2017 Fall

“Phase Transformation *in* Materials”

11.13.2017

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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 for previous class

3.4 Interphase Interfaces in Solids

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

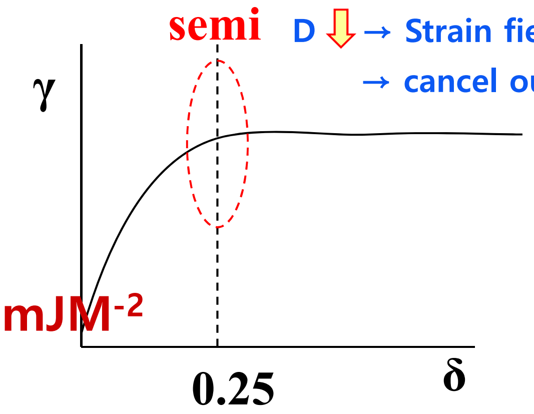
coherent, **Perfect atomic matching at interface**

γ (coherent) = γ_{ch} **γ (coherent) ~ 200 mJM^{-2}**

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

γ_{st} → due to structural distortions caused by the misfit dislocations

γ(semicoherent) ~ 200~500 mJM^{-2}



D ⇩ → Strain field overlap
→ cancel out

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 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

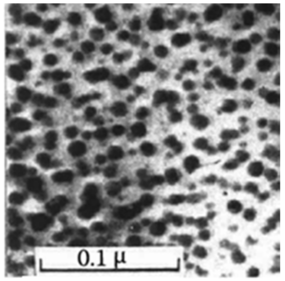
$$\sum A_i\gamma_i + \Delta G_S = minimum$$

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

Fully coherent precipitates

γ_{ch}

different composition



⇨ γ_{ch} + *Lattice misfit* ⇨ γ_{ch} + $\boxed{Volume\ Misfit \quad \Delta = \frac{\Delta V}{V}}$

Coherency strain energy

Chemical and structural interfacial E

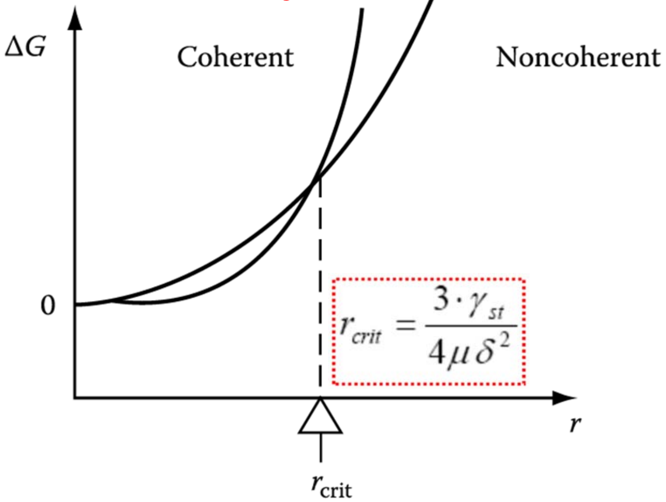
$$\Delta G_S = 4\mu\delta^2 \cdot V$$ **(If v=1/3)** ⬄ $$\Delta G_S = \frac{2}{3}\mu\Delta^2 \cdot V \cdot \boxed{f(c/a)}$$

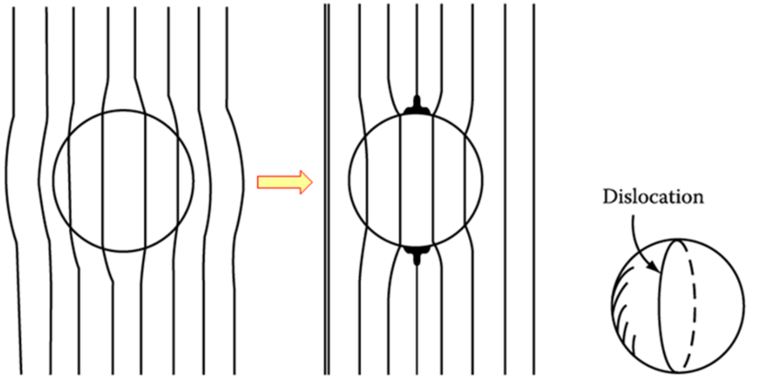
Fully coherent precipitates **Incoherent inclusions**

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

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

"Coherency loss"





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

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

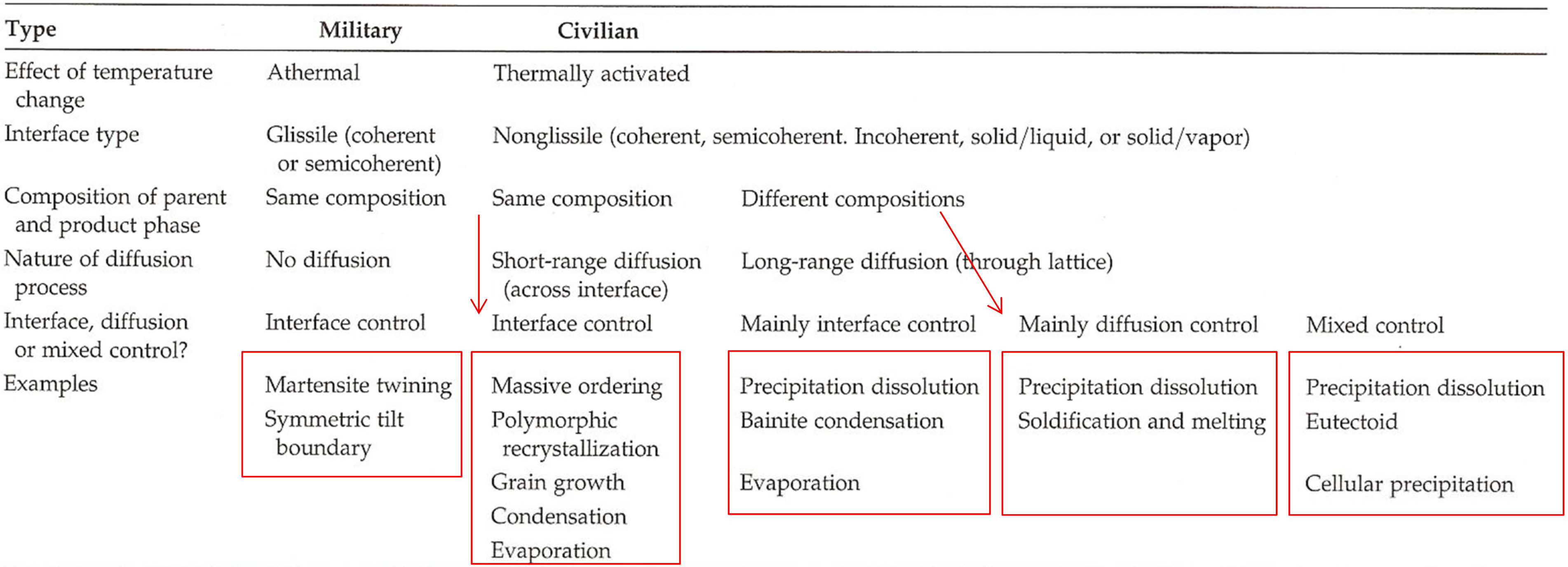
No Nucleation barrier   Ex. Spinodal decomposition (Chapter 5)

Order-disorder transformation

*** Types of Interface** → **Types of transformation**

- **Glissile Interface: Athermal, Shape change** → **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 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)

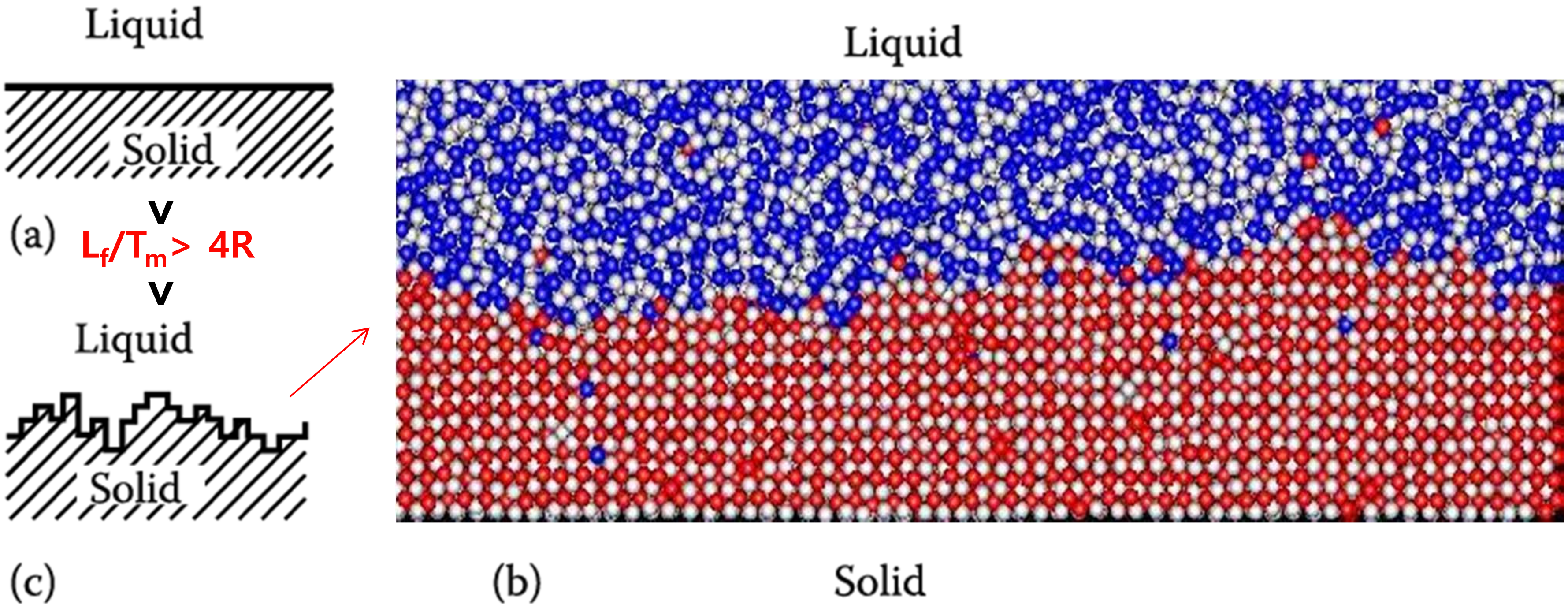
Q: What is the structure of interface between liquids and crystals?

Interphase Interfaces in Solid (α/β)

2) Solid /Liquid Interfaces: consequences for the structure and energy of the interface

Faceted interface Rather narrow transition zone approximately one atom layer thick
~ same as solid/vapor interfaces, i.e., atomically flat close-packed interface

: some intermetallic compounds, elements such as Si, Ge, Sb, and most nonmetals

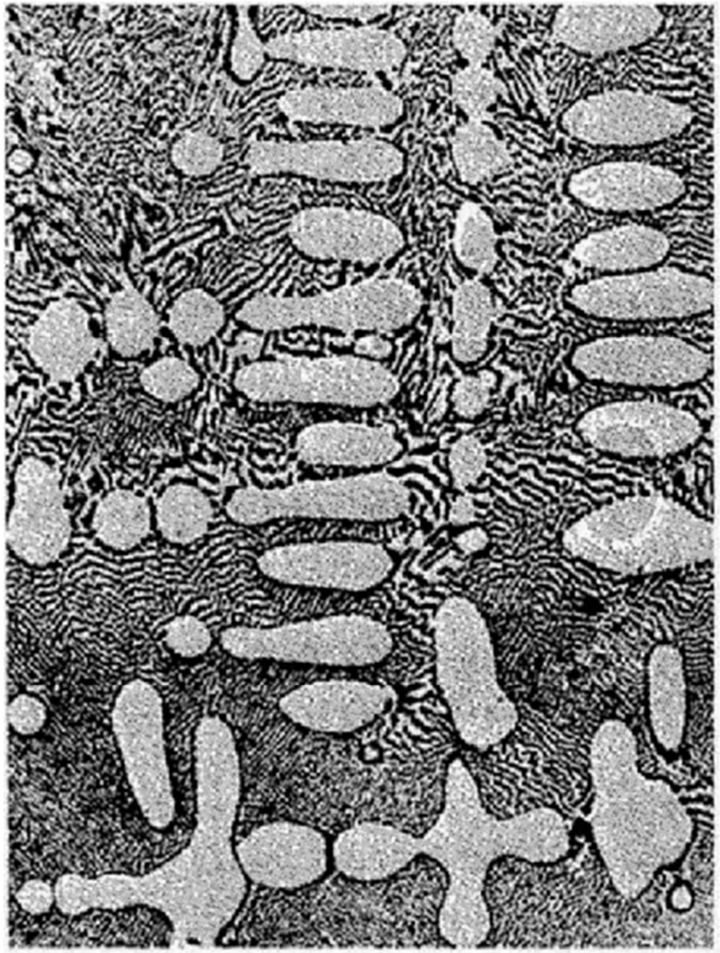


V
$L_f/T_m > 4R$
V

Fig. 3. 63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces.

Diffusion interface (non-faceted) Rather wide transition zone over several atom layers
: most metals, $L_f/T_m \sim R$ (gas constant) ~automatically rough & diffuse interface

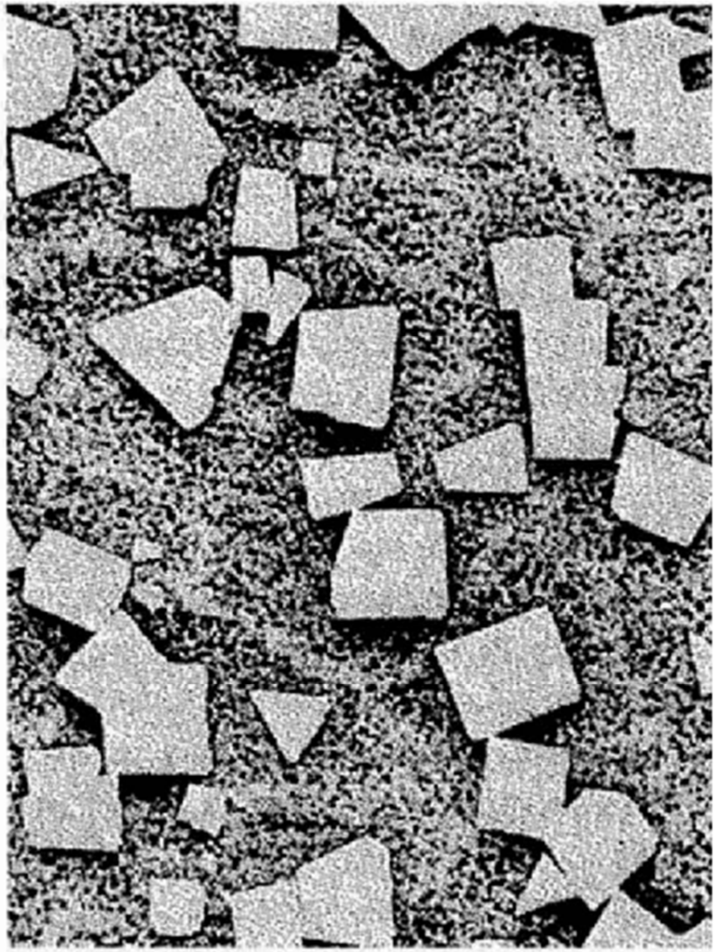
Primary Ag dendrite
in Cu-Ag eutectic matrix



(a) **Non-faceted**

- Free E ~do not vary with crystallographic orientation
- γ-plot ~ spherical

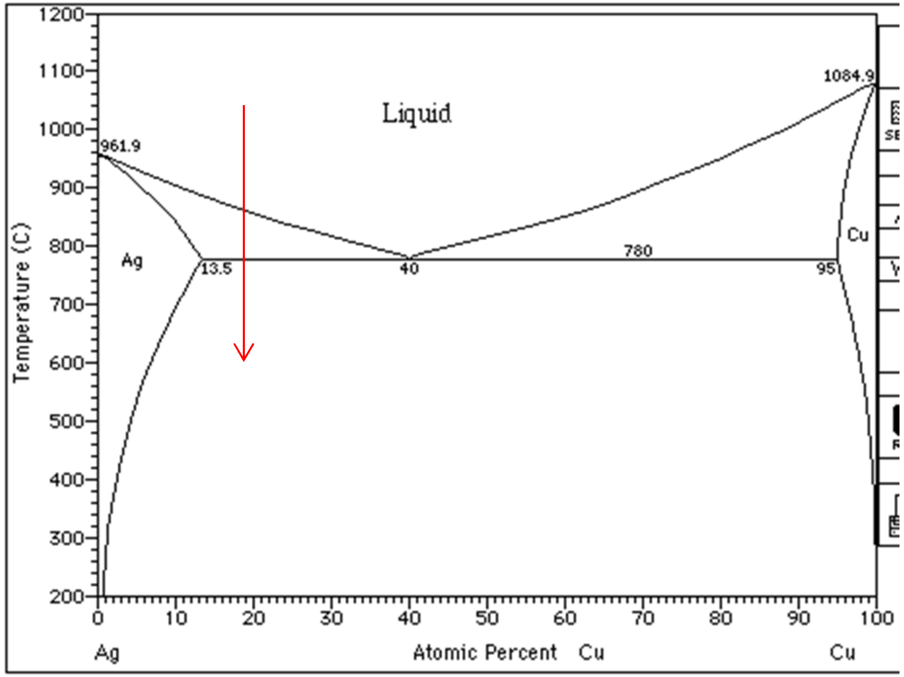
β′-SnSb intermetallic compound
in Sn(Sb) solid solution



(b) **Faceted**

- Strong crystallographic effects
- Solidify with low-index close-packed facets

Primary Ag dendrite
in Cu-Ag eutectic matrix



β′-SnSb intermetallic compound
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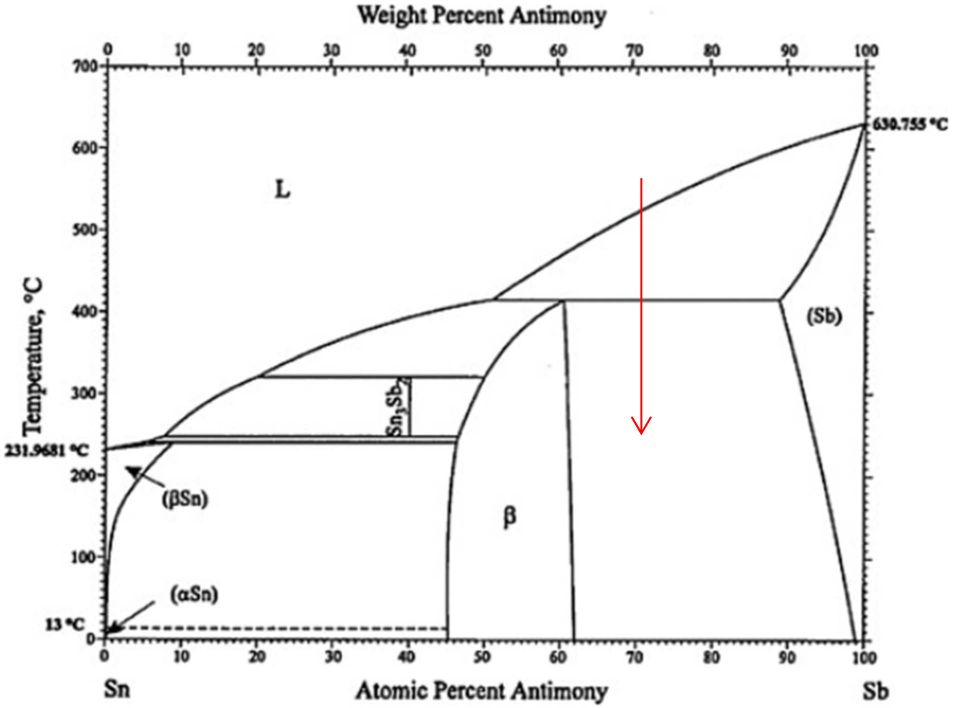
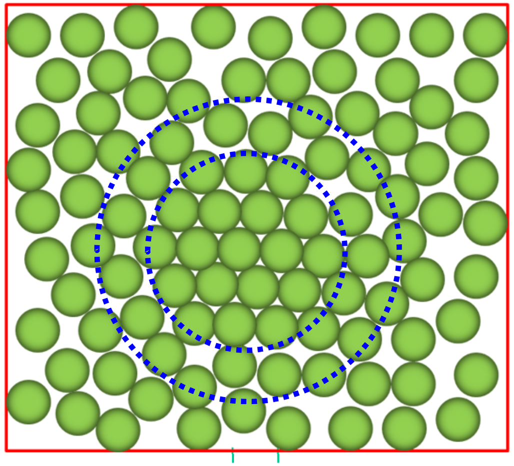
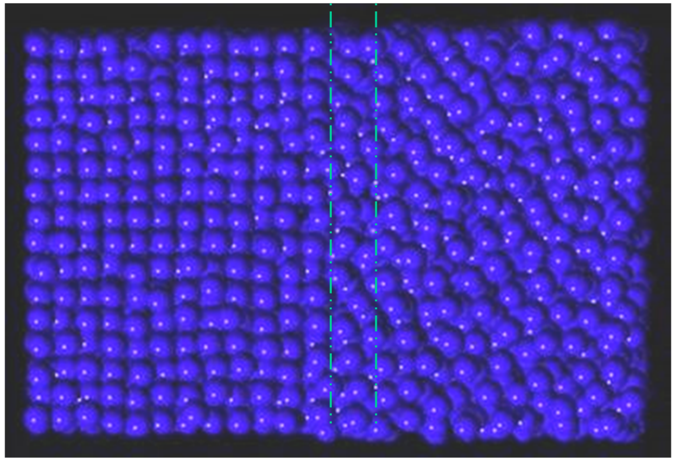


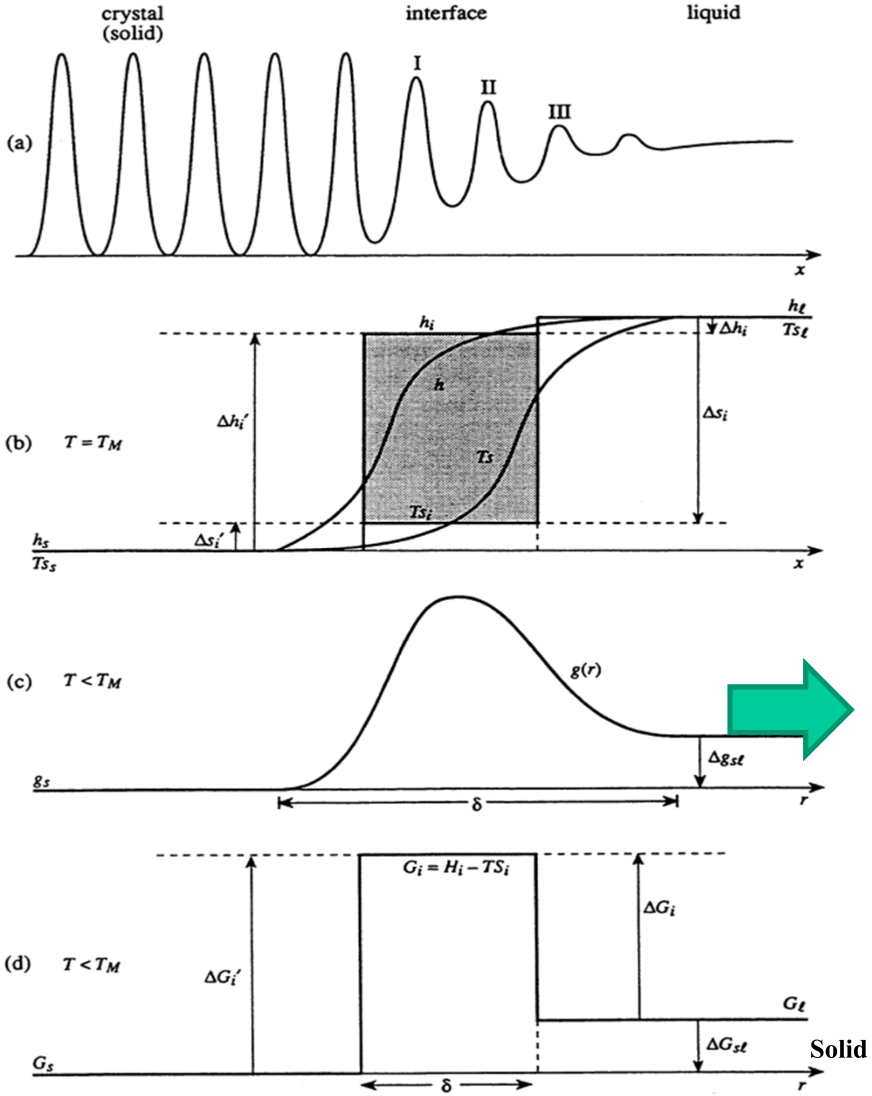
What is the structure of interface between liquids and crystals?

Turnbull’s solid-liquid interface

Turnbull’s insight: Liquid orders substantially near a crystal surface due to entropy decreasing caused by the crystal-melt interfacial tension



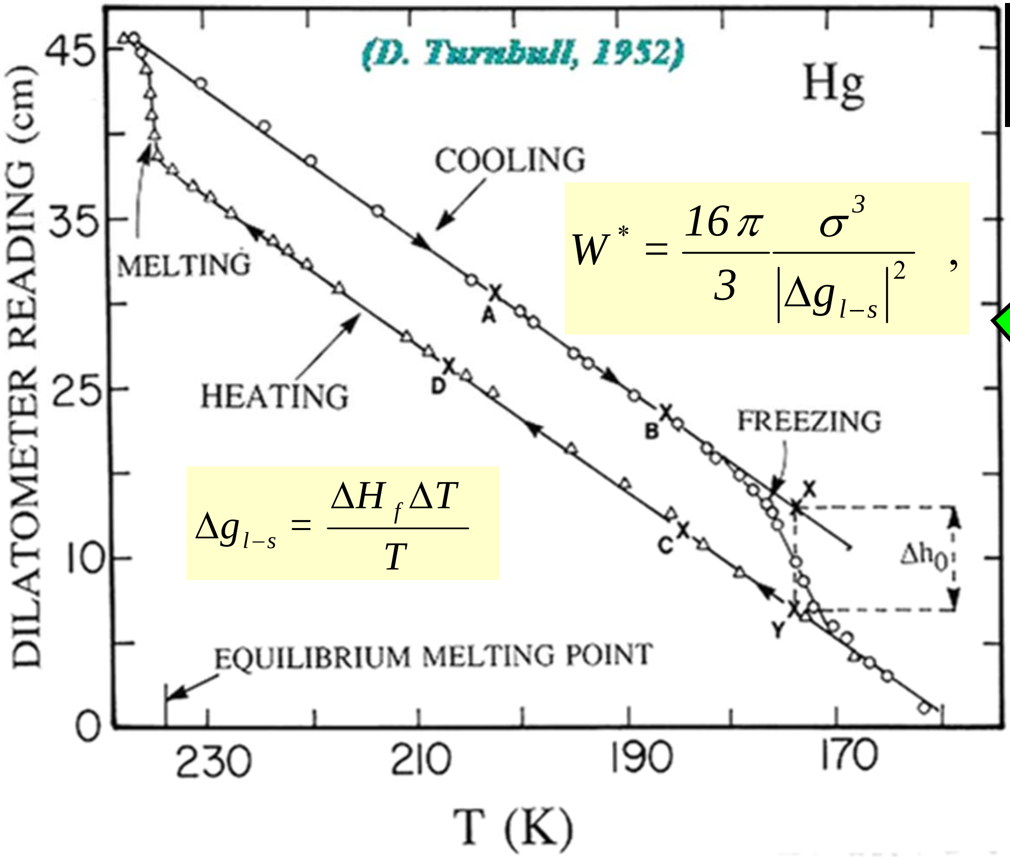




Supercooling

Solid state physics v47, 1 (1994)

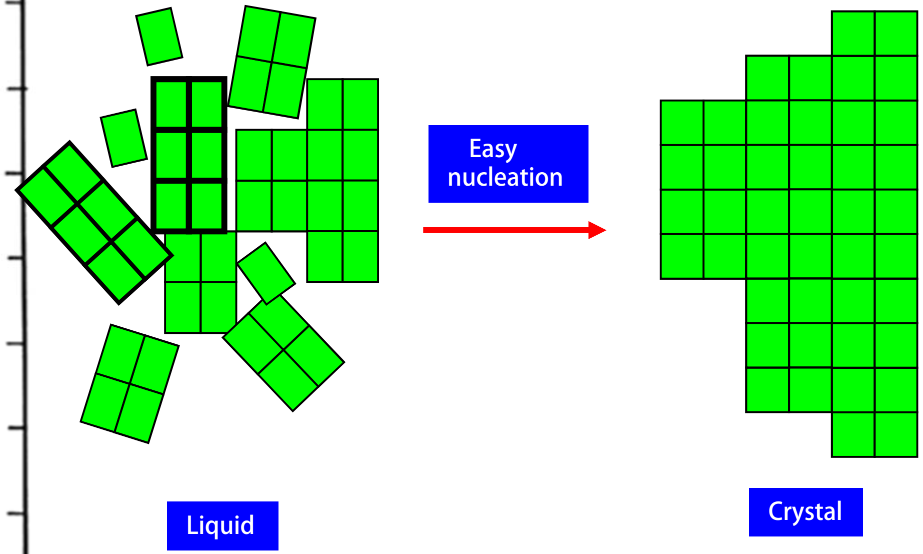
Turnbull's Insight for Supercooling



$$W^* = \frac{16\pi}{3}\frac{\sigma^3}{|\Delta g_{l-s}|^2} \ ,$$

$$\Delta g_{l-s} = \frac{\Delta H_f \Delta T}{T}$$

Microcrystalline structure for liquid metals
–*Same short range order with crystals*!



- ◆ **How does the liquid metals resist on the crystallization?**
- ◆ **What the origin of high nucleation barrier against the crystallization?**

* Broken bond model → calculation of the E of solid/ liquid interface

$0.5L_f / N_a \rightarrow 0.45L_f / N_a$ (엔트로피 효과로 감소)

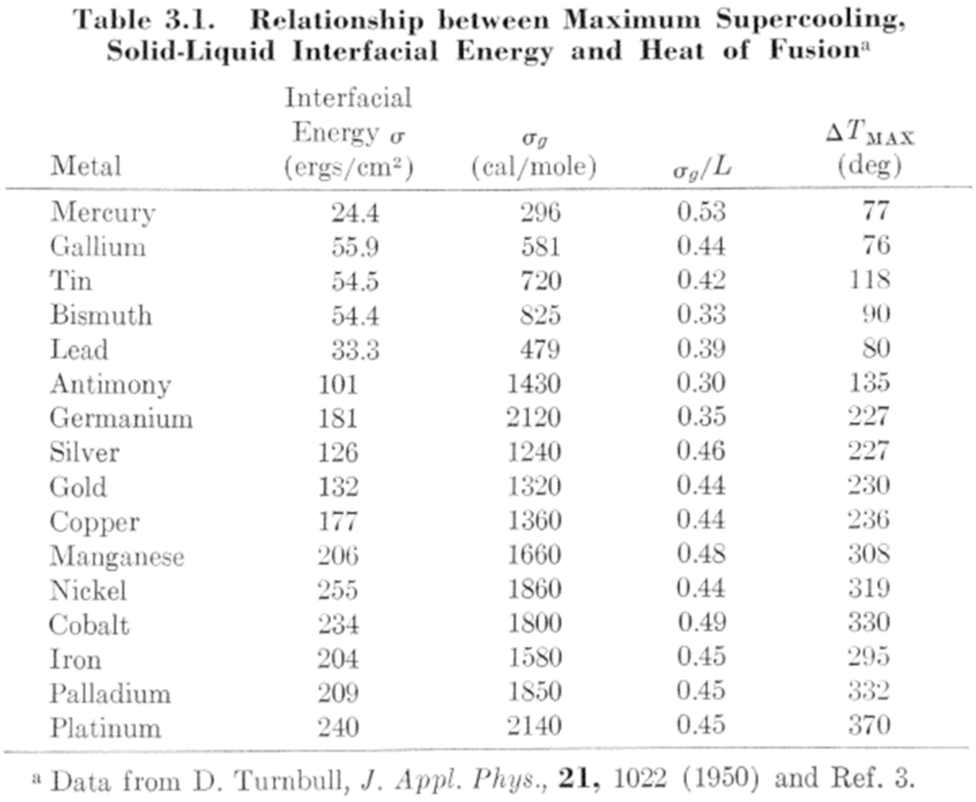


Table 3.1. Relationship between Maximum Supercooling, Solid-Liquid Interfacial Energy and Heat of Fusion[a]

Metal	Interfacial Energy σ (ergs/cm²)	σ_g (cal/mole)	σ_g/L	ΔT_{MAX} (deg)
Mercury	24.4	296	0.53	77
Gallium	55.9	581	0.44	76
Tin	54.5	720	0.42	118
Bismuth	54.4	825	0.33	90
Lead	33.3	479	0.39	80
Antimony	101	1430	0.30	135
Germanium	181	2120	0.35	227
Silver	126	1240	0.46	227
Gold	132	1320	0.44	230
Copper	177	1360	0.44	236
Manganese	206	1660	0.48	308
Nickel	255	1860	0.44	319
Cobalt	234	1800	0.49	330
Iron	204	1580	0.45	295
Palladium	209	1850	0.45	332
Platinum	240	2140	0.45	370

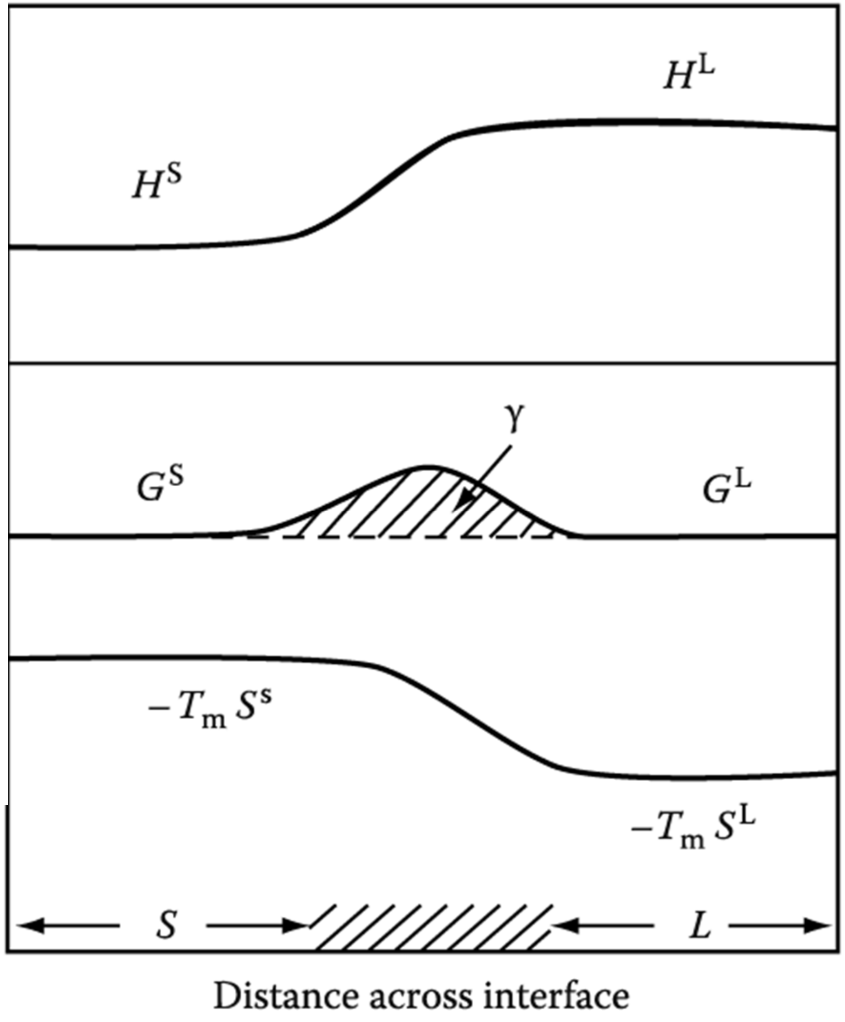
[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

$\gamma_{SL} \approx 0.45\ \gamma_b$ $(= 0.15\gamma_{SV})$

for the most metals

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

at equilibrium melting temp.



Showing the origin of the solid/ liquid interfacial energy, γ

4.1.4. 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.

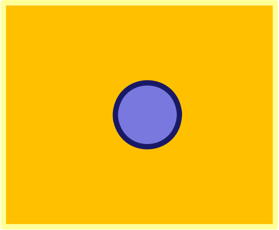
Why?

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

In general, wetting angle = 0 ⇨ **No superheating required!**

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

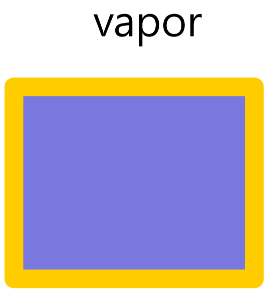
- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid



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)**

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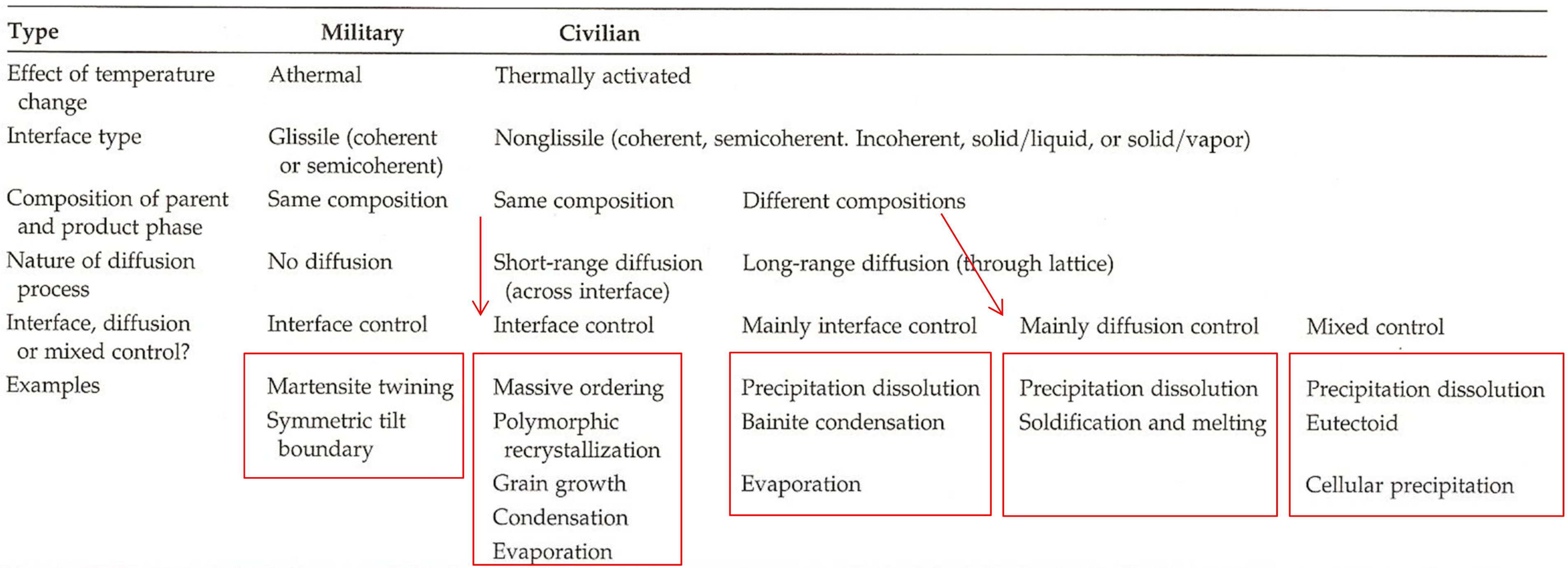
Classification of Nucleation and Growth Transformation



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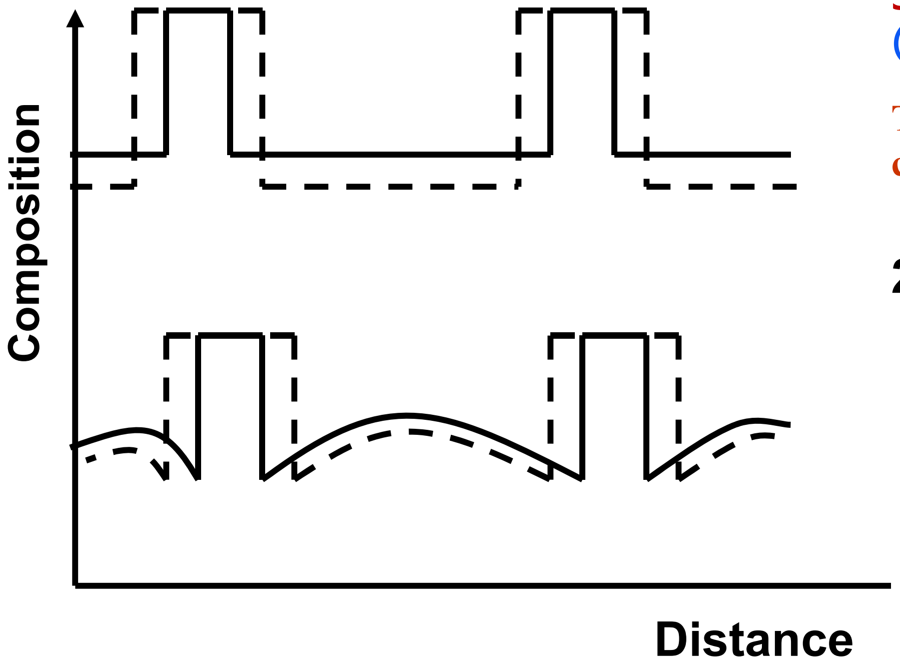
exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface

(need to additional research)

3.5. Interface Migration

* Civilian Transformation



1) Interface control

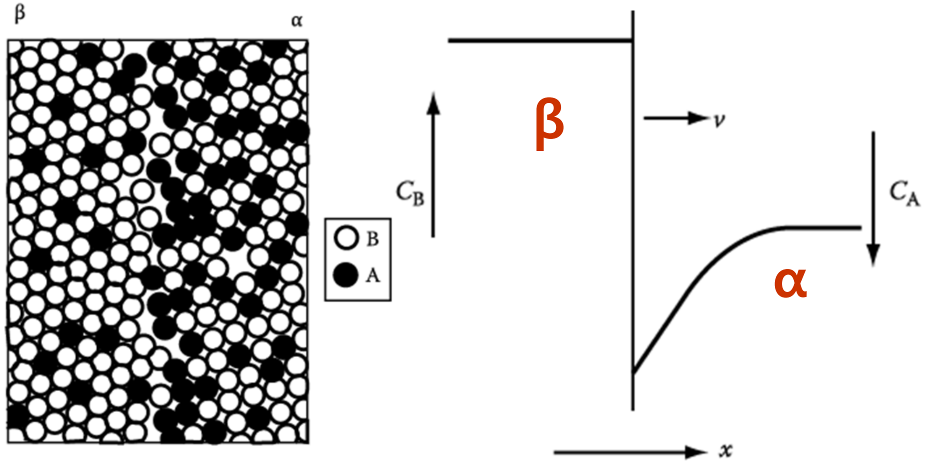
Same composition between parent and product
(Ex. α→γ transformation in pure iron)

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.



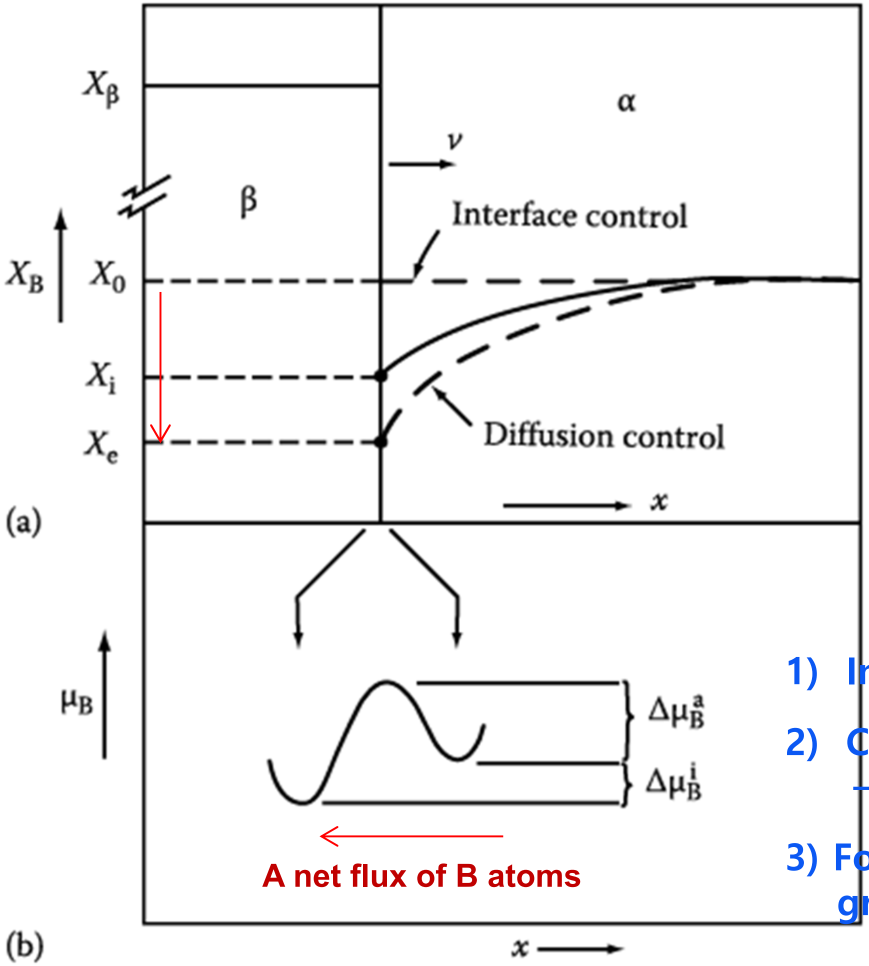
3) Mixed control: interface reaction = diffusion process

3.5.1. Diffusion-Controlled and Interface-Controlled Growth

Fig. 3.67 Interface migration with long-range diffusion

; <u>the migration of interface separating two phases of different composition</u>

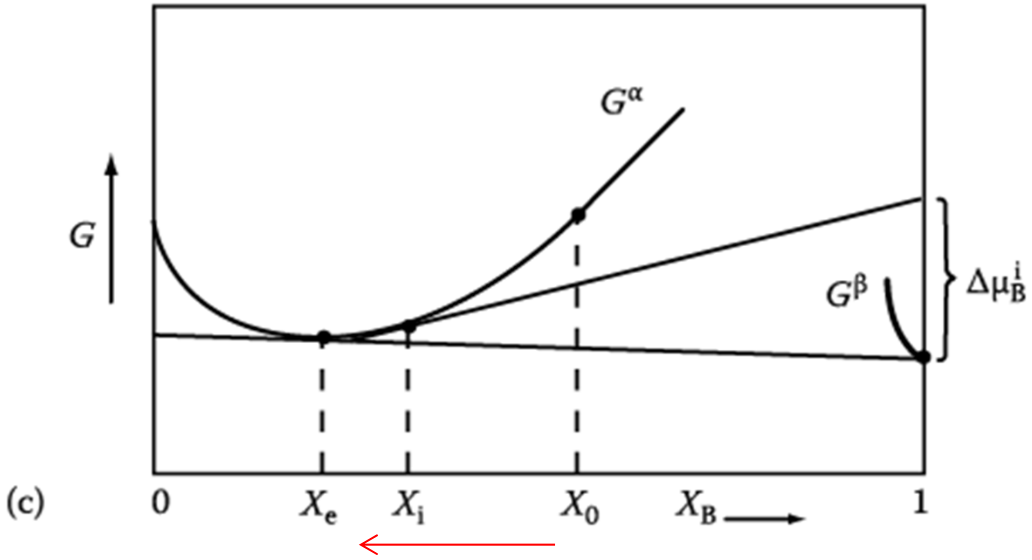
(a) Composition profile across the interface



A net flux of B atoms

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

(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 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 $\boxed{\alpha \rightarrow \alpha + \beta}$ 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)

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

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

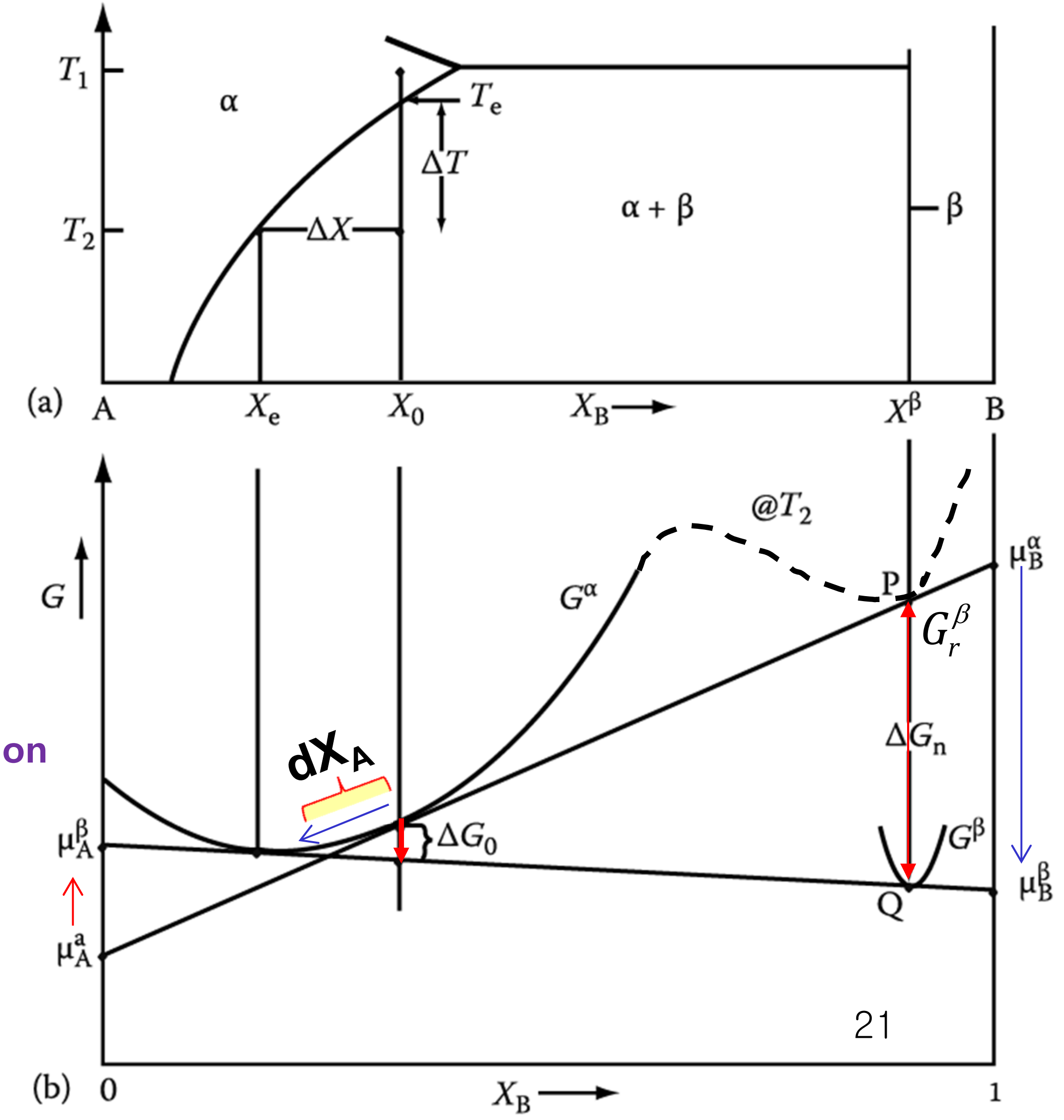
: driving force for β precipitation

For dilute solutions,

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

$$\boxed{\Delta G_V \propto \Delta X \propto \Delta T}$$

∝ undercooling below T_e



3.5.1. Diffusion-Controlled and Interface-Controlled Growth

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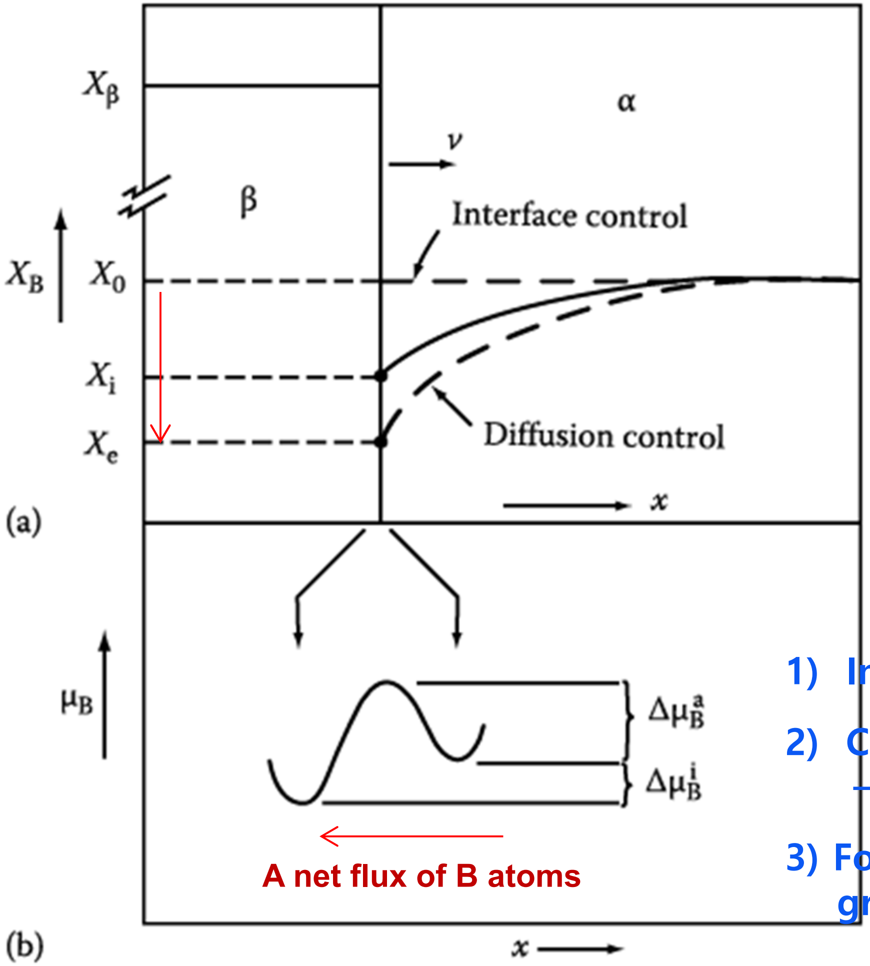
(a) Composition profile across the interface



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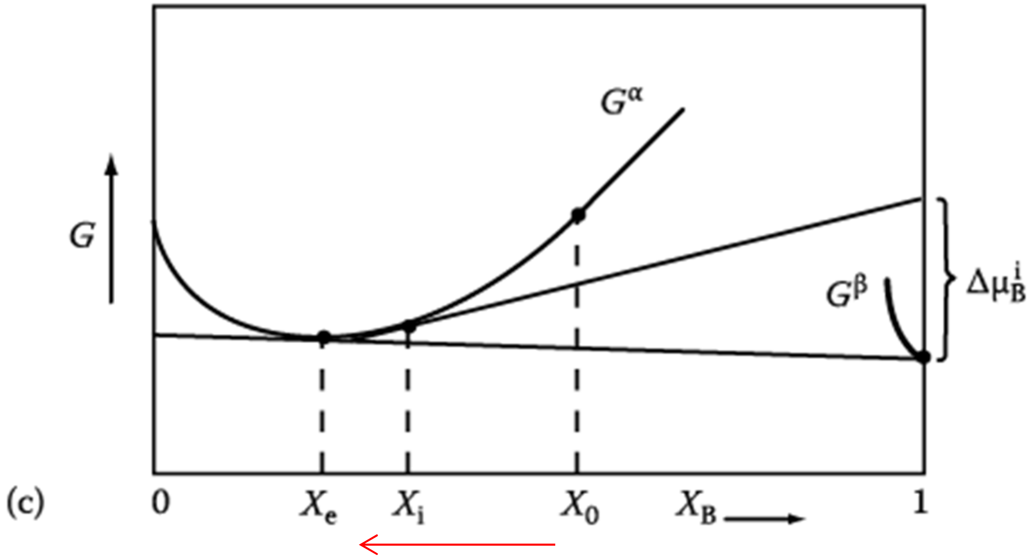

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2) Concentration B in the α phase adjacent to the inteface X_i
→ B concentration in α : $X_0 \rightarrow X_i$

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

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

v ~ ΔG/V_m driving force

→ F = ΔG/V_m

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

rate of grain growth ***dD/dt* ~ *1/D*, exponentially increase with *T***

- Interface velocity of precipitate

$$\boxed{v = M\Delta\mu_B^i / V_m}$$

***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

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

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

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

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

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

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

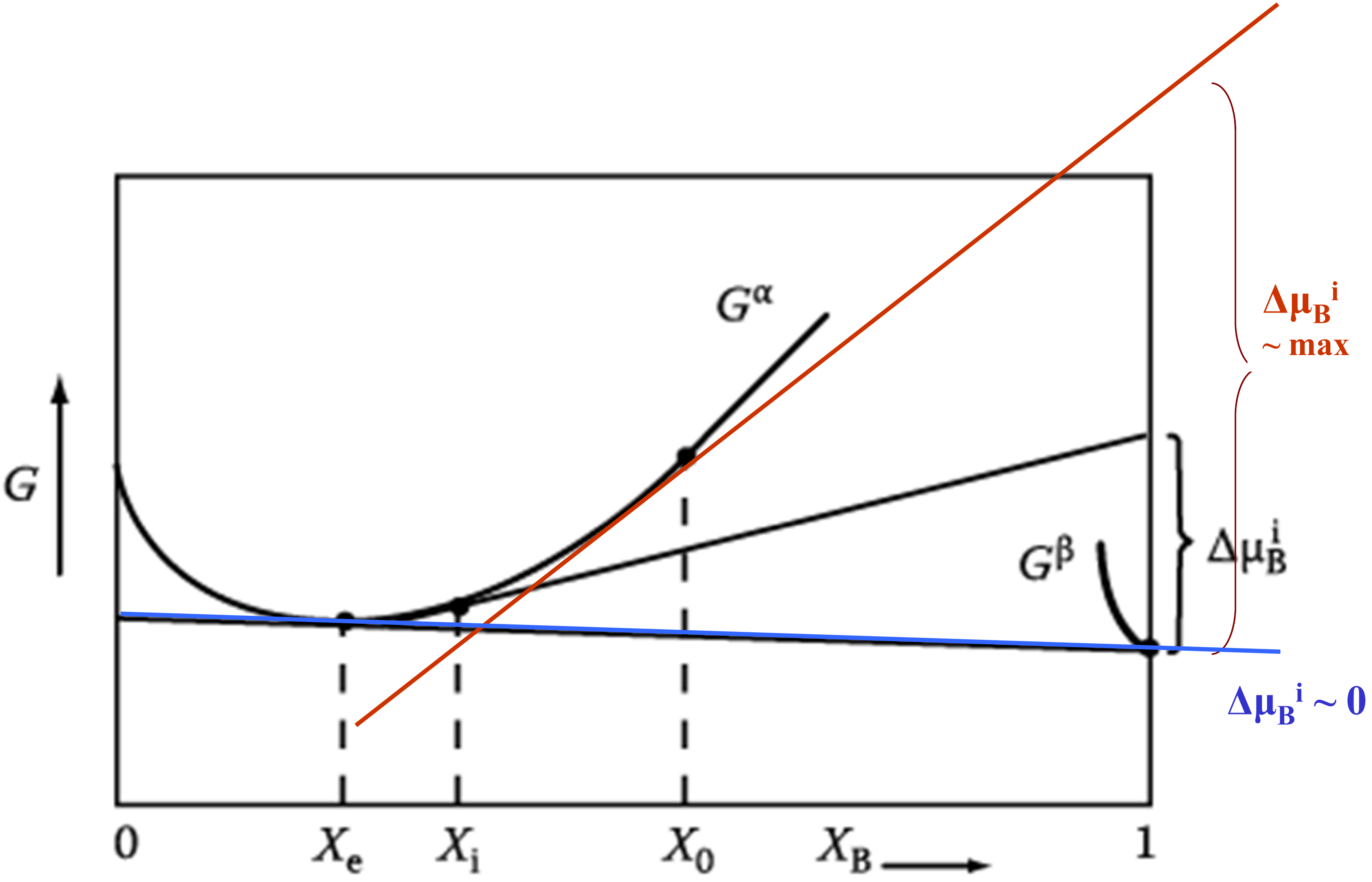
2) When the interface has a low mobility,

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

3) In the limit of a very low mobility,

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

$\Delta\mu_B^i$ 는 최대


G
G^{α}
G^{β}
$\Delta\mu_B^i$
$\Delta\mu_B^i$
~ max
$\Delta\mu_B^i \sim 0$
0
X_e
X_i
X_0
X_B
1

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

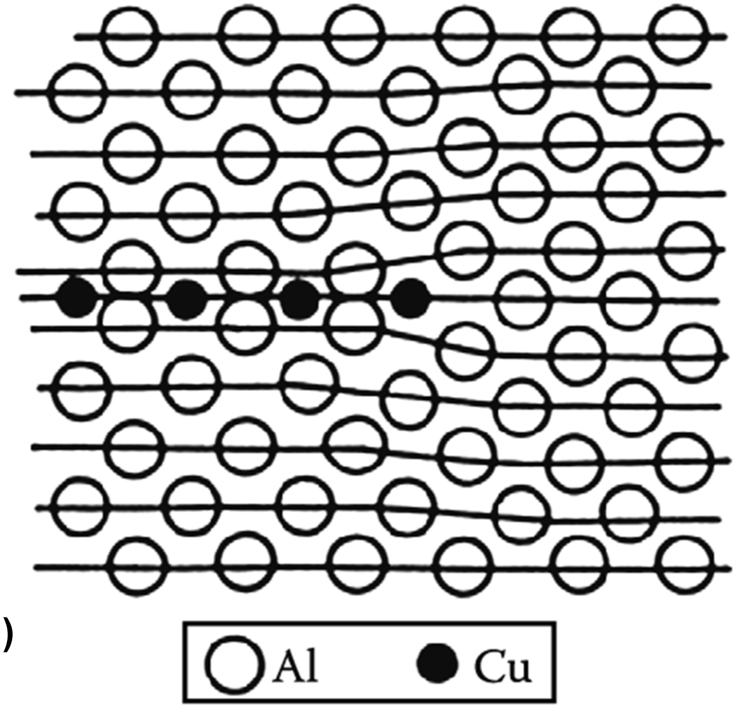
Al-Cu ppt structures

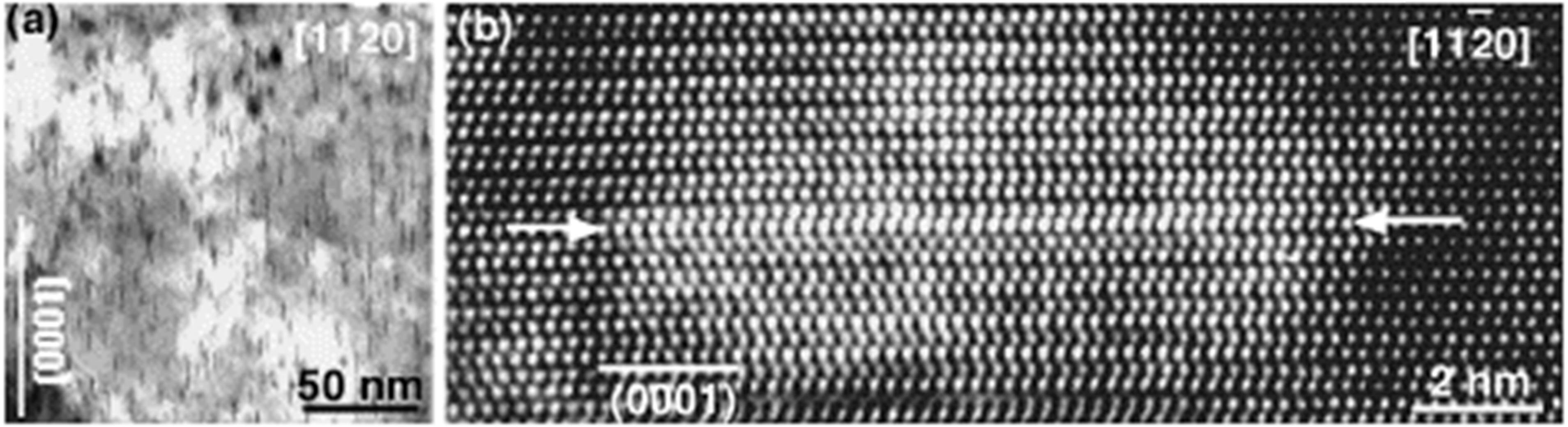
If two phases with different compositions, but the same crystal structure are separated by a coherent interface

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 $(0\ 0\ 0\ 1)_\alpha$ 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

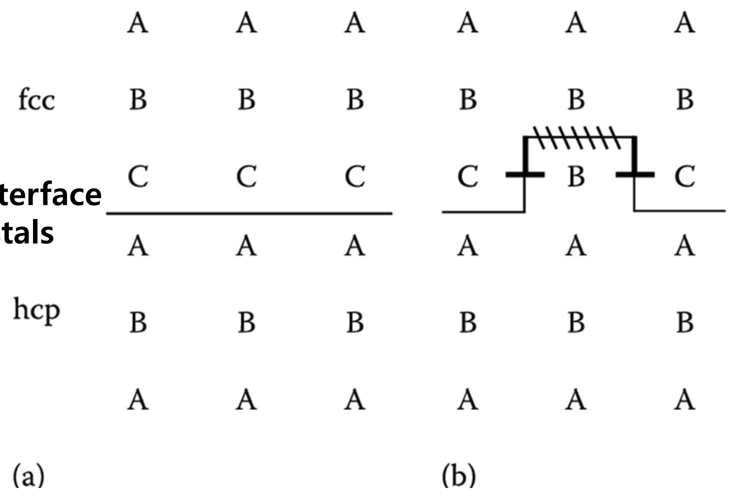
Incoherent interfaces and diffuse interface solid/liquid interfaces,
as high-angle grain boundaries = value of A close to unity ➡ "diffusion control"

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

Ex) Interface control

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

Coherent close-packed interface between fcc and hcp crystals



A loop of Shorkley partial disl.

~ high E/ unstable configuration
→ force back to its original position

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

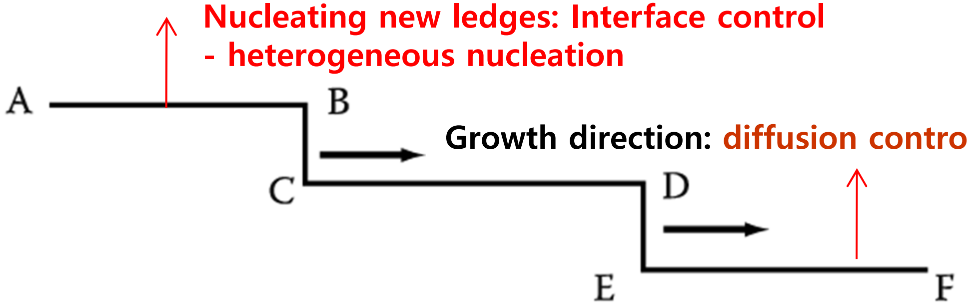
hcp phase growth by individual atomic jumps (i.e., so-called continuous growth) ~ very difficult
(very low accommodation factors and low mobility)

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



Nucleating new ledges: Interface control
\- heterogeneous nucleation

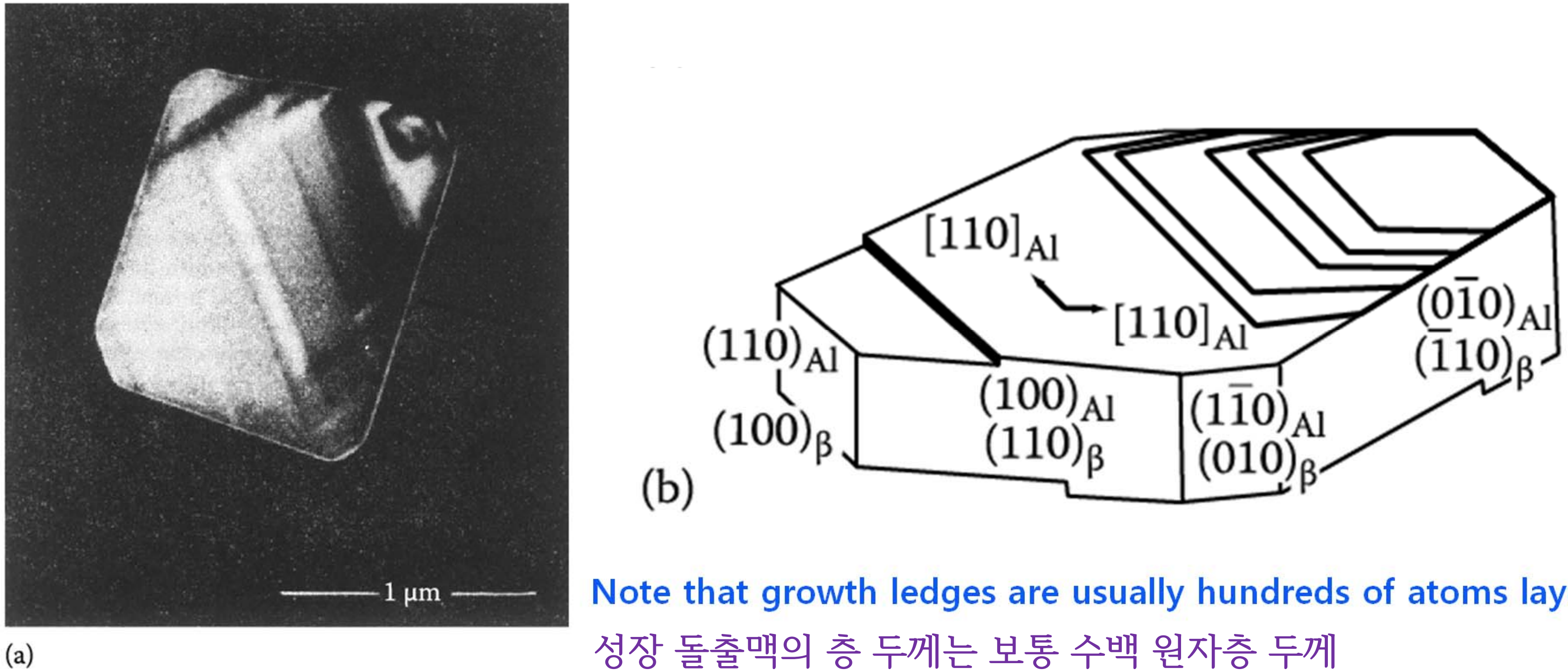
Growth direction: diffusion control

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 Al-1.5 wt% Mg_2Si, solution treated and aged 2h at 350 ℃. Dark field micrograph.

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



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

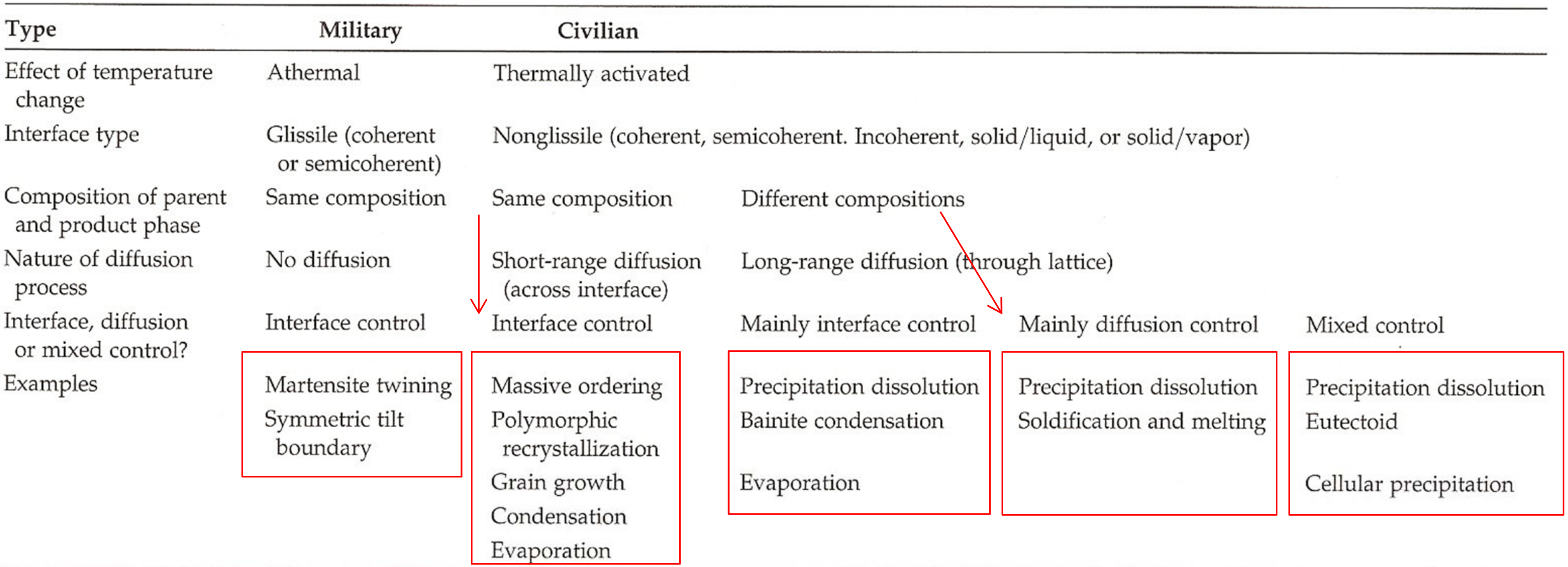
성장 돌출맥의 층 두께는 보통 수백 원자층 두께

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 $\gamma i / \gamma c$**
  - **b) (in practice) "relative rates" at which the coherent and incoherent interface can migrate**

정합/ 부정합 계면의 상대적인 이동속도 차에 의해 형상 변화

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)

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

until 20th November (before class)

Good Luck!!

Contents in Phase Transformation

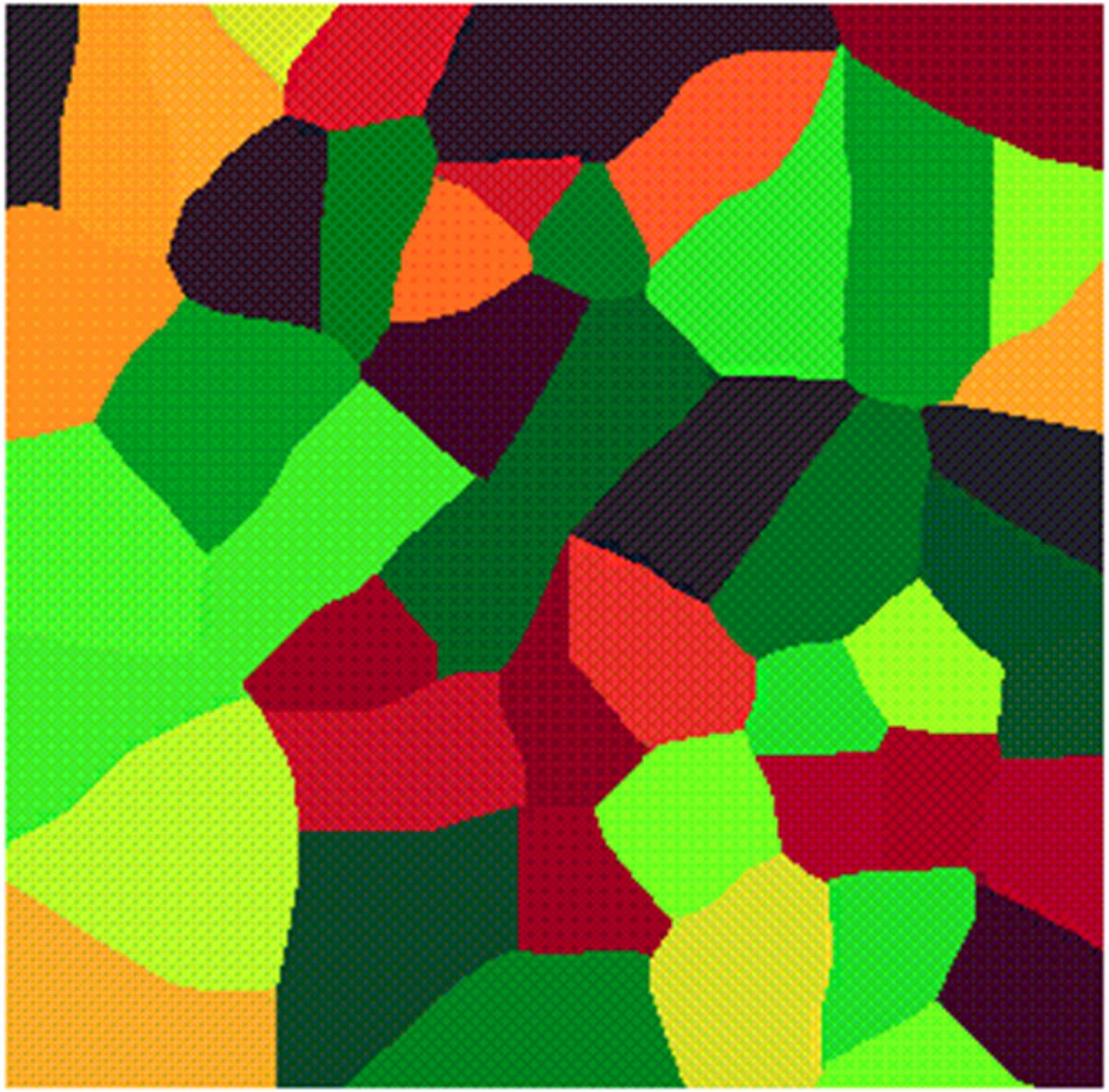
Background to understand phase transformation

- **(Ch1) Thermodynamics and Phase Diagrams**
- **(Ch2) Diffusion: Kinetics**
- **(Ch3) Crystal Interface and Microstructure**

Representative Phase transformation

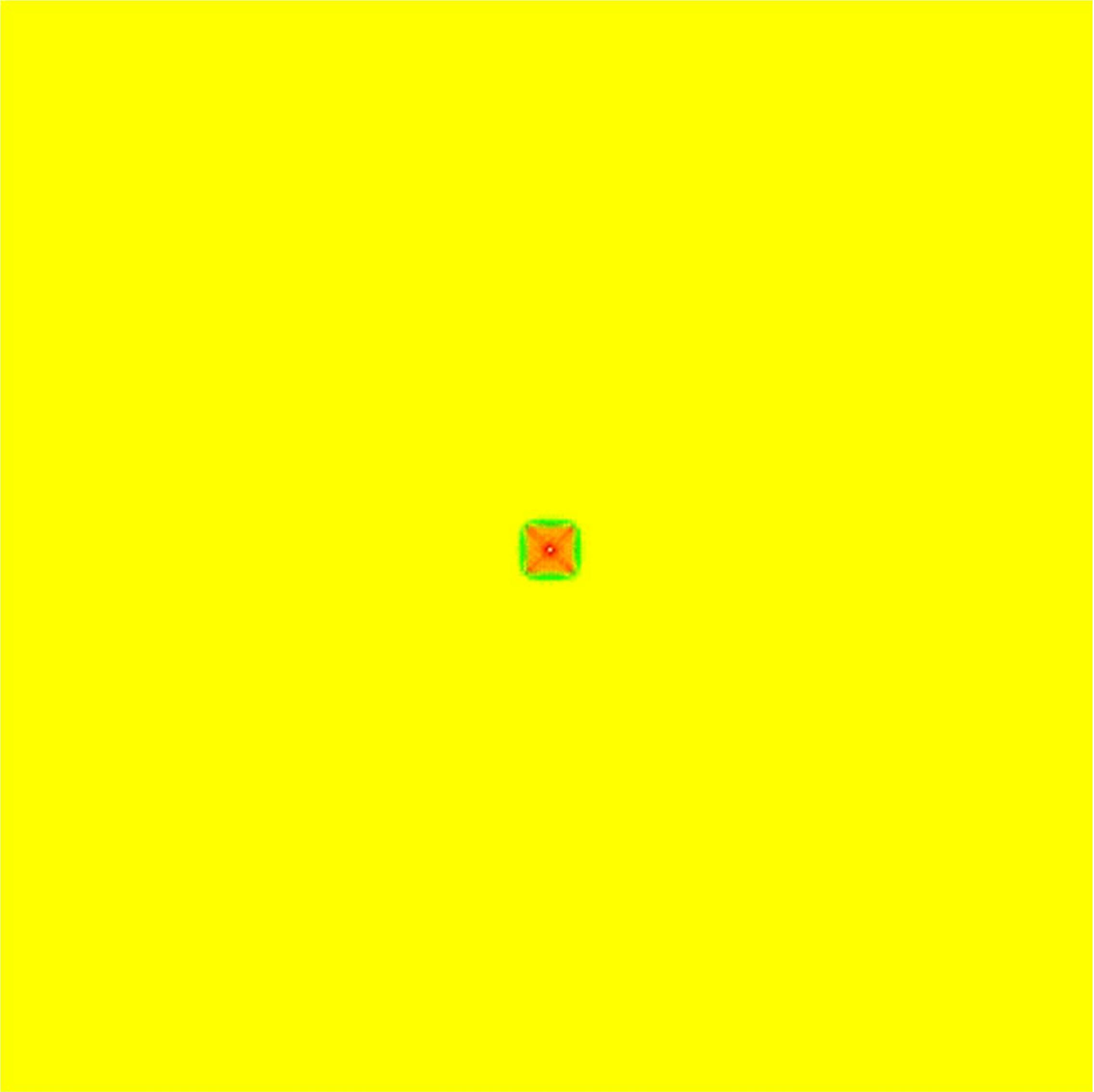
- **(Ch4) Solidification: Liquid → Solid**
- **(Ch5) Diffusional Transformations in Solid: Solid → Solid**
- **(Ch6) Diffusionless Transformations: Solid → Solid**

Solidification: Liquid → 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 of sharply defined interface
- Heat Flow and Interface Stability

Q: Undercooling of homogenous vs heterogenous nucleation ?

Solidification: Liquid → Solid

- casting & welding
- single crystal growth
- directional solidification
- rapid solidification

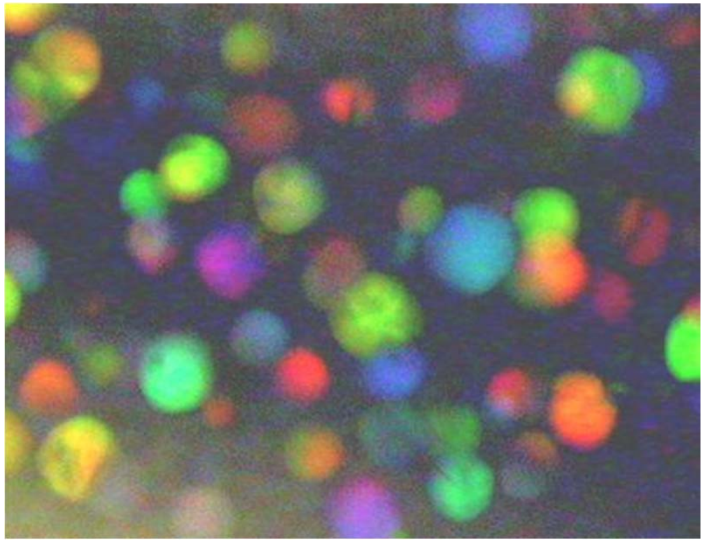
4.1. Nucleation in Pure Metals

T_m : $G_L = G_S$

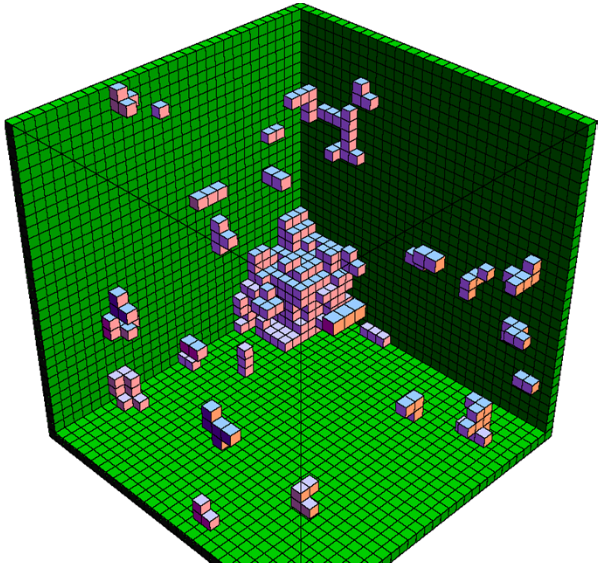
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

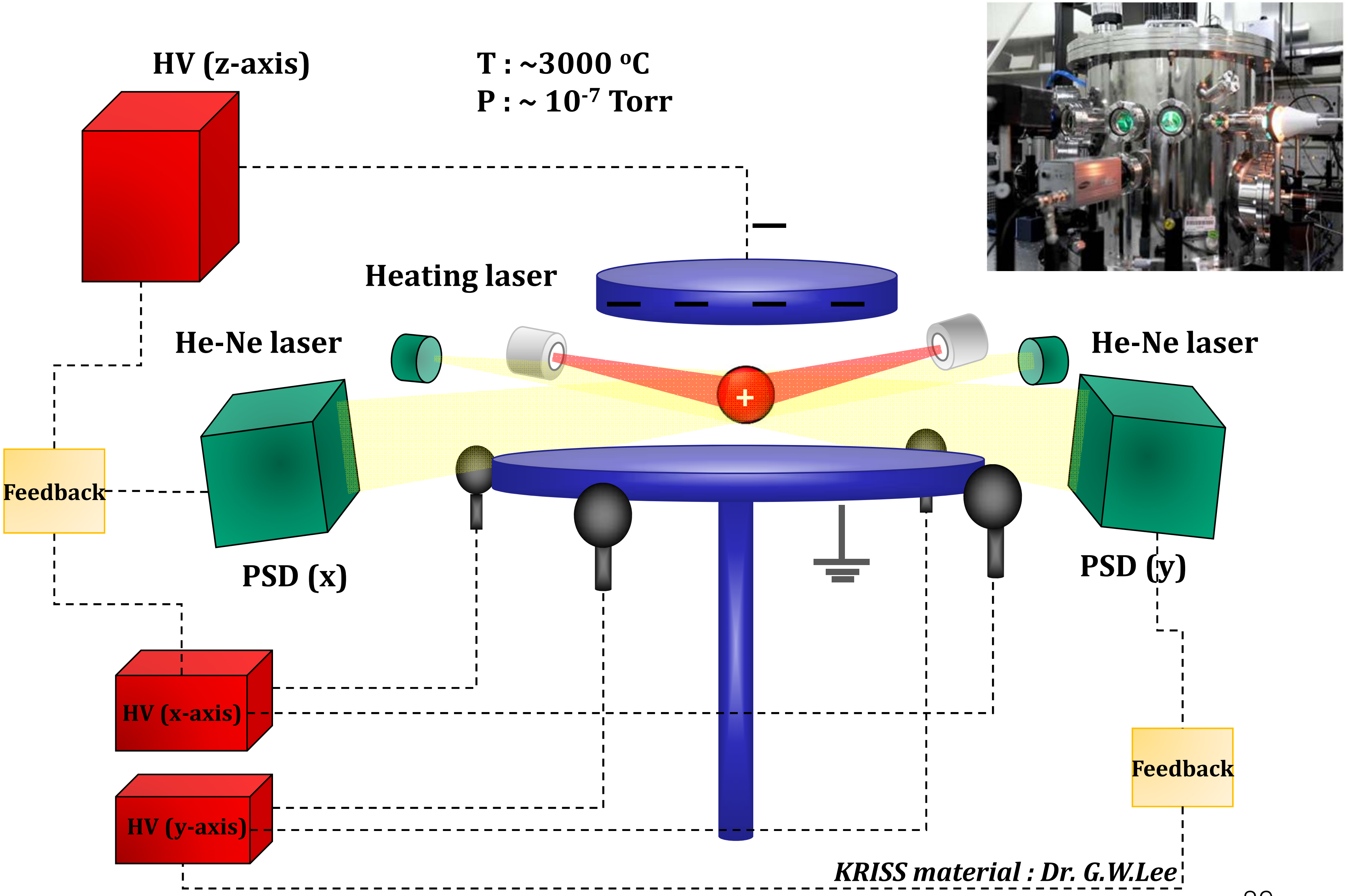
- Homogeneous nucleation



- Heterogeneous nucleation

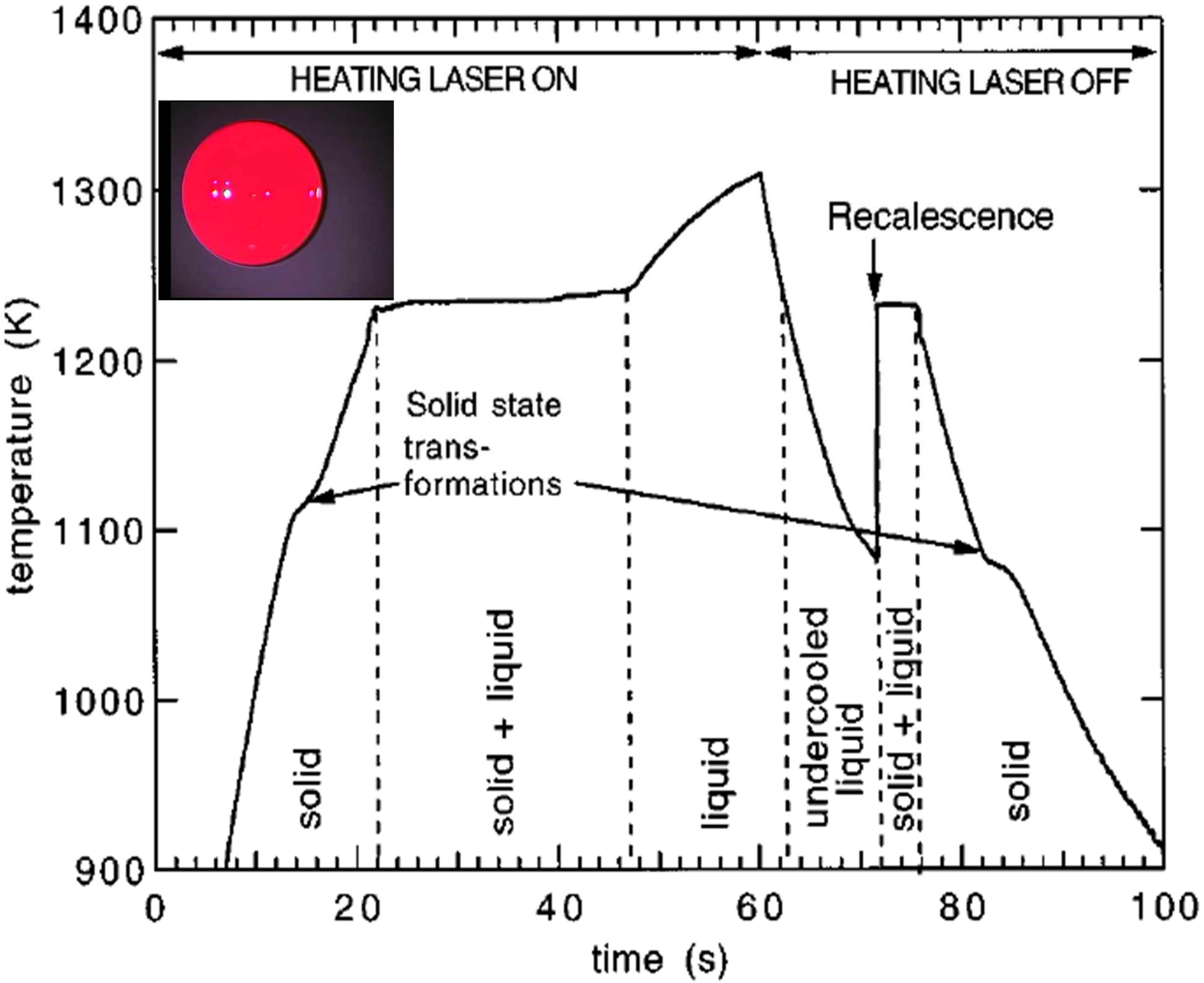


Electrostatic levitation in KRISS

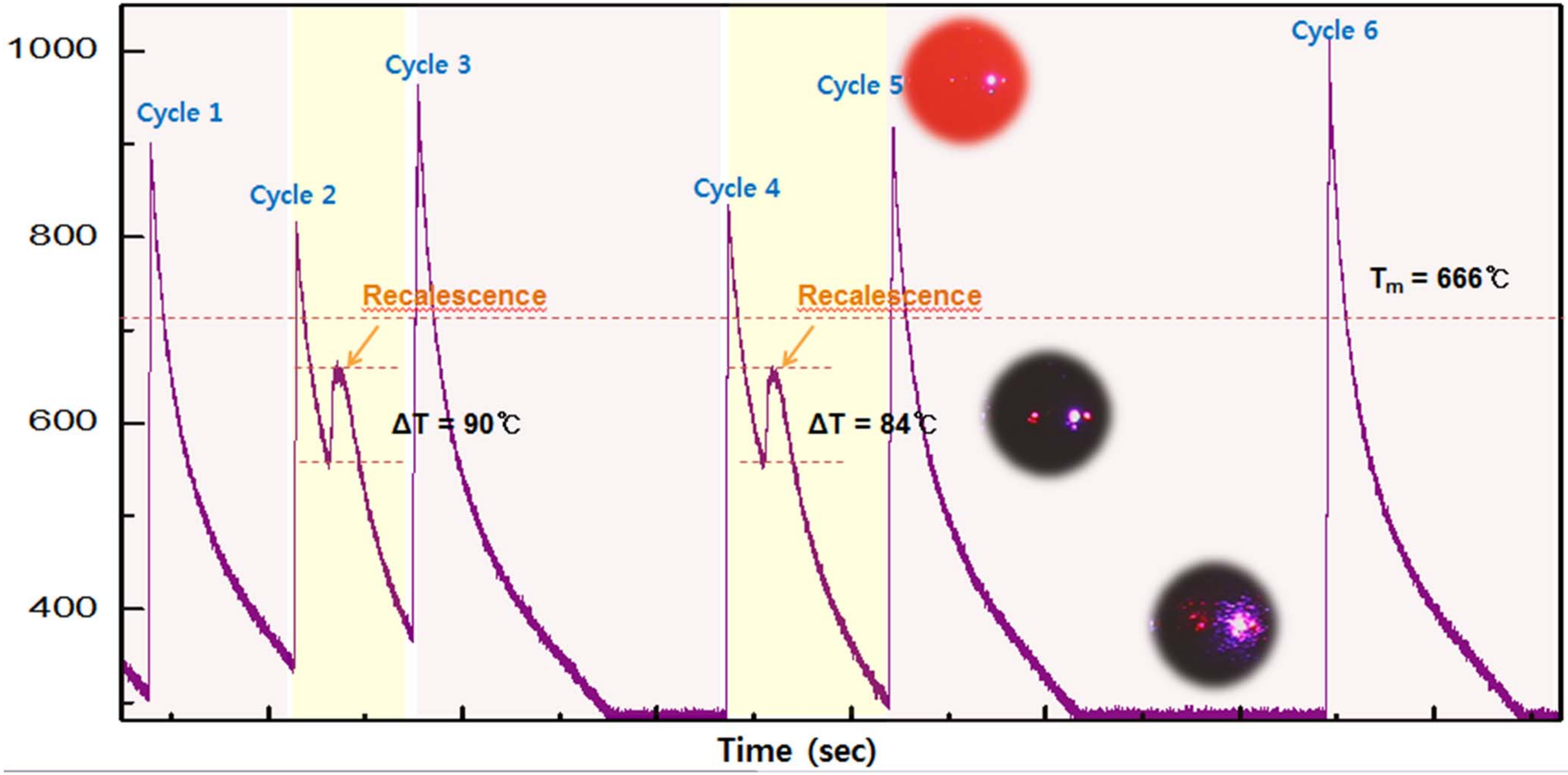


T : ~3000 °C
P : ~ 10^{-7} Torr

KRISS material : Dr. G.W.Lee


HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans- formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

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

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

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

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

$L : \Delta H = H^L - H^S$

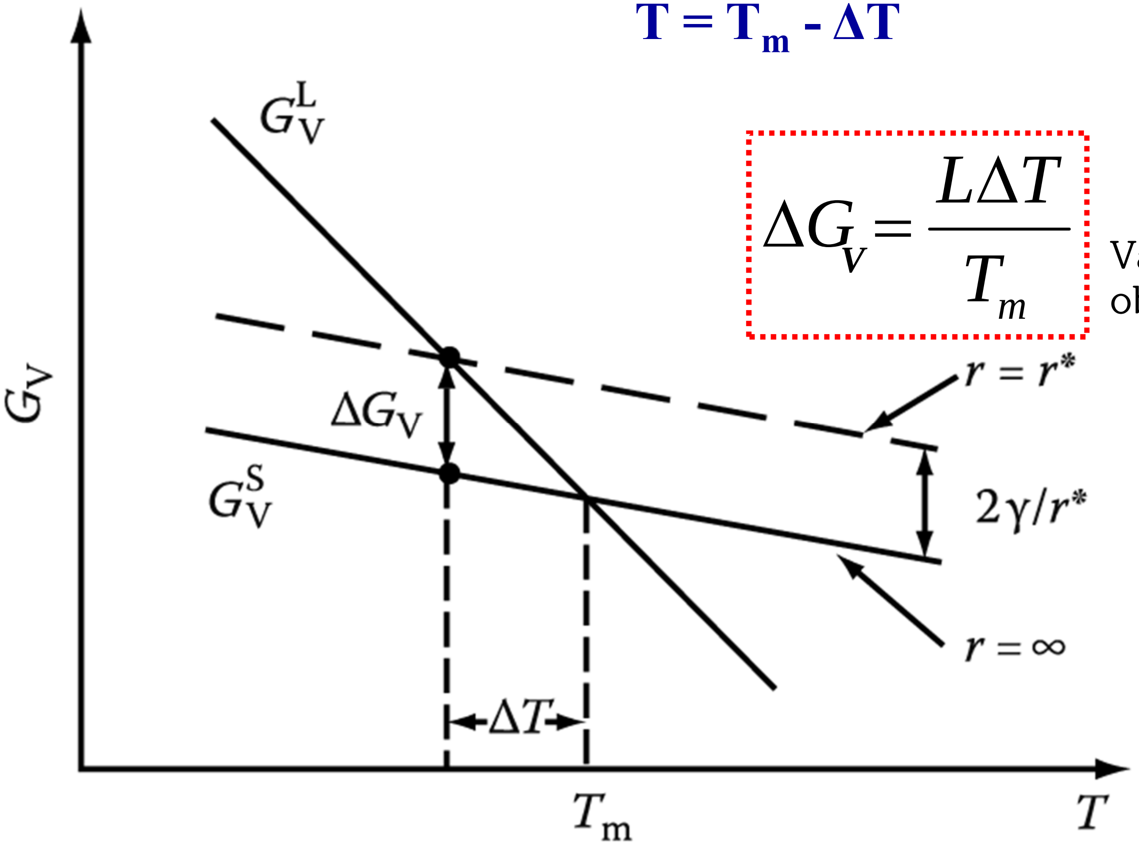
(Latent heat)

$T = T_m - \Delta T$

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

$\Delta S = \Delta H / T_m = L / T_m$

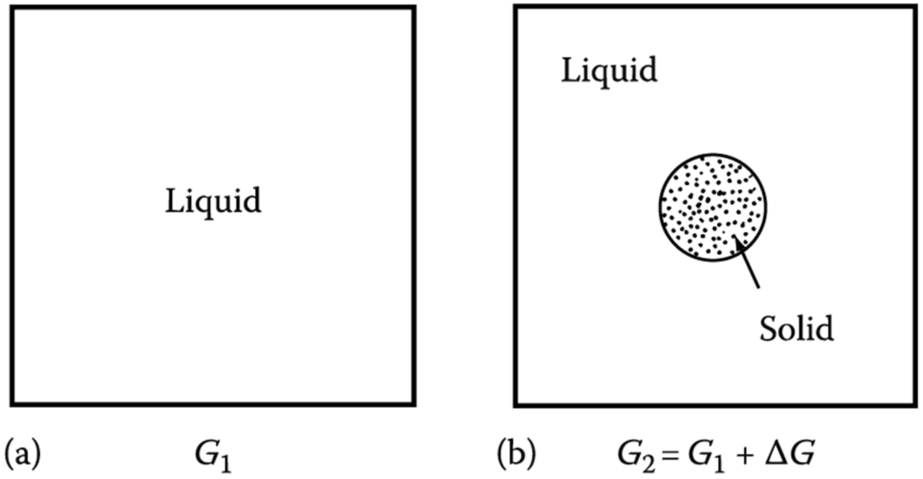
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$



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

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

4.1.1. Homogeneous Nucleation



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

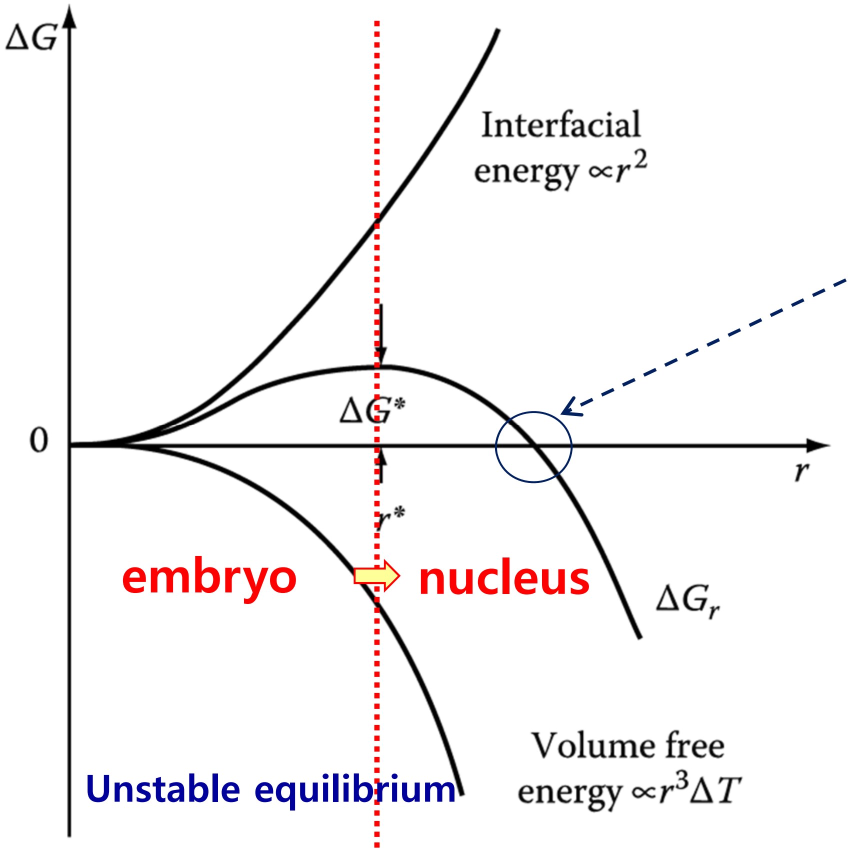
G_V^S, G_V^L : **free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

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* ⟹ dG=0

Gibbs-Thompson Equation

Critical ΔG of nucleation at r*

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

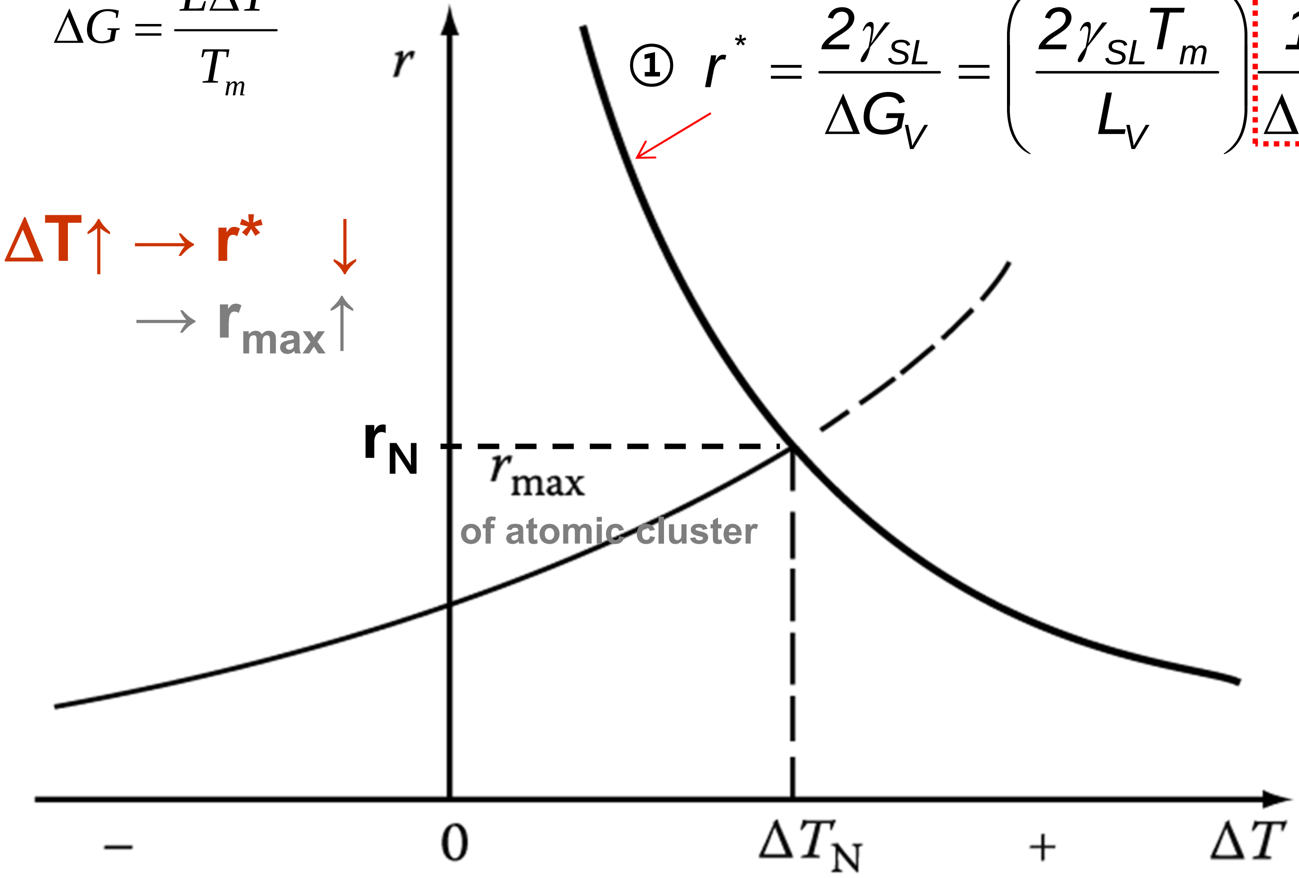
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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

Q: How do we define ΔT_N?

The creation of a critical nucleus ~ thermally activated process

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



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

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

$\rightarrow r_{max}\uparrow$

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

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

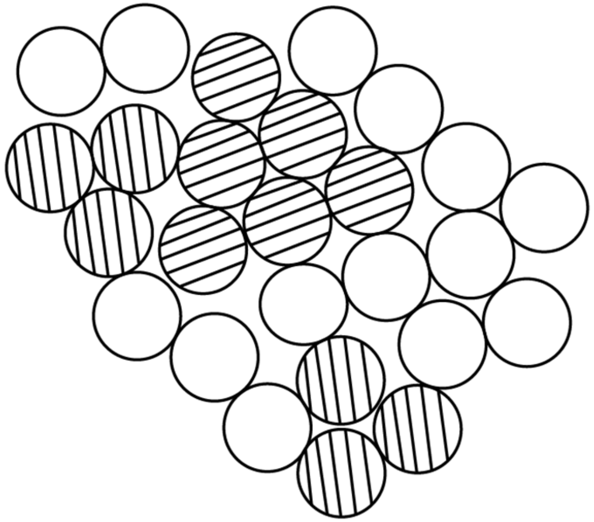
→ Condition for nucleation:

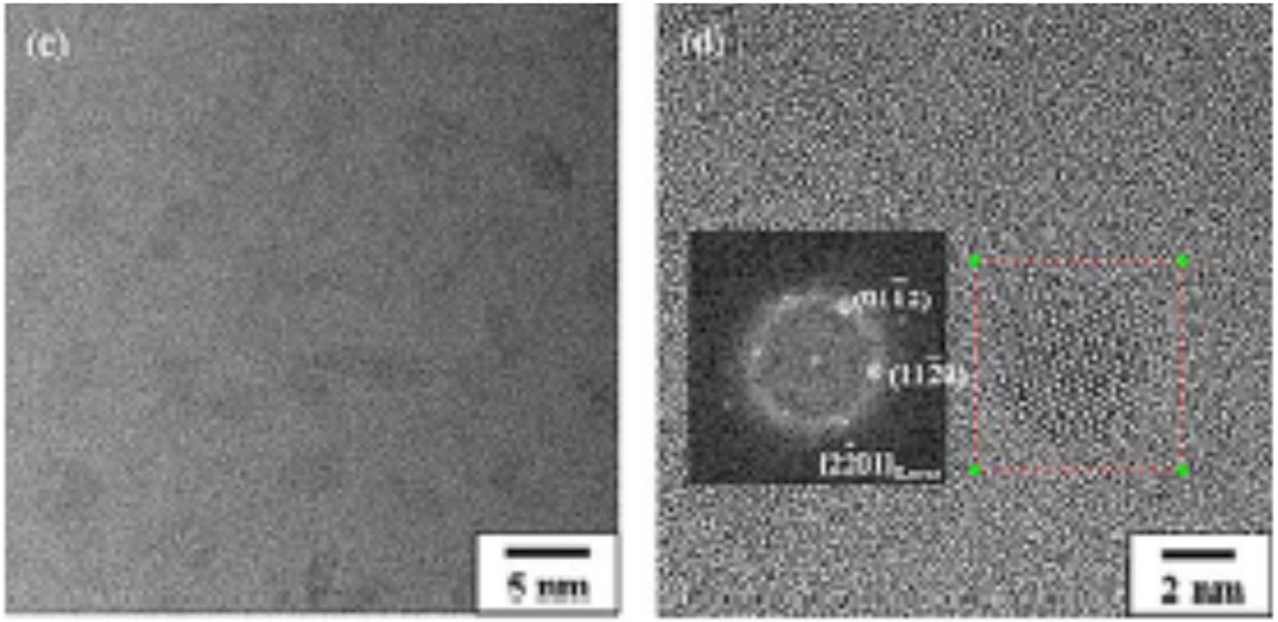
The number of clusters with r^* at $T < \Delta T_N$ is negligible.

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?

$$A_1 \to A_2 \to A_3 \to A_4 \to \cdots \to A_{m-1} \to A_m$$

$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1\to 2}}{kT}\right)$$

Excess free E associated with the cluster of 1→2 atoms

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

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

$$\vdots$$

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

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

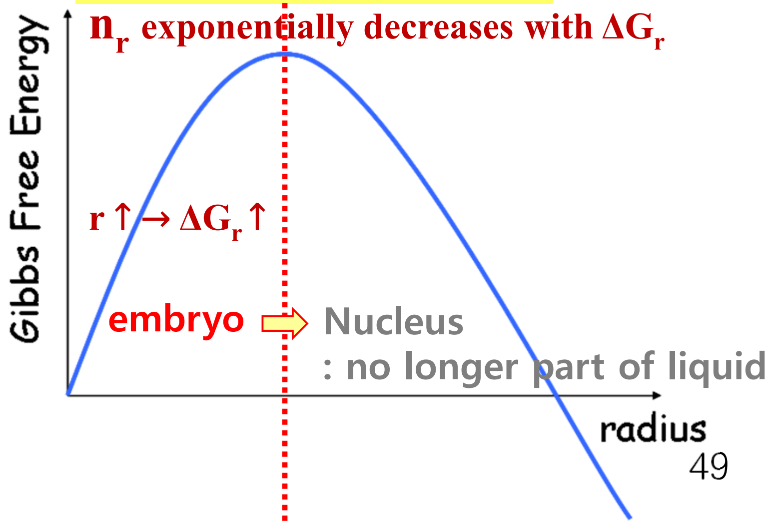
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1\to m}}{kT}\right)$$

반지름 r인 구상의 군집체 수

# of cluster of radius r

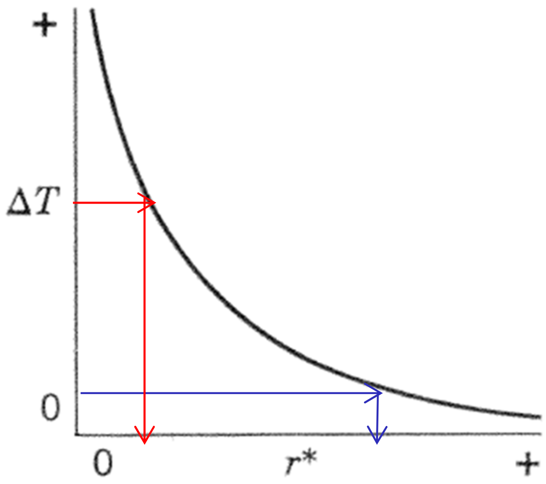
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

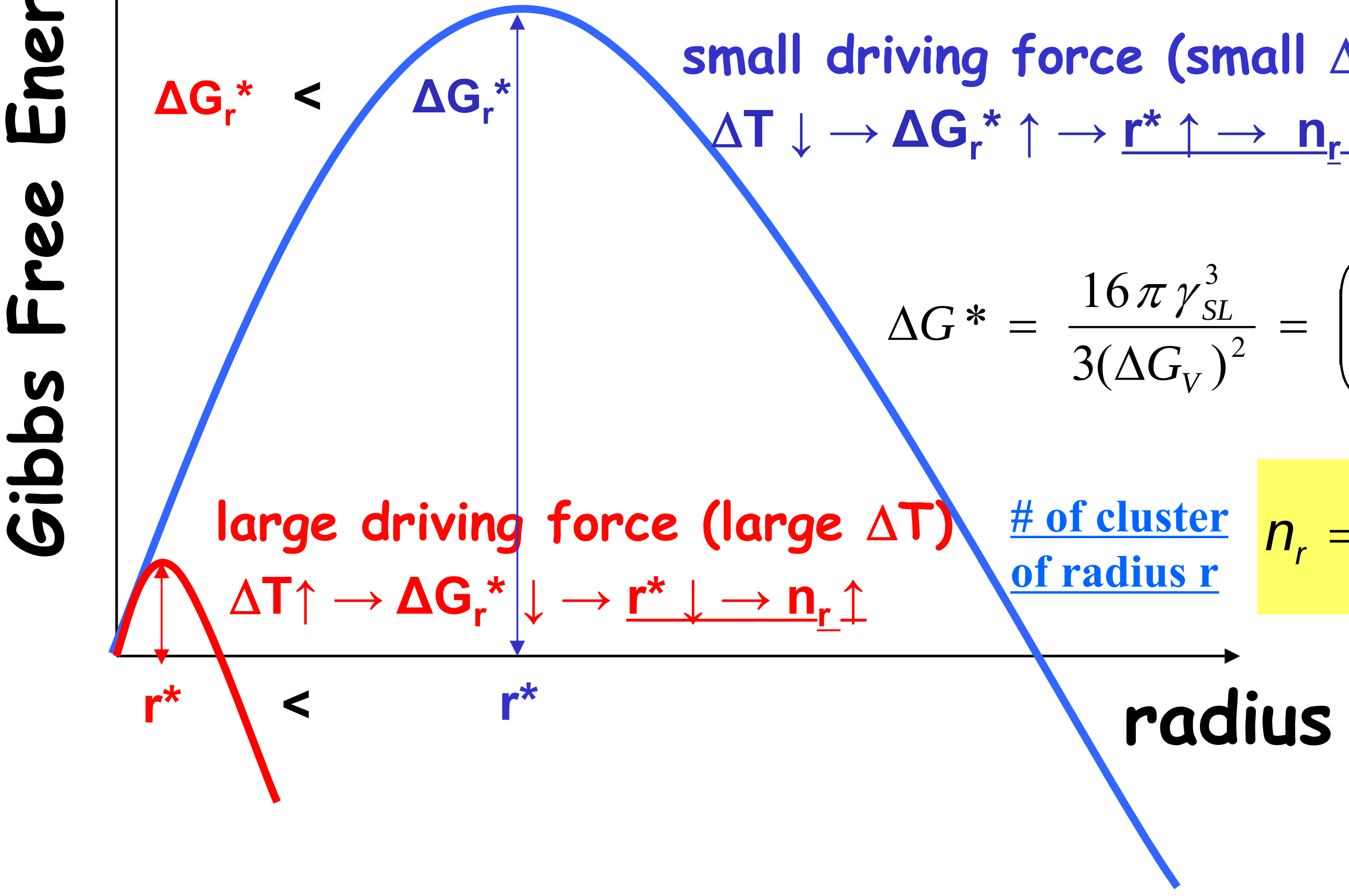
n_r exponentially decreases with ΔG_r



Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.





small driving force (small ΔT)

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

large driving force (large ΔT)

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

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

# 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 $r \le r^*$

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

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

- n_r exponentially decreases with ΔG_r

Ex. 1 mm^3 of copper at its melting point (n_0: 10^{20} atoms)

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

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

→ effectively a maximum cluster size, ~ 100 atoms
~ 10^{-8} clusters mm^{-3} or 1 cluster in ~ 10^7 mm^3

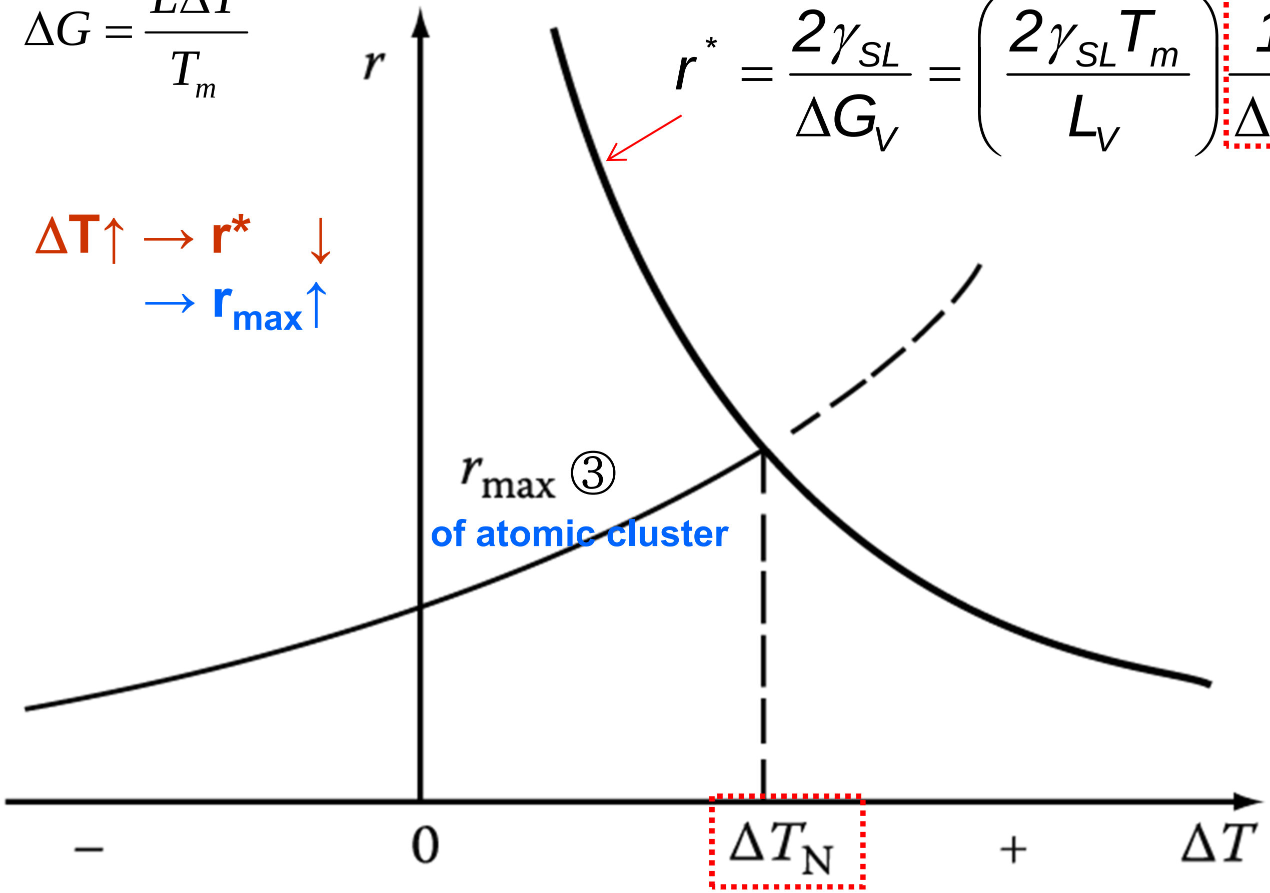
The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow r_{max}\uparrow$



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

$$C^* = C_0 \exp\left(-\frac{\Delta G^*_{\mathrm{hom}}}{kT}\right)$$ **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

$$N_{\mathrm{hom}} = f_0 C_o \exp\left(-\frac{\Delta G^*_{\mathrm{hom}}}{kT}\right)$$ **nuclei / m^3·s**

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

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

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

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

Reasonable nucleation rate

4.1.2. The homogeneous nucleation rate - kinetics

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

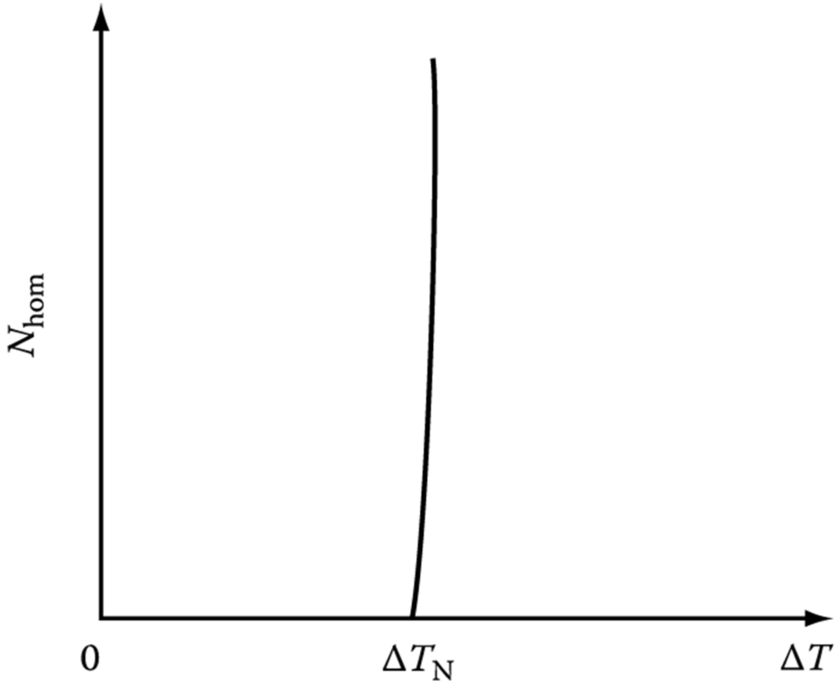
where $A = \dfrac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2 kT}$

A = relatively insensitive to Temp.

How do we define ΔT_N?

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

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, ΔT_N~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.

* Copper Homogeneous nucleation

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

If nucleus is spherical shape,

$V = 4.2 * 10^{-21}$ cm^3 ~ 360 atoms (∵ 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.**

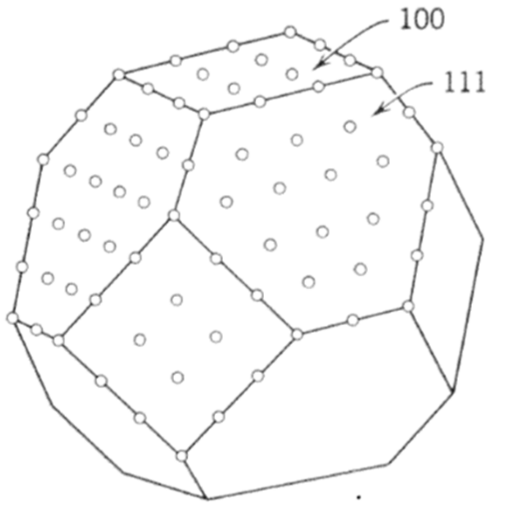


Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

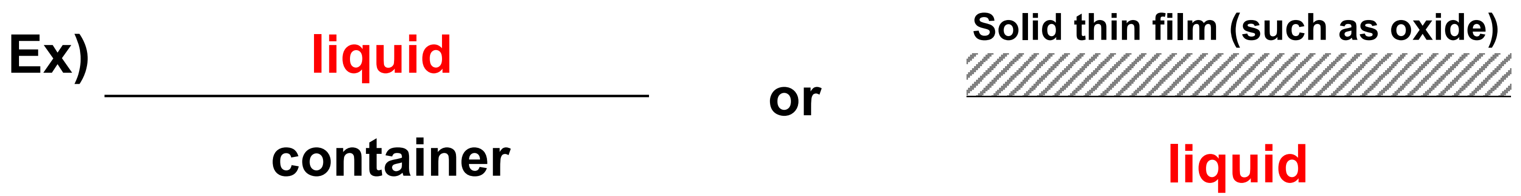
Real behavior of nucleation: metal $\Delta T_{\text{bulk}} < \Delta T_{\text{small drop}}$

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"



Why this happens? What is the underlying physics?

Which equation should we examine?

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

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