

**2021 Spring**

# **“Phase Equilibria *in* Materials”**

**03.02.2021**

**Eun Soo Park**

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**Office hours: by an appointment**

# ***Introduction***

- **Web lecture assistance: <http://etl.snu.ac.kr>**
  - **All materials will be posted at the webpage.**
  - **text message will be sent for the important and urgent notice.**
- **Hand out copied materials or scanned materials in website**

**Text: A. PRINCE, "Alloy Phase Equilibria",**

Elsevier publishing company (1966)\_an out-of-printed book

**Prerequisite coursework: Thermodynamics, Phase transformation in Materials**

**References: 1) "Phase Diagrams in Metallurgy",**

Frederick N. Rhines, McGraw-Hill Book Company, INC (1956)

2) **"Principles of Phase Diagrams in Materials Systems",**

Paul Gordon, McGraw-Hill Book Company, INC (1968)

3) **"Phase Transformations in Metals and Alloys",**

D.A. Porter and K.E. Eastering, Nelson thornes Ltd (2001)

**Additional reading materials will be provided.**

# ***Course Goals***

This course provides the fundamental concepts and advanced understandings of phase equilibria in materials, including relationship of free energy to phase diagram. The course will address some kinetic and non-equilibrium concepts and some phenomenological discussions. In particular, phase and composition determinations in ternary and quaternary systems, relationship between phase diagrams and thermodynamic data, and cooling paths during cooling of the ternary melts will be covered. This course can provide a working knowledge of how to construct and read phase diagrams and use them to solve problems involving materials and process design.

# ***Schedule***

- week 1 Introductory Thermodynamics
- week 2 Thermodynamics of Solutions
- week 3 Binary Phase Diagrams: Two-phase Equilibrium
- week 4 Binary Phase Diagrams: Three-phase Equilibrium
- week 5 Binary Phase Diagrams: Limited Solubility in Both the Liquid and Solid State
- week 6 Binary Phase Diagrams: Reactions in the Solid State
- week 7 Binary Phase Diagrams: Allotropy of the Components
- week 8 Ternary Phase Diagrams: Two-phase Equilibrium
- week 9 Ternary Phase Diagrams: Three-phase Equilibrium
- week 10 Ternary Phase Diagrams: Four-phase Equilibrium
- week 11 Ternary Phase Diagrams: Intermediate Phases
- week 12 Ternary Phase Diagrams: Liquid Immiscibility
- week 13 Ternary Phase Diagrams: Four-phase Equilibrium Involving Allotropy of One Component
- week 14 The Association of Phase Regions
- week 15 Quaternary Phase Diagrams I
- week 16 Quaternary Phase Diagrams II

# ***Components of Your Grade:***

## **1) Exams (mid: 35% + final: 40%)**

There will be two exams, each of which takes place in class for 2 hours. The exams will be conceptual and difficult.

## **2) Reports or Presentation (15%)**

Assignments handed in after the start of class lose credit depending on the timing. If you wish, you may work together on homework assignments. But, you must hand in your own work, in your own words.

## **3) Attendance (10%)**

**REMARK: The percentage can be changed under 5%.**

# ***Policies and Procedures***

- ***All homework are due by the start of class on the stated deadline.***
  - Late assignments go to my office. If I'm not around, slide it under my door and leave me an email so that I know when you turned it in.
  - You lose 20% of the full assignment value per day late. Since homework are due on **Thursday**, you can get 80% credit if you turn it in on **Friday**, 50% on next Monday, nothing thereafter.
- ***If you wish, you may work together on homework assignments. BUT, you must hand in your own work, in your own words.***
- **IMPORTANT:** ***you MUST reference your sources appropriately, including texts, journals web sites, etc.***
  - Article authors, title, journal, volume, year, pages
  - Book authors, title, publisher, year, pages
  - Web address
  - etc.

# Microstructure-Properties Relationships

*Alloy design & Processing*

*Performance*

*“Phase Transformation”*

*Microstructure*  
*down to atomic scale*

*Properties*

*“Tailor-made Materials Design”*

**Important!!!**

***Understanding and Controlling***  
**Phase Transformation of Materials**



# Contents in Phase Transformation

D.A. Porter and K.E. Eastering, "Phase Transformations in Metals and Alloys"

Basic concept  
for understanding  
Phase Transformation

(Ch1) **Thermodynamics** and Phase Diagram

(Ch2) **Diffusion: Kinetics**

(Ch3) **Crystal Interface and Microstructure**

Representative  
Phase Transformation

(Ch4) **Solidification: Liquid → Solid**

(Ch5) **Diffusional Transformations in Solids: Solid → Solid**

(Ch6) **Diffusionless Transformations: Solid → Solid**

# Phase Equilibria in Materials

*Thermodynamics*

*Phase diagrams*

*Binary, Ternary, Quarternary phase diagram*

**2021 Spring**

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# Phase Equilibria in Materials

*Thermodynamics*

*Phase diagrams*

*Binary, Ternary, Quarternary phase diagram*

## Contents for today's class

# CHAPTER 1 Introductory Thermodynamics

- **Equilibrium**

- **Single component system**

  - Gibbs Free Energy as a Function of **Temp.** and **Pressure**

- **Phase Transformation**

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

  - Driving force for solidification

- **Classification of phase transition**

  - First order transition/Second order transition



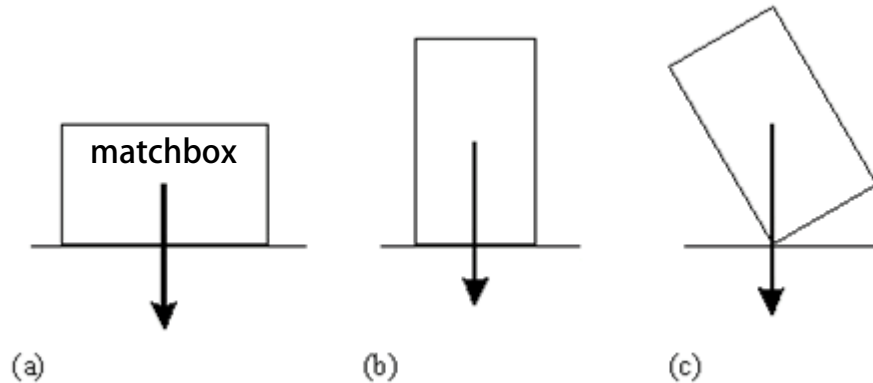
**Q1: “thermodynamic equilibrium”?**

**Lowest possible value of Gibb’s Free Energy**

# Chapter 1

## Equilibrium

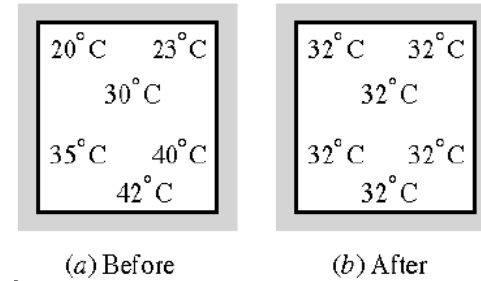
### Mechanical equilibrium



: total potential energy of the system is a minimum.

### Thermal equilibrium

: absence of temperature gradients in the system



### Chemical equilibrium

: no further reaction occurs between the reacting substances  
i.e. the forward and reverse rates of reaction are equal.

## Thermodynamic equilibrium

: the system is under mechanical, thermal and chemical equilibrium

The properties of the system-P, T, V, concentrations-do not change with time.

**Thermodynamic free energy**, the energy in a physical system that can be converted to do work,

When no useful work is being extracted from the sub-system,  $dX \leq 0$

The energy  $X$  reaching a minimum at equilibrium, when  $dX=0$ .

If no chemical species can enter or leave the sub-system, then  $\sum \mu_{iR} N_i$  can be ignored.

If furthermore the temperature of the sub-system is such that  $T$  is always equal to  $T_R$ ,

then  $X = E - TS + \text{const}' = A + \text{const}'$

in particular:

**Helmholtz free energy**, the energy that can be converted into work at a constant temperature and volume

If the volume  $V$  is constrained to be constant, then

where  $F$  is the thermodynamic potential called Helmholtz free energy,  $F=E-TS$ .

Under constant volume conditions therefore,  $dF < 0$  if a process is to go forward;

and  $dF=0$  is the condition for equilibrium.  $X = E - TS + \text{const}' = A + \text{const}'$

Helmholtz free energy :  $F=E-TS$ .

Useful when  $V$  is constrained during thermodynamic process.

**Gibbs free energy**, the energy that can be converted into work at a uniform temperature and pressure throughout a system

If the sub-system pressure  $P$  is constrained to be equal to the external reservoir pressure  $P_R$ ,

$$X = E - TS + PV + \text{const} = G + \text{const}$$

,where  $G$  is the Gibbs free energy,  $G=E-TS+PV$ . Therefore under constant pressure conditions, if  $dG \leq 0$ , then the process can occur spontaneously, because the change in system energy exceeds the energy lost to entropy.  $dG=0$  is the condition for equilibrium. This is also commonly written in terms of enthalpy, where  $H=E+PV$ .  $G=H-TS$

Gibbs free energy :  $G=E +PV-TS=H-TS$

**Useful when P is constrained during thermodynamic process.**

# Chapter 1.1

Relative Stability of a System → Gibbs Free Energy

$$G = H - TS$$

***H*** : *Enthalpy* ; Measure of the heat content of the system

$$H = E + PV$$

$$H \cong E \text{ for Condensed System}$$

**E** : **Internal Energy**, Kinetic + Potential Energy of a atom within the system

Kinetic Energy :

Atomic Vibration (Solid, Liquid)

Translational and Rotational Energy in liquid and gas.

Potential Energy : Interactions or Bonds between the atoms within the system

***T*** : *The Absolute Temperature*

***S*** : *Entropy*, The *Randomness* of the System

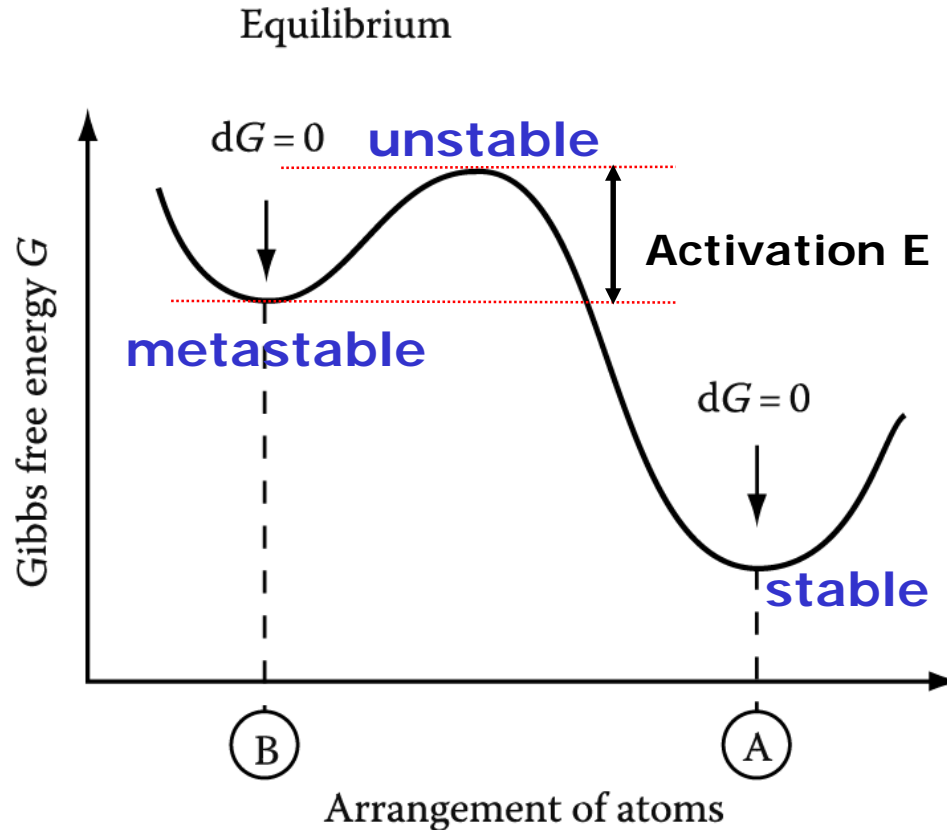
# Chapter 1.1

## Equilibrium

$$dG = 0$$

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



Phase Transformation

$$\Delta G = G_2 - G_1 < 0$$

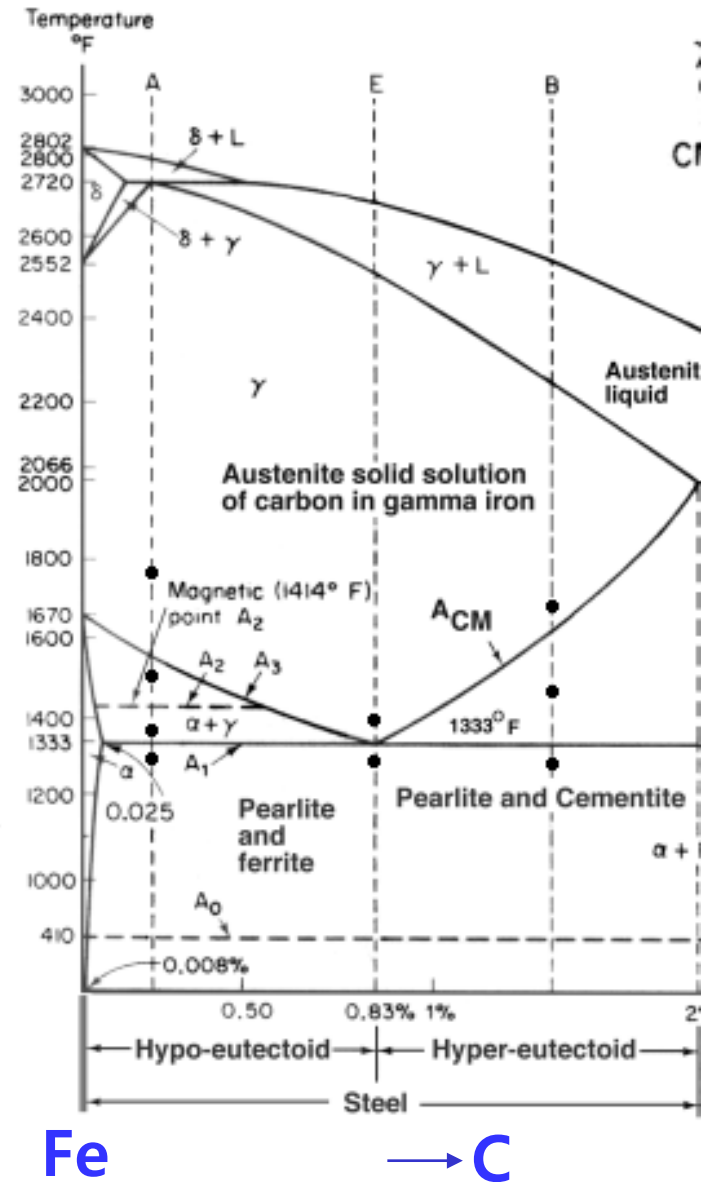
**Q2: What is single component system?**

# 1.2 Single component system

One element (Al, Fe)

One type of molecule (H<sub>2</sub>O)

Allotropic form?



$$G = H - TS$$



1.2.1 Gibbs Free Energy as a Function of Temp. 14



\* What is the role of temperature on equilibrium?

**Q3:  $C_v$  vs.  $C_p$  ?**

**Specific heat**

**(the quantity of heat (in joules) required to raise the temperature of substance by 1K)  
at constant volume VS. at constant pressure**

$$H = E + PV \longrightarrow dE = \delta Q - P \cdot dV$$

When V is constant,

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P \frac{dV}{dT} \xrightarrow{0}$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V dT$$

Experimentally, it is easy to keep constant P (Cp) than constant V because it is difficult to make constant V (Cv) → pressure ex) 1 atm,

When pressure is constant,

$$H \equiv E + PV \longrightarrow dH = dE + PdV + VdP$$

$$= \delta Q - \delta w + PdV + VdP$$

$$dE = \delta Q - P \cdot dV$$

$$= \delta Q - PdV + PdV + VdP$$

$$= \delta Q + VdP$$

$$\rightarrow \frac{dH}{dT} = \frac{\delta Q}{dT} + V \frac{dP}{dT}$$

$$\rightarrow \frac{dP}{dT} = 0 \quad \text{when } P \text{ is constant}$$

$$\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P$$

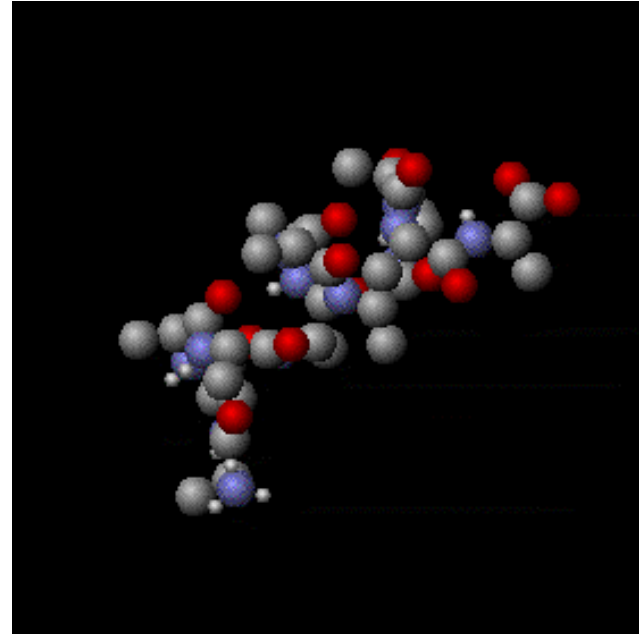
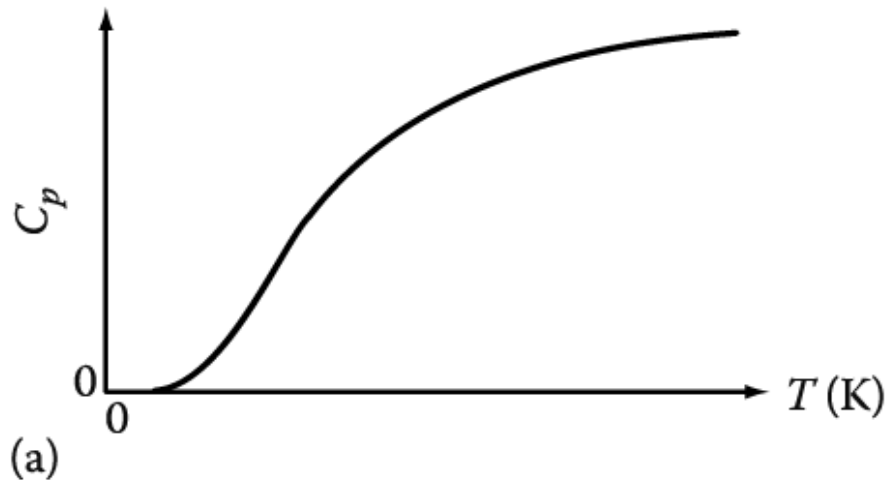
$$H = \int C_P dT$$

In alloy work one usually consider systems at constant pressure so that enthalpy changes are more important than energy changes.

$C_p$ ; temperature-dependent function

$$C_p = a + bT + CT^{-2}$$

(empirical formula above room temp)



Molecules have internal structure because they are composed of atoms that have different ways of moving within molecules. Kinetic energy stored in these internal degrees of freedom contributes to a substance's specific heat capacity and not to its temperature.

## Table of specific heat capacities

Substance	Phase	$C_p$ J / g·K	$C_p$ J / mol·K	$C_v$ J / mol·K	Volumetric heat capacity J / cm <sup>3</sup> ·K
Aluminium	Solid	0.897	24.2		2.422
Copper	solid	0.385	24.47		3.45
Diamond	solid	0.5091	6.115		1.782
Gold	solid	0.1291	25.42		2.492
Graphite	solid	0.710	8.53		1.534
Iron	solid	0.450	25.1		3.537
Lithium	solid	3.58	24.8		1.912
Magnesium	solid	1.02	24.9		1.773
Silver	solid	0.233	24.9		
Water	liquid (25 °C)	4.1813	75.327	74.53	4.184
Zinc	solid	0.387	25.2		

All measurements are at 25 °C unless otherwise noted.

\* What is the role of temperature on equilibrium?

**Q4: How is  $C_p$  related with H and S?**

# Draw the plots of (a) $C_p$ vs. $T$ , (b) $H$ vs. $T$ and (c) $S$ vs. $T$ .

*How is  $C_p$  related with  $H$  and  $S$ ?*

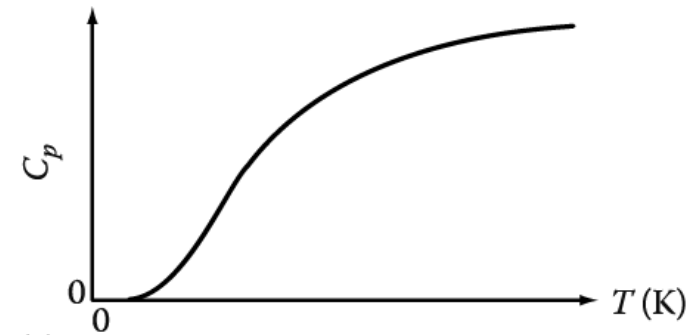
$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad H = ? \quad H = \int_{298}^T C_P dT$$

**$H = 0$  at 298K for a pure element  
in its most stable state.**

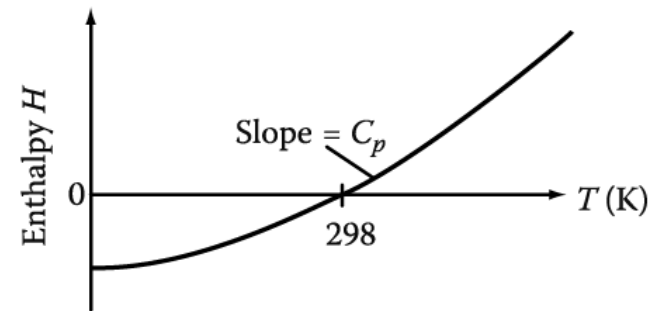
: When considering a phase transformation or a chemical reaction, the important thing is not the value of the thermodynamic function, but **the amount of change.**

Entropy :  $S = \frac{q}{T}$

$$S = ? \quad \frac{C_P}{T} = \left( \frac{\partial S}{\partial T} \right)_P \quad S = \int_0^T \frac{C_P}{T} dT$$



(a)



(b)

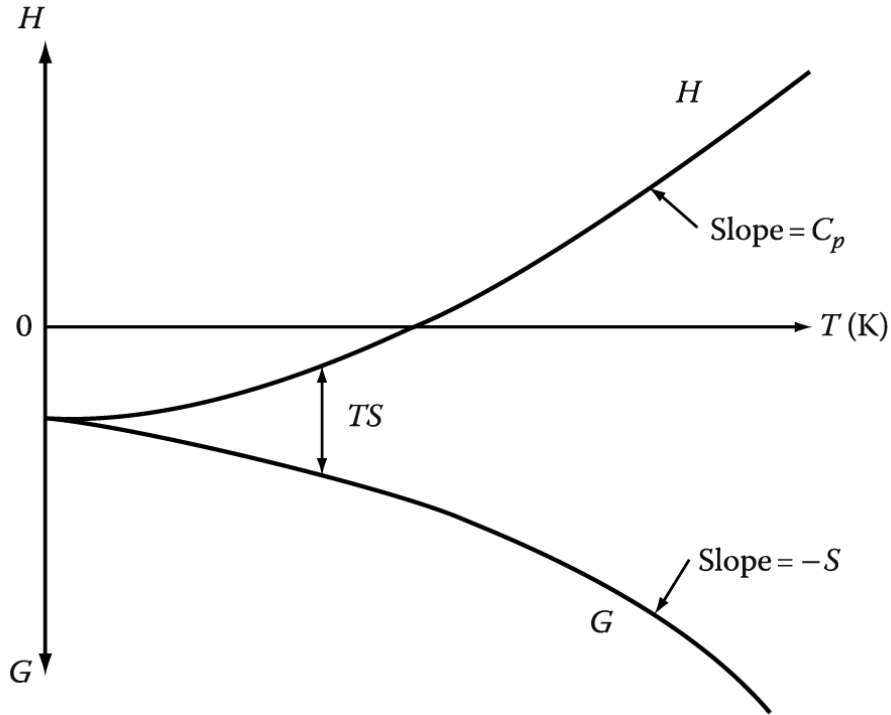


(c)

**\* What is the role of temperature on equilibrium?**

**Q5: How to draw the plots of H vs.T and G vs. T in single component system?**

# Compare the plots of H vs.T and G vs. T.



$$G = G(T, P)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP$$

$$G = H - TS$$

$$dG = dH - d(TS) = dE + d(PV) - d(TS)$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$= VdP - SdT$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S, \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

$$dG = VdP - SdT$$

$$G(P, T) = G(P_0, T_0) + \int_{P_0}^{P_1} V(T_0, P) dP - \int_{T_0}^{T_1} S(P, T) dT$$



**\* What is the role of temperature on equilibrium?**

**Q6:  $G^S$  vs  $G^L$  as a function of temperature?**

## 1.2.1 Gibbs Free Energy as a Function of Temp.

- Which is larger,  $H^L$  or  $H^S$ ?
- $H^L > H^S$  at all temp.
- Which is larger,  $S^L$  or  $S^S$ ?
- $S^L > S^S$  at all temp.

→ Gibbs free energy of the liquid decreases more rapidly with increasing temperature than that of the solid.

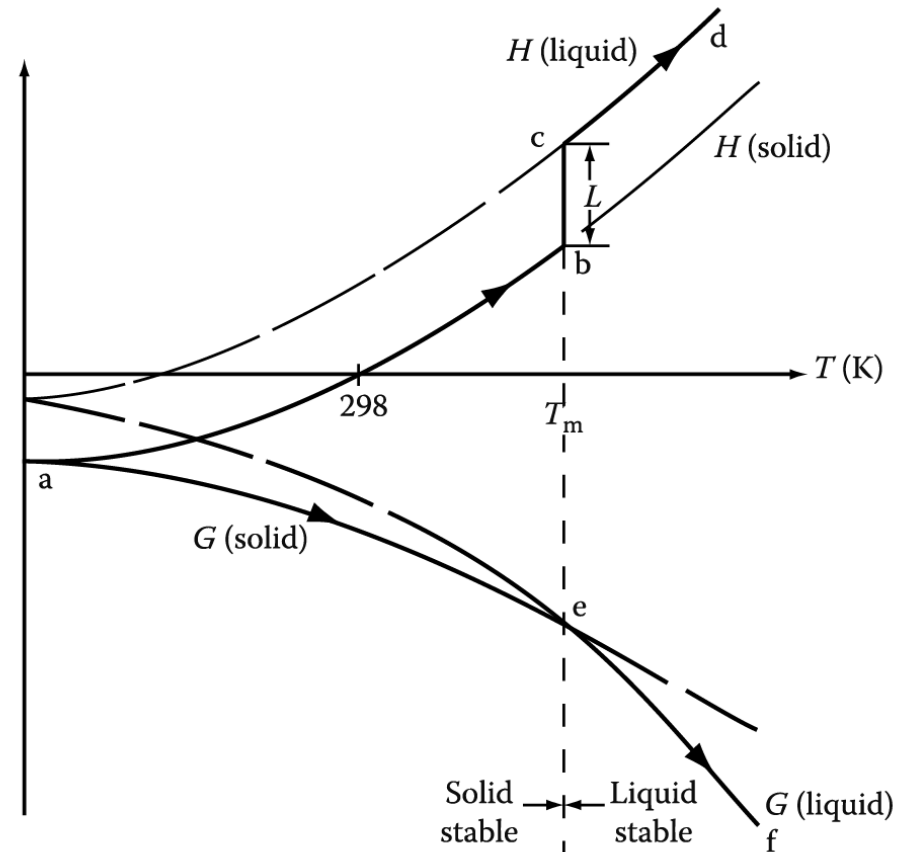


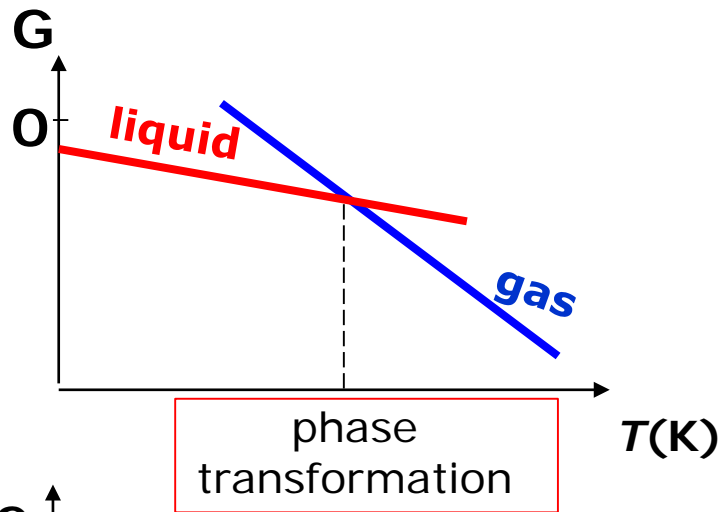
Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting,  $T_m$  the Equilibrium melting temperature.

- Which is larger,  $G^L$  or  $G^S$  at low T?
- $G^L > G^S$  (at low Temp) and  $G^S > G^L$  (at high Temp)

Considering  $P, T$   $G = G(T, P)$

$$dG = VdP - SdT$$

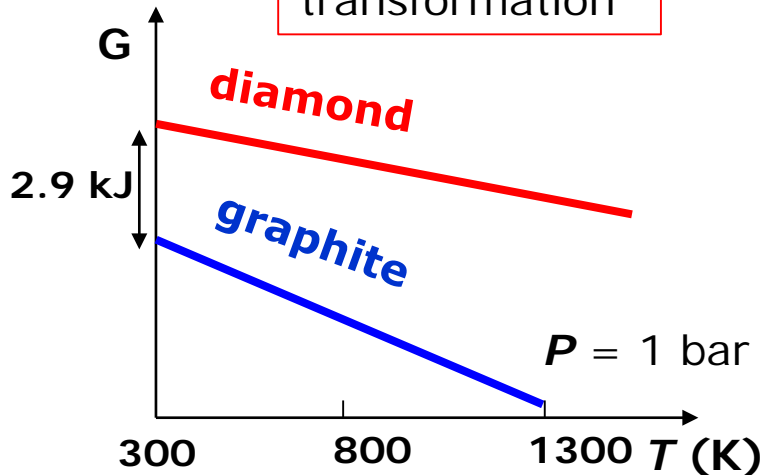
$$G(P, T) = G(P_0, T_0) + \int_{P_0}^{P_1} V(T_0, P)dP - \int_{T_0}^{T_1} S(P, T)dT$$



$$S(\text{water}) = 70 \text{ J/K}$$

$$S(\text{vapor}) = 189 \text{ J/K}$$

$$\left( \frac{\partial G}{\partial T} \right)_P = -S$$



$$S(\text{graphite}) = 5.74 \text{ J/K,}$$

$$S(\text{diamond}) = 2.38 \text{ J/K,}$$

## Q7: What is the role of pressure on equilibrium?

$$* \textit{ Clausius-Clapeyron Relation } : \left( \frac{dP}{dT} \right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

(applies to all coexistence curves)

## 1.2.2 Pressure Effects

When the two phases with different molar volumes are in equilibrium, if the pressure changes, the equilibrium temperature  $T$  should also change with pressure.

If  $\alpha$  &  $\beta$  phase are equilibrium,

$$dG^\alpha = V^\alpha dP - S^\alpha dT$$

$$dG^\beta = V^\beta dP - S^\beta dT$$

At equilibrium,

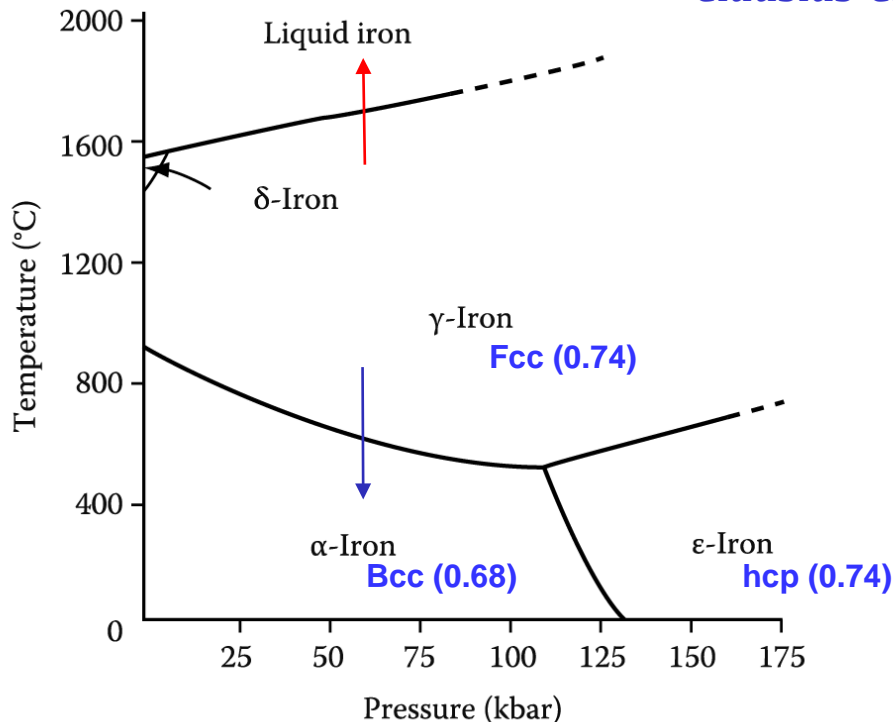
$$dG^\alpha = dG^\beta$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S}{\Delta V}$$

Here,  $\Delta S = \frac{\Delta H}{T_{eq}}$

\* *Clausius-Clapeyron Relation* :  $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$

(applies to all coexistence curves)



For,  $\gamma \rightarrow$  liquid;  $\Delta V (+)$ ,  $\Delta H(+)$

$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq} \Delta V} > 0$$

For,  $\alpha \rightarrow \gamma$ ;  $\Delta V (-)$ ,  $\Delta H(+)$

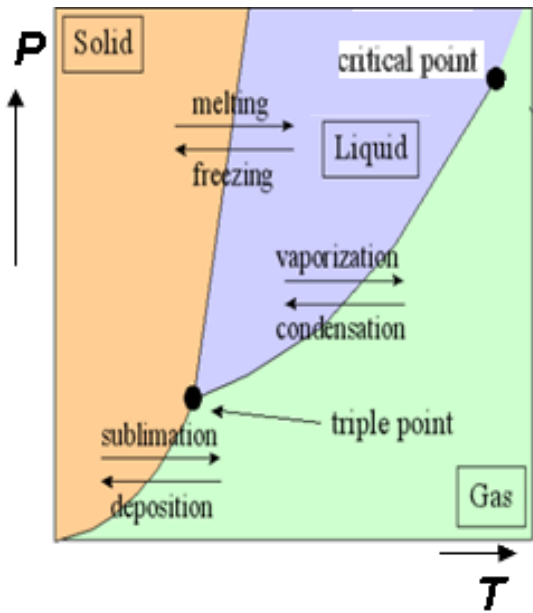
$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq} \Delta V} < 0$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

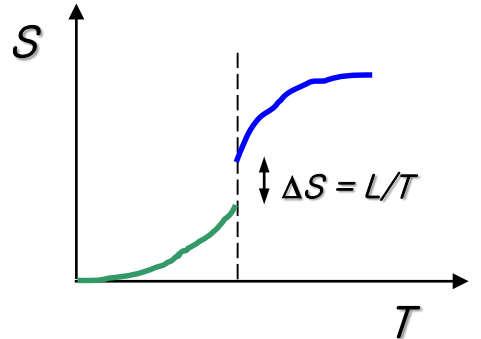
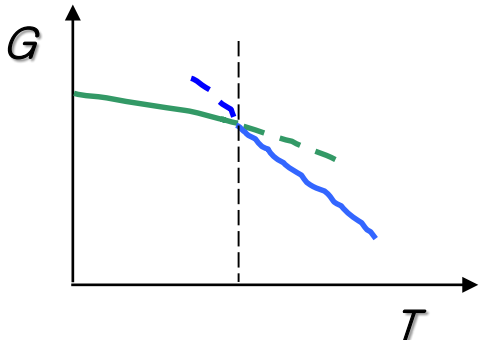
## Q8: How to classify phase transition?

**“First order transition” vs “Second order transition”**

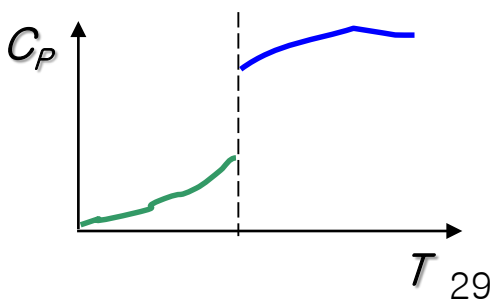


# The First-Order Transition

Latent heat  
Energy barrier  
Discontinuous entropy, heat capacity



$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P,N}$$



• First Order Phase Transition at  $T_T$ :

- $G$  is **continuous** at  $T_T$
- First derivatives of  $G$  ( $V, S, H$ ) are **discontinuous** at  $T_T$

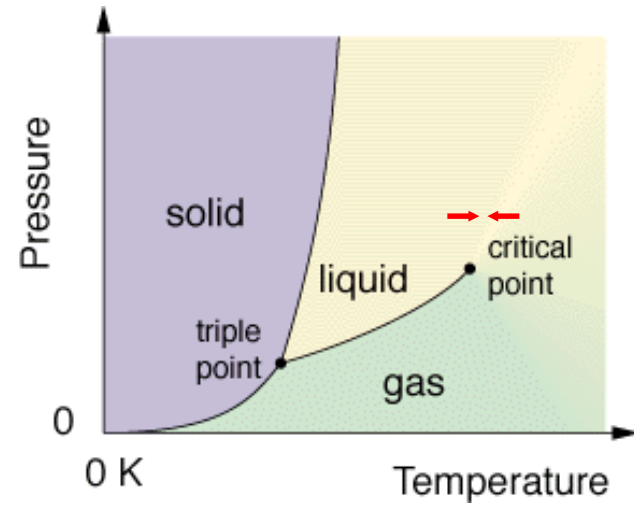
$$V = \left( \frac{\partial G}{\partial P} \right)_T \quad S = - \left( \frac{\partial G}{\partial T} \right)_P \quad H = G - T \left( \frac{\partial G}{\partial T} \right)_P$$

- Second derivatives of  $G$  ( $\alpha, \beta, C_p$ ) are **discontinuous** at  $T_T$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \beta = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

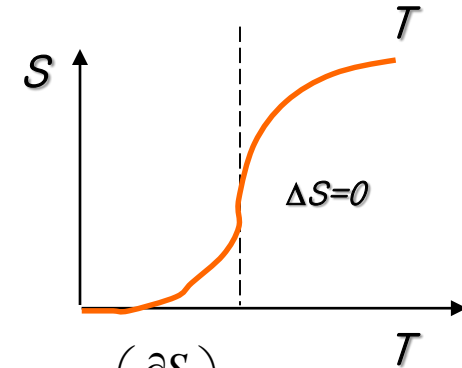
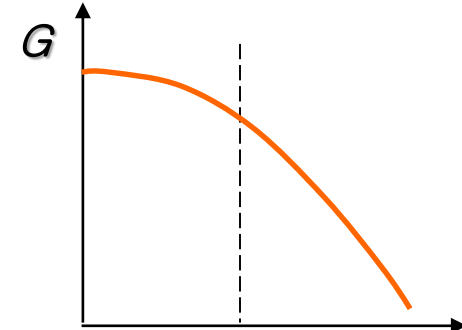
- **Examples:** Vaporization, Condensation, Fusion, Crystallization, Sublimation.

# The Second Order Transition

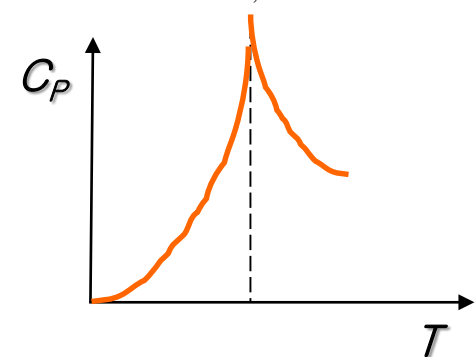


No Latent heat  
Continuous entropy

Second-order transition



$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P,N} \rightarrow \infty$$



• Second Order Phase Transition at  $T_T$ :

–  $G$  is **continuous** at  $T_T$

– First derivatives of  $G$  ( $V, S, H$ ) are **continuous** at  $T_T$

$$V = \left( \frac{\partial G}{\partial P} \right)_T \quad S = - \left( \frac{\partial G}{\partial T} \right)_P \quad H = G - T \left( \frac{\partial G}{\partial T} \right)_P$$

– Second derivatives of  $G$  ( $\alpha, \beta, C_p$ ) are **discontinuous** at  $T_T$

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \beta = \frac{-1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

– **Examples:** Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

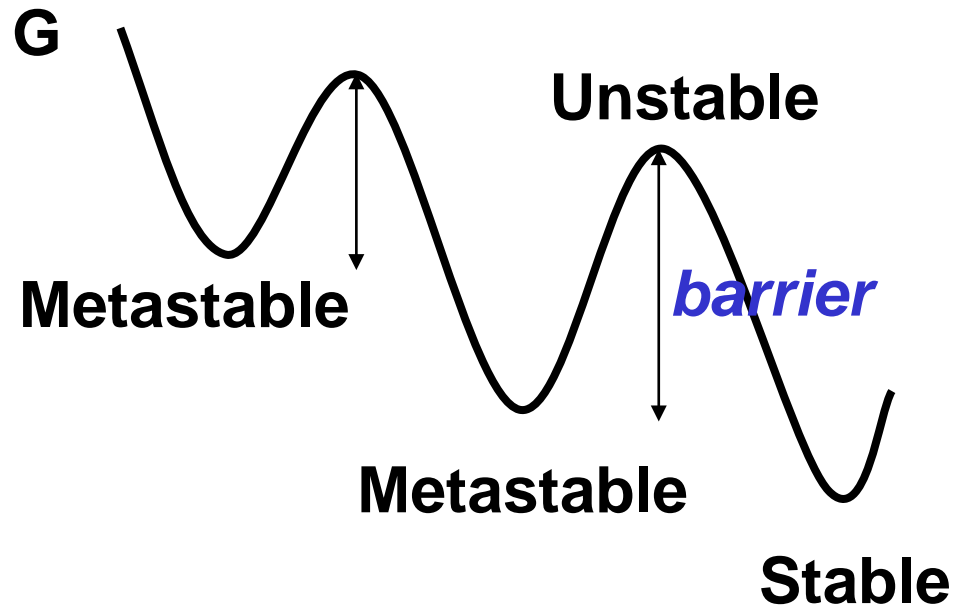


**Q9: What is the driving force for  
“Solidification: Liquid → Solid”?**

# Phase Transformation

Change to another phase  $\rightarrow$  metastable state  
structure or composition or order

$$\Delta G = G_2 - G_1 < 0$$



## 1.2.3 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)

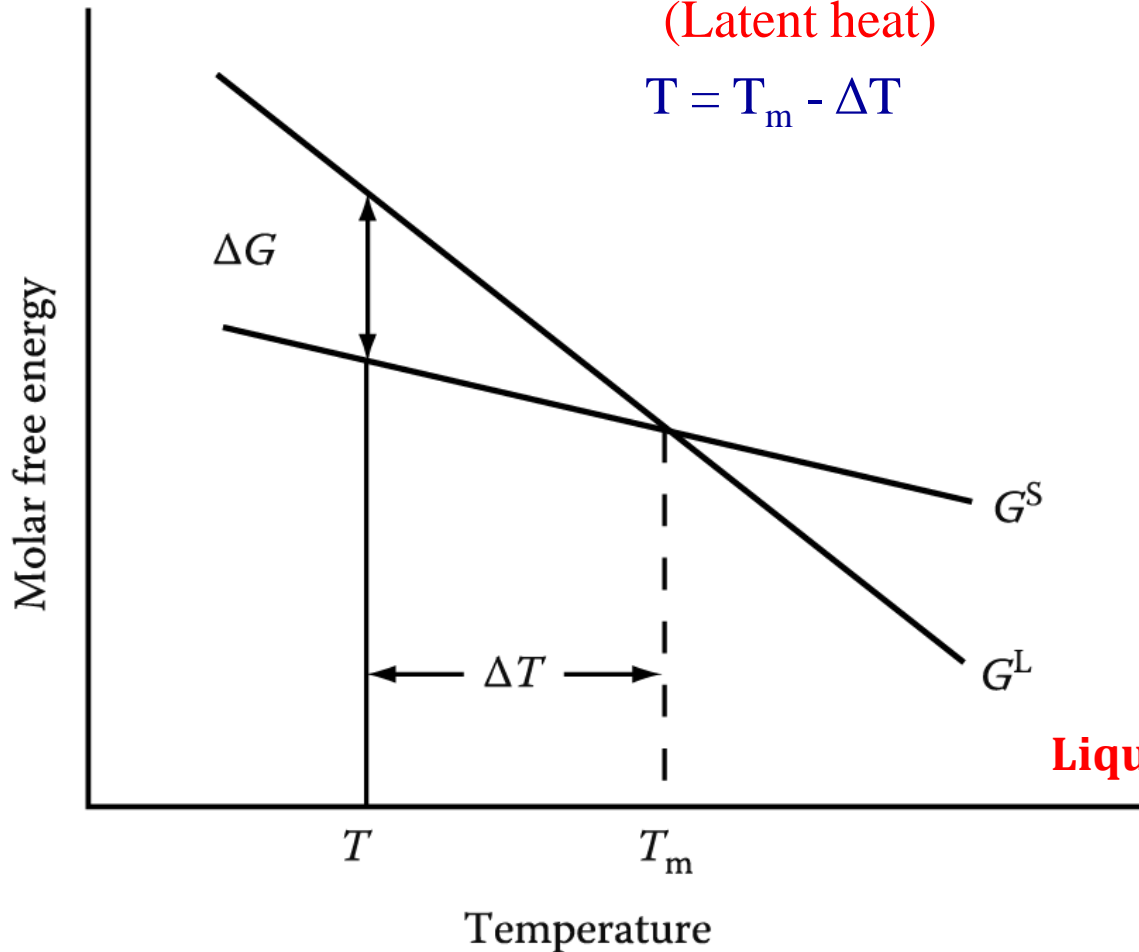
$$T = T_m - \Delta T$$

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

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

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

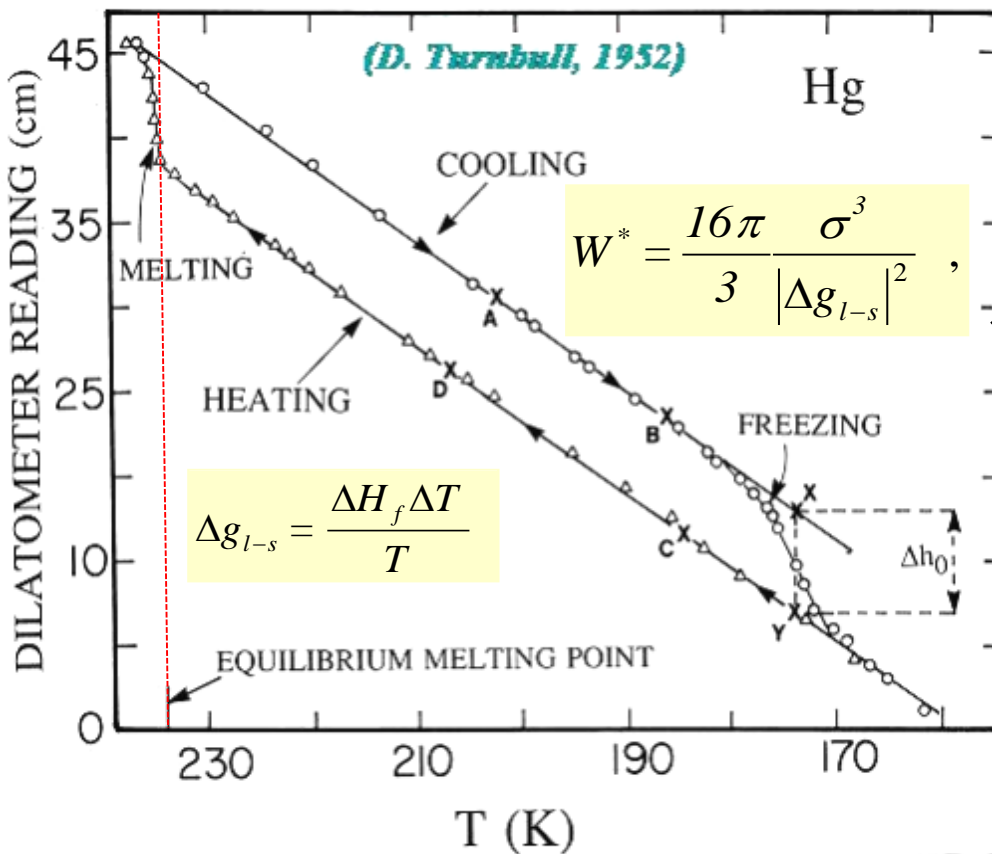
(eq. 1.17)



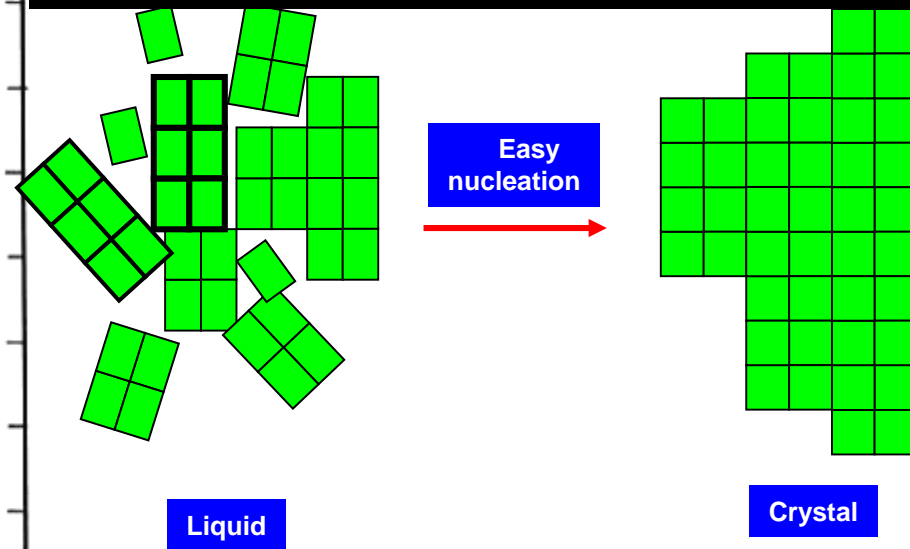
$$\Delta G = \frac{L\Delta T}{T_m}$$

**Liquid** → **Solid** transformation?

# Turnbull's Insight for Supercooling



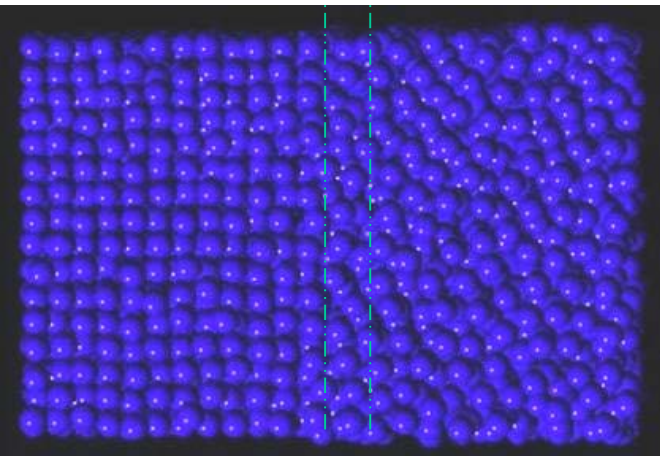
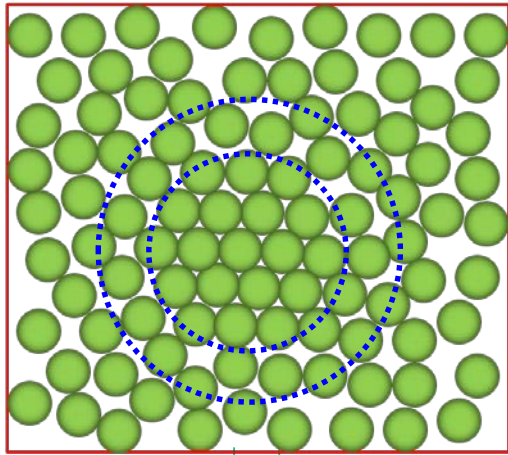
Microcrystalline structure for liquid metals  
 – Same short range order with crystals!



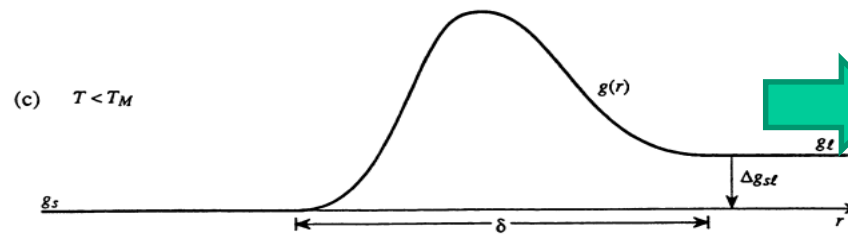
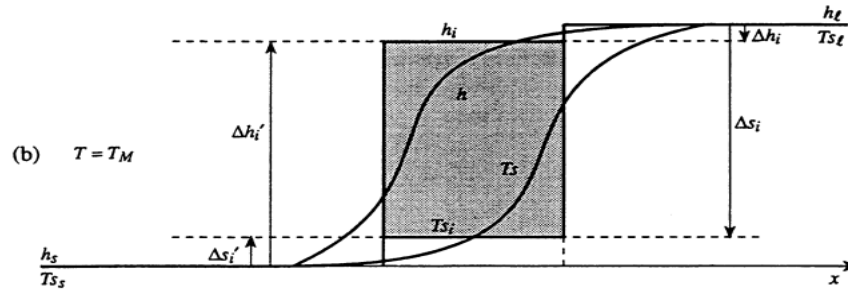
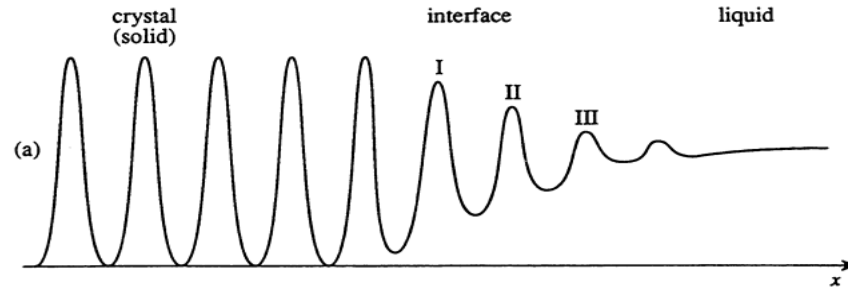
- ◆ How does the liquid metals resist on the crystallization?
- ◆ What is the origin of high nucleation barrier against the crystallization?
- What is the structure of interface between liquids and crystals?
- ◆ What is the local order of liquid metals?

# Turnbull's solid-liquid interface

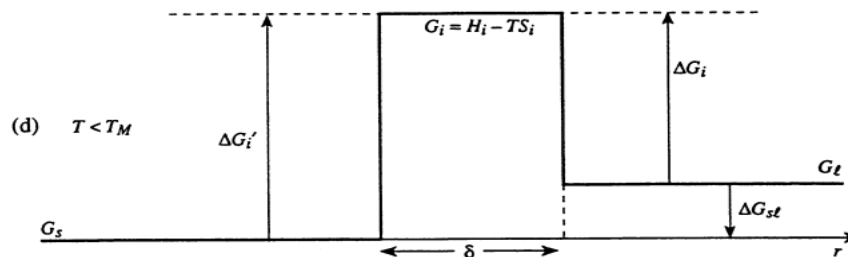
Turnbull's insight : Liquid orders substantially near a crystal surface due to entropy decreasing caused by the crystal-melt interfacial tension



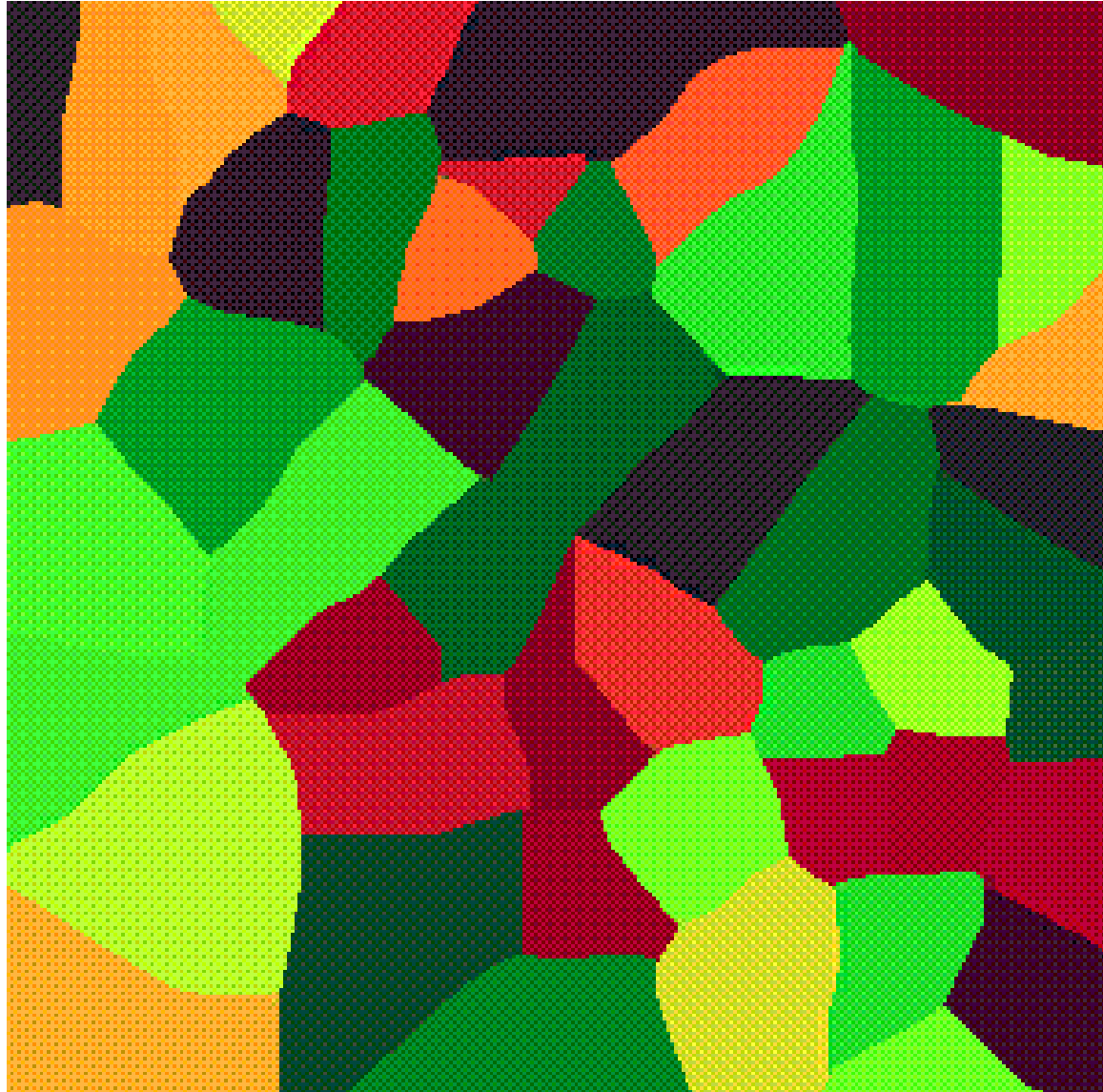
Solid state physics v47, 1 (1994)



Supercooling

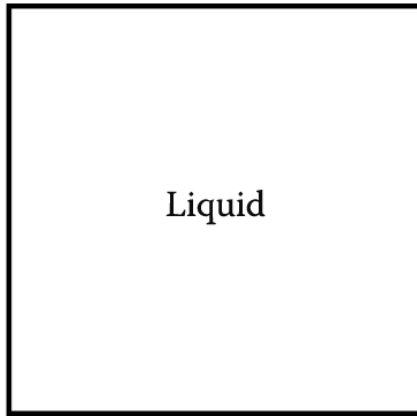


4. Solidification: Liquid  $\longrightarrow$  Solid



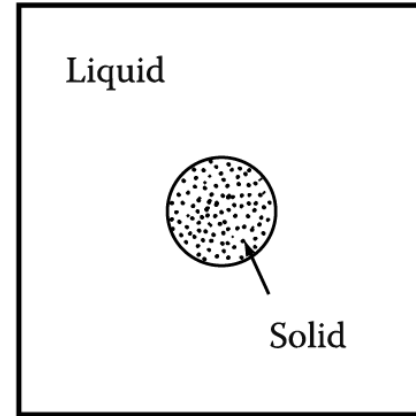
4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

## 4.1.1. Homogeneous Nucleation



(a)  $G_1$

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



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

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

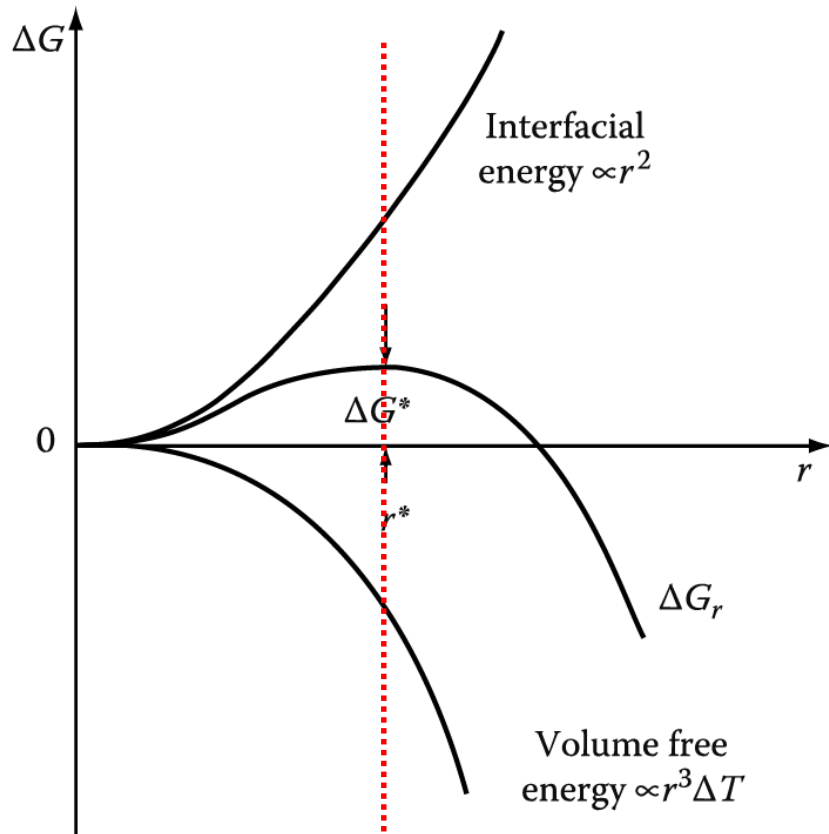
$G_V^S, G_V^L$  : free energies per unit volume

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

for spherical nuclei (isotropic) of radius :  $r$

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

# 4.1.1. Homogeneous Nucleation



**Unstable equilibrium**

Fig. 4.2 The free energy change associated with homogeneous nucleation of a sphere of radius  $r$ .

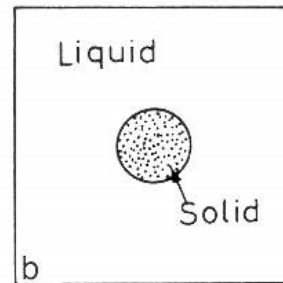
**Why  $r^*$  is not defined by  $\Delta G_r = 0$ ?**

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

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

$r^*$  : **critical nucleus size**

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



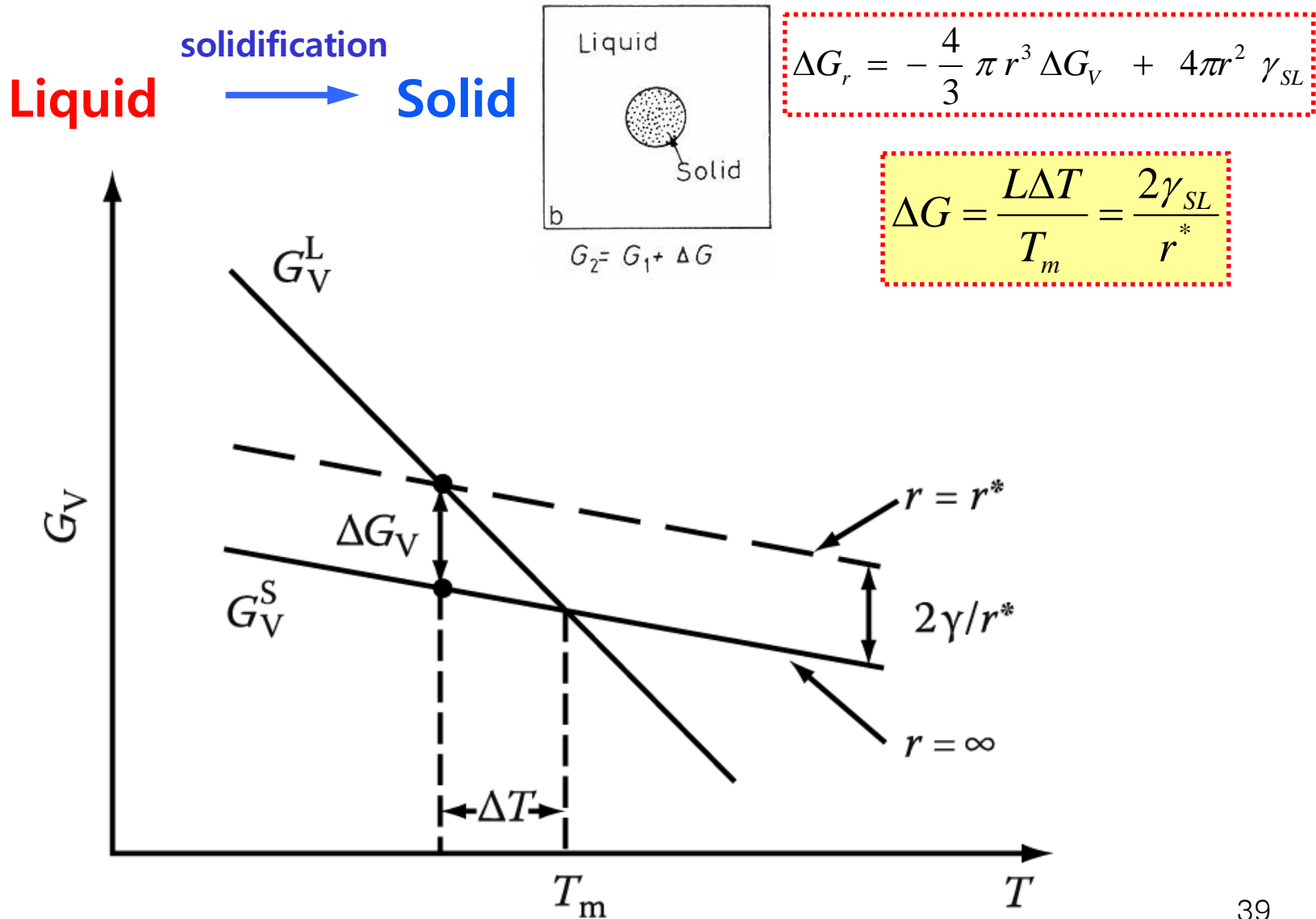
$$G_2 = G_1 + \Delta G$$

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

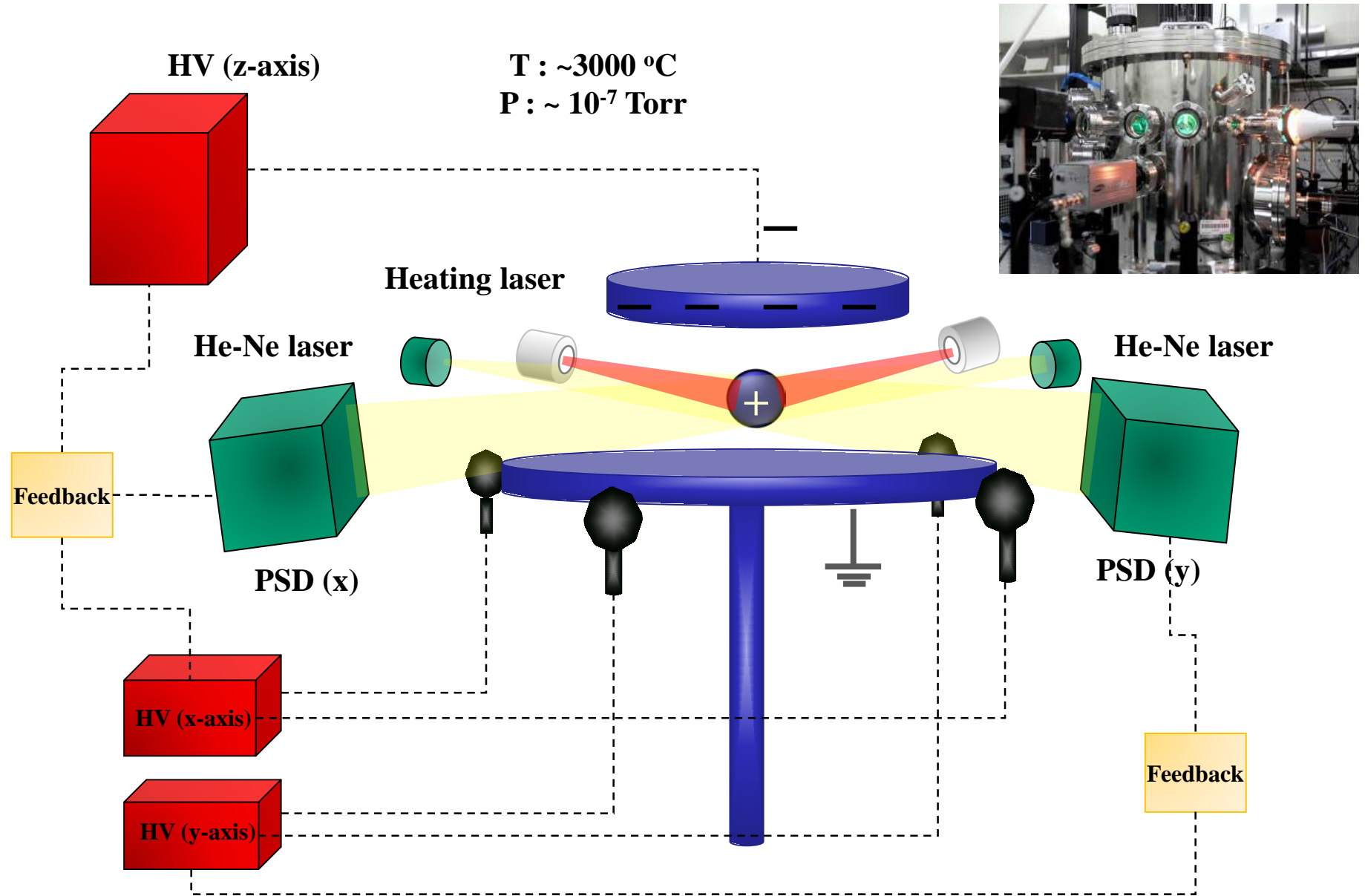
$$\Delta G^* = \frac{2\gamma_{SL}}{r^*}$$

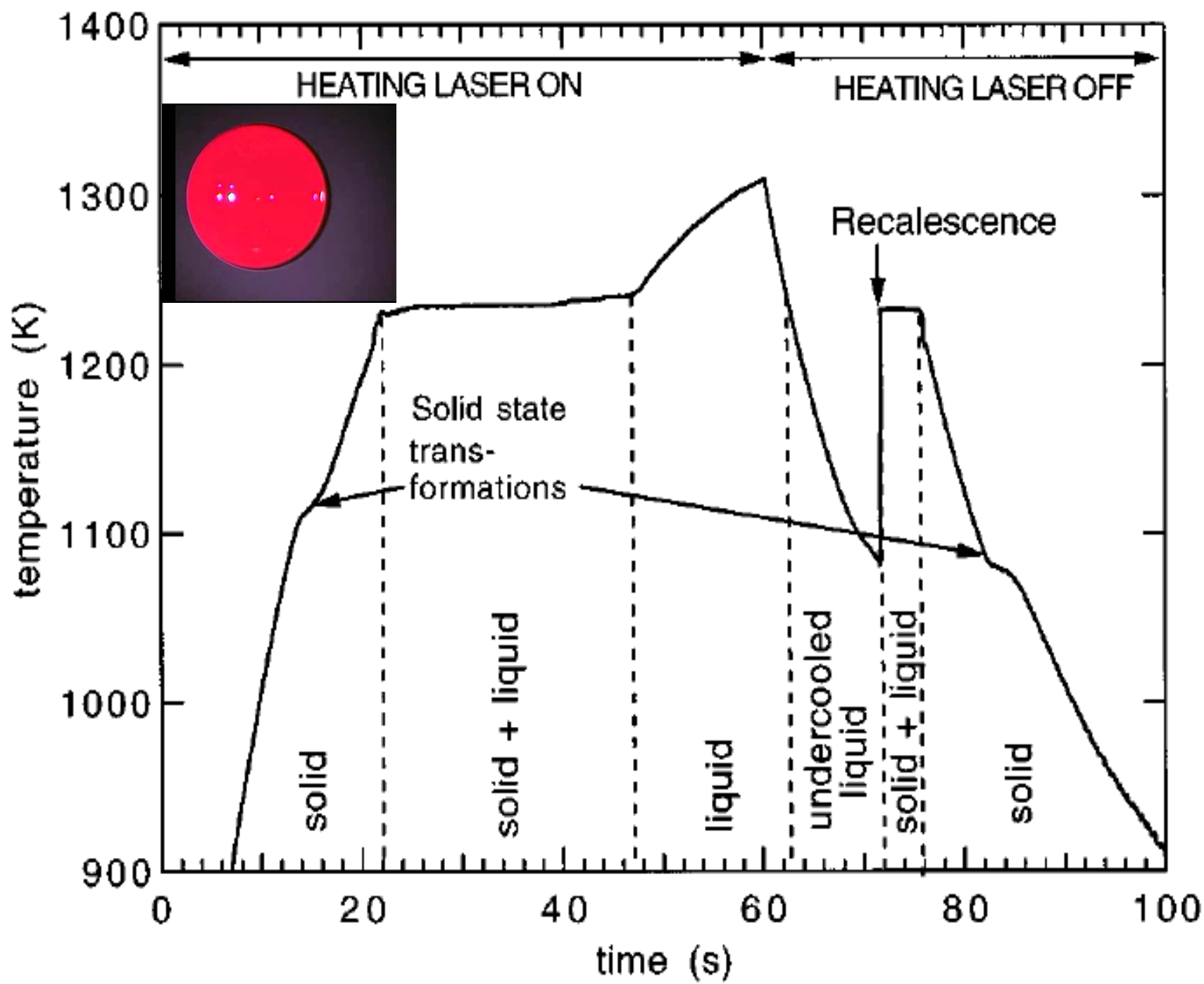


## 1.2.3 Driving force for solidification

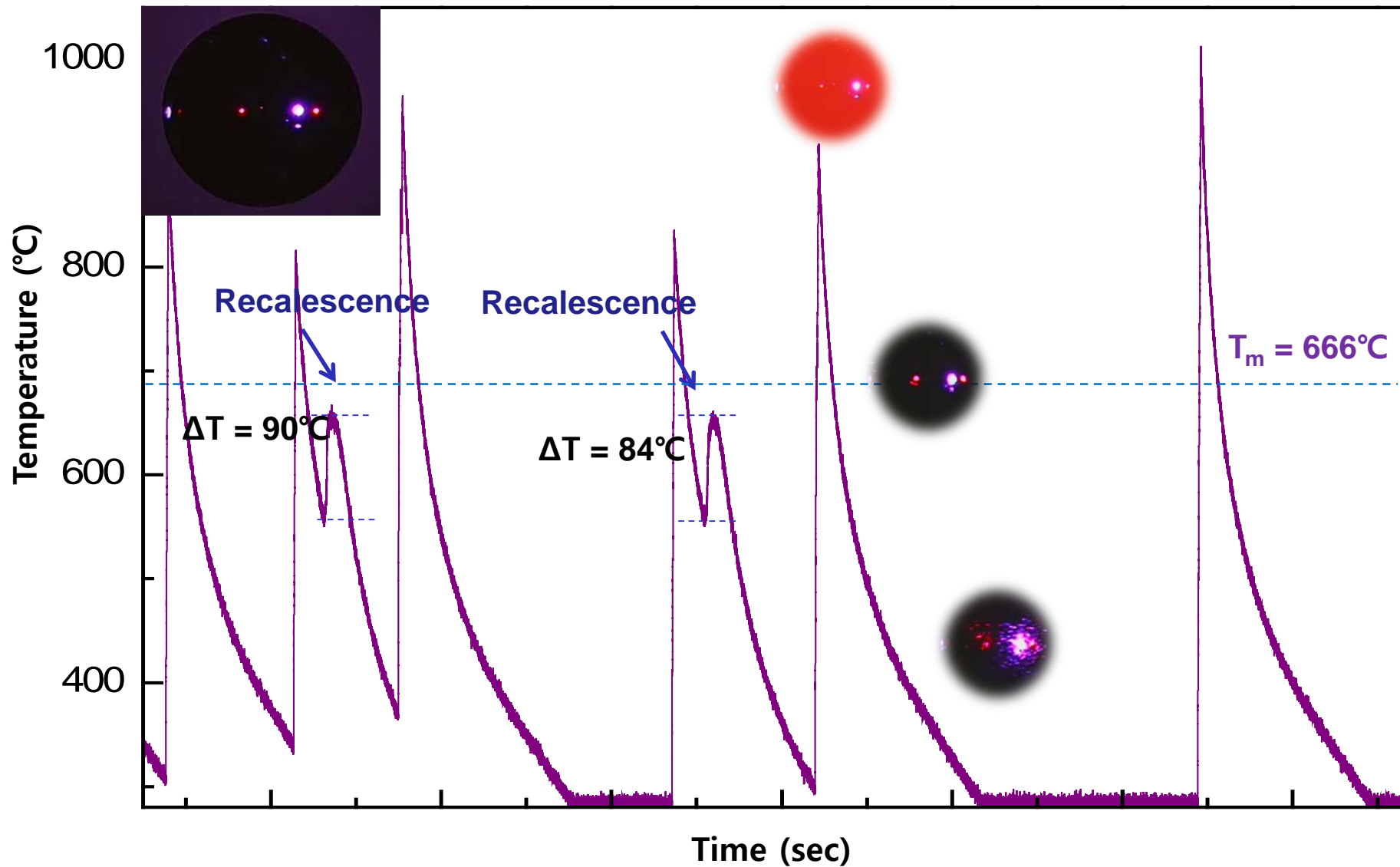


# Electrostatic levitation in KRISS





# Cyclic cooling curves of $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$



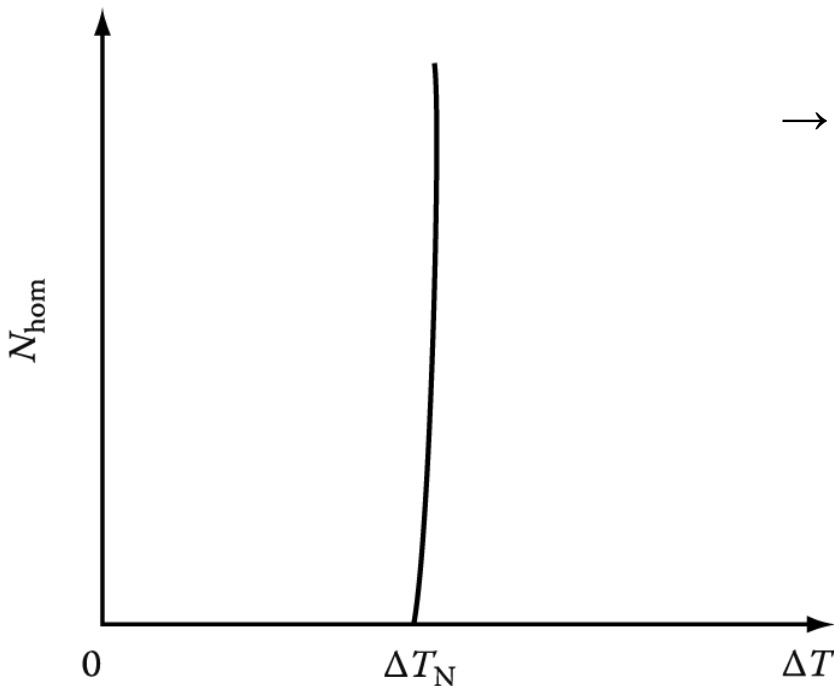
## \* The homogeneous nucleation rate - kinetics

$$I = \frac{nkT}{h} \exp\left(-\frac{G_A}{kT}\right) \exp\left(-\frac{16\pi\sigma_{SL}^3 T_E^2}{3L^2(\Delta T)^2 kT}\right)$$

: insensitive to Temp.

How do we define nucleation temperature,  $\Delta T_N$  ?

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



→ **critical value for detectable nucleation**

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

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

The homogeneous nucleation rate as a function of undercooling  $\Delta T$ .

$\Delta T_N$  is **the critical undercooling** for homogeneous nucleation.

## \* Relationship between Maximum Supercoolings and $T_m$

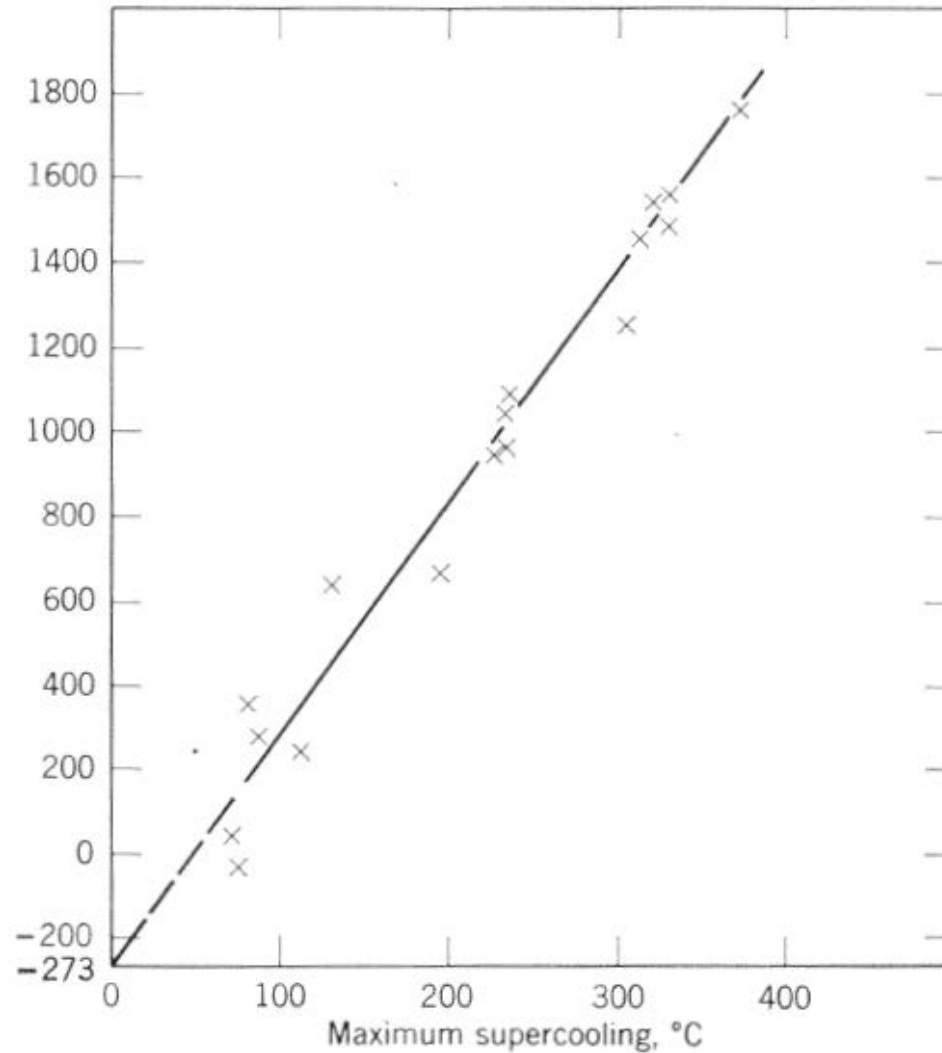


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

# Solidification: **Liquid** $\longrightarrow$ **Solid**

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

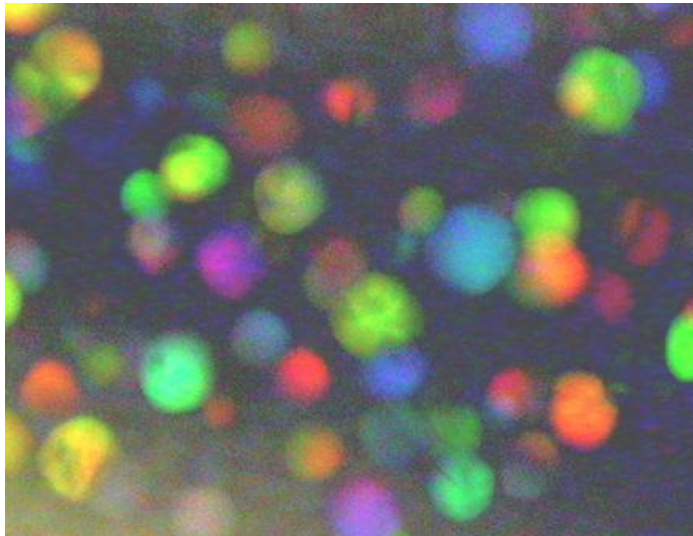
## Nucleation in Pure Metals

$$T_m : G_L = G_S$$

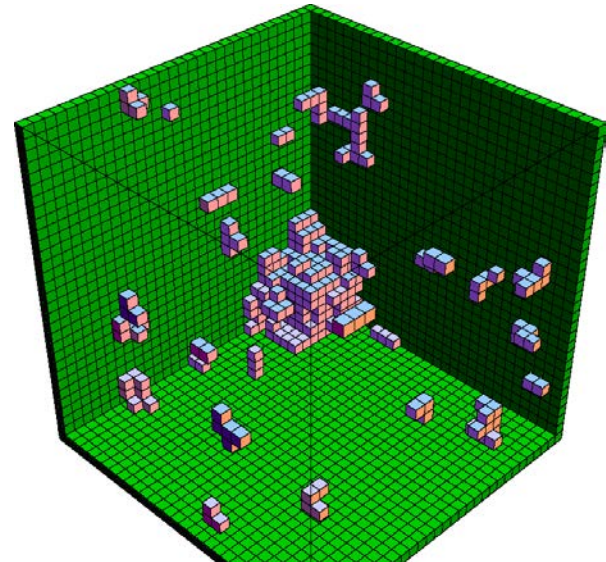
- Undercooling (supercooling) for nucleation: 250 K  $\sim$  1 K

<Types of nucleation>

- **Homogeneous nucleation**



- **Heterogeneous nucleation**



**Q10: What is the driving force for  
“Melting: Solid → Liquid”?**



# \* Driving force for melting

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

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

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

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

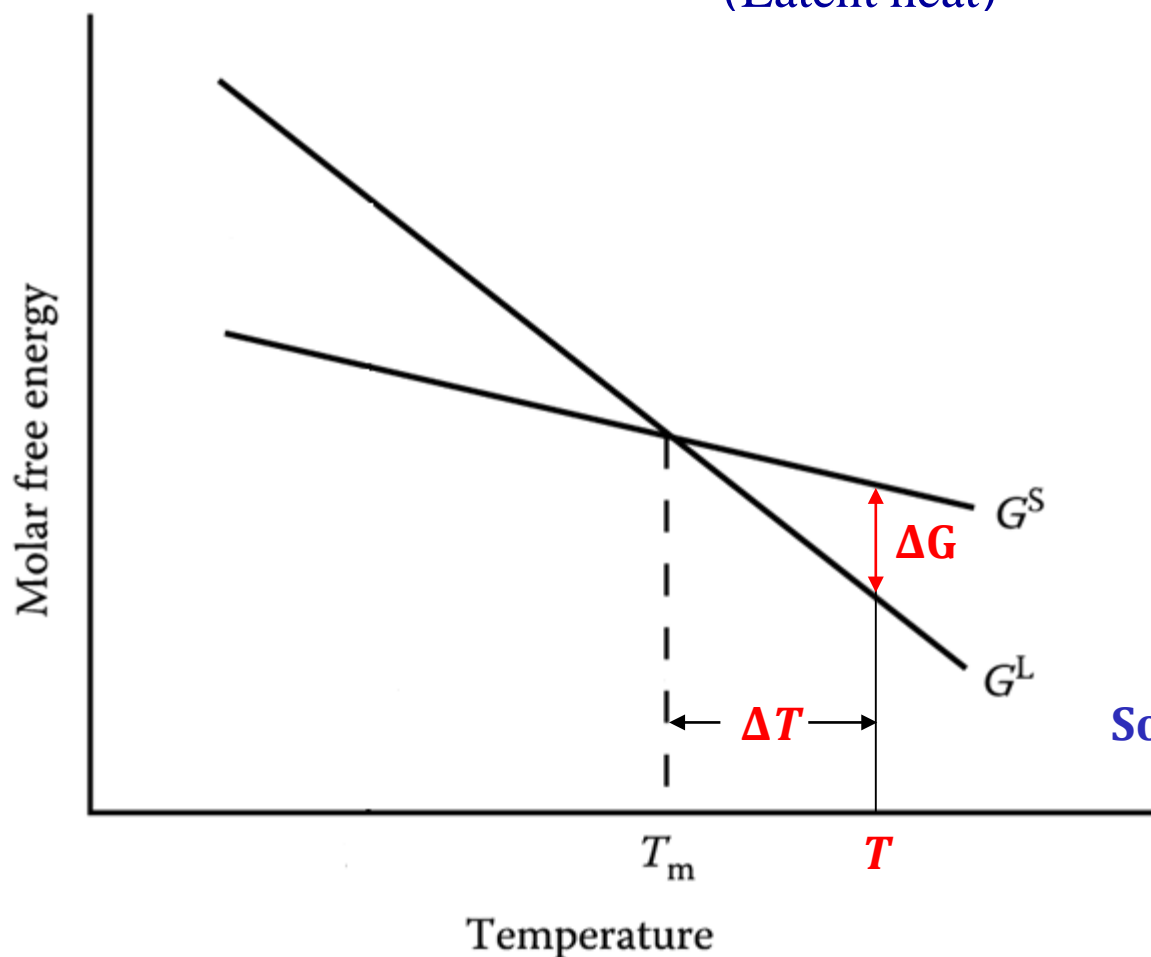
(Latent heat)

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

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

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

(eq. 1.17)



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

**Solid** → **Liquid** transformation?

# 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?

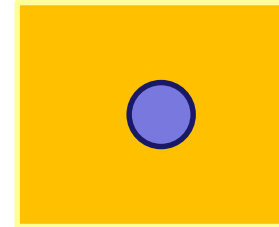
$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} \quad (\text{commonly})$$



In general, wetting angle = 0 → No superheating required!

# Melting and Crystallization are Thermodynamic Transitions

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



<Thermodynamic>

- Interfacial energy  $\Rightarrow \Delta T_N$

Liquid

$T_m$  Undercooled Liquid

Solid

No superheating required!

- Interfacial energy  $\Rightarrow$  No  $\Delta T_N$

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

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



## Contents for today's class

# CHAPTER 1 Introductory Thermodynamics

- **Equilibrium** -  $dG = 0$       **Lowest possible value of G**  
*No desire to change ad infinitum*

- **Single component system**

Gibbs Free Energy as a Function of **Temp.** and **Pressure**

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

*Clausius-Clapeyron Relation*

- **Phase Transformation**       $\Delta G = G_2 - G_1 < 0$

- **Classification of phase transition**

First order transition: **CDD**/Second order transition: **CCD**

- **Solidification: Liquid** → **Solid**      *Thermodynamic transition*

Driving force for solidification

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