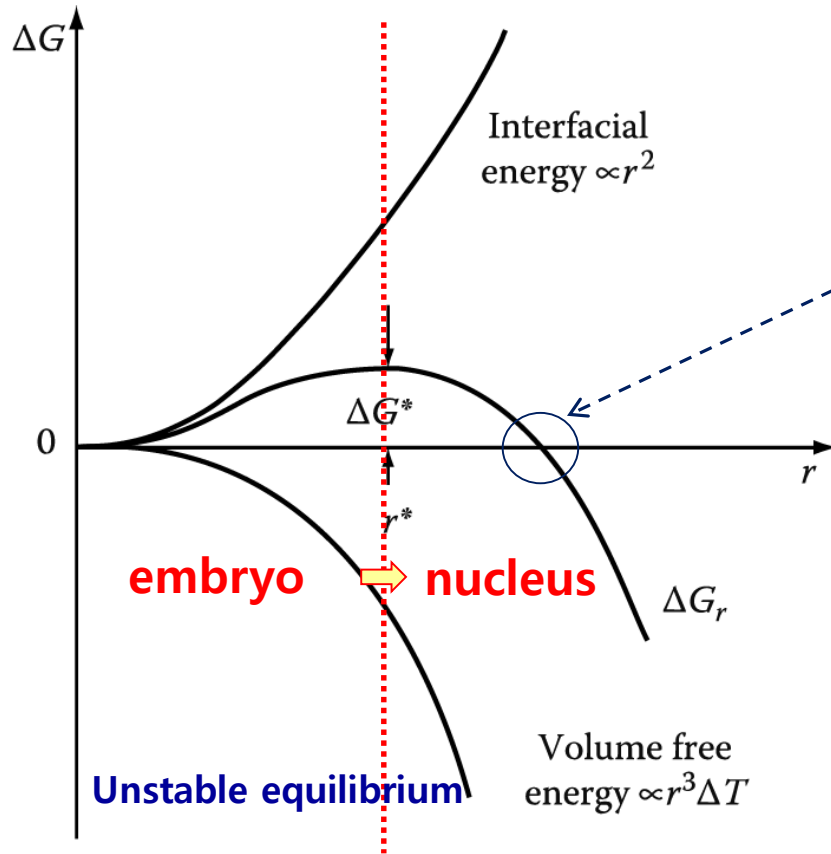
G_V^S, G_V^L : free energies per unit volume

$$\Delta G = G_2 - G_1 = -V_S (G_V^L - G_V^S) + A_{SL} \gamma_{SL}$$

for spherical nuclei (isotropic) of radius : r

$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

Calculation of critical radius, r^*



$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

Why r^* is not defined by $\Delta G_r = 0$?

$r < r^*$: **unstable** (lower free E by reduce size)

$r > r^*$: **stable** (lower free E by increase size)

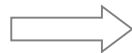
r^* : critical nucleus size

$$r^* \Rightarrow dG=0$$

Gibbs-Thompson Equation

Critical ΔG of nucleation at r^*

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$



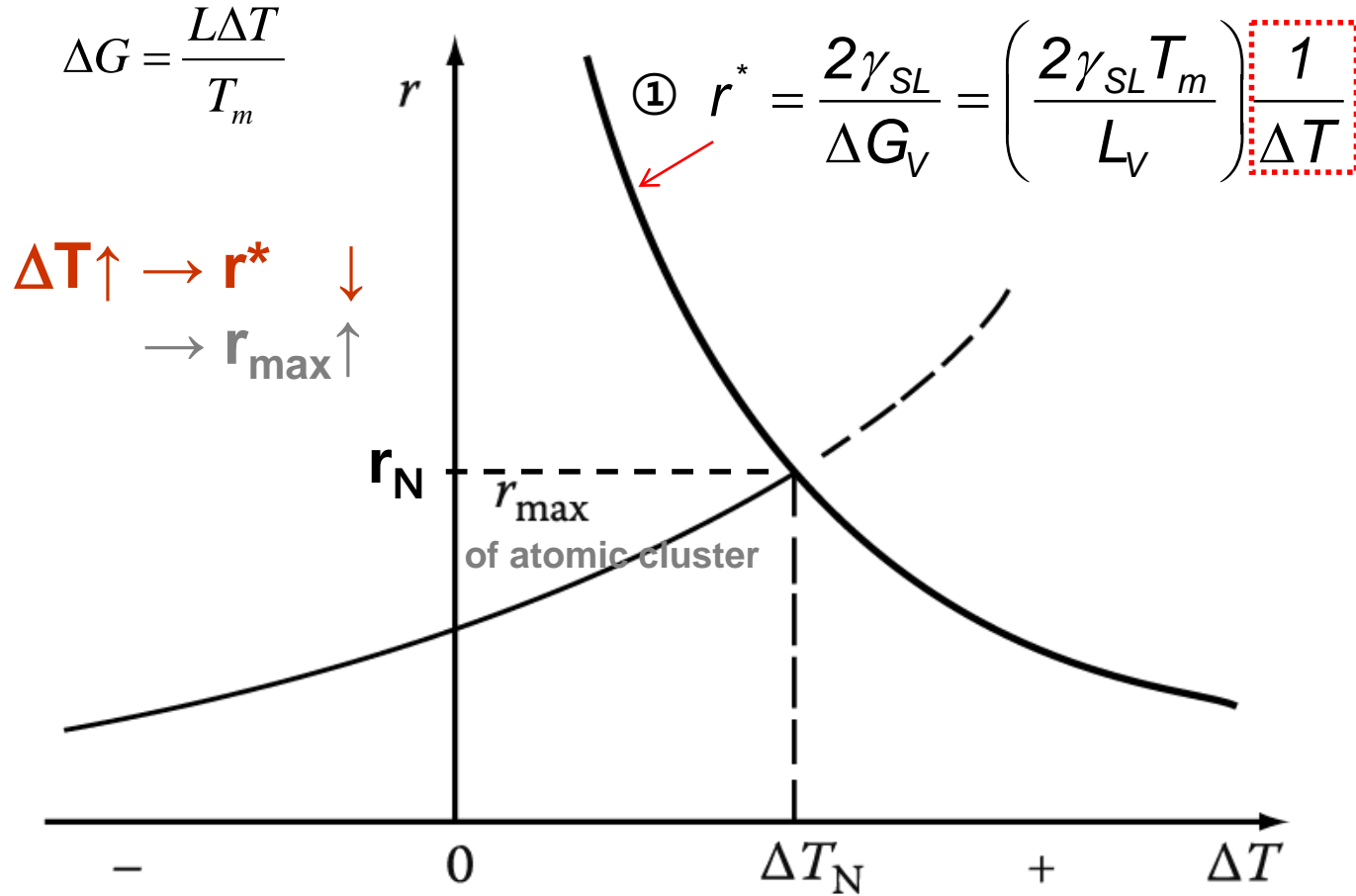
$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2}$$

$$\Delta G_r = -\frac{4}{3} \pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

$$\Delta G_V = \frac{L\Delta T}{T_m}$$

Q: How do we define ΔT_N ?

The creation of a critical nucleus ~ thermally activated process



ΔT_N is **the critical undercooling** for homogeneous nucleation.

Fig. 4.5 The variation of r^* and r_{\max} with undercooling ΔT

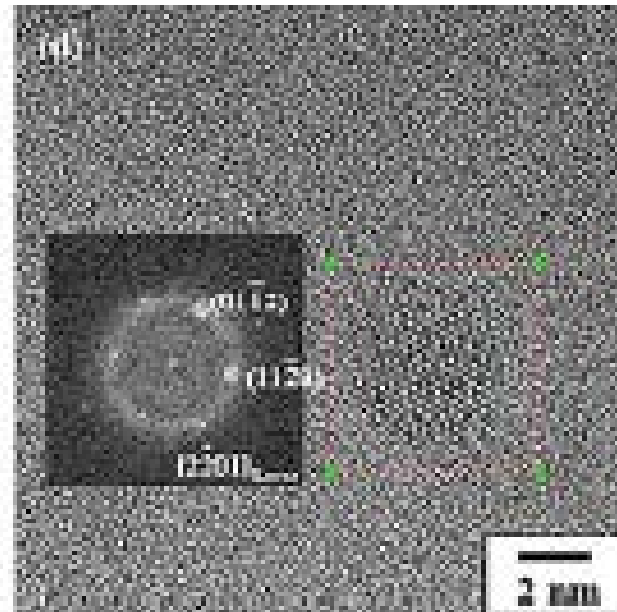
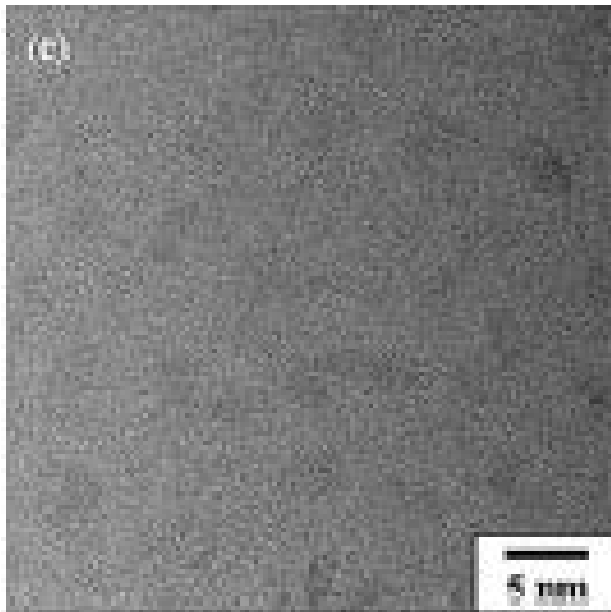
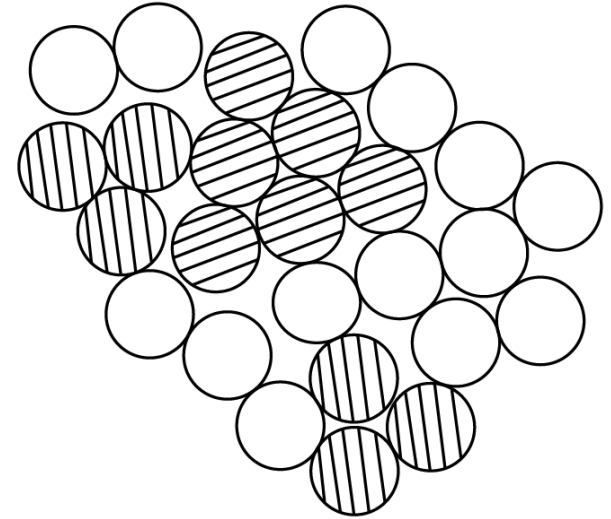
→ Condition for nucleation:

The number of clusters with r^* at $T < \Delta T_N$ is negligible.

② Formation of Atomic Cluster

At the T_m , the liquid phase has a volume 2-4% greater than the solid.

Fig. 4.4 A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are instantaneously formed.

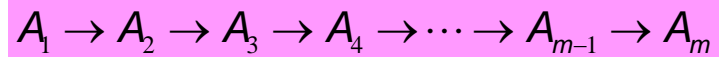


Formation of Atomic Cluster

When the free energy of the atomic cluster with radius r is by

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL},$$

how many atomic clusters of **radius r** would exist in the presence of the total number of atoms, n_0 ?



$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow 2}}{kT}\right) \quad \text{Excess free E associated with the cluster of } 1 \rightarrow 2 \text{ atoms}$$

$$n_3 = n_2 \exp\left(-\frac{\Delta G^{2 \rightarrow 3}}{kT}\right)$$

$$n_4 = n_3 \exp\left(-\frac{\Delta G^{3 \rightarrow 4}}{kT}\right)$$

$$\vdots$$

$$n_m = n_{m-1} \exp\left(-\frac{\Delta G^{m-1 \rightarrow m}}{kT}\right)$$

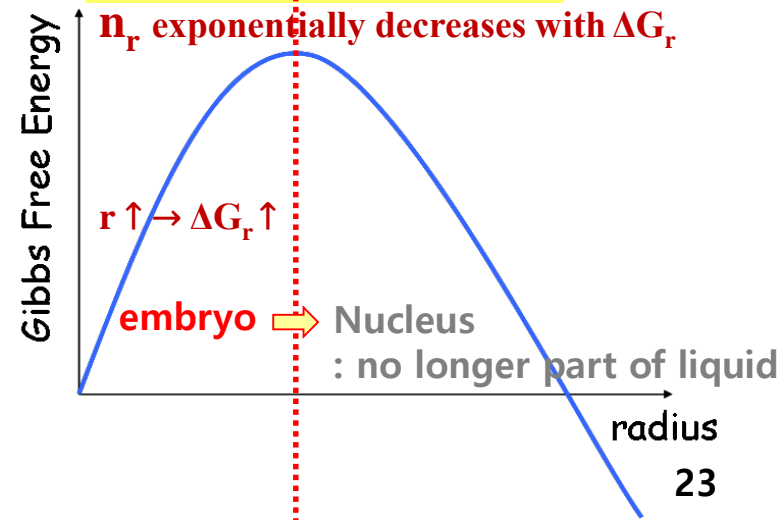
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow 2} + \Delta G^{2 \rightarrow 3} + \dots + \Delta G^{m-1 \rightarrow m}}{kT}\right)$$

$$n_m = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow m}}{kT}\right)$$

반지름 r 인 구상의 균집체 수

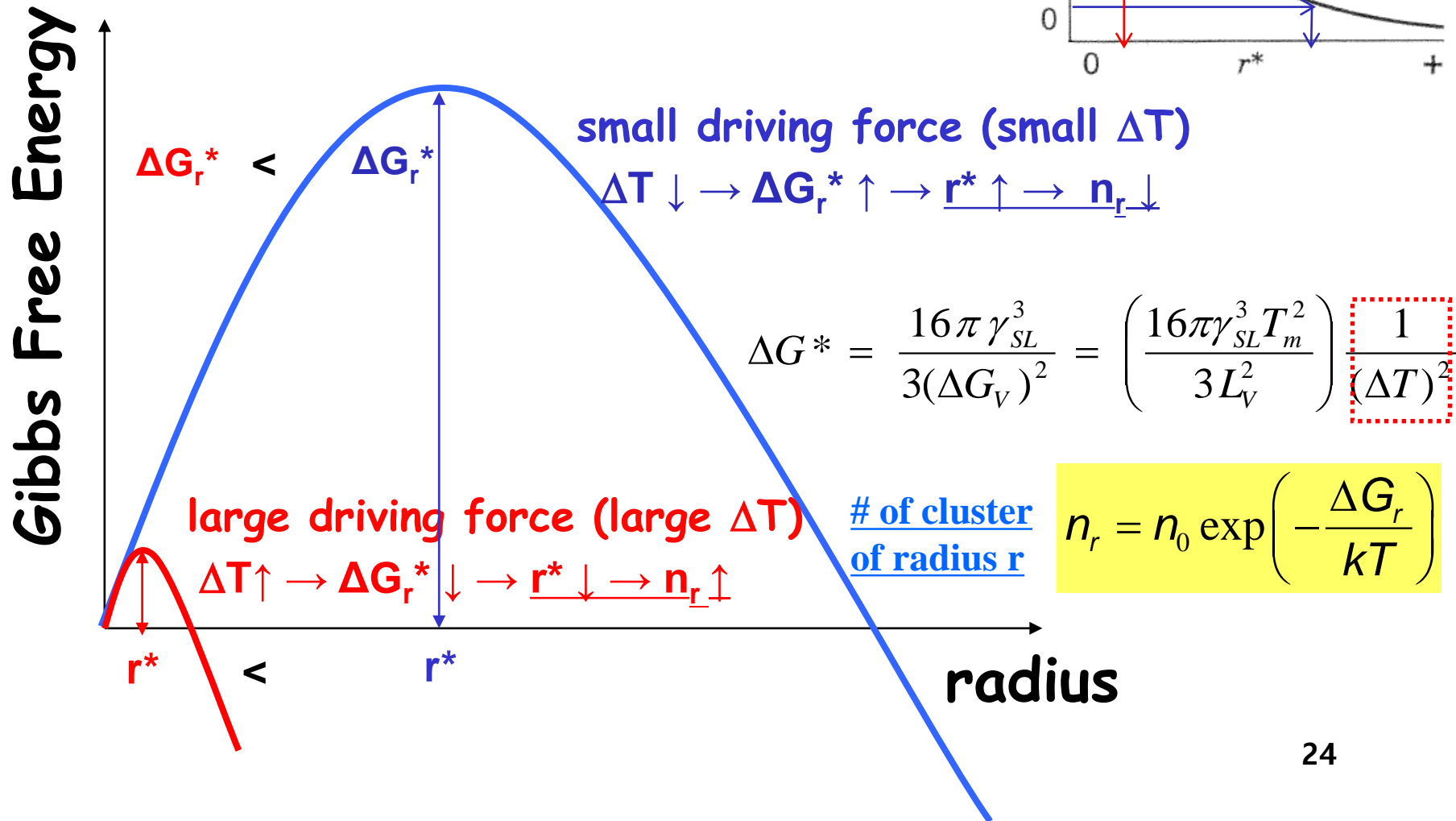
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

of cluster of radius r



Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.



Formation of Atomic Cluster

n_0 : total # of atoms.

ΔG_r : excess free energy associated with the cluster

k : Boltzmann's constant

of cluster of radius r

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

- holds for $T > T_m$ / $T < T_m$ and $r \leq r^*$

Apply for all r / $r \leq r^*$

($\because r > r^*$: no longer part of the liquid)

- n_r exponentially decreases with ΔG_r

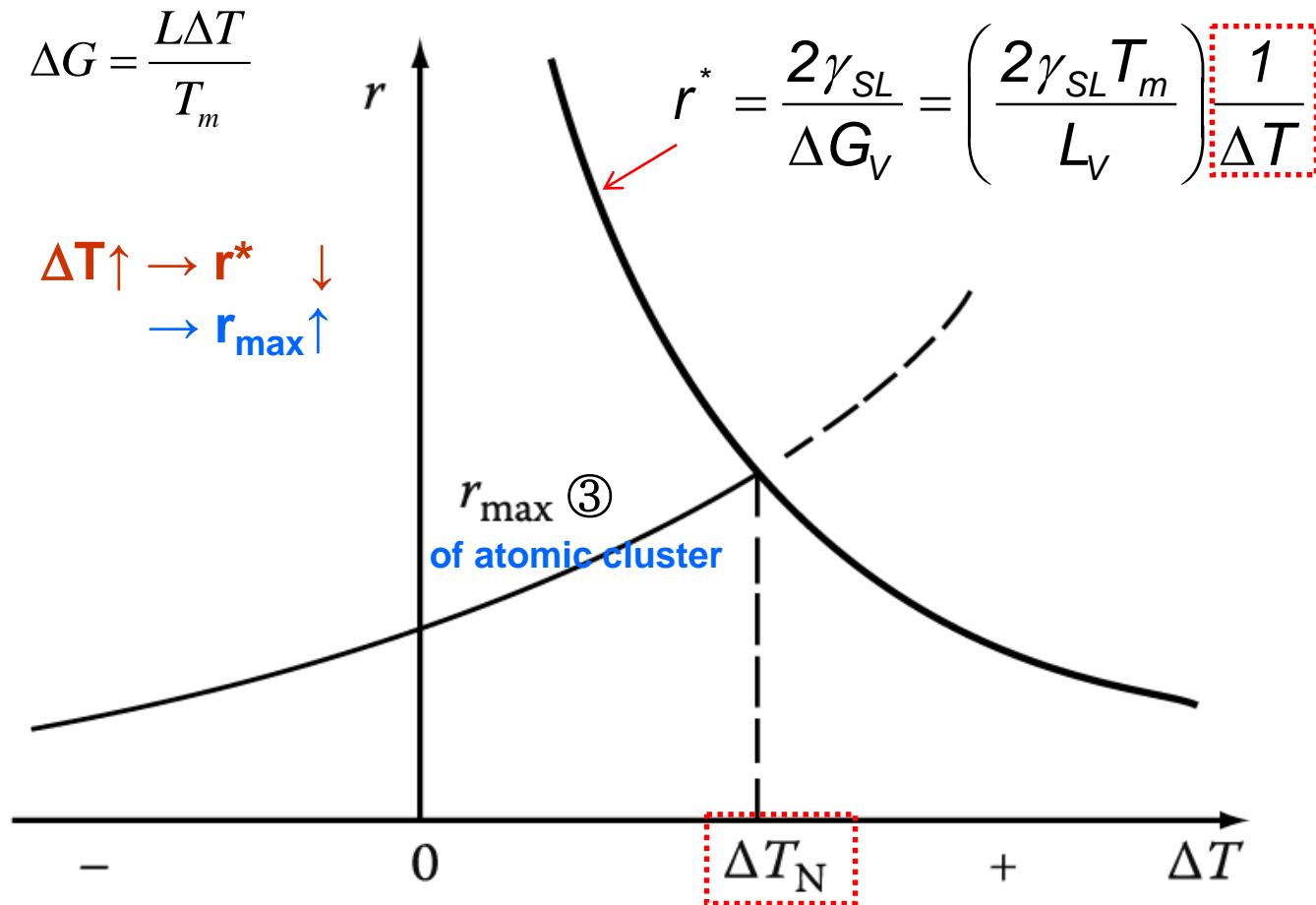
Ex. 1 mm³ of copper at its melting point (n_0 : 10²⁰ atoms)

$r \downarrow \rightarrow n_r \uparrow \rightarrow \sim 10^{14}$ clusters of 0.3 nm radius (i.e. ~ 10 atoms)

$r \uparrow \rightarrow n_r \downarrow \rightarrow \sim 10$ clusters of 0.6 nm radius (i.e. ~ 60 atoms)

\rightarrow **effectively a maximum cluster size, ~ 100 atoms**
 $\sim 10^{-8}$ clusters mm⁻³ or 1 cluster in $\sim 10^7$ mm³

The creation of a critical nucleus ~ thermally activated process



ΔT_N is **the critical undercooling** for homogeneous nucleation.

Fig. 4.5 The variation of r^* and r_{\max} with undercooling ΔT

The number of clusters with r^* at $\Delta T < \Delta T_N$ is negligible.

4.1.2. The homogeneous nucleation rate - kinetics

How fast solid nuclei will appear in the liquid at a given undercooling?

C_0 : atoms/unit volume

C^* : # of clusters with size of C^* (critical size) 임계핵 크기의 cluster 수

$$C^* = C_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right) \quad \text{clusters / m}^3$$

The addition of one more atom to each of these clusters will convert them into stable nuclei. 한 개 원자 추가로 확산시 핵생성

Homogeneous
Nucleation rate

$$N_{\text{hom}} = f_0 C_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right) \quad \text{nuclei / m}^3 \cdot \text{s}$$

$f_0 \sim 10^{11} \text{ s}^{-1}$: frequency \propto vibration frequency energy of diffusion in liquid surface area (const.)

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2}$$

$C_0 \sim \text{typically } 10^{29} \text{ atoms/m}^3$

$$N_{\text{hom}} \approx 1 \text{ cm}^{-3} \text{ s}^{-1} \quad \text{when } \Delta G^* \sim 78 kT$$

4.1.2. The homogeneous nucleation rate - kinetics

$$N_{\text{hom}} \approx f_0 C_o \exp\left\{-\frac{A}{(\Delta T)^2}\right\}$$

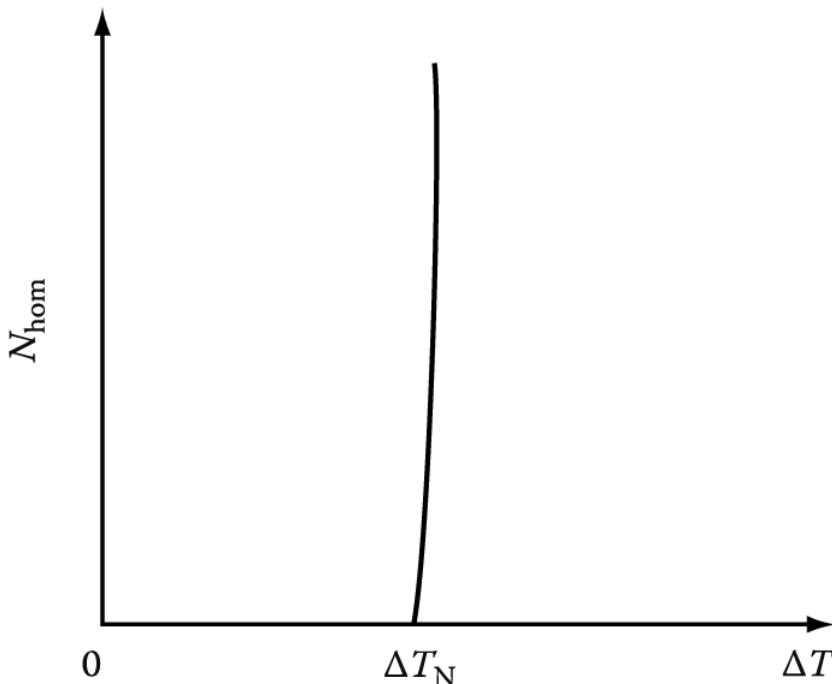
where $A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2 kT}$

A = relatively insensitive to Temp.

How do we define ΔT_N ?

$$N_{\text{hom}} \sim \frac{1}{\Delta T^2}$$

Changes by orders of magnitude from essentially zero to very high values over a very narrow temperature range



→ critical value for detectable nucleation

- critical supersaturation ratio
- critical driving force
- critical supercooling

→ for most metals, $\Delta T_N \sim 0.2 T_m$ (i.e. $\sim 200\text{K}$)

Fig. 4.6 The homogeneous nucleation rate as a function of undercooling ΔT . ΔT_N is **the critical undercooling** for homogeneous nucleation.

* **Copper** Homogeneous nucleation

$$\Delta T = 230 \text{ K} \rightarrow r^* \sim 10^{-7} \text{ cm} < 4 * (\text{Diameter of Cu atom})$$

If nucleus is spherical shape,

$$V = 4.2 * 10^{-21} \text{ cm}^3 \sim 360 \text{ atoms} (\because \text{one Cu atom } 1.16 * 10^{-23} \text{ cm}^3)$$

“Typically in case of metal” $\Delta T^* \sim 0.2 T_E / \sigma_{SL} \sim 0.4 L$

→ r^* (critical nucleus for homogeneous nucleation) of metal ~ 200 atoms

But, if cluster radius \sim (only 4 * atom diameter),

“no spherical shape”

(large deviation from spherical shape) →

→ **Possible structure for the critical nucleus of Cu**
: bounded only by {111} and {100} plane

- σ_{SL} may vary with the crystallographic nature of the surface.
- The faces of this crystal are close to their critical size for 2D nucleation at the critical temp for the nucleus as a whole.

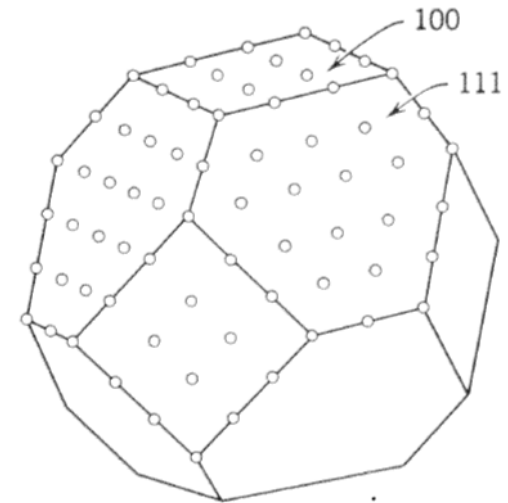


Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

Real behavior of nucleation: metal $\Delta T_{\text{bulk}} < \Delta T_{\text{small drop}}$

Under suitable conditions, **liquid nickel** can be **undercooled** (or **supercooled**) to 250 K below T_m (1453°C) and held there indefinitely without any transformation occurring.



Normally undercooling as large as 250 K are not observed.

The nucleation of solid at undercooling of only ~ 1 K is common.

The formation of a nucleus of critical size can be catalyzed by a suitable surface in contact with the liquid. → “Heterogeneous Nucleation”

Ex)

liquid

container

or

Solid thin film (such as oxide)



liquid

Why this happens? What is the underlying physics?

Which equation should we examine?

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2} \right) \frac{1}{(\Delta T)^2}$$

$$N_{\text{hom}} = f_0 C_o \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right)$$

**Q: Real behavior of nucleation:
“Heterogeneous nucleation”**

4.1.3. Heterogeneous nucleation

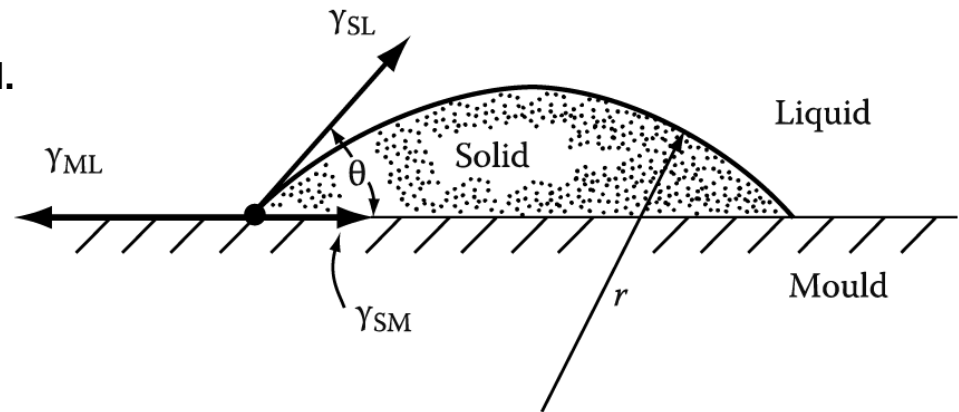
From
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2}$$

Nucleation becomes easy if $\gamma_{SL} \downarrow$ by forming nucleus from mould wall.

Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.

$$\gamma_{ML} = \gamma_{SL} \cos \theta + \gamma_{SM}$$

$$\cos \theta = (\gamma_{ML} - \gamma_{SM}) / \gamma_{SL}$$



$$\Delta G_{het} = -V_S \Delta G_v + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}$$

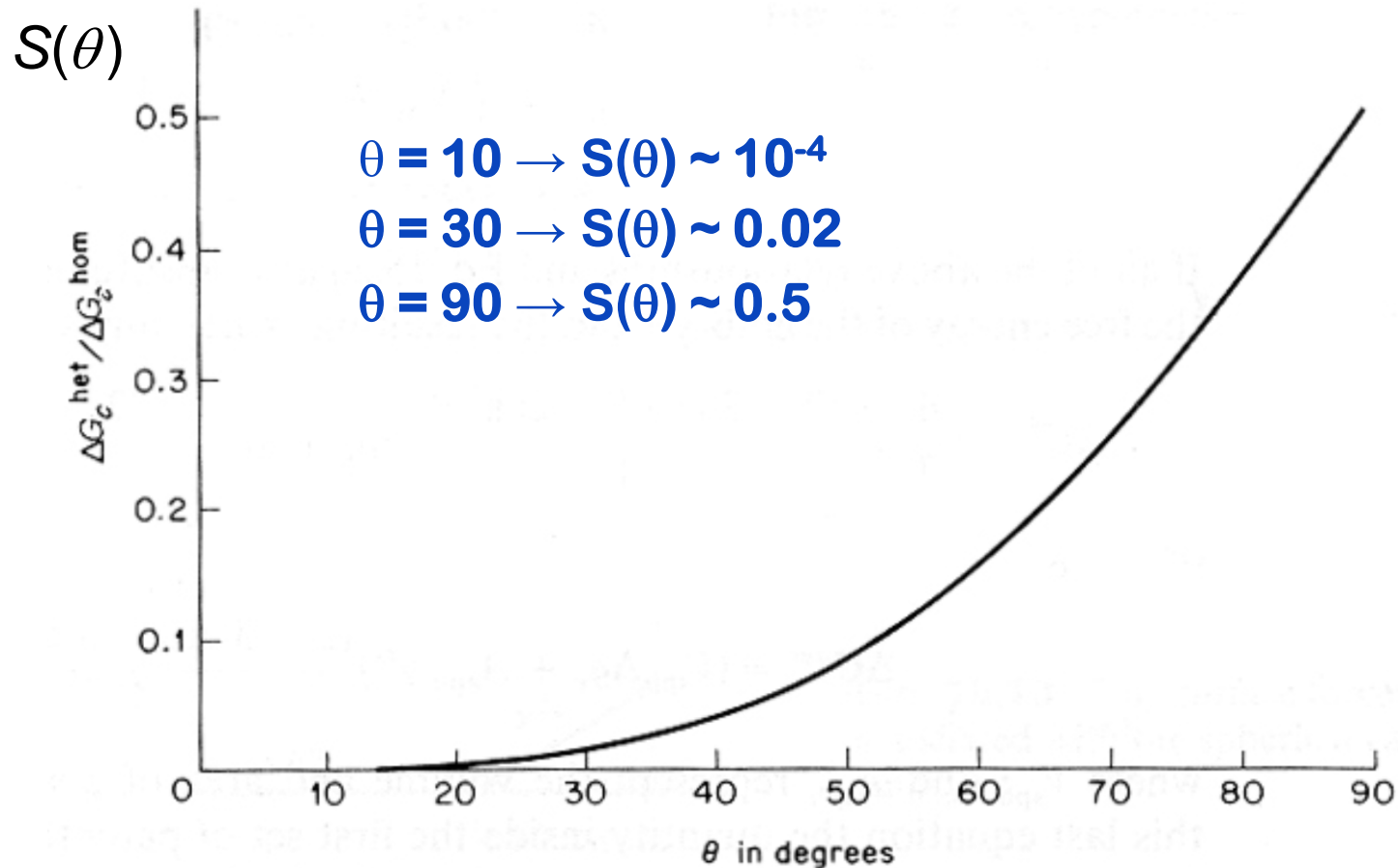
In terms of the wetting angle (θ) and the cap radius (r) (Exercies 4.6)

$$\Delta G_{het} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \right\} S(\theta)$$

where $S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$

$S(\theta)$ has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G_{het}^* = S(\theta) \Delta G_{hom}^* \quad \Rightarrow \quad r^* = \frac{2 \gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_V^2} \cdot S(\theta)$$



$S(\theta)$ has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G_{het}^* = S(\theta) \Delta G_{hom}^*$$



$$r^* = \frac{2 \gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16 \pi \gamma_{SL}^3}{3 \Delta G_V^2} \cdot S(\theta)$$

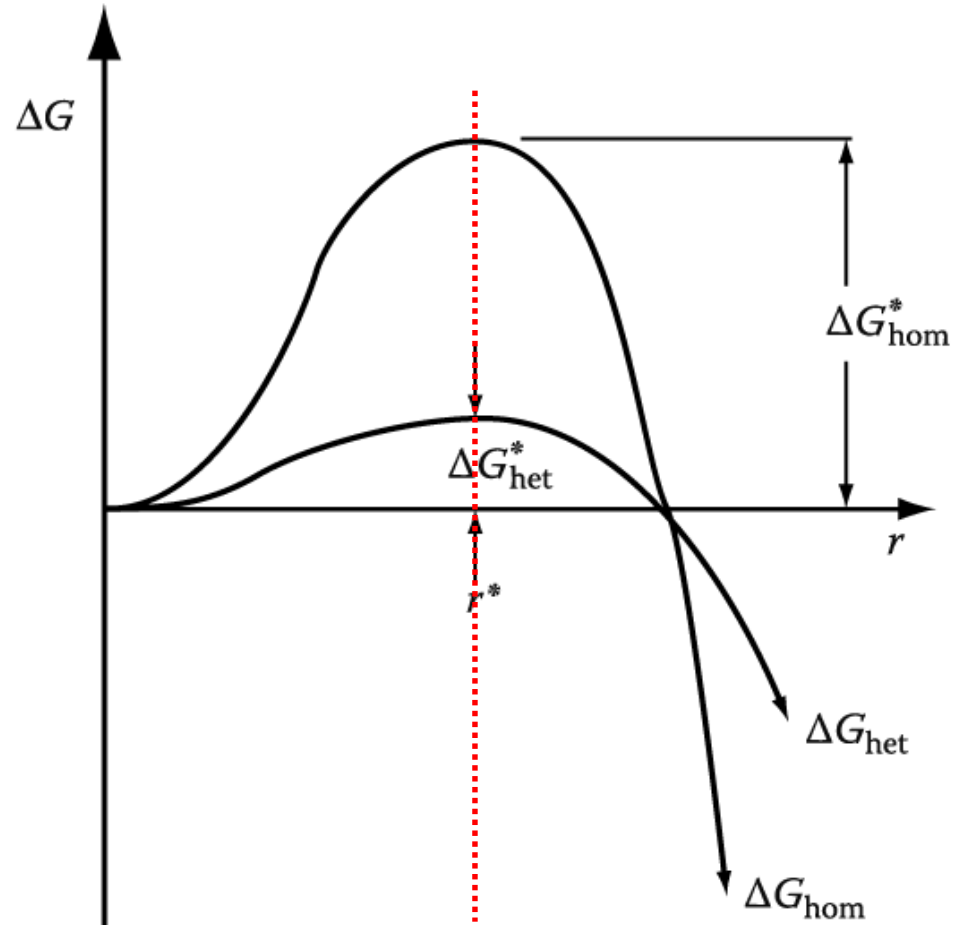


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r^* is independent of the nucleation site.

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom} ?

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_v^2} \right) \frac{1}{(\Delta T)^2}$$

$$\Rightarrow \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$

n_1 atoms in contact
with the mold wall

$$n^* = n_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

$$N_{het} = f_1 C_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

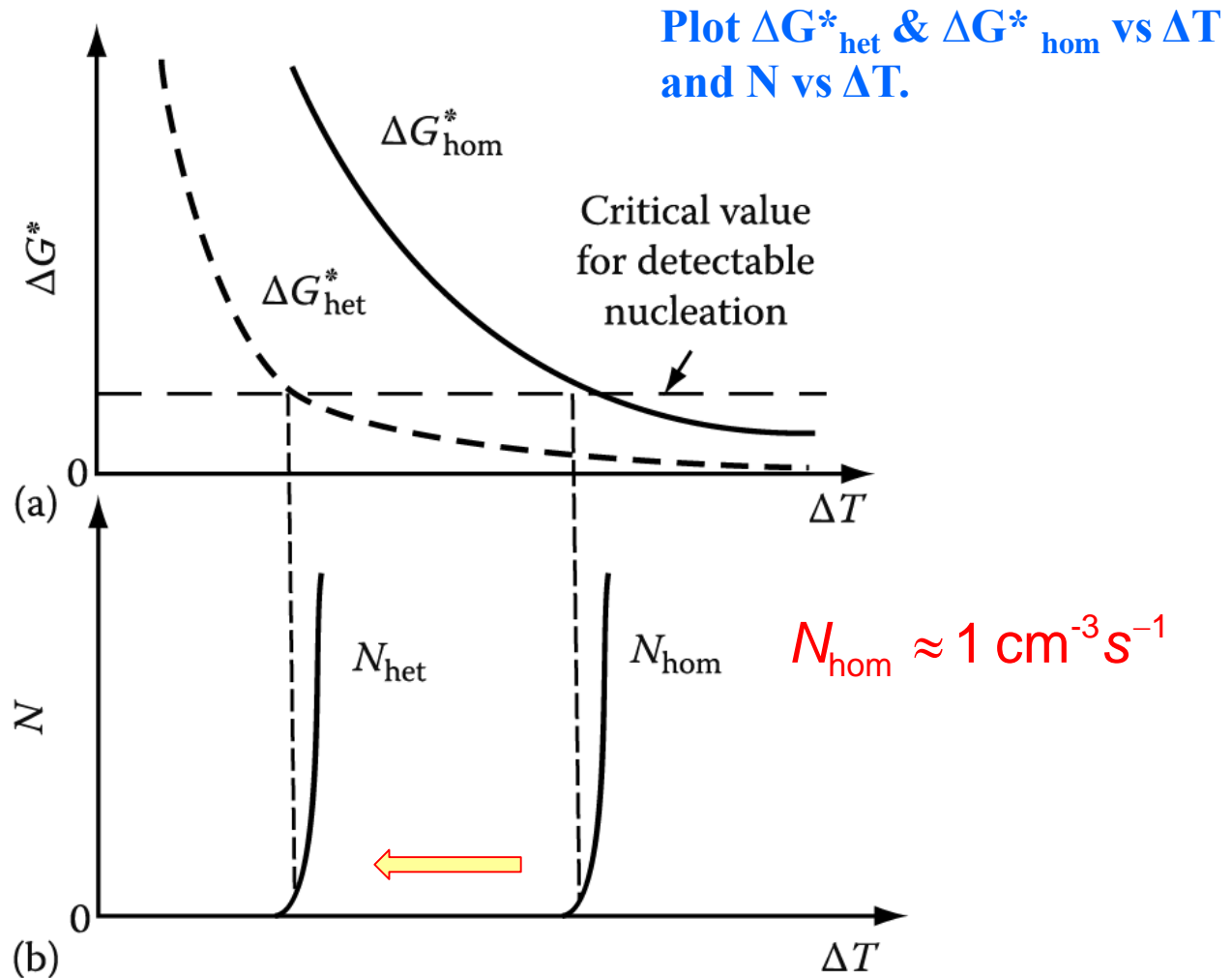


Fig. 4.9 (a) Variation of ΔG^* with undercooling (ΔT) for homogeneous and heterogeneous nucleation.
(b) The corresponding nucleation rates assuming the same critical value of ΔG^*

$\theta \downarrow \rightarrow V_c / V \downarrow \rightarrow \text{embryo radius } (r_{\max}) \uparrow$

\rightarrow condition for heterogeneous nucleation as a function of θ

Assumption 1: angle of contact is independent of temp.

2: substrate is flat.

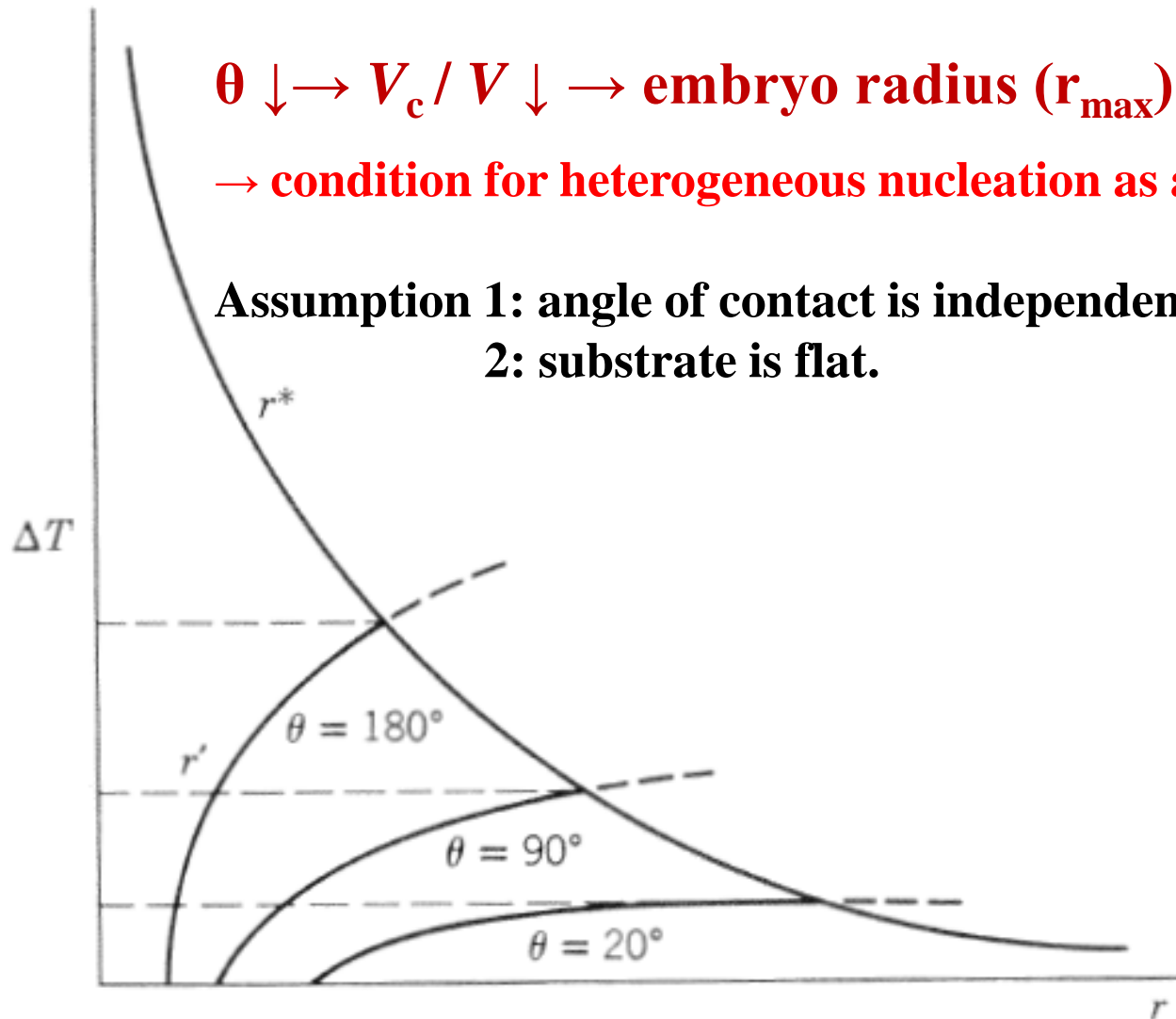
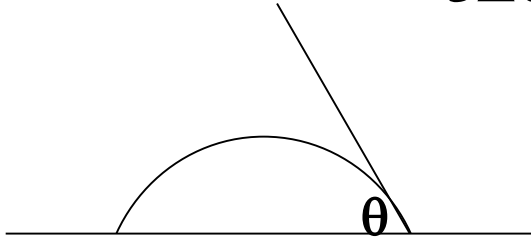


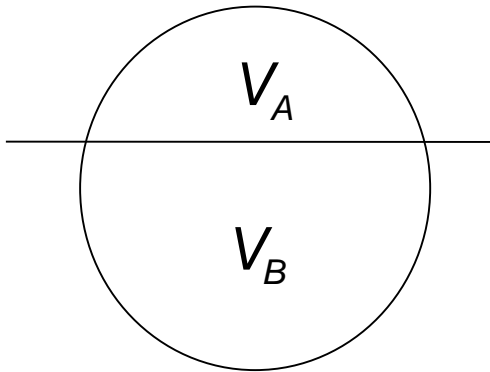
Fig. 3.15. Condition for heterogeneous nucleation (schematic).

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2 - 3\cos\theta + \cos^3\theta)}{4}$$



$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*$$



$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right)$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

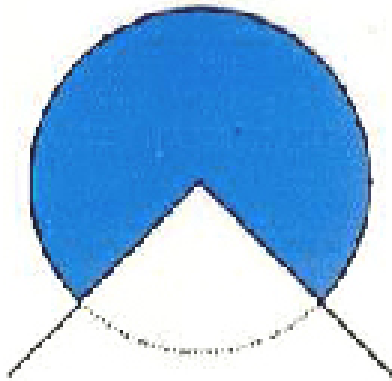
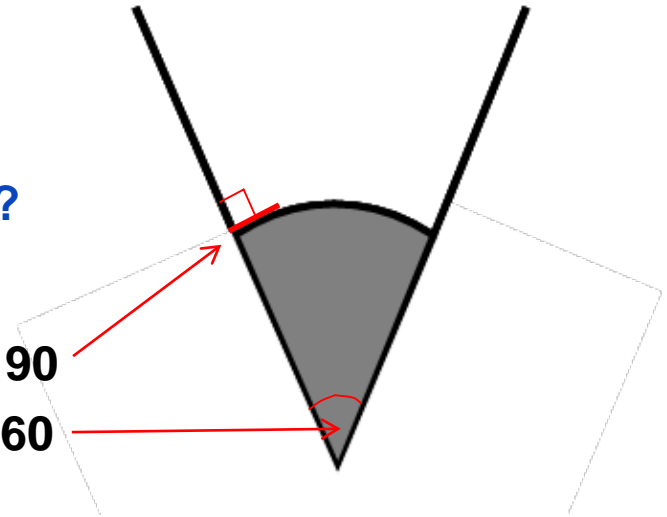
How about the nucleation at the crevice or at the edge?

Nucleation Barrier at the crevice

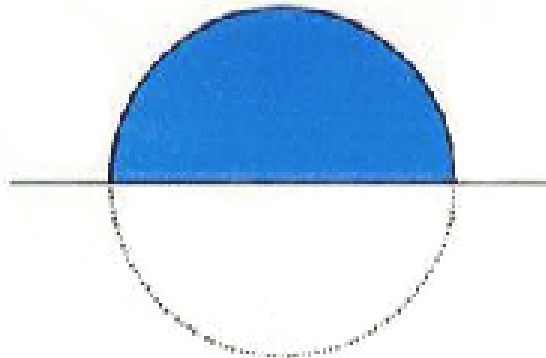
What would be the shape of nucleus and the nucleation barrier for the following conditions?

$$\frac{1}{6} \Delta G_{\text{homo}}^*$$

contact angle = 90
groove angle = 60



$$\frac{3}{4} \Delta G_{\text{homo}}^*$$

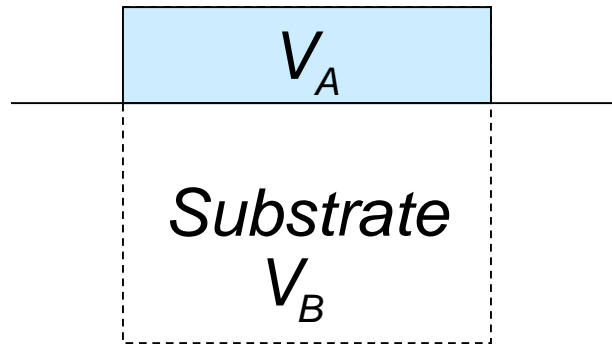


$$\frac{1}{2} \Delta G_{\text{homo}}^*$$

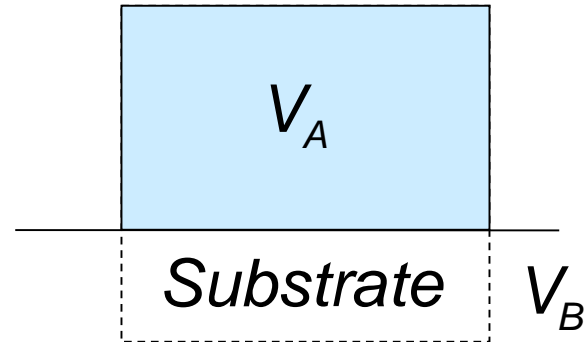


$$\frac{1}{4} \Delta G_{\text{homo}}^*$$

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{V_A}{V_A + V_B} \right)$$

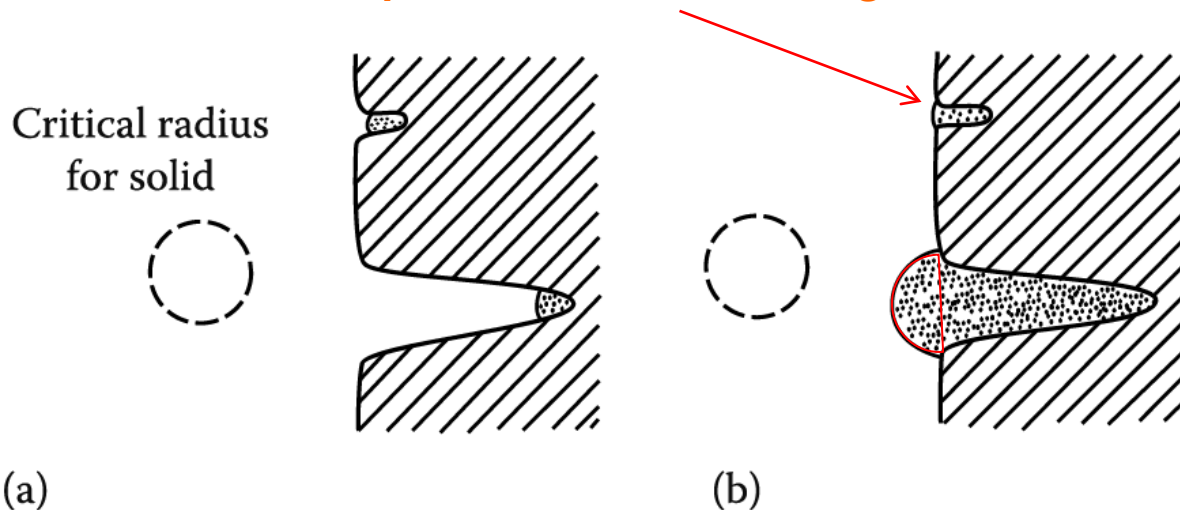
Effect of good and bad wetting on substrate

Extreme form of a concave substrate: **Nucleation inside the crevice**

So far it has been assumed that the mold wall is microscopically flat.

In practice, however, it is likely to contain many microscopic cracks or crevices.

Nucleation from cracks or crevices should be able to occur at very small undercoolings even when the wetting angle θ is relatively large. However, that for the crack to be effective the crack opening must be large enough to allow the solid to grow out without the radius of the solid/liquid interface decreasing below r^* .



In both of the nucleation types considered so far it can be shown that

Formation of a nucleus
on such a surface

$$\Delta G^* = \frac{1}{2} V^* \Delta G_V$$

몰드 표면에서 핵생성 될 때 필요한 에너지

V^* : volume of the critical nucleus (**cap or sphere**)

Inoculants ~ low values of $\theta \rightarrow$ low energy interface, fine grain size

3.7 The Nucleation of Melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Because, melting can apparently, start at crystal surfaces without appreciable superheating.

Why?

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} \quad (\text{commonly})$$

In the case of gold,

γ_{SL}	solid-liquid	132 ergs/cm
γ_{LV}	liquid-vapor	1128 ergs/cm
γ_{SV}	solid-vapor	1400 ergs/cm



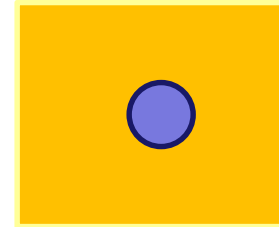
In general, wetting angle = 0 \Rightarrow No superheating required!

Melting and Crystallization are Thermodynamic Transitions

Solidification: **Liquid** \longrightarrow **Solid**

<Thermodynamic>

- Interfacial energy $\Rightarrow \Delta T_N$



Liquid

T_m

Undercooled Liquid

Solid

No superheating required!

- Interfacial energy \Rightarrow No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

Melting: **Liquid** \longleftarrow **Solid**

vapor



Contents for today's class

Solidification: Liquid \longrightarrow Solid

- Nucleation in Pure Metals
- Homogeneous Nucleation

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V}$$

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2}\right) \frac{1}{(\Delta T)^2}$$

r^* & ΔG^* \downarrow as ΔT \uparrow

$$N_{\text{hom}} \approx f_0 C_o \exp\left\{-\frac{A}{(\Delta T)^2}\right\} \sim \frac{1}{\Delta T^2}$$

- Heterogeneous Nucleation

$$\Delta G_{\text{het}}^* = S(\theta) \Delta G_{\text{hom}}^*$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

- Nucleation of melting

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

(commonly)

- Undercooling ΔT
- Interfacial energy γ_{SL} / $S(\theta)$ wetting angle

