2023 Fall

"Phase Transformation *in* Materials"

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Chapter 3 Crystal Interfaces and Microstructure

1) Interfacial Free Energy (vs E_{sv})

2) Solid/Vapor Interfaces

4) Boundaries in Single-Phase Solids

5) Interphase Interfaces in Solid (α/β)

3) Solid/Liquid Interfaces

6) Interface migration

Contents for previous class

3.5 Interphase Interfaces in Solids

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

coherent,
Perfect atomic matching at interface

$$\gamma \text{ (coherent)} = \gamma_{ch}$$ **γ (coherent) ~ 200 mJM^{-2}**

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

semi   D ⇩ → **Strain field overlap**
→ **cancel out**

γ_{st} → **due to structural distortions caused by** <u>the misfit dislocations</u>

γ(semicoherent) ~ 200~500 mJM^{-2}

γ

0.25   **δ 전위간 거리**

δ=4: 1 dislocation per 4 lattices
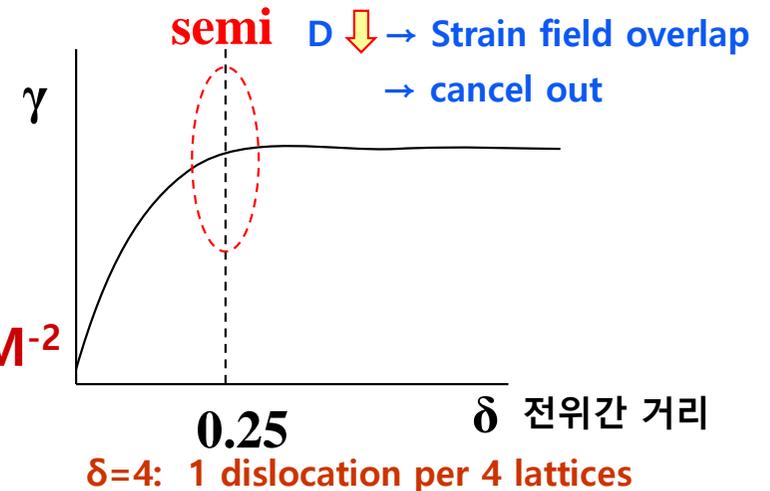
incoherent
1) δ > 0.25 **No possibility of good matching across the interface**

2) different crystal structure (in general)

γ (incoherent) ~ 500~1000 mJM^{-2}

Complex Partial Coherent 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°.)   **3**

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

3.5 Interphase Interfaces in Solids

$$\sum A_i \gamma_i + \Delta G_S = minimum$$

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

Fully coherent precipitates

γ_{ch}

different composition

0.1 μ

γ_{ch} + *Lattice misfit* $\Longrightarrow$ γ_{ch} + Volume Misfit $\Delta = \dfrac{\Delta V}{V}$
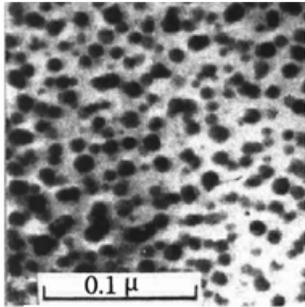
Coherency strain energy

$$\Delta G_S = 4\mu\delta^2 \cdot V \quad \text{(If v=1/3)} \Longleftrightarrow \Delta G_S = \frac{2}{3}\mu\Delta^2 \cdot V \cdot f(c/a)$$

Fully coherent precipitates   **Incoherent inclusions**

Chemical and structural interfacial E

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

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

Incoherent inclusions

"Coherency loss"

ΔG

Coherent   Noncoherent

0

$$r_{crit} = \frac{3 \cdot \gamma_{st}}{4\mu\delta^2}$$

r

r_{crit}

Dislocation

(a) **Coherent with strain E** (b) **Coherency strain replace** (c) **Precipitate**
                                     by dislocation loop.   **with dislocation**

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Contents for today's class

- **Interphase Interfaces in Solid (α/β)**

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

  - **Second-Phase Shape** — **Interface Energy Effects**

    $$\sum A_i \gamma_i + \Delta G_S = minimum$$

    Coherent / Semi-coherent / incoherent

    Misfit Strain Effects

  - **Coherency Loss**

  - **Glissil Interfaces** ⟺ **Non-Glissil Interfaces**

    e.g. Solid/Liquid Interfaces

- **Interface migration**

  - **Interface controlled growth** ⟺ **Diffusion controlled growth**

⟹ **Classification of Heterogeneous** (Nucleation and Growth) **Transformation**   5

Glissil Interfaces ⟺ **Non-Glissil Interfaces**

Q: What is Glissile interface?

Glissile interface → coordinated glide of the interfacial disl. → (α→β) phase transformation

1) Glissile Interfaces (평활 이동 계면)

: epitaxial; Can't move forward or backward

(interface//burgers vector) ⟶ **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.[7]

Fig. 3. 51 The nature of a glissile interface.

Low-Angle tilt Boundaries

Bugers vector = edge dislocation

But, this is not interphase interface.

∵ crystal structure is same,
only lattice rotation

$$D = \frac{b}{\theta}$$
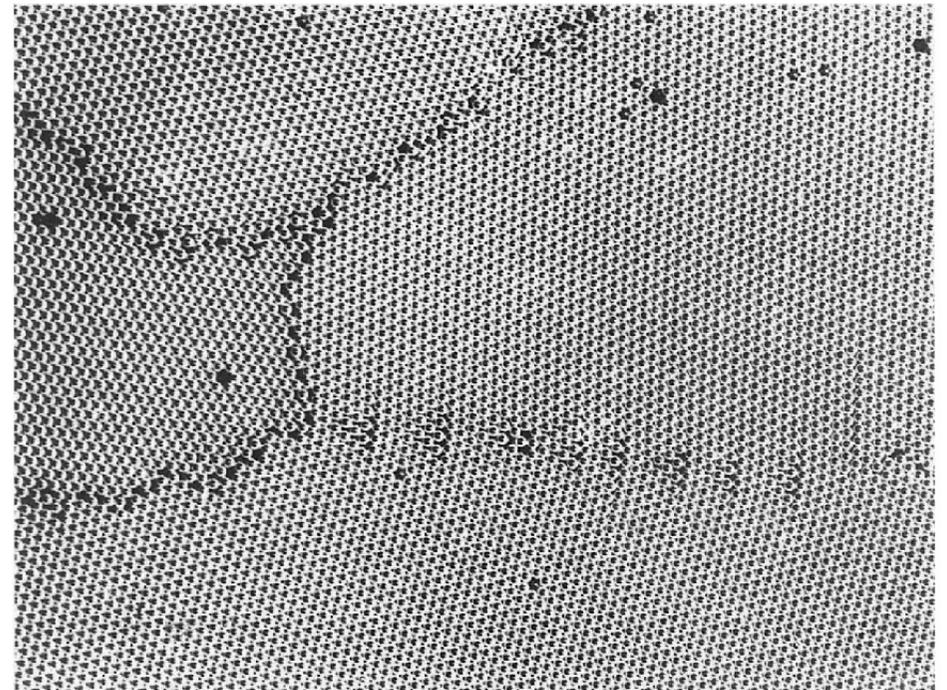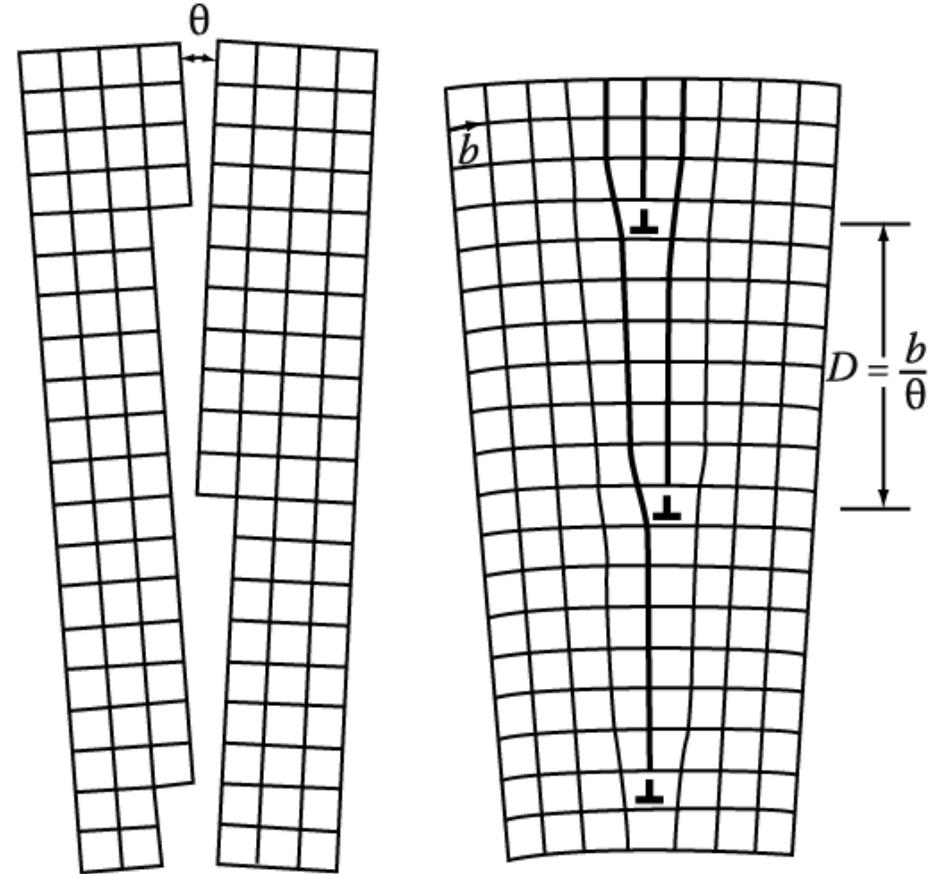
* As disl. glide at low-angle grain boundary
: no change in crystal structure,
  just rotation of the lattice into the other grain

Glissile Interfaces between two lattices

Shockley partial dislocation

HCP: ABABABAB…

close packed plane: (0001)

close packed directions: $<11\bar{2}0>$
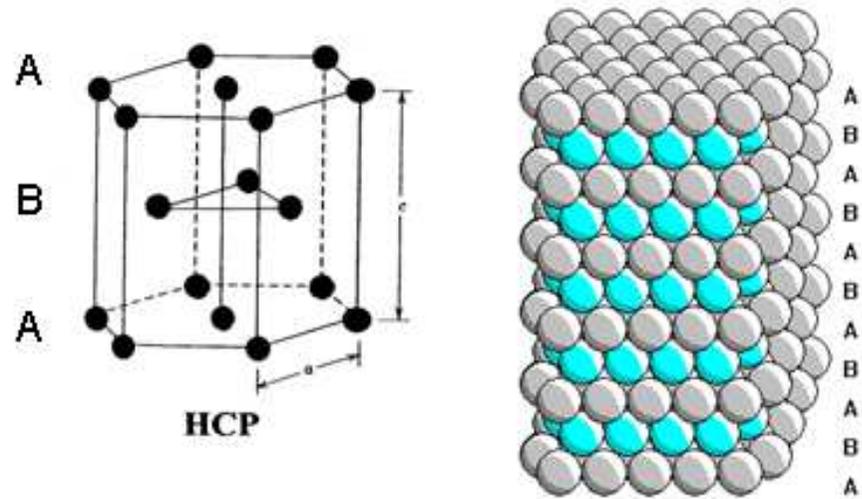
FCC: ABCABCAB…

close packed planes: {111}

close packed directions: $<110>$

HCP

FCC
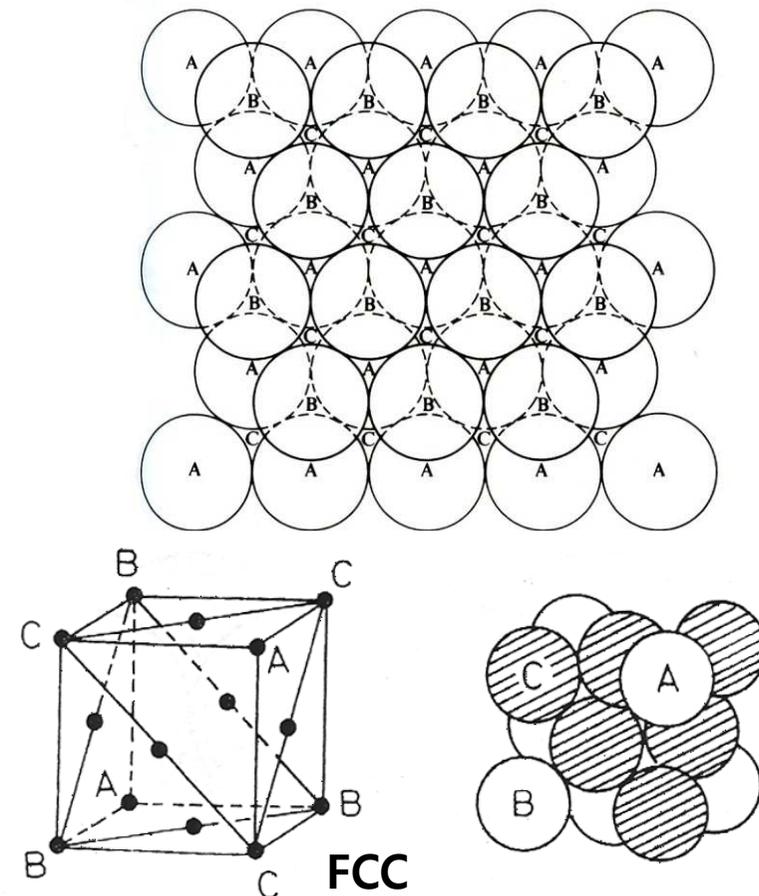
1) Perfect dislocation

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

In C layer, atoms move
   C' → C''

: remain a cubic close-packed arrangement with a fcc unit cell

< FCC → FCC >
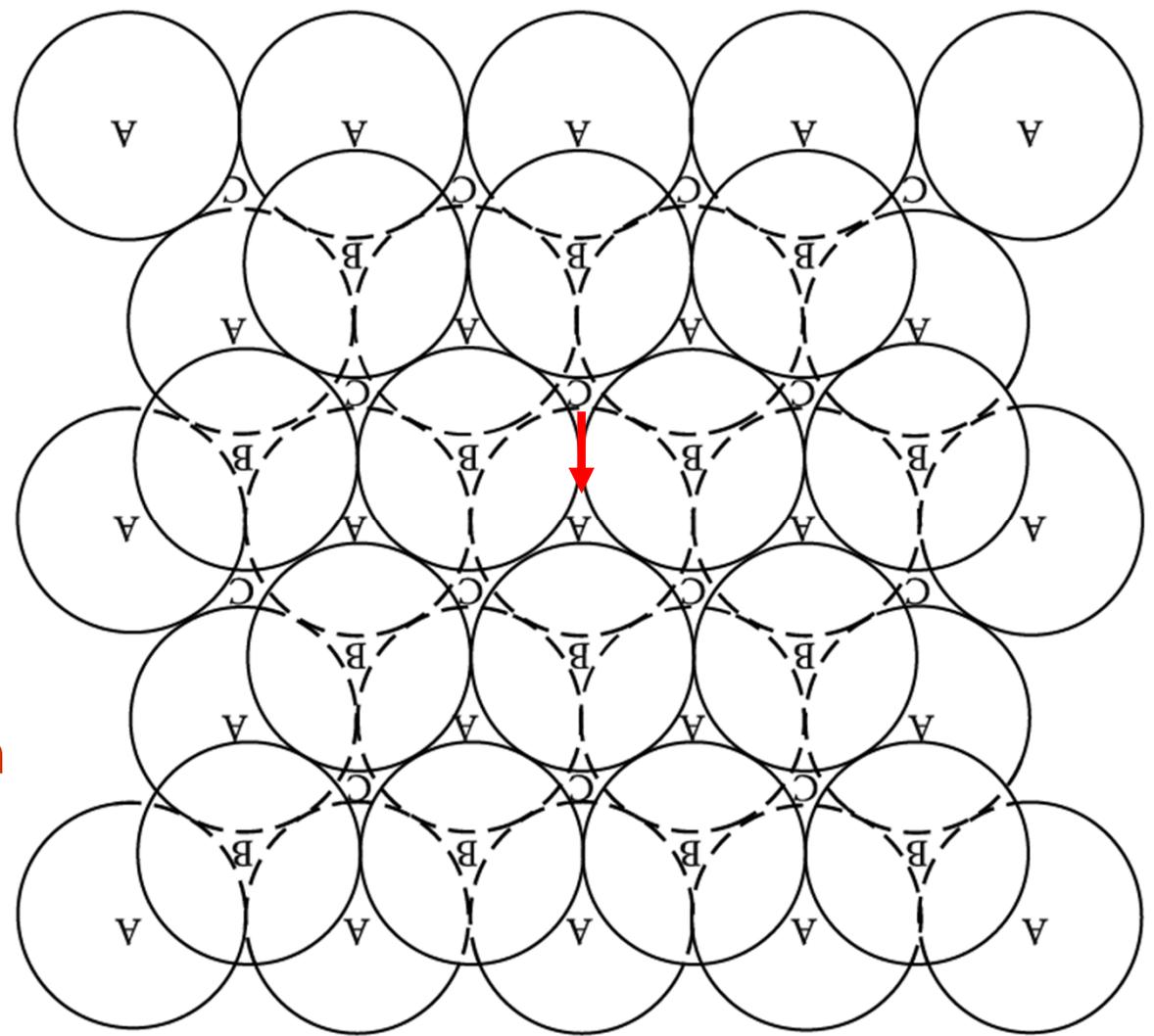
2) Shockley partial dislocation

when atoms move: C' → C''
possible to move C' → A → 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)

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

$$\frac{a}{6}[11\bar{2}]$$

$$\frac{a}{6}[2\bar{1}\bar{1}]$$

C'

A

C''

10
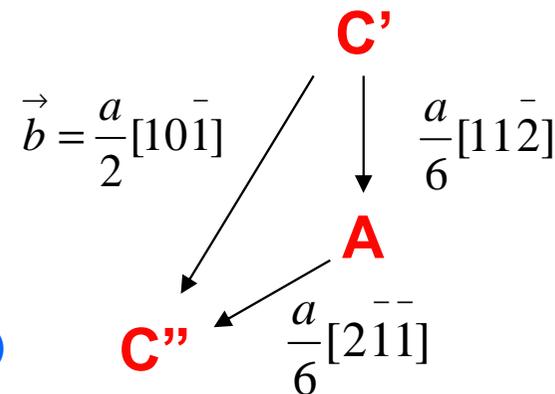
< FCC → HCP: phase transformation by stacking fault over the area of glide plane swept by the disl.>

Gliding of Shockley partial dislocations ➡ Stacking fault region
적층결함

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

$b = \frac{a}{6}[11\bar{2}]$

Slip plane (111)

(a)

Dislocation sliding

FCC

7	A	B
6	C	A
5	B	C
4	A	A
3	C	C
2	B	B
1	A	A

hcp
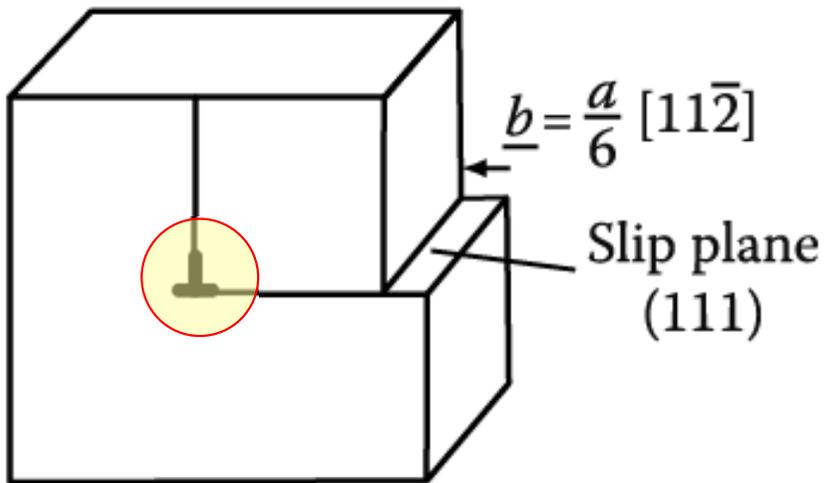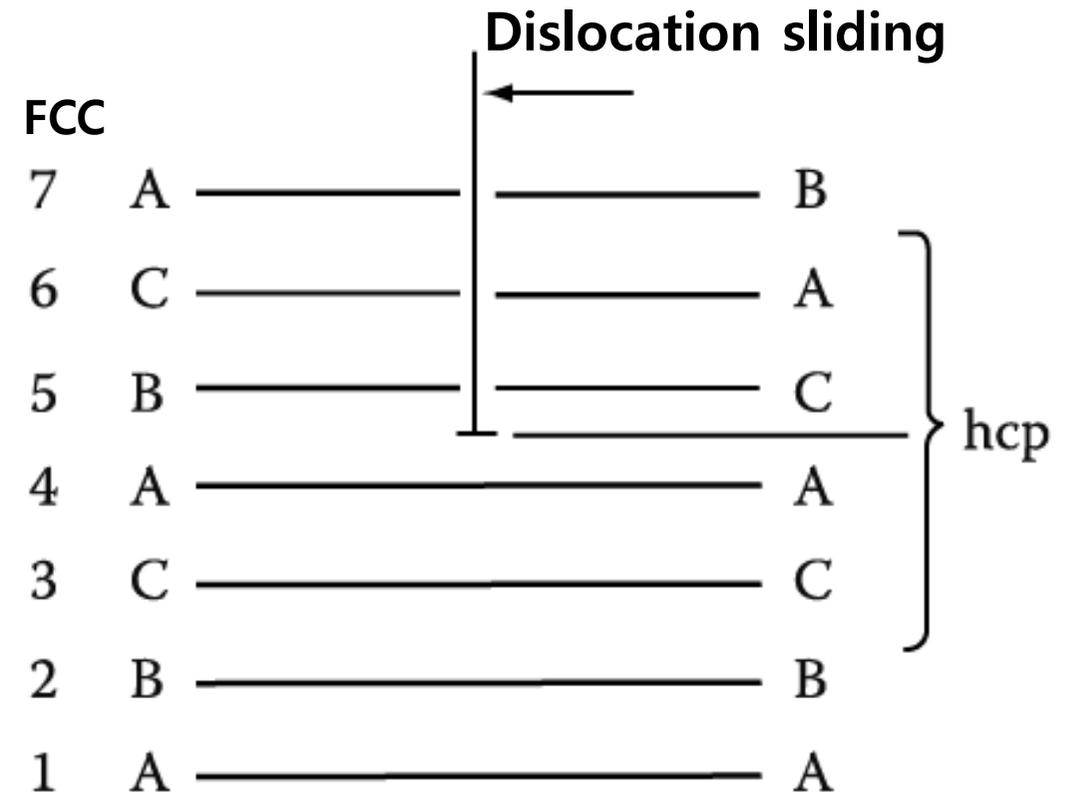
(b)

Fig. 3. 52 (a) An edge dislocation with a Burgers vector b $=\frac{a}{6}$[112] on (11$\bar{1}$). (shockley partial dislocation.)
(b) The same dislocation locally changes the stacking sequence from fcc to hcp.

If FCC lattice is <u>only metastable with respect to the HCP structure</u> → stacking fault E ~ effectively

negative → gliding of partial dislocation: easy due to decrease the free energy of system
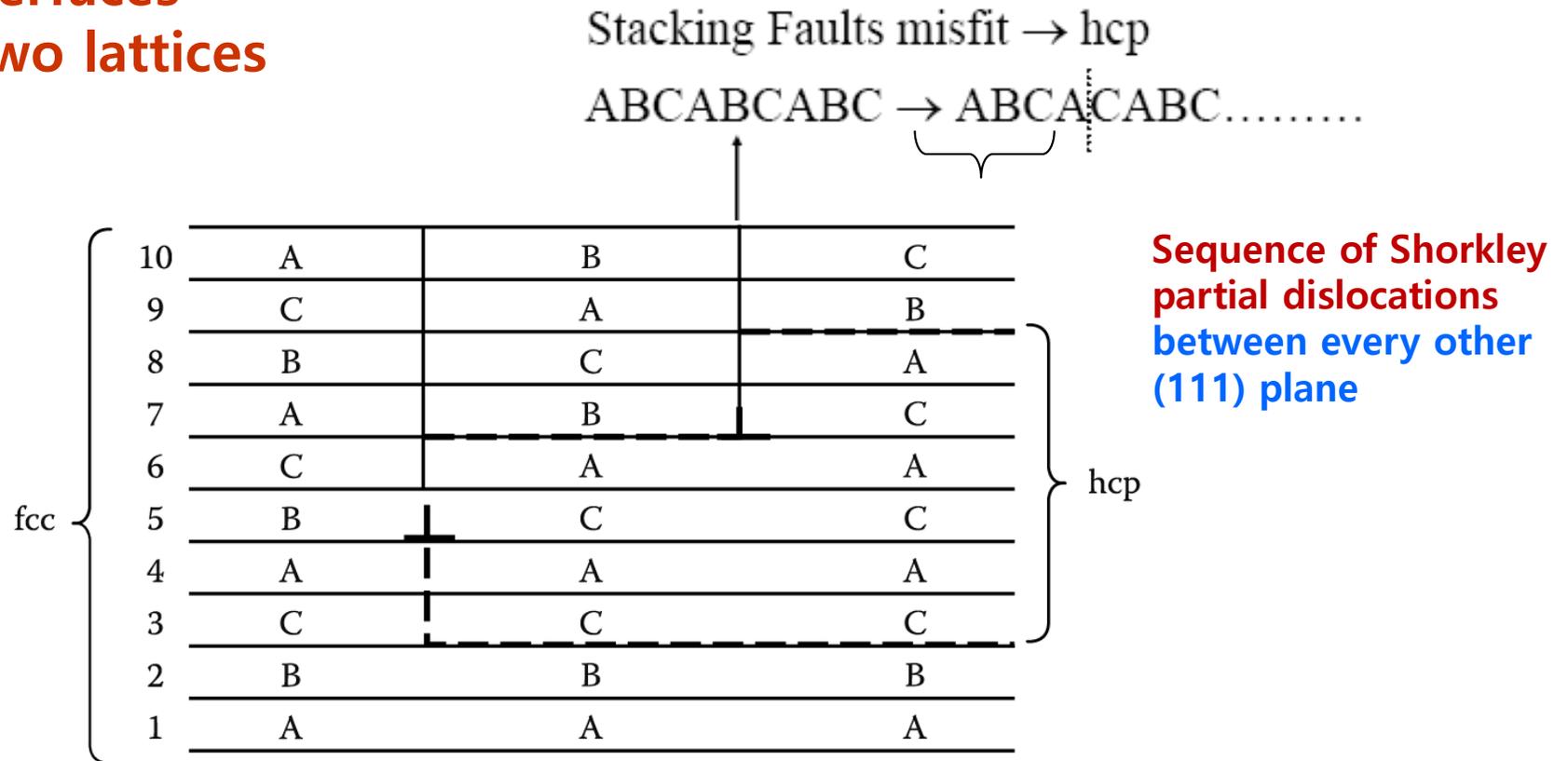
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Glissile Interfaces between two lattices

Stacking Faults misfit → hcp

ABCABCABC → ABCACABC..........

10	A	B	C
9	C	A	B
8	B	C	A
7	A	B	C
6	C	A	A
5	B	C	C
4	A	A	A
3	C	C	C
2	B	B	B
1	A	A	A

fcc

hcp

Sequence of Shorkley partial dislocations between every other (111) plane

Fig. 3. 53 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

FCC {111} plane

Macroscopic interface plane

fcc

hcp

HCP (0001) plane

Fig. 3.54 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

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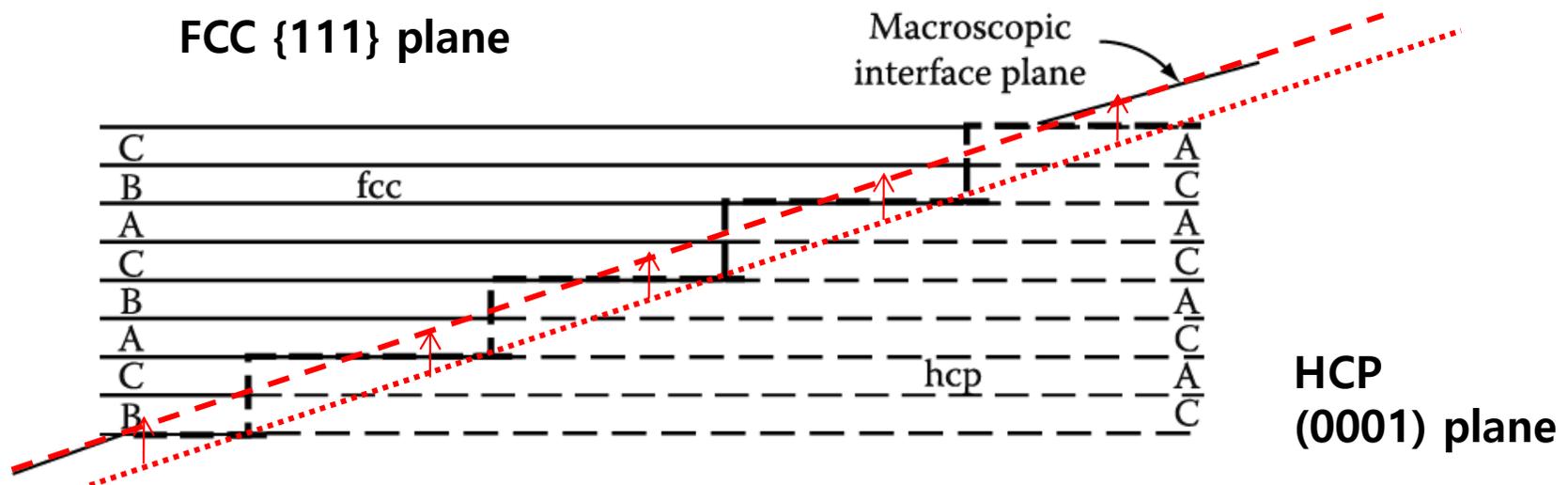
An important characteristic of glissile dislocation interfaces
  → they can produce a macroscopic shape change in the crystal.

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

  → Pure shear deformation
  → Fcc → Hcp
  → shape change

(a)   fcc   →   hcp

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

C'

$$\vec{b} = \frac{a}{2}[10\bar{1}]$$ $$\frac{a}{6}[11\bar{2}]$$

A

C" $$\frac{a}{6}[2\bar{1}\bar{1}]$$
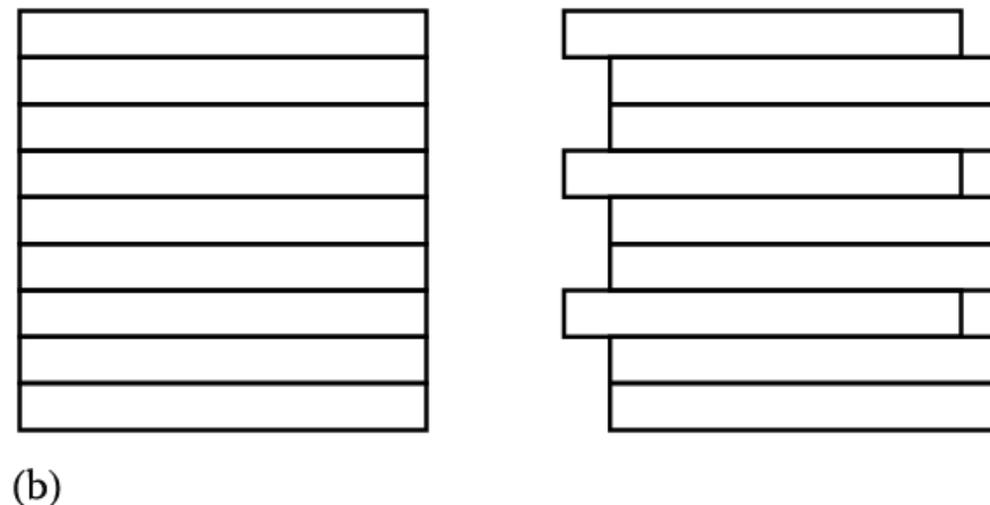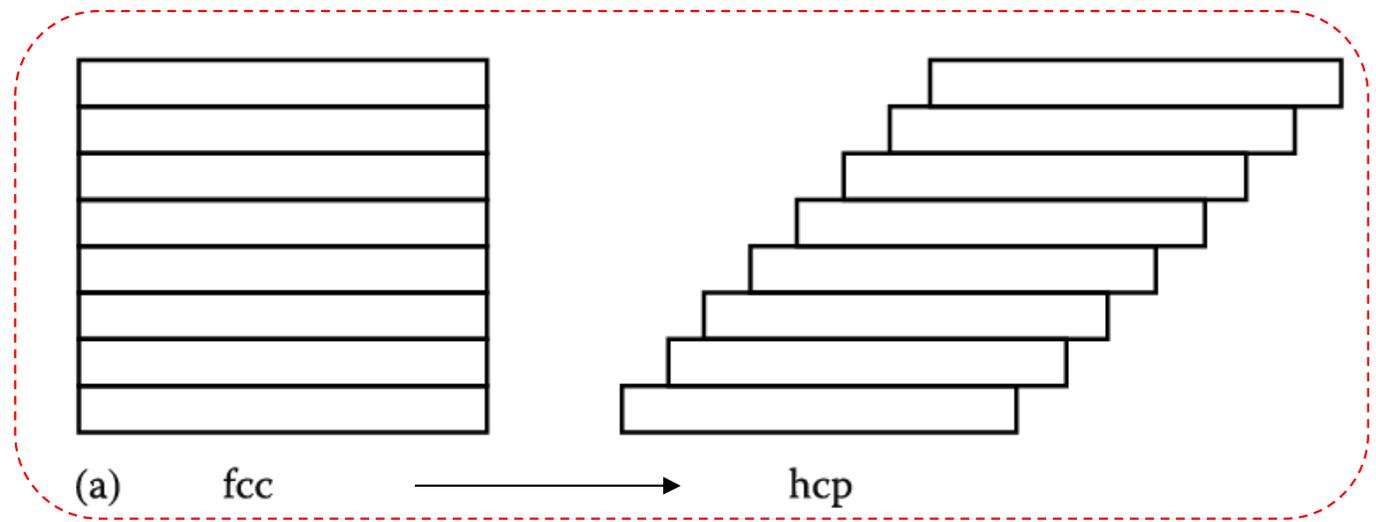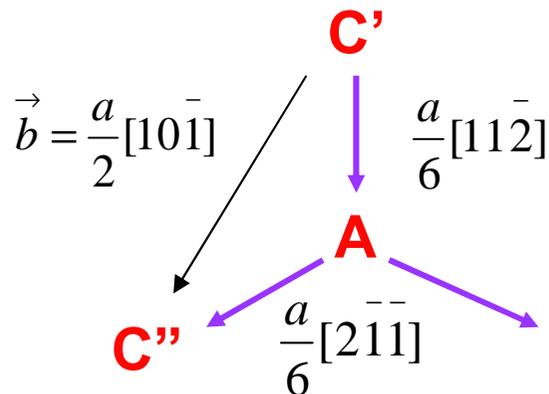
→ No overall shape change

(b)

Fig. 3. 55 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   **13**
  → 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
- <u>most of transformation product</u> 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** ⟶ **Military transformation**
  Dislocation gliding

- **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 Soldification 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)

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Table 3.3 Classification of Nucleation and Growth Transformation

Type	Civilian (Diffusional)				Diffusional-Displacive	Military (Displacive)
Effect of Temperature	Thermally activated				Thermally activated	Athermal
Interface type	Non-glissile				Glissile or ledge	Glissile
	(coherent, partly coherent, incoherent, solid/liquid or solid/vapor)				(coherent or partly coherent)	(coherent or partly coherent)
Composition of parent and product phases	Same	Different			Different	Same
Nature of diffusion processes	Short-range (across interface)	Long-range (through lattice)			Long-range	No diffusion
Interface, diffusion or mixed control?	Interface control	Mainly interface control	Mainly diffusion control	Mixed control	Mainly diffusion control	Interface control
Example	Massive Ordering Polymorphic Recrystallization Grain growth Condensation Evaporation	Precipitation Dissolution Condensation Evaporation	Precipitation Dissolution Solidification Melting	Precipitation Dissolution Eutectoid Cellular Precipitation	Bainite γ' (Ag2Al) pptn.	Martensite (Twining, Symmetric, tilt boundary, migration)

Source: Modification of classification given in J.W. Christian, 'Phase transformations in metals and alloys-an introduction', in phase transformation, Vol. 1, p.1, Institute of Metallurgists, 1979.

3.5. Interface Migration

* Civilian Transformation

1) Interface control

Same composition between parent and product
(Ex. α→γ transformation in pure iron)

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

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

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Fig. 3. 56 Composition changes in a substitutional alloy caused by interface migration when the two adjoining phases have different compositions.

3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.57 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

(a)

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

(c)

1) Initial composition of A-rich α phase X_0

2) Concentration B in the α phase adjacent to the inteface 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.

Total Free Energy Decrease per Mole of Nuclei ΔG_0

: Driving force for phase transformation of system

Driving Force for Precipitate Nucleation $\boxed{\alpha \to \alpha + \beta}$ ΔG_V

$$\Delta G_1 = \mu_A^\alpha X_A^\beta + \mu_B^\alpha X_B^\beta$$

: **Decrease of total free E of system**
 by removing a small amount of material
 with the nucleus composition (X_B^β) (P point)

$$\Delta G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta$$

: **Increase of total free E of system**
 by forming β phase with composition X_B^β
 (Q point)

$$\Delta G_n = \Delta G_2 - \Delta G_1 \quad \text{(length PQ)}$$

$$\boxed{\Delta G_V} = \frac{\Delta G_n}{V_m} \quad per\ unit\ volume\ of\ \beta$$

: **driving force for β precipitation**

For dilute solutions,

$$\Delta G_V \propto \Delta X \quad where\ \Delta X = X_0 - X_e$$

$$\Delta G_V \propto \Delta X \propto \left(\Delta T\right)$$

∝undercooling below T_e

(a) Plot: axes T_1, T_e, ΔT, T_2, ΔX, regions α, α + β, β; points X_e, X_0, X_B, X^β, A, B

(b) Plot: G vs X_B; @T_2; G^α, G^β, G_r^β; dX_A; μ_A^β, μ_A^a, μ_B^α, μ_B^β; ΔG_0, ΔG_n; points P, Q

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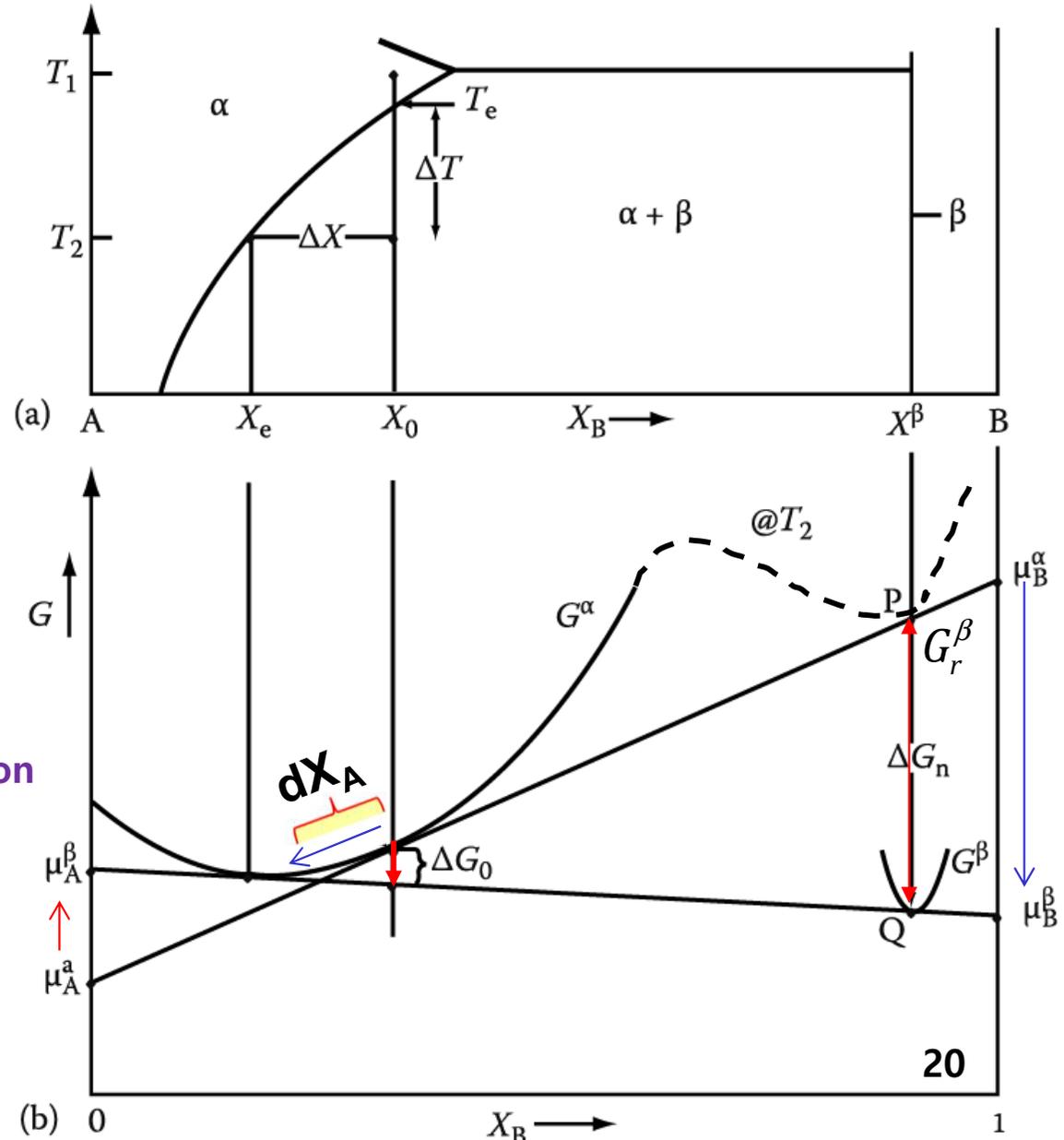
3.5.1. Diffusion-Controlled and Interface-Controlled Growth

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

(a)

(b)

(c)

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

A net flux of B atoms
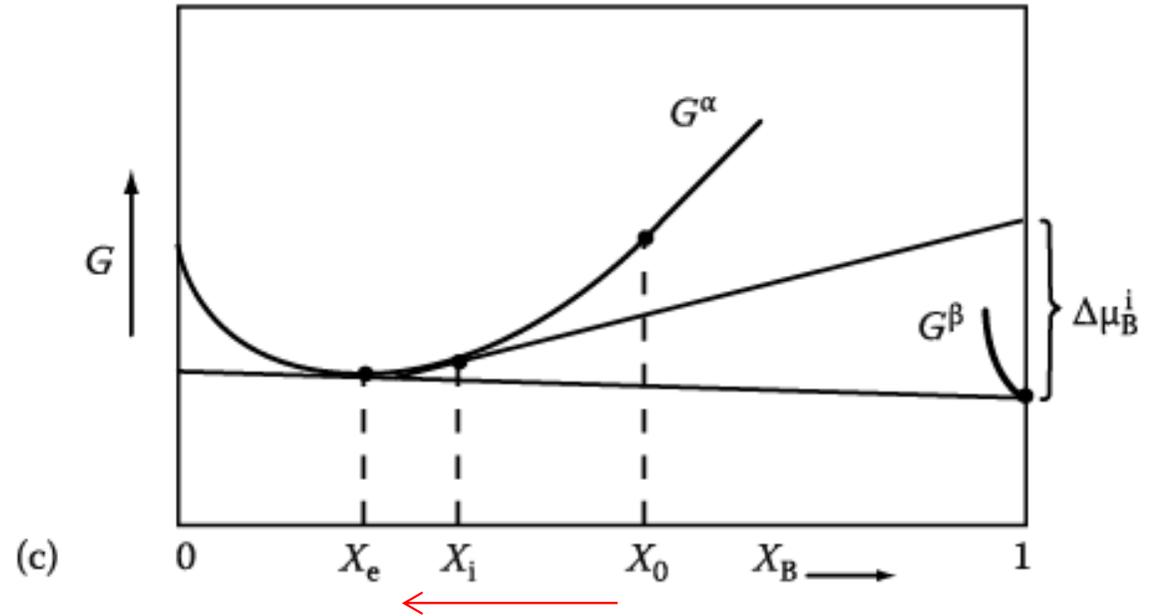
1) Initial composition of A-rich α phase X_0

2) Concentration B in the α phase adjacent to the inteface 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.

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)

  β ⟵ α

  $$J_B^i = -C_B^i v_B$$

  $$= -\frac{1}{V_m}(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m})$$

  $$= J_B^\alpha = -D(\frac{\partial C_B}{\partial X})_{\text{interface}}$$

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

  Steady state at interface,

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

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  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)

$$\boxed{J_B^i} = -C_B^i v_B$$

$$= -\frac{1}{V_m}\left(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}\right)$$

$$= \boxed{J_B^\alpha} = -D\left(\frac{\partial C_B}{\partial X}\right)_{\text{interface}}$$

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

Steady state at interface,

$$\boxed{J_B^i = J_B^\alpha}$$

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: $Xi \approx X_o$, $\left(\dfrac{\partial C}{\partial X}\right)_{\text{intrface}} \approx 0$; Interface-Control

$\Delta\mu_B{}^i$ 는 최대

G

G^{α}

G^{β}

$\Delta\mu_B^i$
$\sim max$

$\Delta\mu_B^i$

$\Delta\mu_B^i \sim 0$

$0 \qquad X_e \quad X_i \qquad X_0 \qquad X_B \longrightarrow \qquad 1$

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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)

○ Al   ● Cu
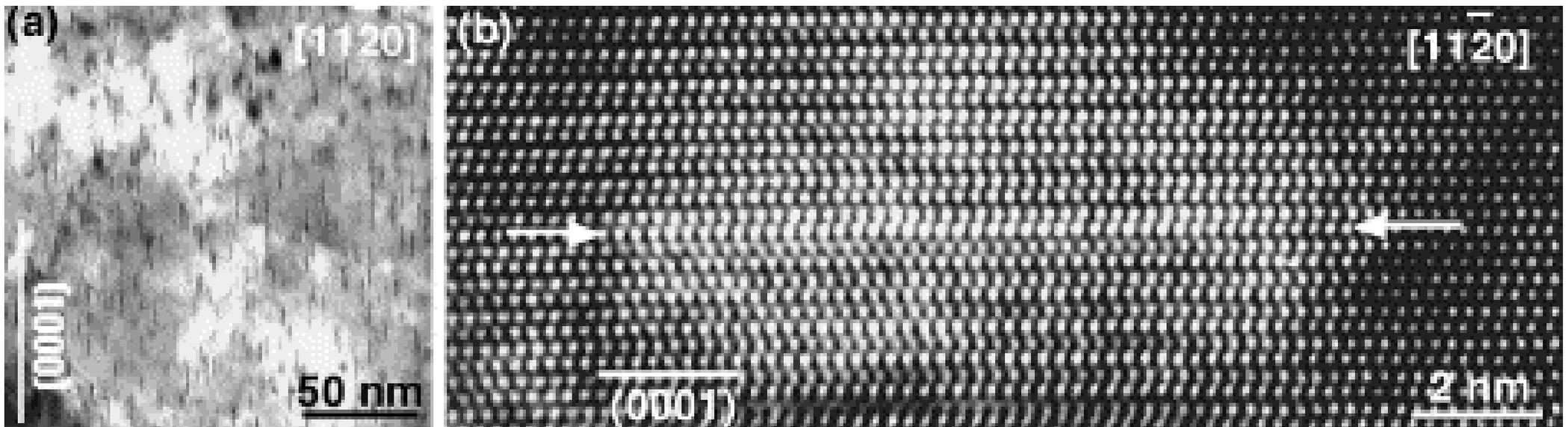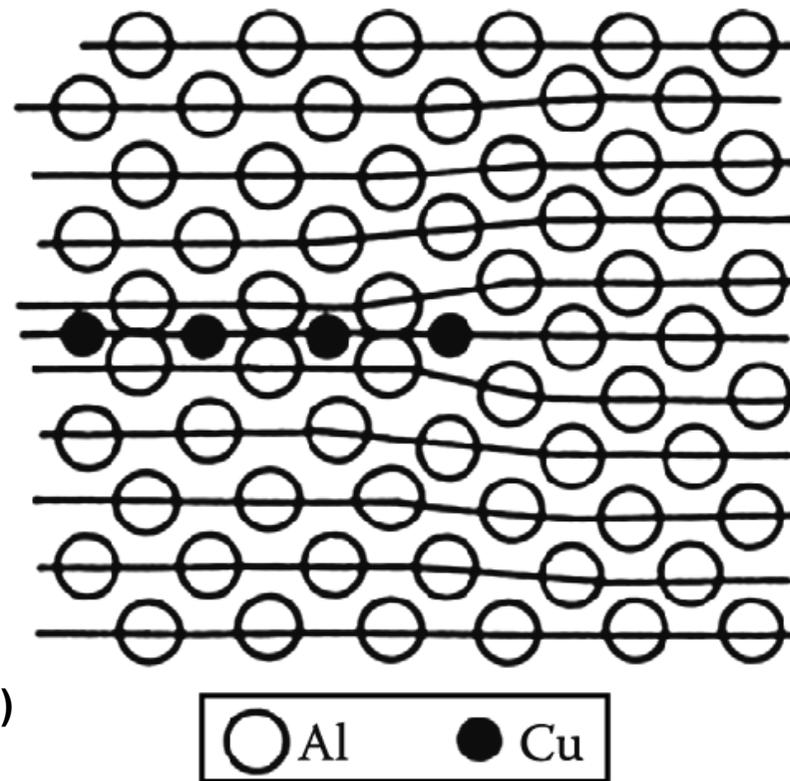
(a) Bright-field TEM image showing G.P. zones, and (b) HRTEM image of a G.P. zone formed on a single $(0\,0\,0\,1)_\alpha$ plane. Electron beam is parallel to in both (a) and (b).

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 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"**

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Ex) Interface control

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

```
        A     A     A     A     A     A

 fcc    B     B     B     B     B     B

 Coherent close-packed interface   C    C    C    C    B    C      A loop of Shorkley partial disl.
 between fcc and hcp crystals      _____    ~ high E/ unstable configuration
        A     A     A     A     A     A       → force back to its original position

 hcp    B     B     B     B     B     B

        A     A     A     A     A     A

       (a)                        (b)
```
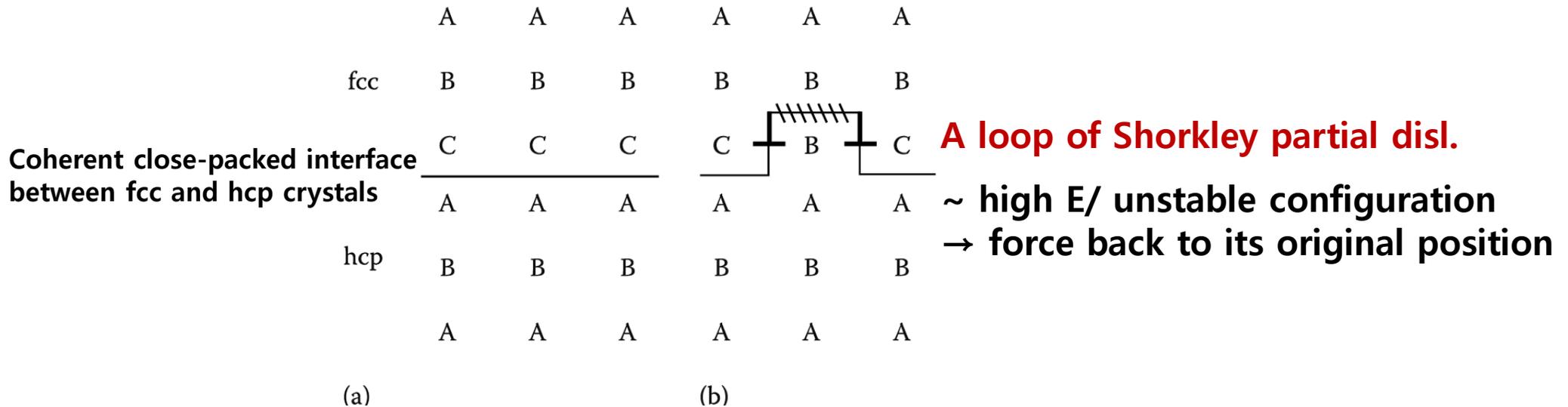
Fig. 3. 58 Problems associated with the continuous growth of coherent interfaces between phases with different crystal structures.

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**

Nucleating new ledges: Interface control
- heterogeneous nucleation

Growth direction: diffusion control

"Growth by ledge mechanism"

**Facets: AB, CD, EF
Ledge: BC, DE**
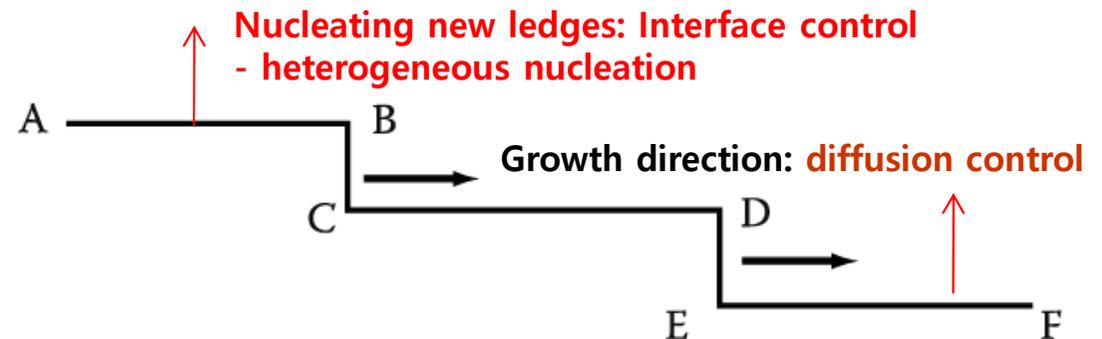
Fig. 3. 59 The ledge mechanism.

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

Fig. 3. 60 (a) Growth ledges at an Mg$_2$Si plate in Al-1.5 wt% Mg$_2$Si, solution treated and aged 2h at 350 ℃. Dark field micrograph.

(b) Schematic diagram of (a) showing ledges on Mg$_2$Si plate.

(a)
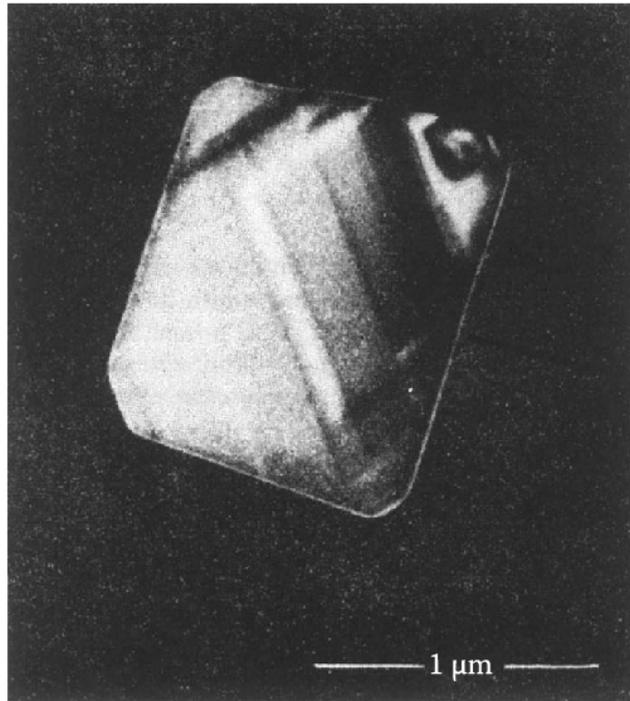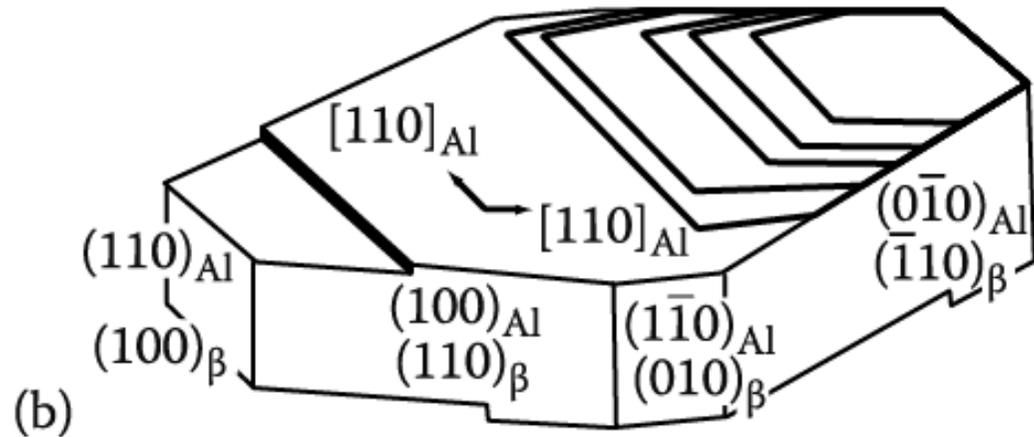
Note that growth ledges are usually hundreds of atoms layers high.
성장 돌출맥의 층 두께는 보통 수백 원자층 두께

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** γi / γc
  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** **Interface Energy Effects**

    $$\sum A_i \gamma_i + \Delta G_s = minimum$$

    Coherent / Semi-coherent / incoherent

    Misfit Strain Effects

  - **Coherency Loss**

  - **Glissil Interfaces** ⟺ **Non-Glissil Interfaces**

    e.g. Solid/Liquid Interfaces

- **Interface migration**

  - **Interface controlled growth** ⟺ **Diffusion controlled growth**

⟹ **Classification of Heterogeneous** (Nucleation and Growth) **Transformation**   30

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 Soldification 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)

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Chapter 3 Crystal Interfaces and Microstructure

1) **Interfacial Free Energy (vs E_{sv})**

2) **Solid/Vapor Interfaces**

4) **Boundaries in Single-Phase Solids**

5) **Interphase Interfaces in Solid (α/β)**

3) Solid/Liquid Interfaces

6) **Interface migration**

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 → Solid

(Ch5) Diffusional Transformations in Solid: Solid → Solid

(Ch6) Diffusionless Transformations: Solid → Solid

* Homework 3 : Exercises 3 (pages 193-196)

until 30th October

* Mid-term?

Good Luck!!

"Phase Transformation *in* Materials"

10.25.2023

Eun Soo Park

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Office hours: by an appointment

Chapter 3 Crystal Interfaces and Microstructure

1) Interfacial Free Energy (vs E_{sv})

2) Solid/Vapor Interfaces

4) Boundaries in Single-Phase Solids

5) Interphase Interfaces in Solid (α/β)

3) Solid/Liquid Interfaces

6) Interface migration

Contents for today's class

- **Interphase Interfaces in Solid (α/β)**

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

  - **Second-Phase Shape** ⎰ **Interface Energy Effects**

    $$\sum A_i \gamma_i + \Delta G_s = minimum$$

    Coherent / Semi-coherent / incoherent

    Misfit Strain Effects

  - **Coherency Loss**

  - **Glissil Interfaces** ⟺ **Non-Glissil Interfaces**

    e.g. Solid/Liquid Interfaces

- **Interface migration**

  - **Interface controlled growth** ⟺ **Diffusion controlled growth**

⟹ **Classification of Heterogeneous** (Nucleation and Growth) **Transformation**   3

Coherency Loss

{ Precipitates with coherent interfaces=low interfacial E + coherency strain E
Precipitates with non-coherent interfaces=higher interfacial E }

If a coherent precipitate grows, it should lose coherency to maintain minimum interfacial free E.

$$\Delta G(coherent) = 4\mu\delta^2 \cdot \frac{4}{3}\pi r^3 + 4\pi r^2 \cdot \gamma_{ch} \Longleftrightarrow \Delta G(non-coherent) = 4\pi r^2 \cdot (\gamma_{ch} + \gamma_{st})$$
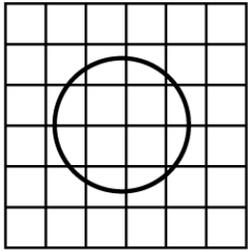
Coherency strain energy Eq. 3.39   **Chemical interfacial E**   **Chemical and structural interfacial E**
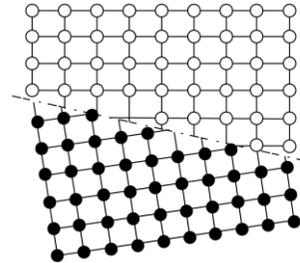
$$\frac{4}{3}\pi r^3 \left(4\pi\mu\delta^2\right) + 4\pi r^2 \left(\gamma_{ch}\right) = 4\pi r^2 \left(\gamma_{st} + \gamma_{ch}\right)$$

coherent ΔG_s-relaxed

$$\therefore r_{crit} = \frac{3 \cdot \gamma_{st}}{4\mu\delta^2}$$

$$for\ small\ \delta,\quad \gamma_{st} \propto \delta$$

(semi-coherent interface)

$$\approx \frac{1}{\delta} \quad (\delta = (d_\beta - d_\alpha)/d_\alpha : \mathbf{misfit})$$
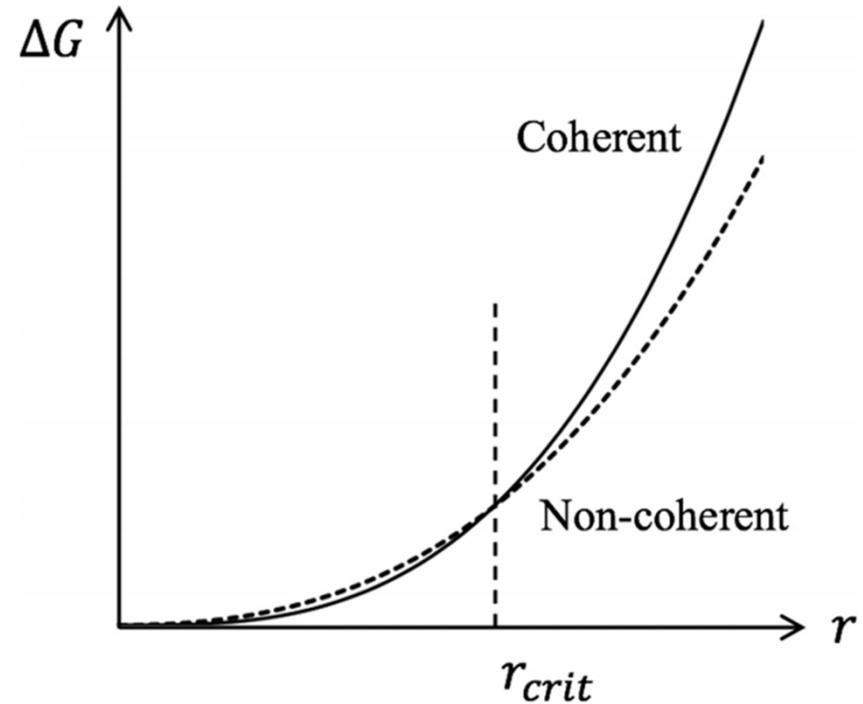
Fig. 3. 71 The total energy of matrix + precipitate vs. precipitate radius for spherical coherent and <u>non-coherent (semicoherent of incoherent)</u> precipitates.
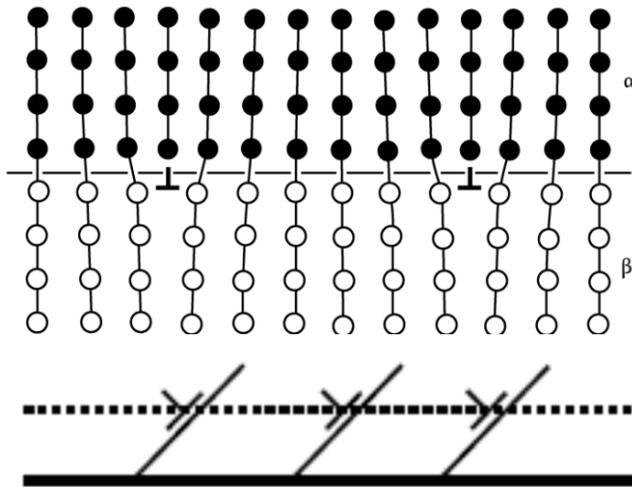
1) Glissile Interfaces (평활 이동 계면)

: epitaxial; Can't move forward or backward

(interface//burgers vector) ⟶ 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.

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

Glissile Interfaces between two lattices
→ Military Transformation

Stacking Faults misfit → hcp

ABCABCABC → ABCACABC..........

Sequence of Shorkley partial dislocations between every other (111) plane

10	A	B	C
9	C	A	B
8	B	C	A
7	A	B	C
6	C	A	A
5	B	C	C
4	A	A	A
3	C	C	C
2	B	B	B
1	A	A	A

fcc

hcp

Fig. 3. 53 Two Shockley partial dislocation on alternate (111) planes create six layers of hcp stacking.

FCC {111} plane

Macroscopic interface plane

fcc

C
B
A
C
B
A
C
B

hcp

A
C
A
C
A
C
A
C

HCP (0001) plane

Fig. 3.54 An array of Shockley partial dislocations forming a glissile interface between fcc and hcp crystals.

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3.5.6. Interface Migration

* Civilian Transformation

1) Interface control

Same composition between parent and product
(Ex. α→γ transformation in pure iron)

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

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

Fig. 3. 56 Composition changes in a substitutional alloy caused by interface migration when the two adjoining phases have different compositions.

3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.57 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

(a)

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

A net flux of B atoms

(c)

1) Initial composition of A-rich α phase X_0

2) Concentration B in the α phase adjacent to the inteface 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.

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

$$J_B^i = -C_B^i v_B$$

$$= -\frac{1}{V_m}\left(M \cdot \Delta\mu_B^i \cdot \frac{1}{V_m}\right)$$

$$= J_B^\alpha = -D\left(\frac{\partial C_B}{\partial X}\right)_{\text{interface}}$$

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

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

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: $Xi \approx X_o$, $\left(\frac{\partial C}{\partial X}\right)_{\text{intrface}} \approx 0$, Interface-Control

$\Delta\mu_B{}^i$ 는 최대

Accommodation factor (A_수용인자)
Probability that an atom crossing the boundary will accommodated on arrival at the new phase

Phase transformation = Interface creation & Migration

Heterogeneous (No nucleation barrier, Growth-interface control) **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)		
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Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Soldification 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)

Table 3.3 Classification of Nucleation and Growth Transformation

Type	Civilian (Diffusional)				Diffusional-Displacive	Military (Displacive)
Effect of Temperature	Thermally activated				Thermally activated	Athermal
Interface type	Non-glissile				Glissile or ledge	Glissile
	(coherent, partly coherent, incoherent, solid/liquid or solid/vapor)				(coherent or partly coherent)	(coherent or partly coherent)
Composition of parent and product phases	Same	Different			Different	Same
Nature of diffusion processes	Short-range (across interface)	Long-range (through lattice)			Long-range	No diffusion
Interface, diffusion or mixed control?	Interface control	Mainly interface control	Mainly diffusion control	Mixed control	Mainly diffusion control	Interface control
Example	Massive Ordering Polymorphic Recrystallization Grain growth Condensation Evaporation	Precipitation Dissolution Condensation Evaporation	Precipitation Dissolution Solidification Melting	Precipitation Dissolution Eutectoid Cellular Precipitation	Bainite γ' (Ag2Al) pptn.	Martensite (Twining, Symmetric, tilt boundary, migration)

Source: Modification of classification given in J.W. Christian, 'Phase transformations in metals and alloys-an introduction', in phase transformation, Vol. 1, p.1, Institute of Metallurgists, 1979.

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 ⟶ Solid

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

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Solidification: Liquid → Solid
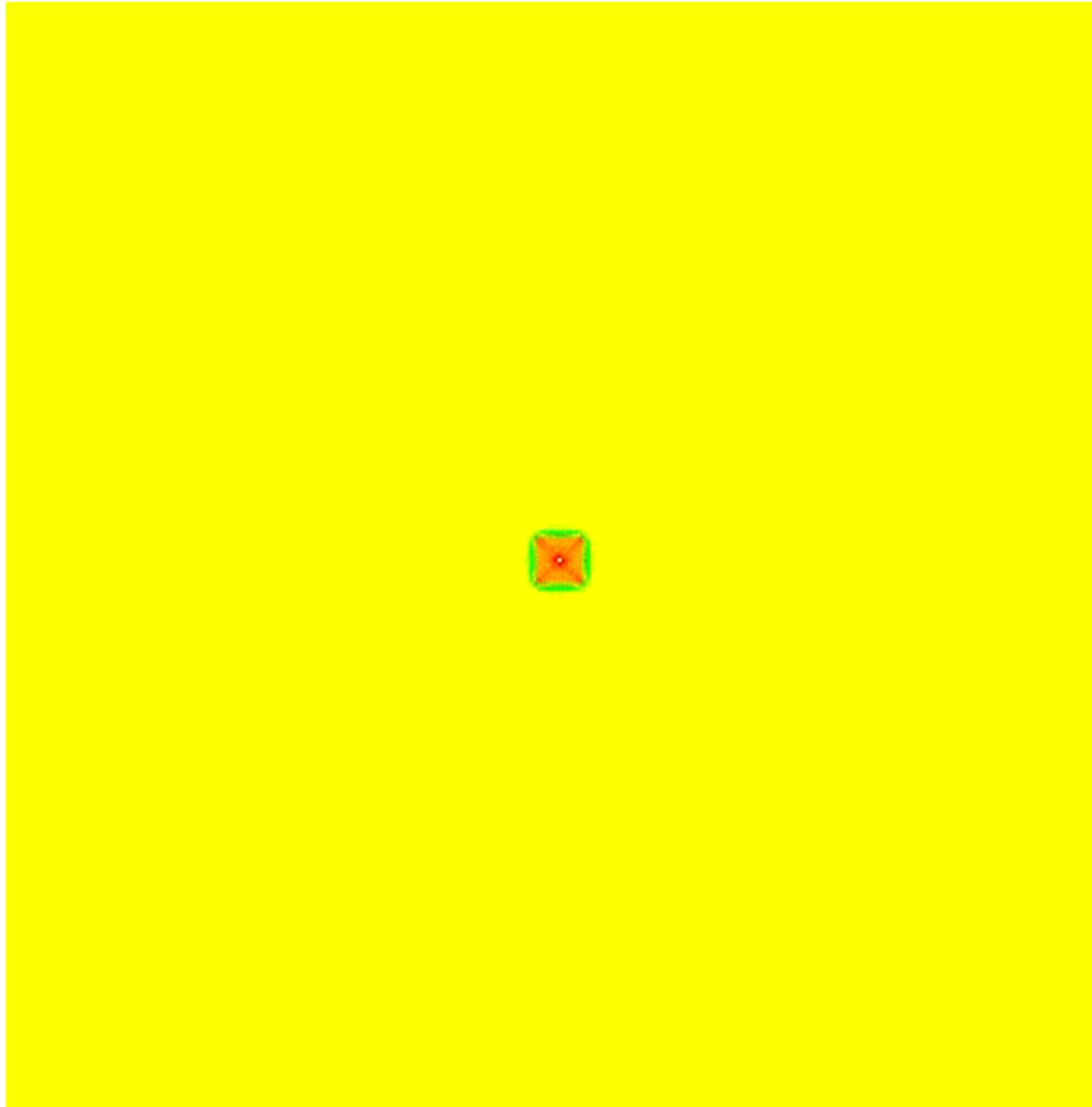
4 Fold Symmetric Dendrite Array

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 of sharply defined interface

- Heat Flow and Interface Stability

Q: Undercooling of homogenous vs heterogenous nucleation ?

Solidification: Liquid $\longrightarrow$ Solid

- casting & welding/<u>additive manufacturing</u>
- 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
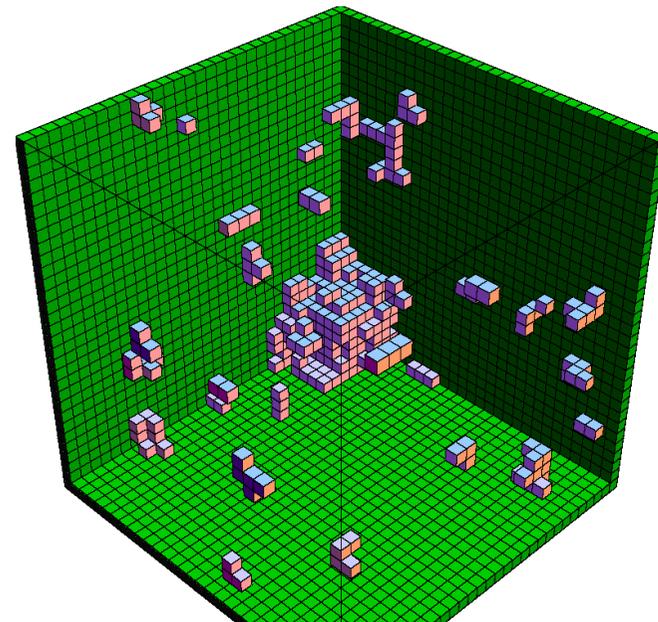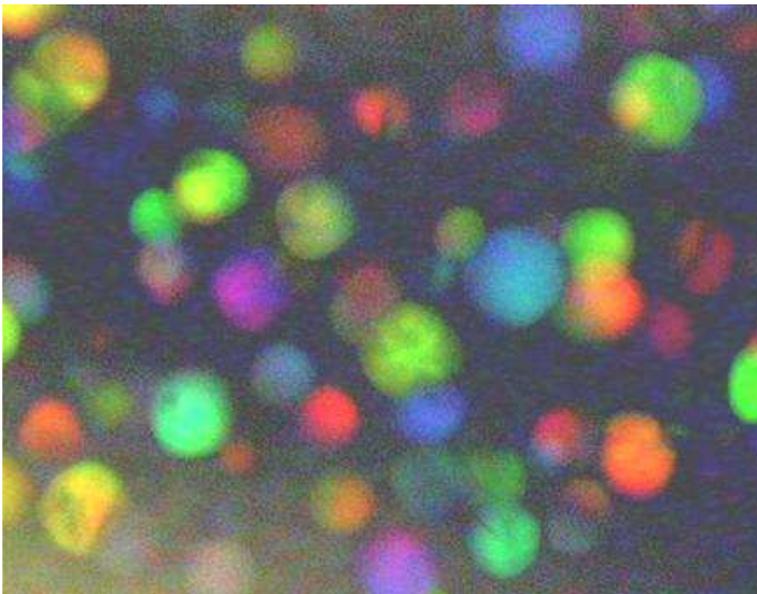
Electrostatic levitation in KRISS

HV (z-axis)

T : ~3000 ºC
P : ~ 10^{-7} Torr

Heating laser

He-Ne laser

He-Ne laser

Feedback

PSD (x)

PSD (y)

HV (x-axis)

HV (y-axis)

Feedback

KRISS material : Dr. G.W.Lee

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HEATING LASER ON | HEATING LASER OFF

Recalescence

Solid state transformations

solid

solid + liquid

liquid

undercooled liquid

solid + liquid

solid

temperature (K)

time (s)

19
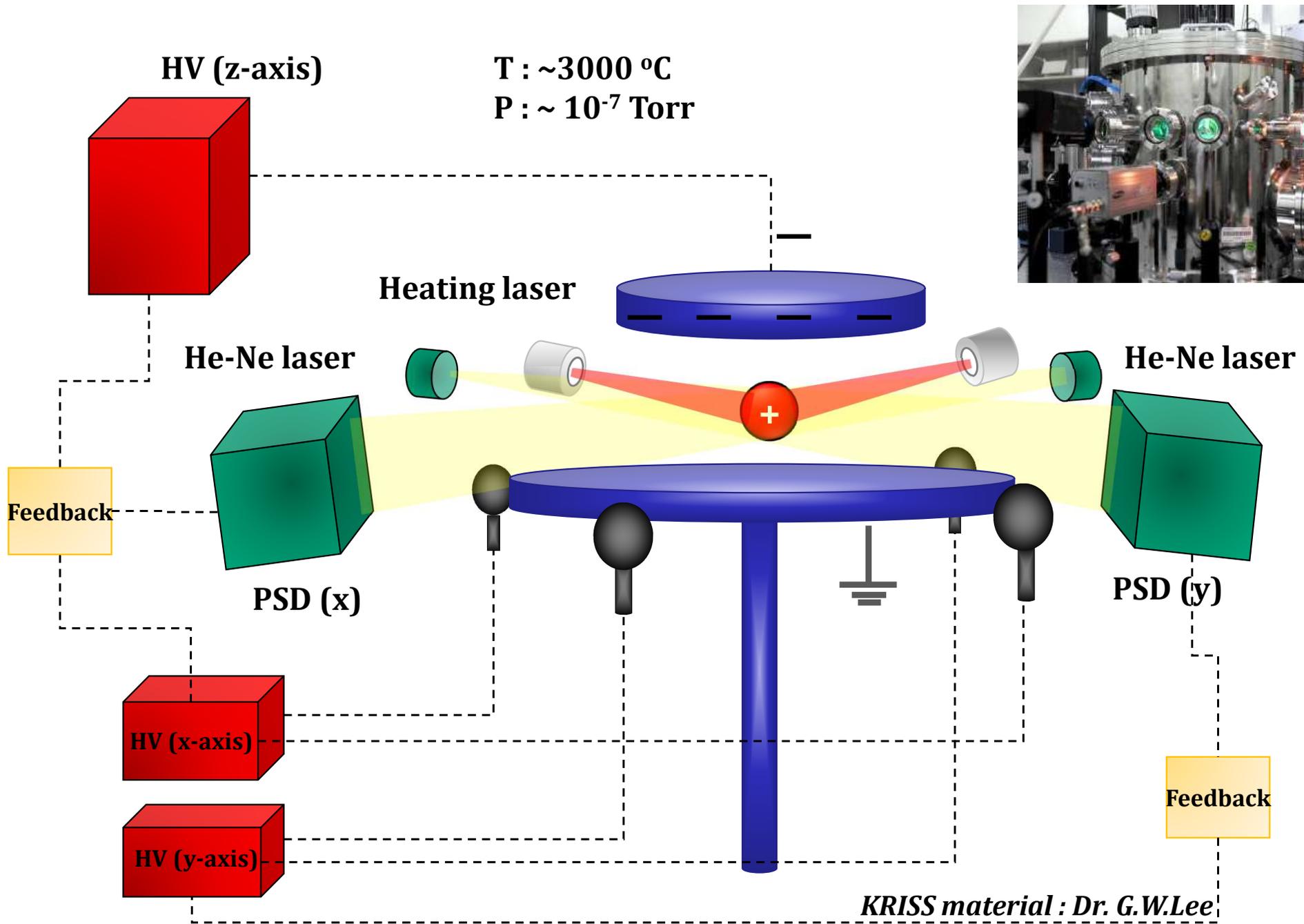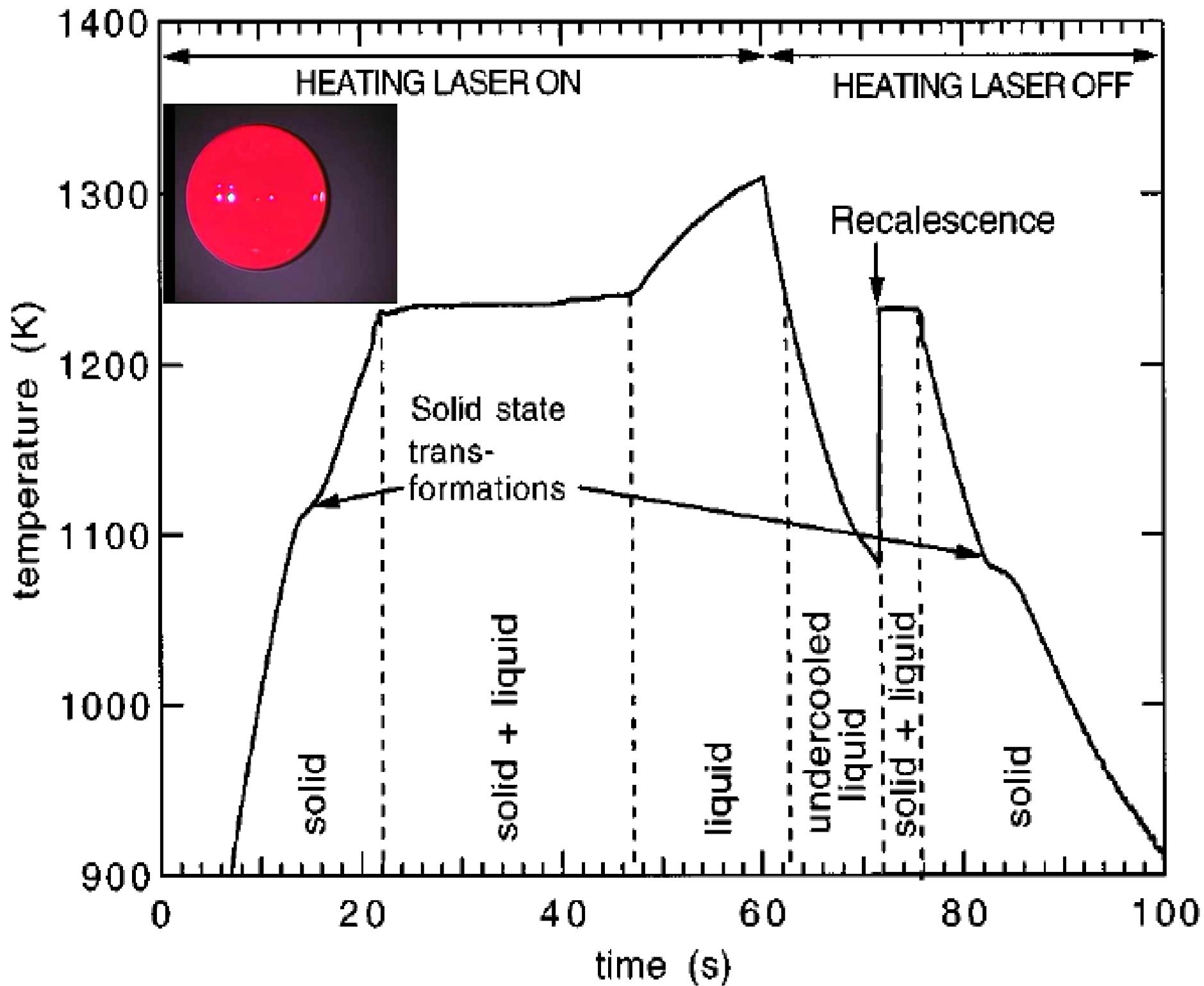
Electrostatic Levitation: cooling curve of Vitreloy 1 system
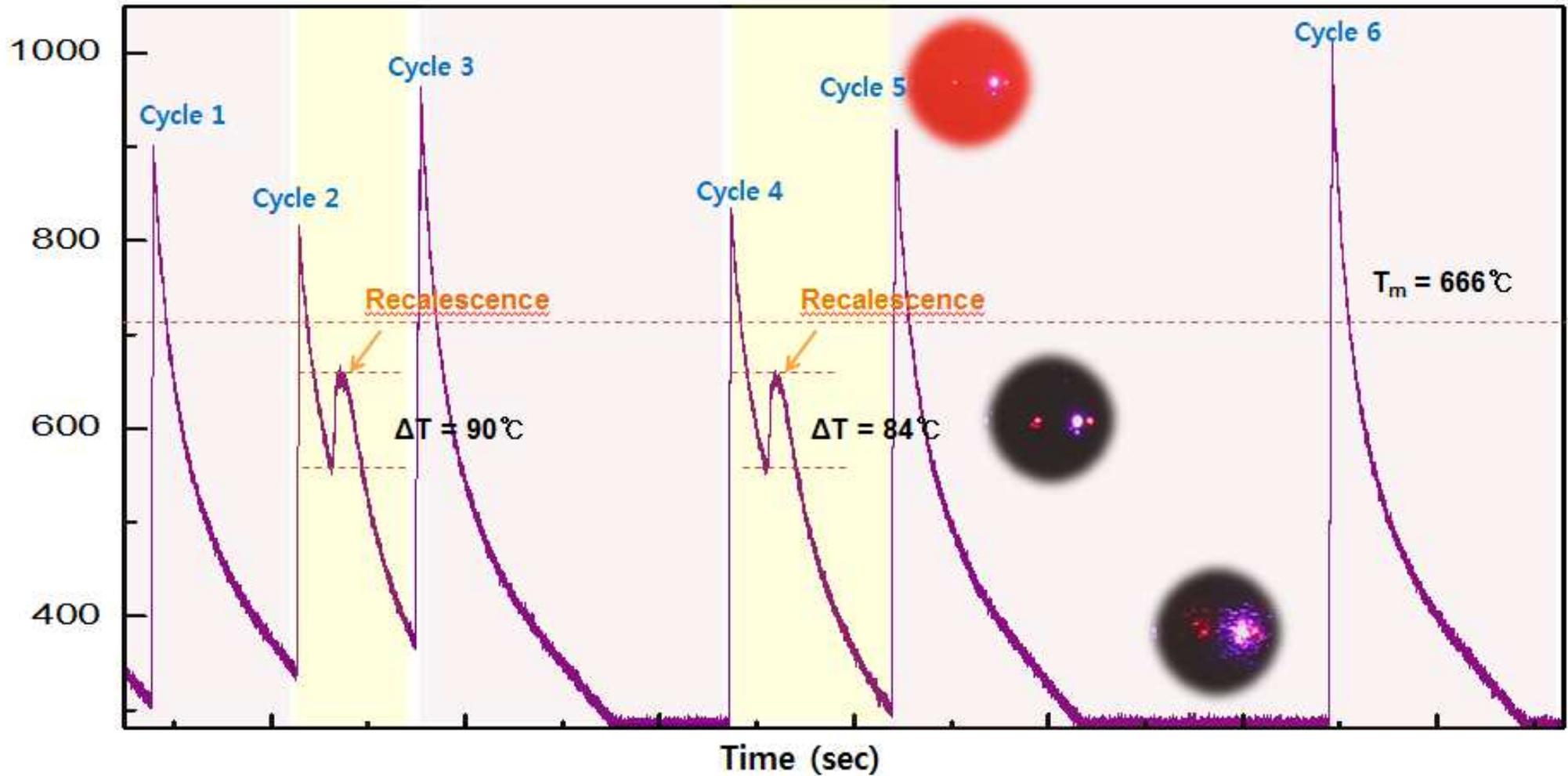
Q: Homogenous nucleation

(a) Driving force for solidification, ΔG_v

(b) Calculation of ΔG_r , r*, ΔG*

4.1.1. Homogeneous Nucleation

Driving force for solidification

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

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

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

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

$$\text{(Latent heat)}$$

$$T = T_m - \Delta T$$

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

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

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

$$\boxed{\Delta G_v = \frac{L \Delta T}{T_m}}$$
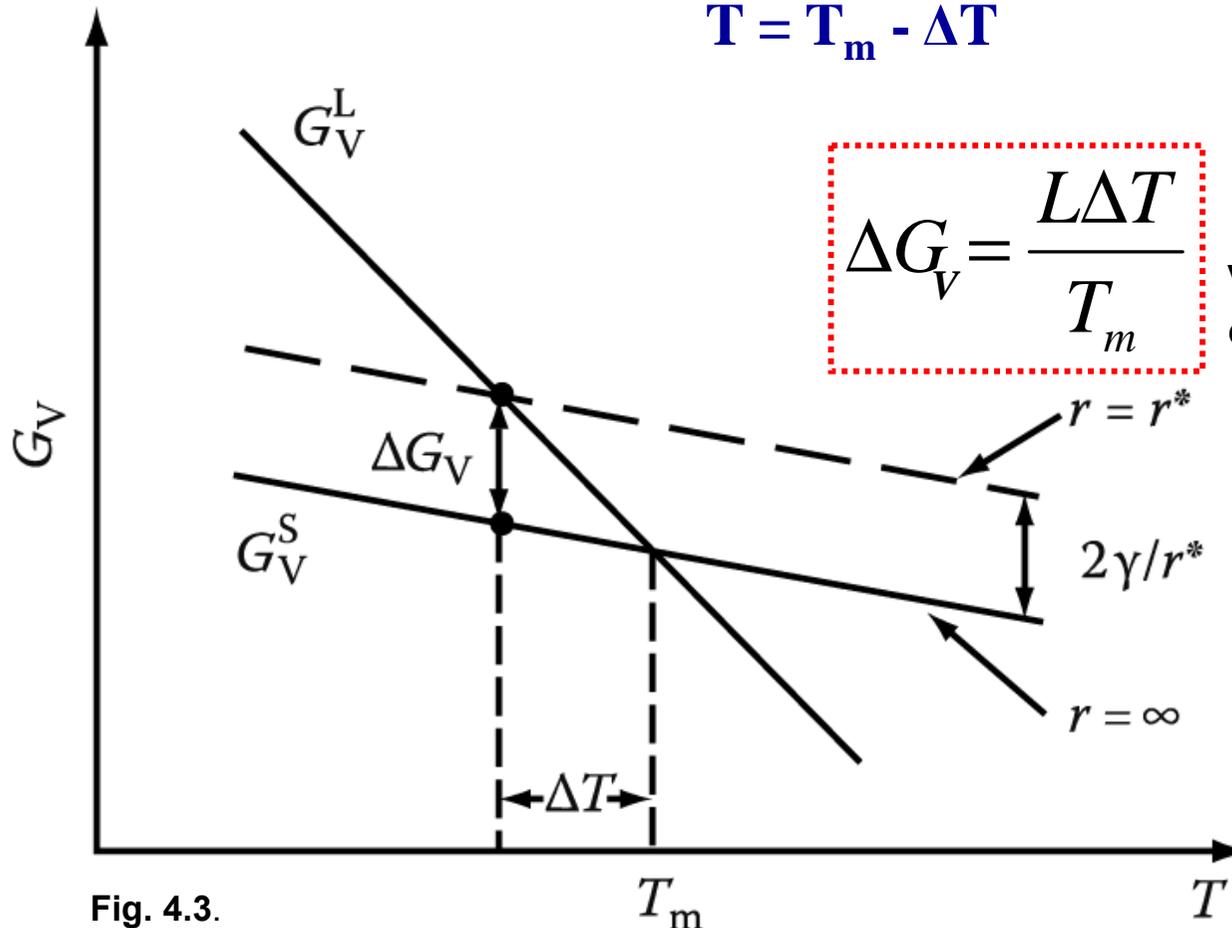
Variation of free energy per unit volume obtained from undercooling (ΔT)

Fig. 4.3.

4.1.1. Homogeneous Nucleation

Fig. 4.1 Homogeneous nucleation.
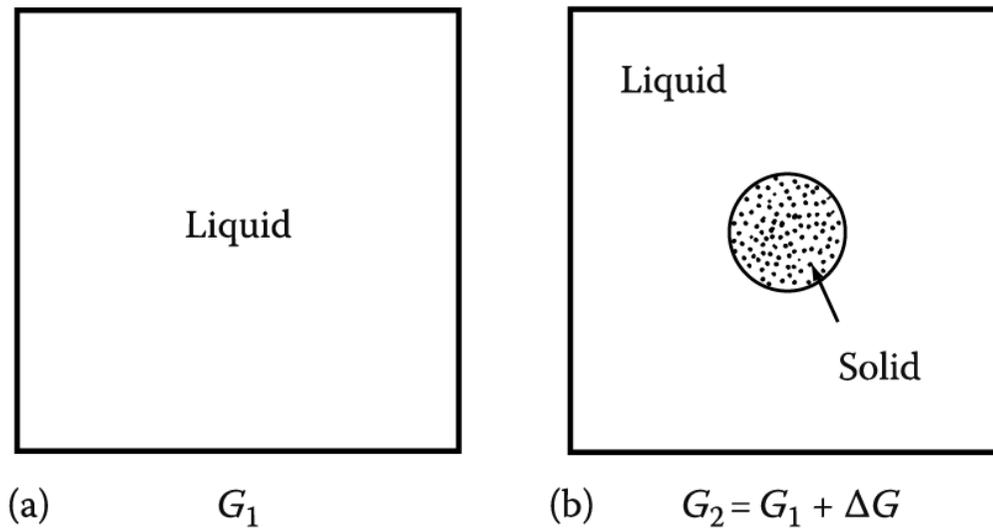
$$G_1 = (V_S + V_L)G_V^L \qquad\qquad G_2 = V_S G_V^S + V_L G_V^L + A_{SL}\gamma_{SL}$$

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*

Fig. 4.2.

ΔG axis, Interfacial energy $\propto r^2$, ΔG^*, r^*, ΔG_r, Volume free energy $\propto r^3 \Delta T$, embryo ⟹ nucleus, Unstable equilibrium
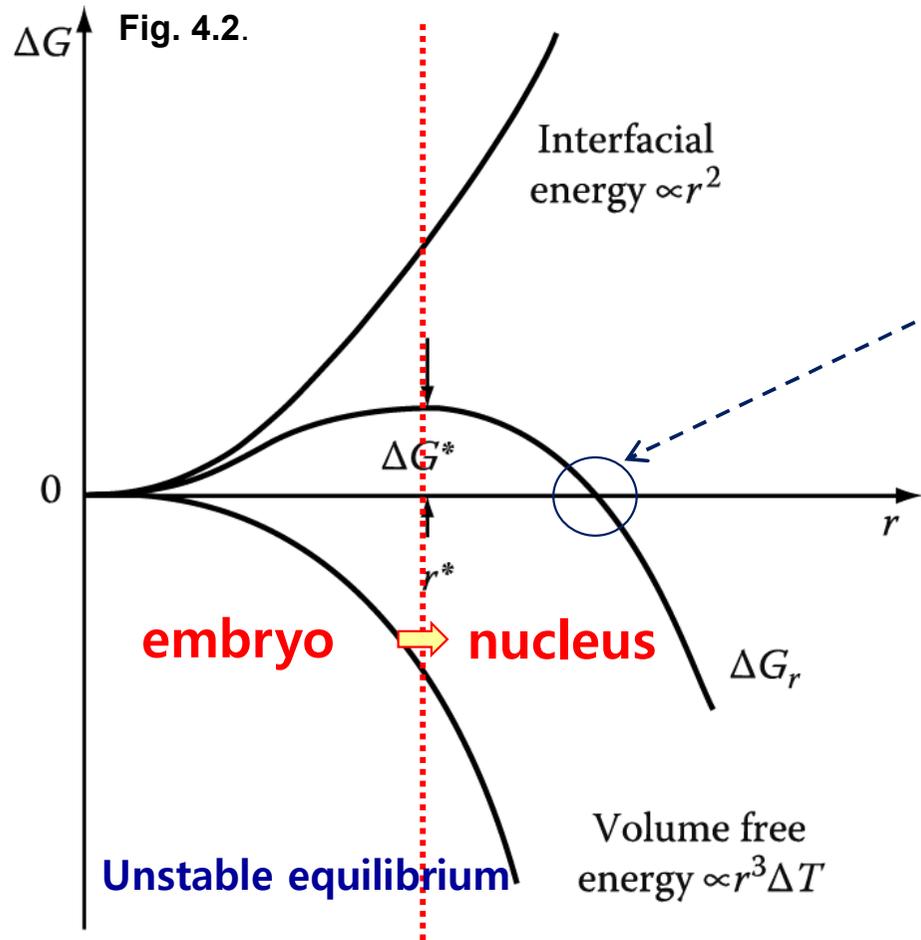
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

Why r* is not defined by ΔG_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* ⟹ **dG=0**

Gibbs-Thompson Equation

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

⟹

Critical ΔG of nucleation at r*

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

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

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

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Q: How do we define ΔT_N?

The creation of a critical nucleus ~ thermally activated process
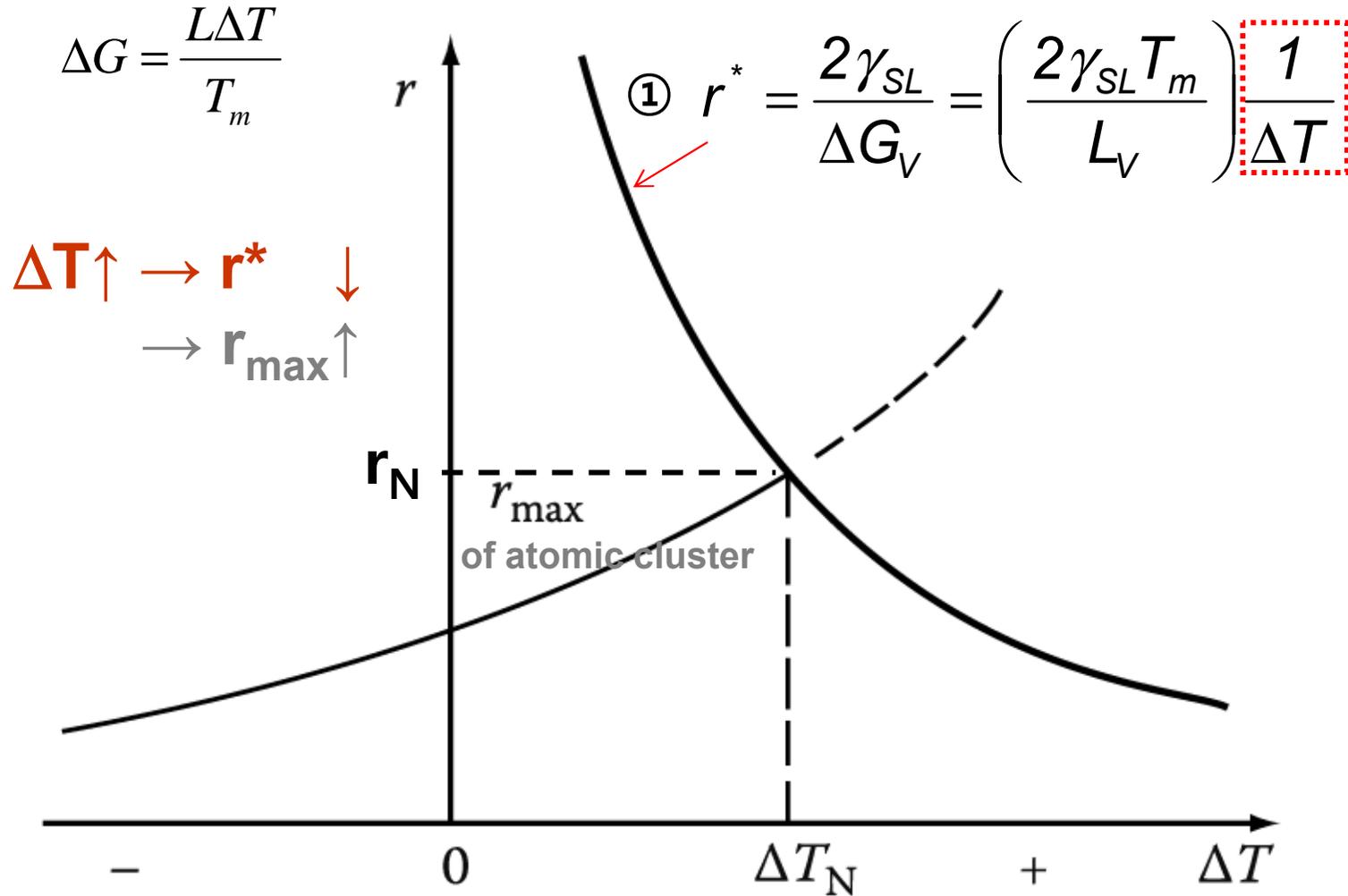
$$\Delta G = \frac{L\Delta T}{T_m}$$

① $\quad r^* = \dfrac{2\gamma_{SL}}{\Delta G_V} = \left(\dfrac{2\gamma_{SL}T_m}{L_V}\right)\dfrac{1}{\Delta T}$

$\Delta T\uparrow \longrightarrow r^* \quad \downarrow$

$\longrightarrow r_{max}\uparrow$

r_N

r_{max}
of atomic cluster

$0 \qquad \Delta T_N \qquad + \qquad \Delta T$

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

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

$\rightarrow$ 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 <u>a volume 2-4% greater</u> than the solid.

Fig. 4.4 <u>A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are instantaneously formed.</u>
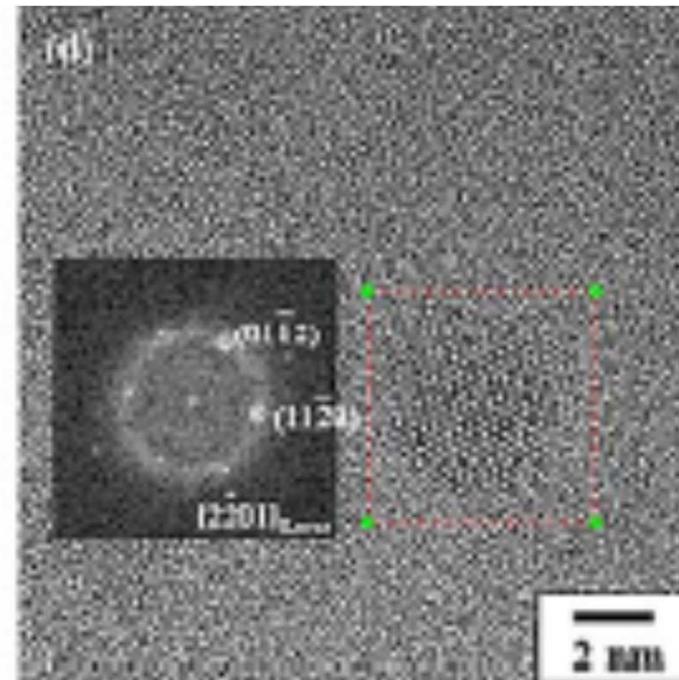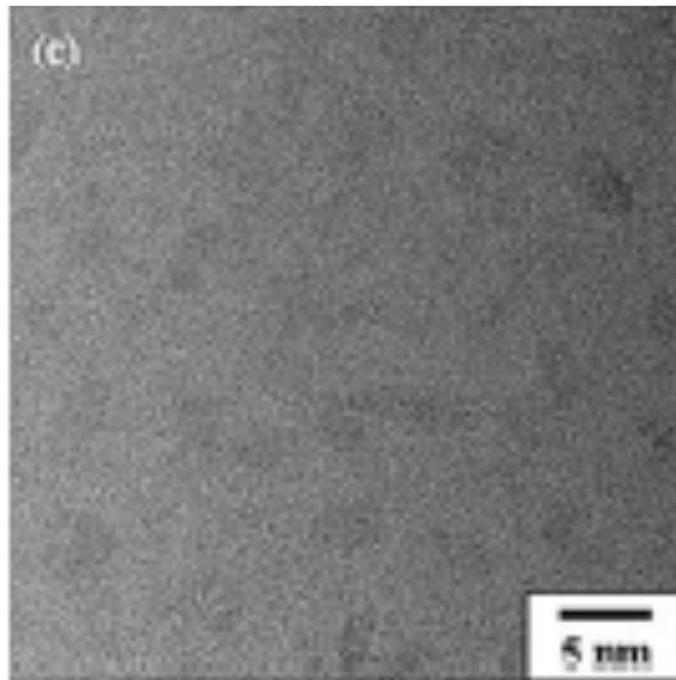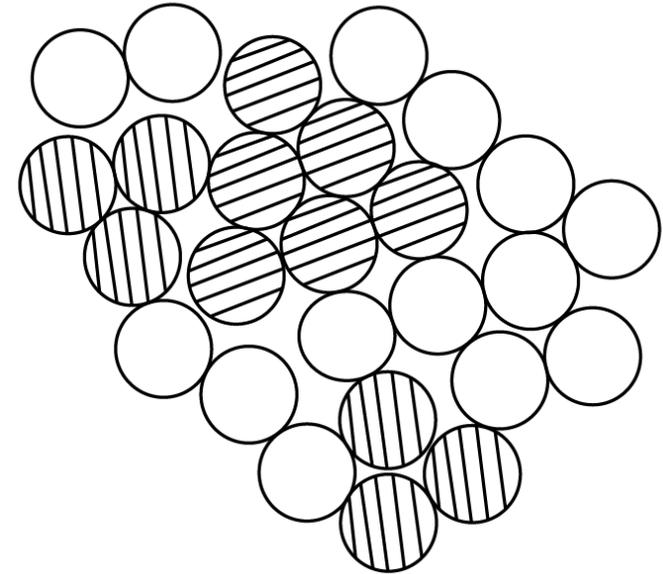
Formation of Atomic Cluster

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?

$$A_1 \rightarrow A_2 \rightarrow A_3 \rightarrow A_4 \rightarrow \cdots \rightarrow A_{m-1} \rightarrow A_m$$
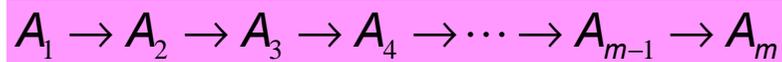
$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1\rightarrow 2}}{kT}\right)$$ **Excess free E associated with the cluster of 1→2 atoms**

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

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

$$\vdots$$

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

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

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

반지름 r인 구상의 군집체 수

# of cluster of radius r

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

n_r exponentially decreases with ΔG_r

Gibbs Free Energy

$r \uparrow \rightarrow \Delta G_r \uparrow$

embryo $\Rightarrow$ Nucleus
: no longer part of liquid
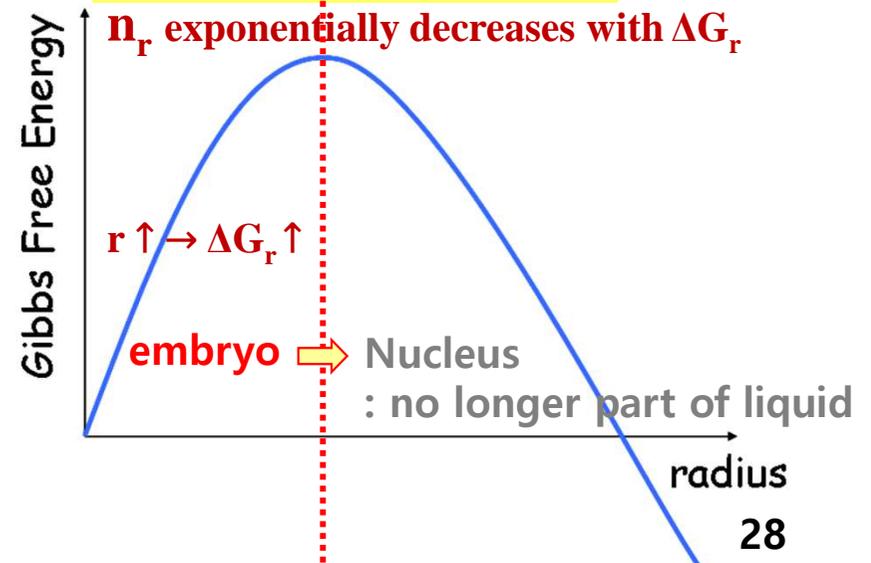
radius

Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.

small driving force (small ΔT)

$\Delta T \downarrow \rightarrow \Delta G_r^* \uparrow \rightarrow r^* \uparrow \rightarrow n_r \downarrow$

$\Delta G_r^* \quad < \quad \Delta G_r^*$

large driving force (large ΔT)

$\Delta T \uparrow \rightarrow \Delta G_r^* \downarrow \rightarrow r^* \downarrow \rightarrow n_r \uparrow$

$r^* \quad < \quad r^*$

radius
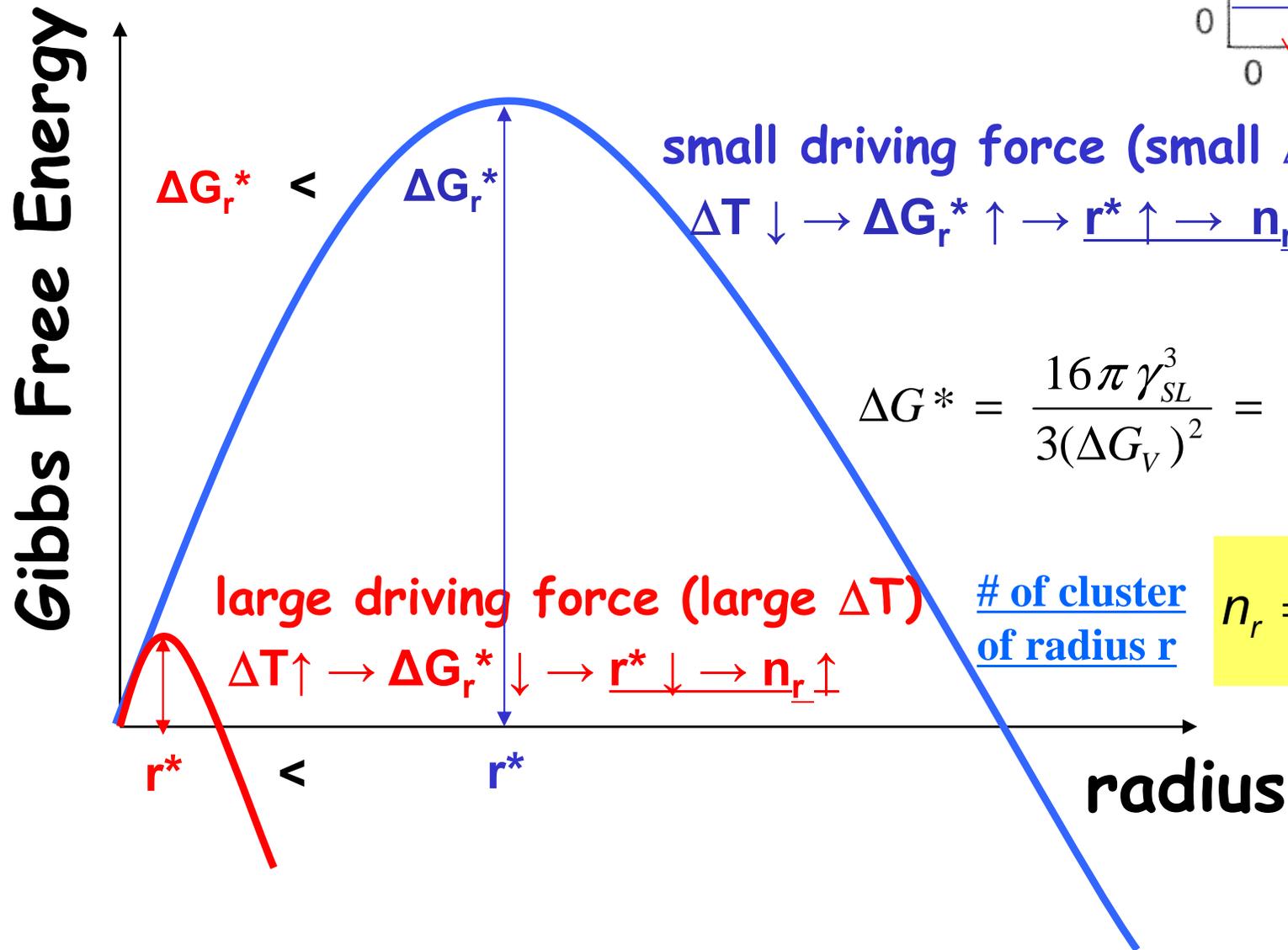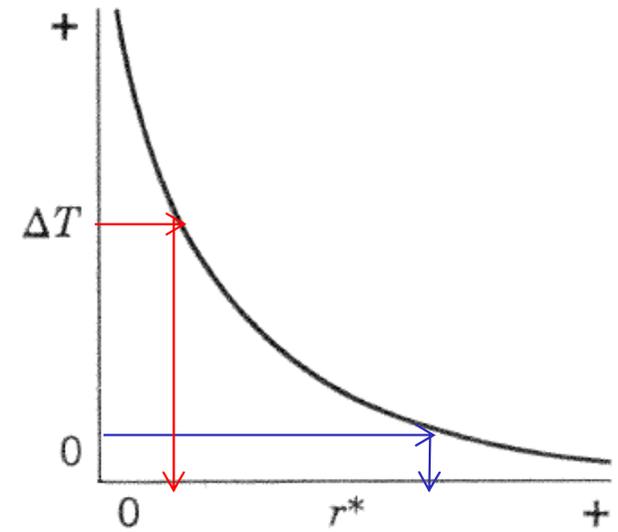
Gibbs Free Energy

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

# of cluster of radius r

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

Formation of Atomic Cluster

n_o : 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 <u>at its melting point</u> (n_0: 10^{20} atoms)

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

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

$\rightarrow$ effectively a maximum cluster size, ~ 100 atoms

~ 10^{-8} clusters mm⁻³ or <u>1 cluster in ~ 10^7 mm³</u>

The creation of a critical nucleus ~ thermally activated process
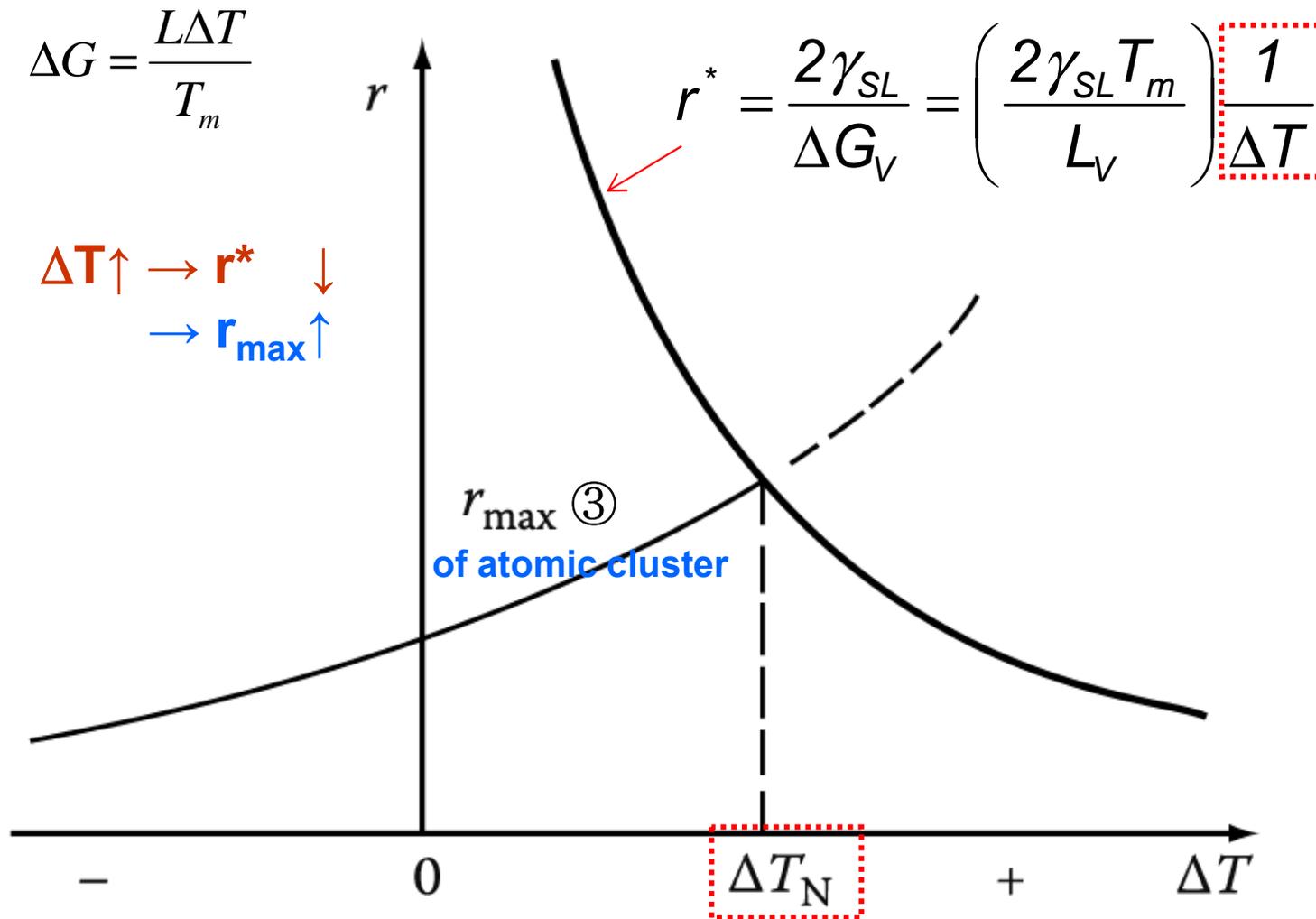
$$\Delta G = \frac{L \Delta T}{T_m}$$

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

$\Delta T\uparrow \rightarrow r^* \quad \downarrow$

$\rightarrow r_{max}\uparrow$

r_{max} ③
of atomic cluster

ΔT_N

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

$$C^* = C_0 \exp(-\frac{\Delta G_{\text{hom}}^*}{kT})$$ **clusters / m³**

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
$$N_{\text{hom}} = f_0 C_o \exp(-\frac{\Delta G_{\text{hom}}^*}{kT})$$ **nuclei / m³·s**

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

$C_o \sim$ typically 10^{29} atoms/m³

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

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

Reasonable nucleation rate

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4.1.2. The homogeneous nucleation rate - kinetics

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

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

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
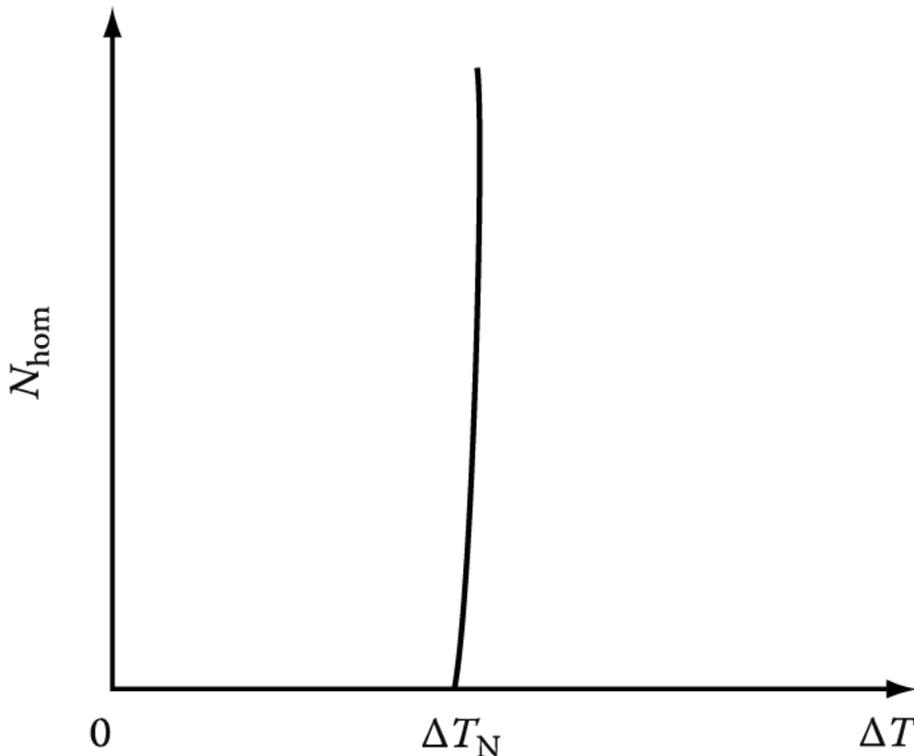
→ **critical value for detectable nucleation**

 - **critical supersaturation ratio**
 - **critical driving force**
 - **critical supercooling**

→ **for most metals, $\Delta T_N \sim 0.2\ T_m$ (i.e. ~200K)**

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

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* **Copper** Homogeneous nucleation

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

If nucleus is spherical shape,

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

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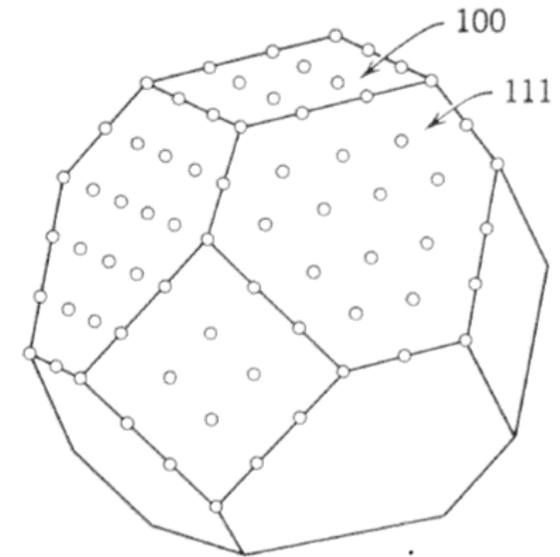
Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

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

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 <u>catalyzed by a suitable surface in contact with the liquid</u>. → "Heterogeneous Nucleation"

Ex)   <u>liquid</u>   or   Solid thin film (such as oxide)

container   liquid

Why this happens?   What is the underlying physics?

Which equation should we examine?

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

$$N_{hom} = f_0 C_o \exp(-\frac{\Delta G^*_{hom}}{kT})$$

Reduction of heterogeneous nucleation site

John H. PEREPEZKO, MSE, 65 (1984) 125-135

: Impurity isolation
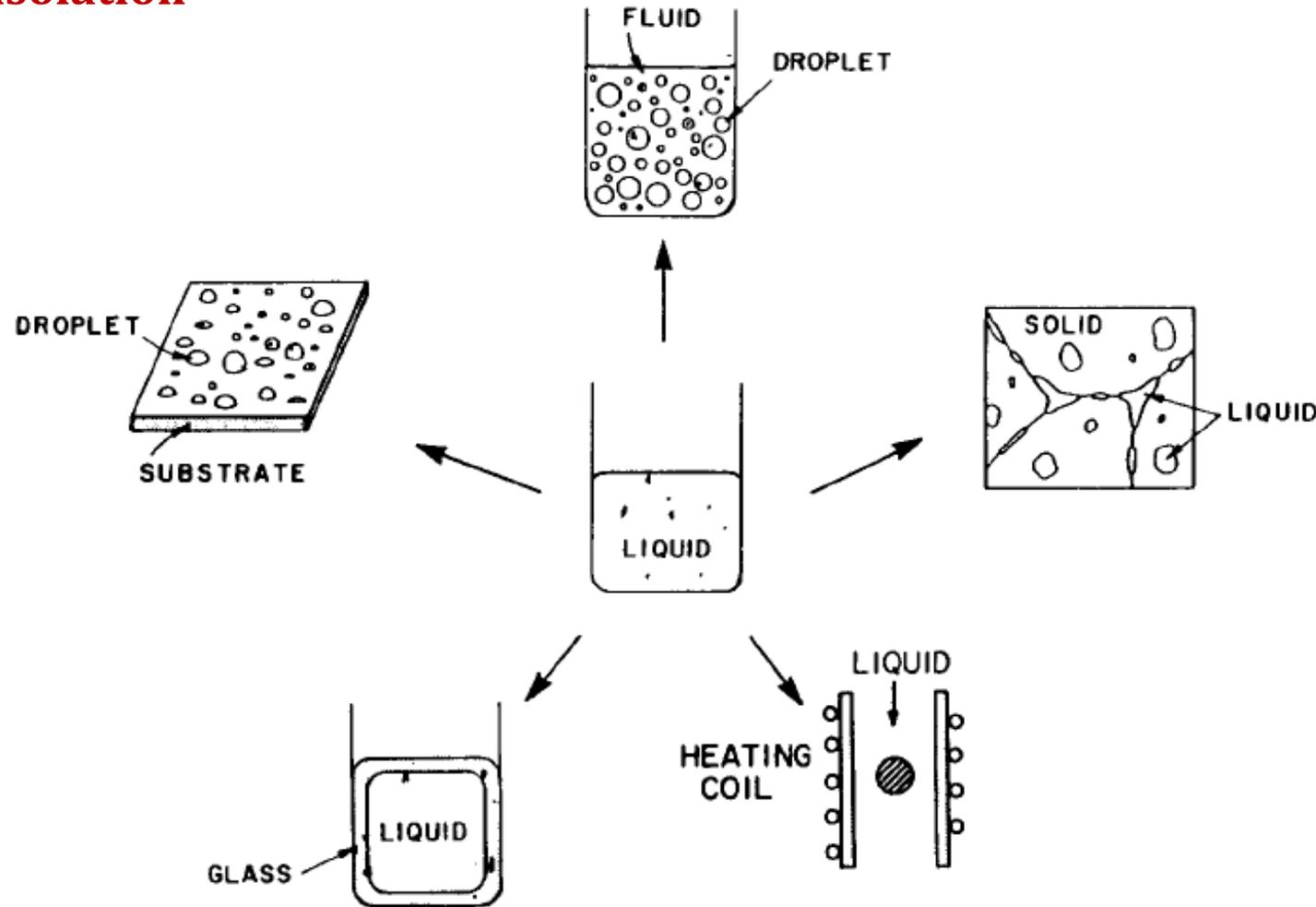
By dispersing a liquid into a large number of small droplets within a suitable medium, the catalytic effects of active nucleants may be restricted to a small fraction of the droplets so that many droplets will exhibit extensive undercooling.