2017 Fall

“Phase Equilibria *in* Materials”

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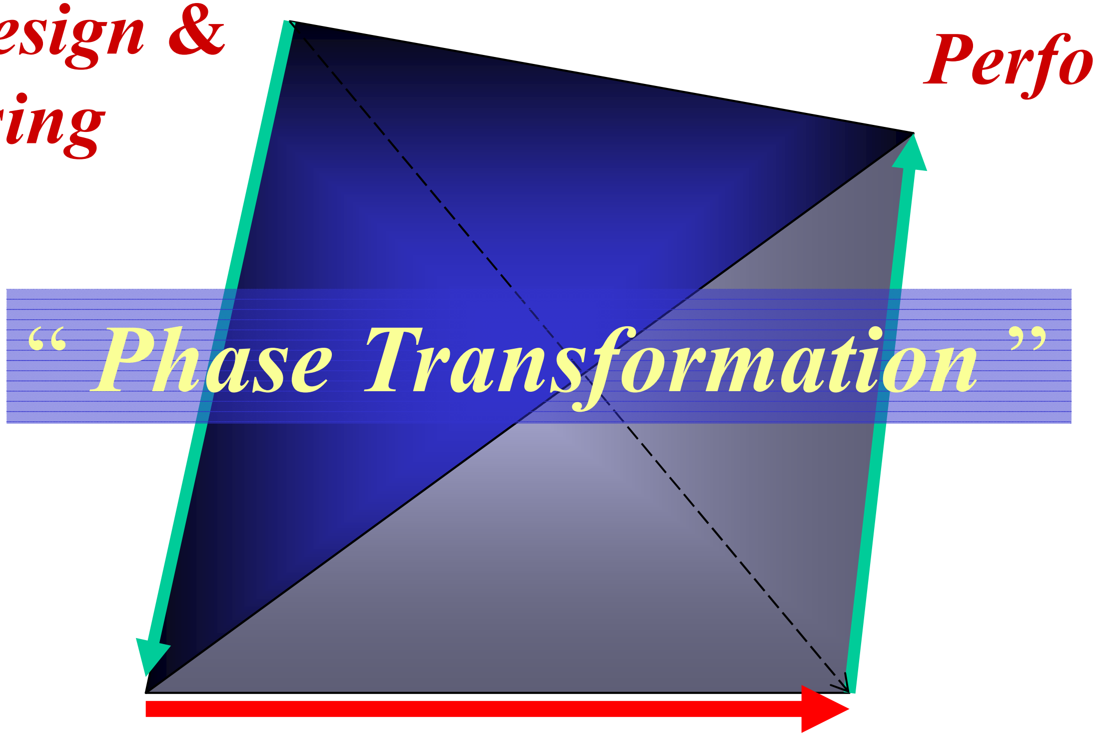
Contents for previous class

Microstructure-Properties Relationships



Alloy design &
Processing

Performance

“ Phase Transformation ”

Microstructure
down to atomic scale

Properties

“Tailor-made Materials Design”

Contents for previous class

Important!!!

Understanding **and** ***Controlling***

Phase Transformation *of* Materials

Contents for previous class

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**

Contents for previous class

Phase Equilibria in Materials

Thermodynamics

Phase diagrams

Binary, Ternary, Quarternary phase diagram

Contents for today's class

CHAPTER 1 Introductory Thermondynamics

- **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

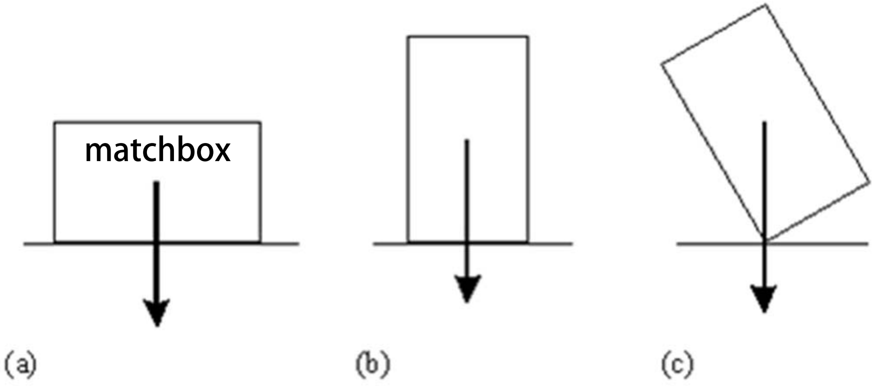
Q1: “thermodynamic equilibrium”?

Lowest possible value of Gibb’s Free Energy

Chapter 1

Equilibrium

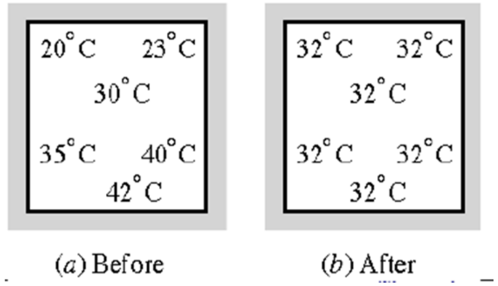
Mechanical equilibrium



: total potential energy of the system is a minimum.

Thermal equilibrium

: absence of temperature gradients in the system



(a) Before (b) After

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, $\boxed{dX \le 0}$

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

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. $\boxed{X = E - TS + const' = A + const'}$

Helmholtz free energy : $\boldsymbol{F=E-TS}$.

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,

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

,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 **:** $\boldsymbol{G=E+PV-TS=H-TS}$

Useful when P is constrained during thermodynamic process.

Chapter 1.1

Relative Stability of a System → Gibbs Free Energy

$$\boxed{G = H - TS}$$

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

$$H = E + PV$$

$$H \cong E \quad \textit{for Condensed System}$$

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*

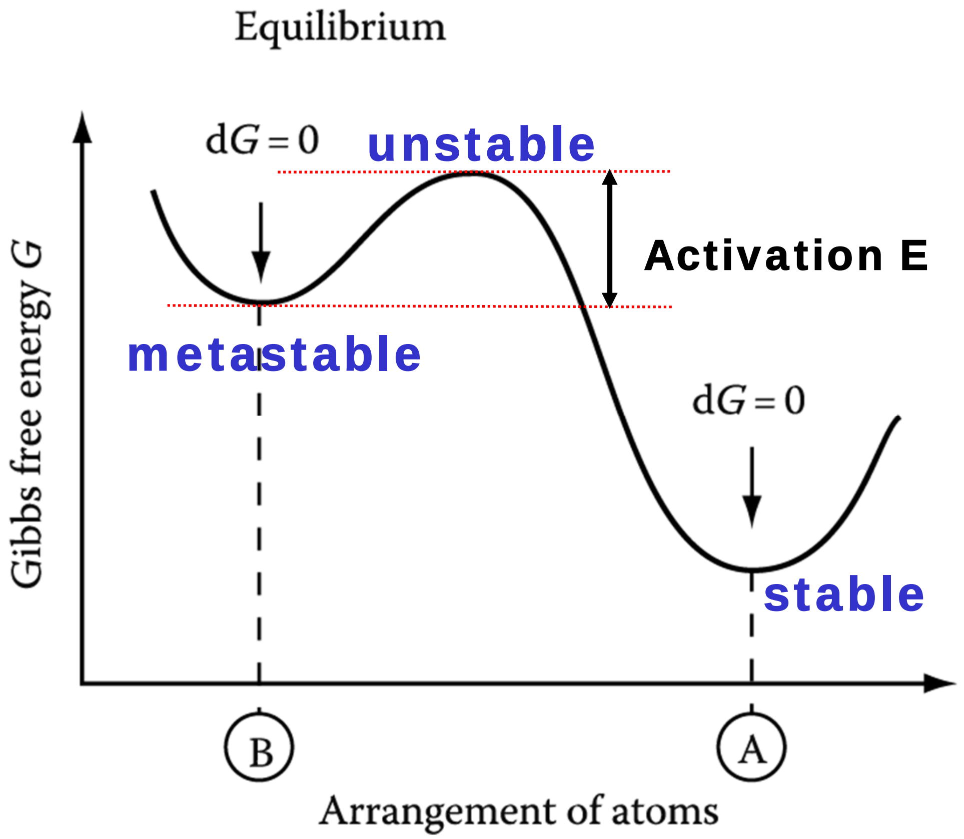
S : Entropy, The *Randomness* of the System

Equilibrium

$$\boxed{dG = 0}$$

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



Phase Transformation $$\boxed{\Delta G = G_2 - G_1 < 0}$$

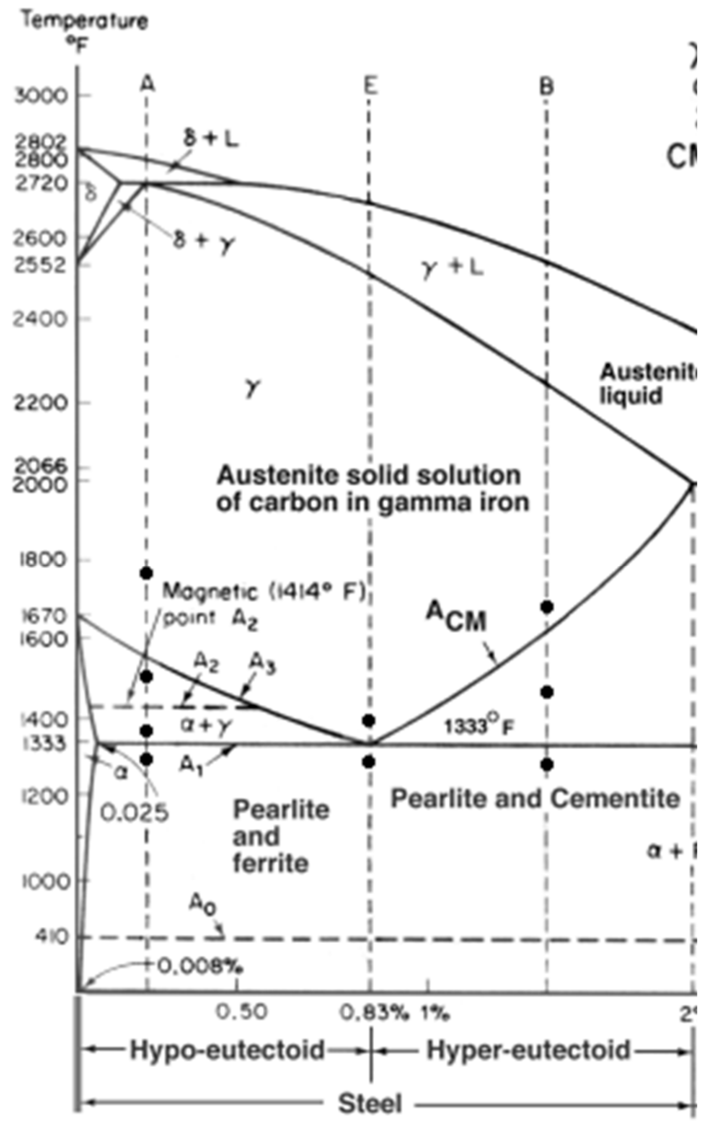
Q2: What is single component system?

1.2 Single component system

One element (Al, Fe)

One type of molecule (H_2O)

Allotropic form?



Fe → **C**

$$G = H - TS$$

1.2.1 Gibbs Free Energy as a Function of Temp.

* 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

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

When V is constant,

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P\cancelto{0}{\frac{dV}{dT}} \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad \boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V \, dT}$$

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,

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

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

$$\boxed{dE = \delta Q - P \cdot dV} \qquad = \delta Q - PdV + PdV + VdP$$

$$= \delta Q + VdP$$

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

➡ $\frac{dP}{dT} = 0$ when P is constant

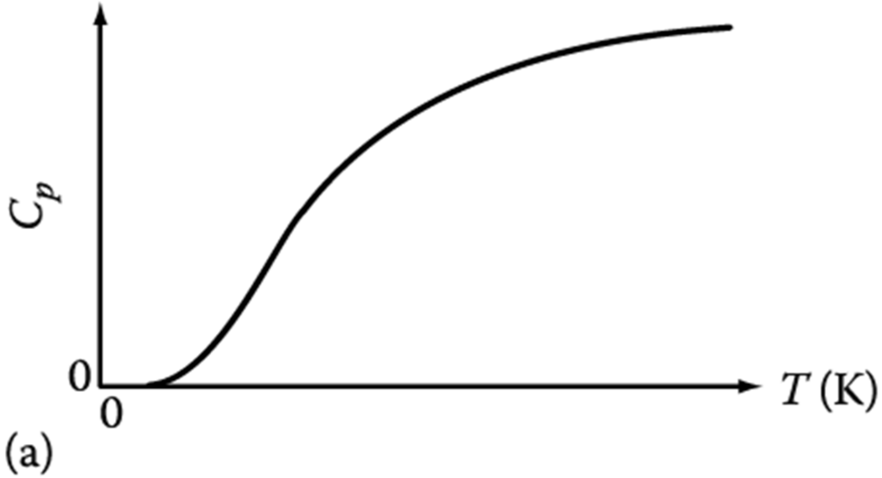
$$\boxed{\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P} \qquad \boxed{H = \int C_p \, dT}$$

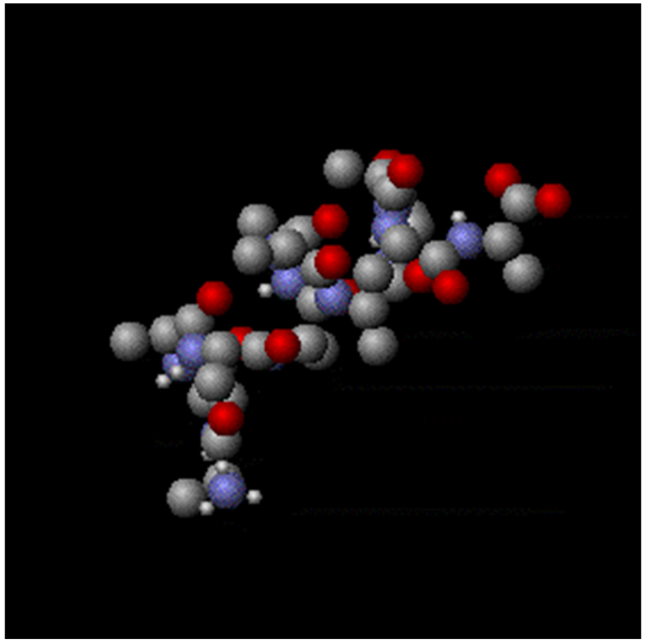
In alloy work one usually consider systems at constant pressure so that enthalpy changes are more important then energy changes.

C_P ; tempeature-dependent function

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

(empirical formula above room temp)





Molecules have <u>internal structure</u> 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^3·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?

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

H = ?

$$\boxed{H = \int_{298}^{T} C_P dT}$$

H = 0 at 298K for a pure element

in its most stable state.

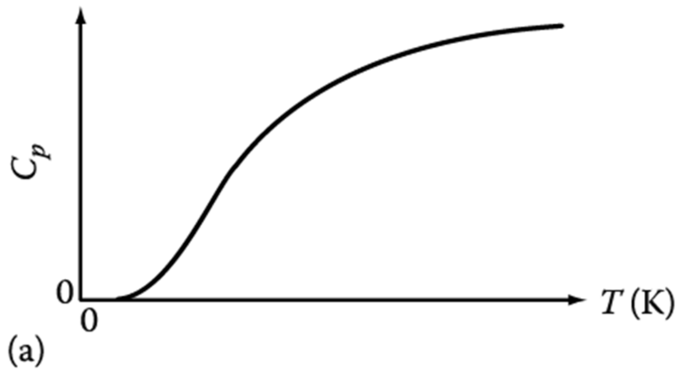
: When considering a phase transformation or a chemical reaction, the important thing is not the value of the thermodynamic function, but <u>the amount of change.</u>

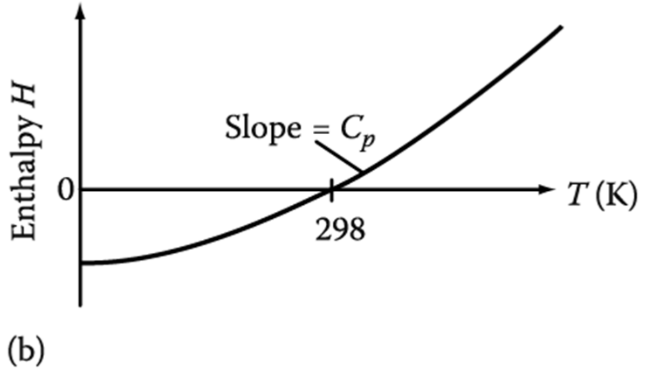
Enropy : $S = \frac{q}{T}$

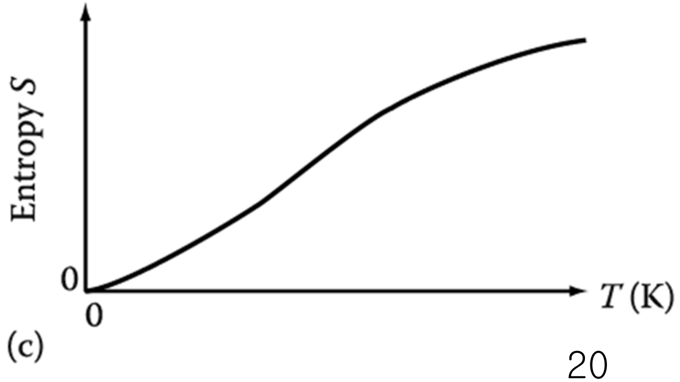
S = ?

$$\boxed{\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P}$$

$$\boxed{S = \int_{0}^{T} \frac{C_P}{T} dT}$$



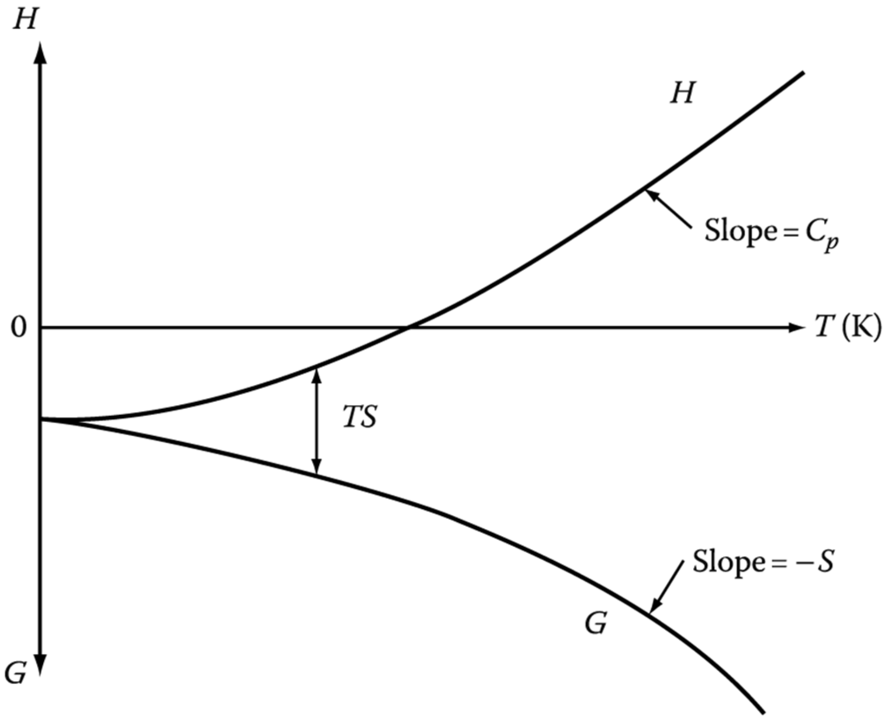




*** What is the role of temperature on equilibrium?**

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.



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

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

$$G = H - TS$$

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

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

$$= VdP - SdT$$

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

$$dG = VdP - SdT$$

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

*** 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.

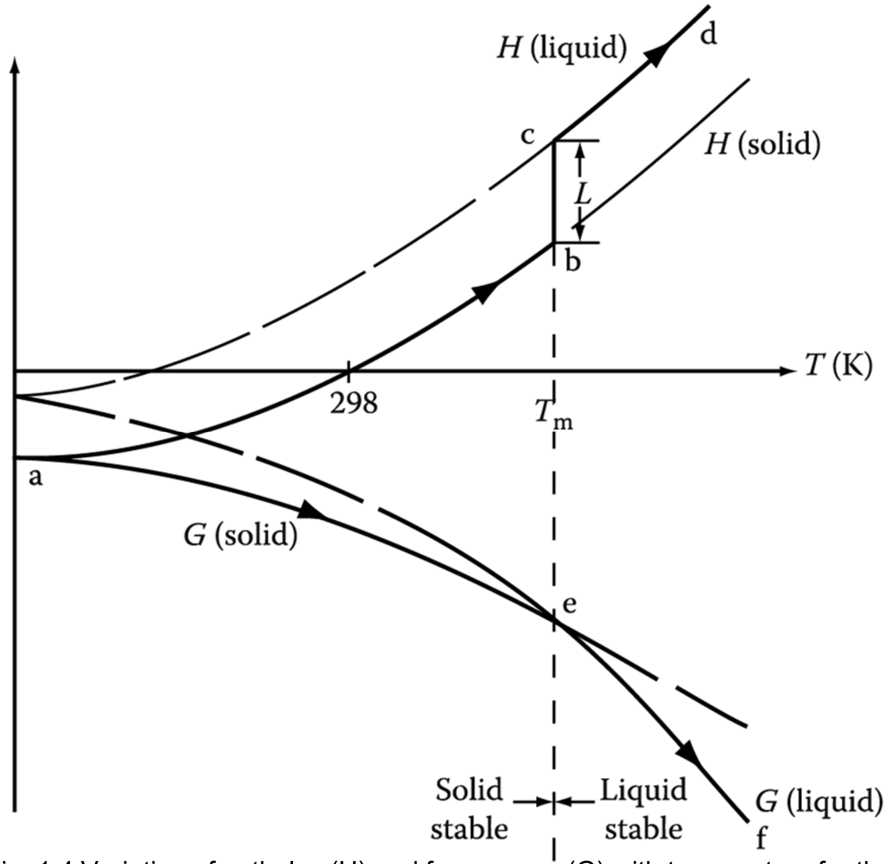


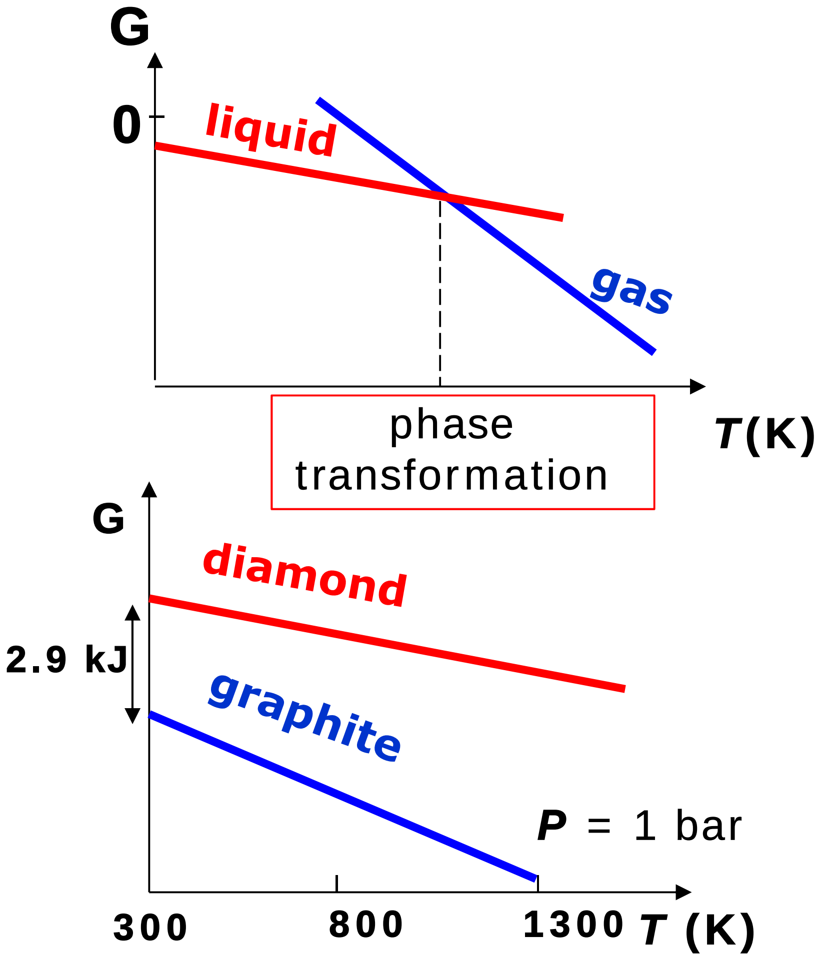
Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting, Tm the Equilibrium melting temperature.

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

$$dG = VdP - SdT$$

$$G(P,T) = G(P_0,T_0) + \int_{P0}^{P1} V(T_0,P)dP - \int_{T0}^{T1} S(P,T)dT$$



S(water) = 70 J/K

S(vapor) = 189 J/K

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

S(graphite) = 5.74 J/K,
S(diamond) = 2.38 J/K,

Q7: What is the role of pressure on equilibrium?

**** 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 α & β 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, $\Delta S = \dfrac{\Delta H}{T_{eq}}$

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

(applies to all coexistence curves)

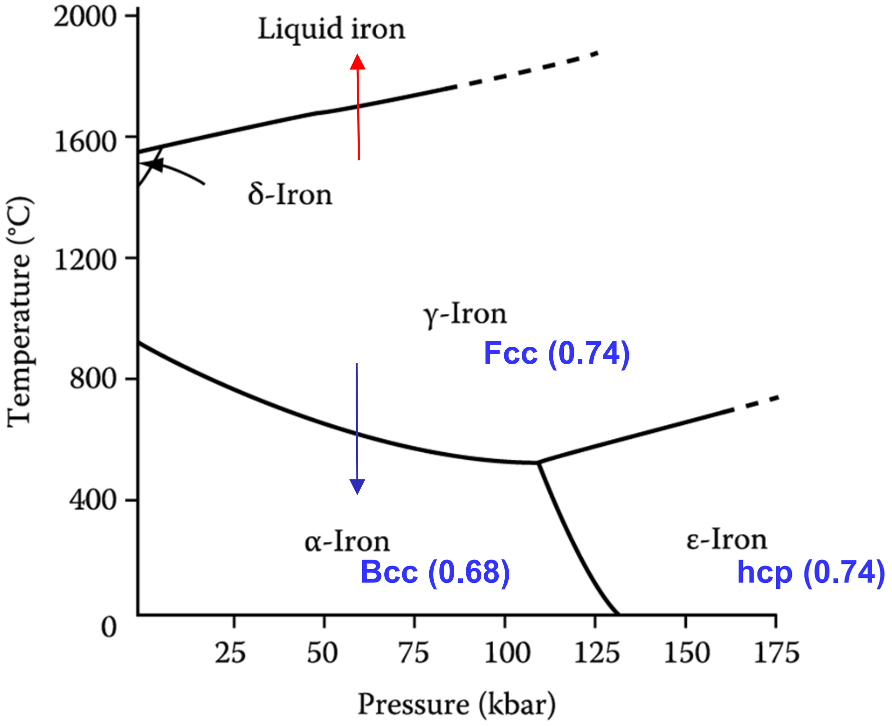


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

For, γ →liquid; ΔV (+), ΔH(+)

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

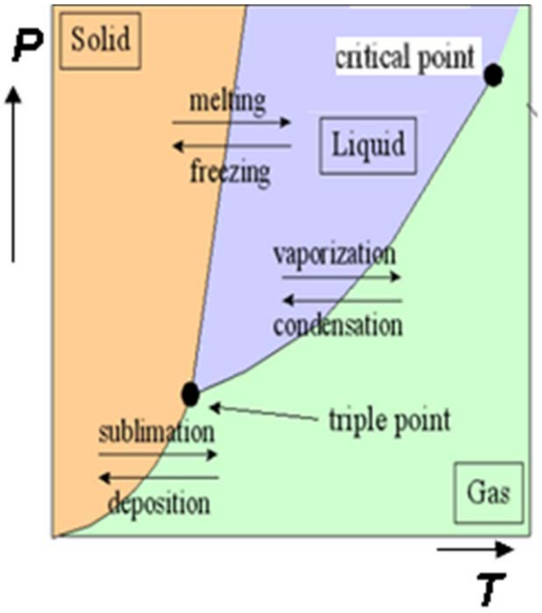
For, α→γ ; ΔV (-), ΔH(+)

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

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

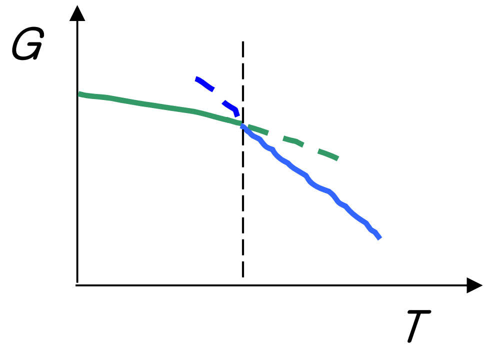
Q8: How to classify phase transition?

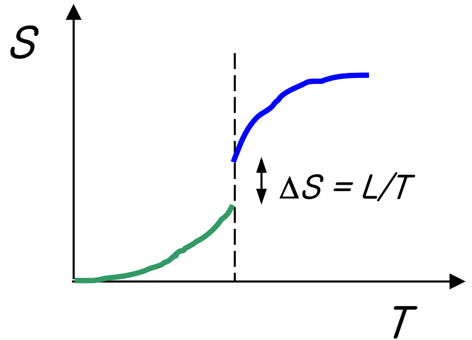
“First order transition” vs “Second order transition”



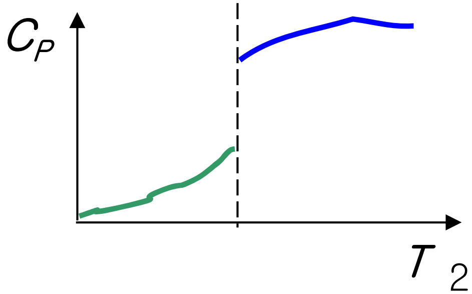
The First-Order Transition

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

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

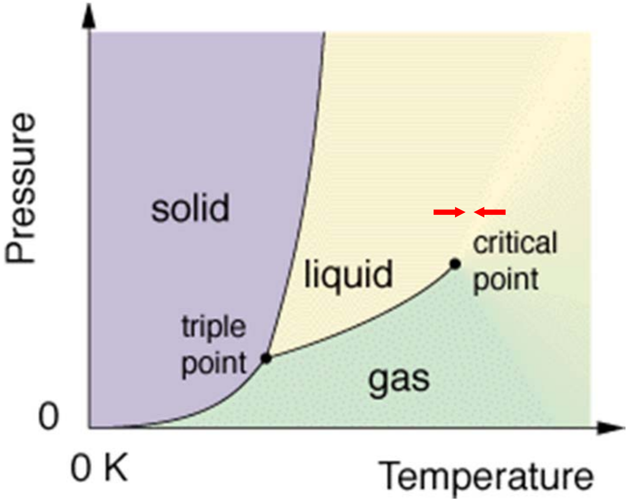
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

The Second Order Transition

No Latent heat
Continuous entropy



- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

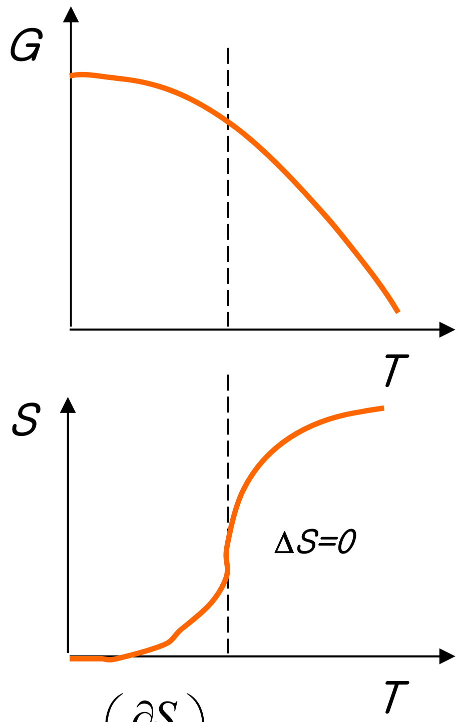
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

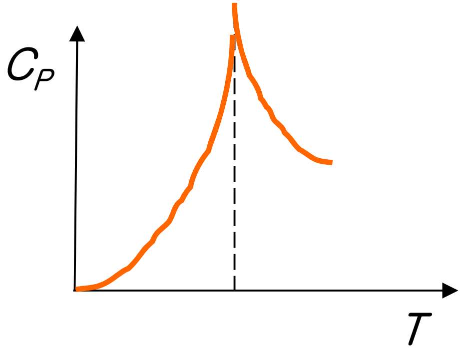
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

Second-order transition



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

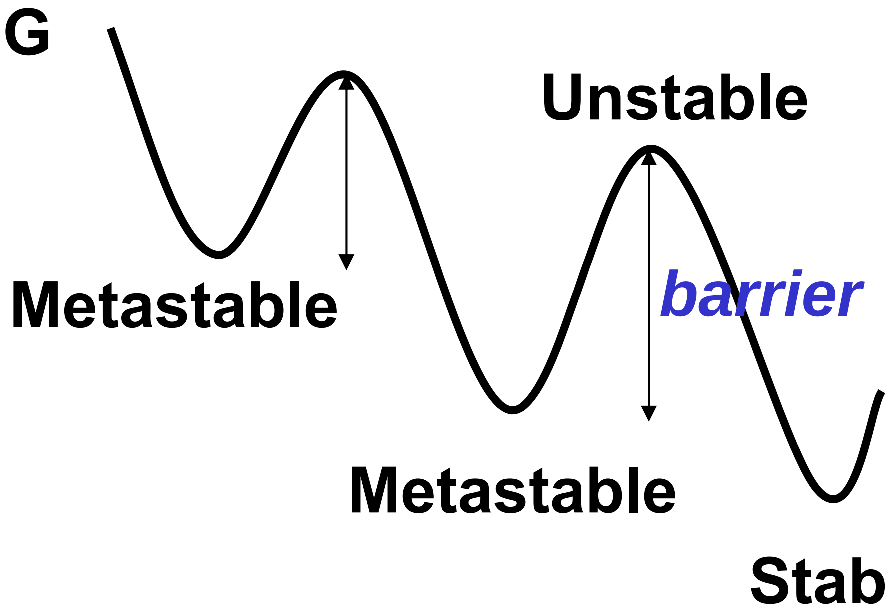


Q9: What is the driving force for “Solidification: Liquid → Solid”?

Phase Transformation

Change to another phase ➡ **metastable state** $\boxed{\Delta G = G_2 - G_1 < 0}$

structure or composition or order



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)

$T = T_m - \Delta T$

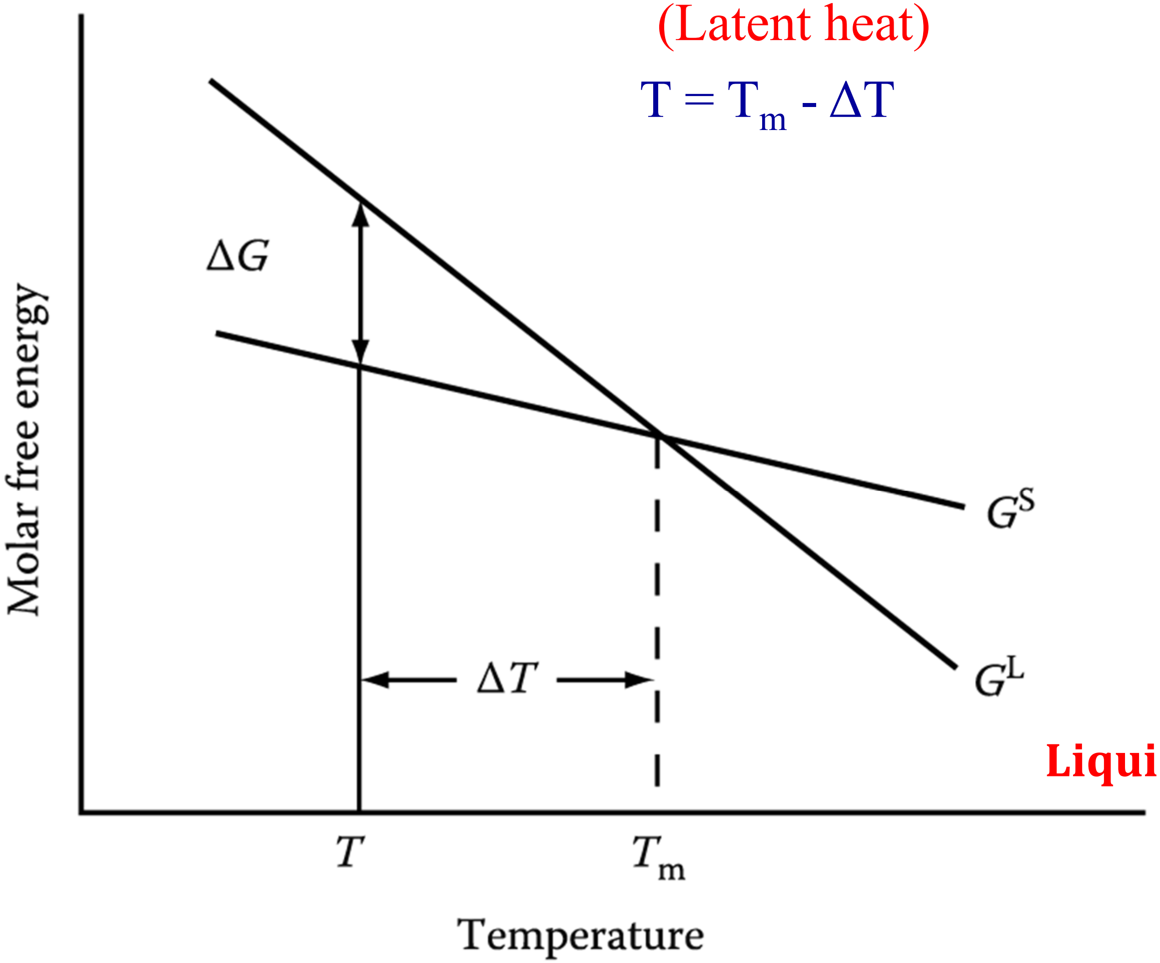
$\Delta G = 0 = \Delta H - T_m \Delta S$

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

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

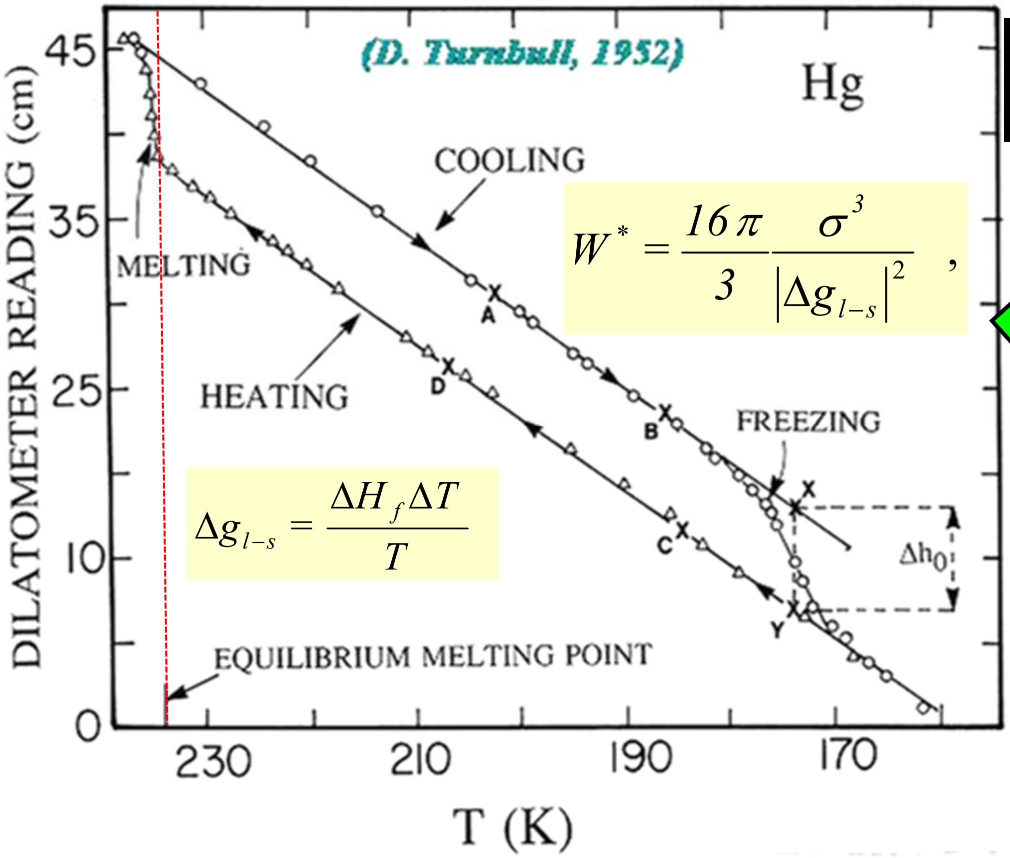
(eq. 1.17)

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



Liquid → Solid transformation?

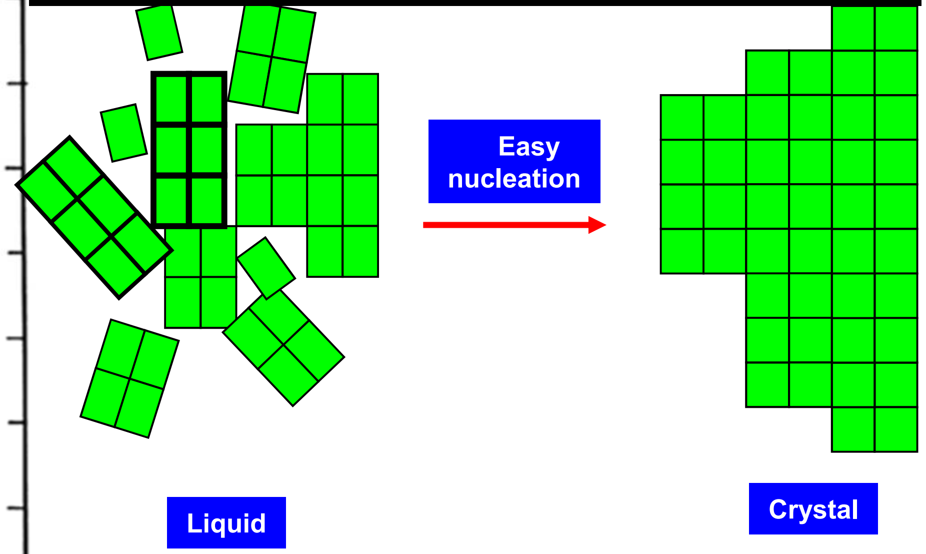
Turnbull's Insight for Supercooling



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

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

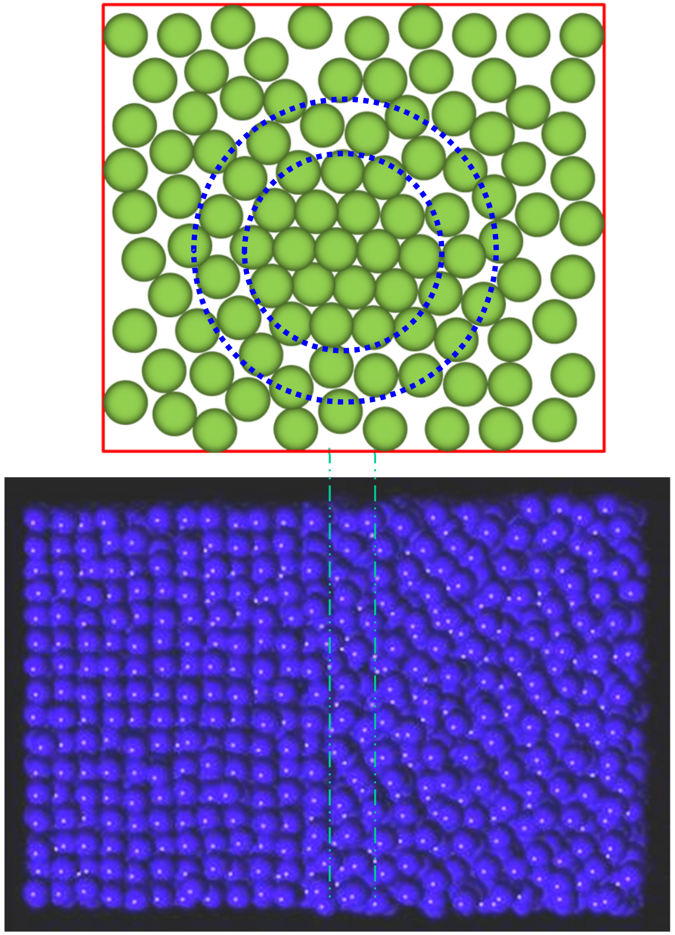
Microcrystalline structure for liquid metals –*Same short range order with crystals*!



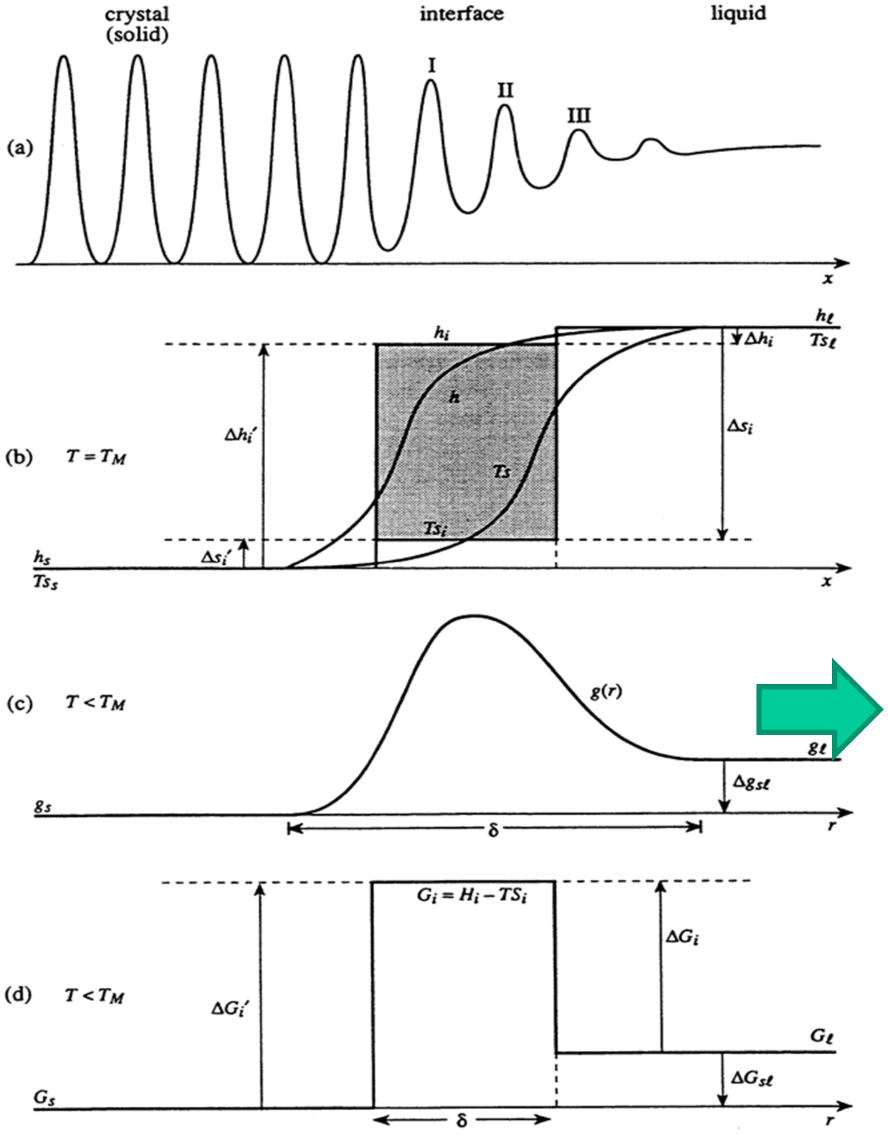
◆ How does the liquid metals resist on the crystallization?
◆ What is the origin of high nucleation barrier against the crystallization?
→ What is the structure of interface between liquids and crystals?
◆ What is the local order of liquid metals?

Turnbull’s solid-liquid interface

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

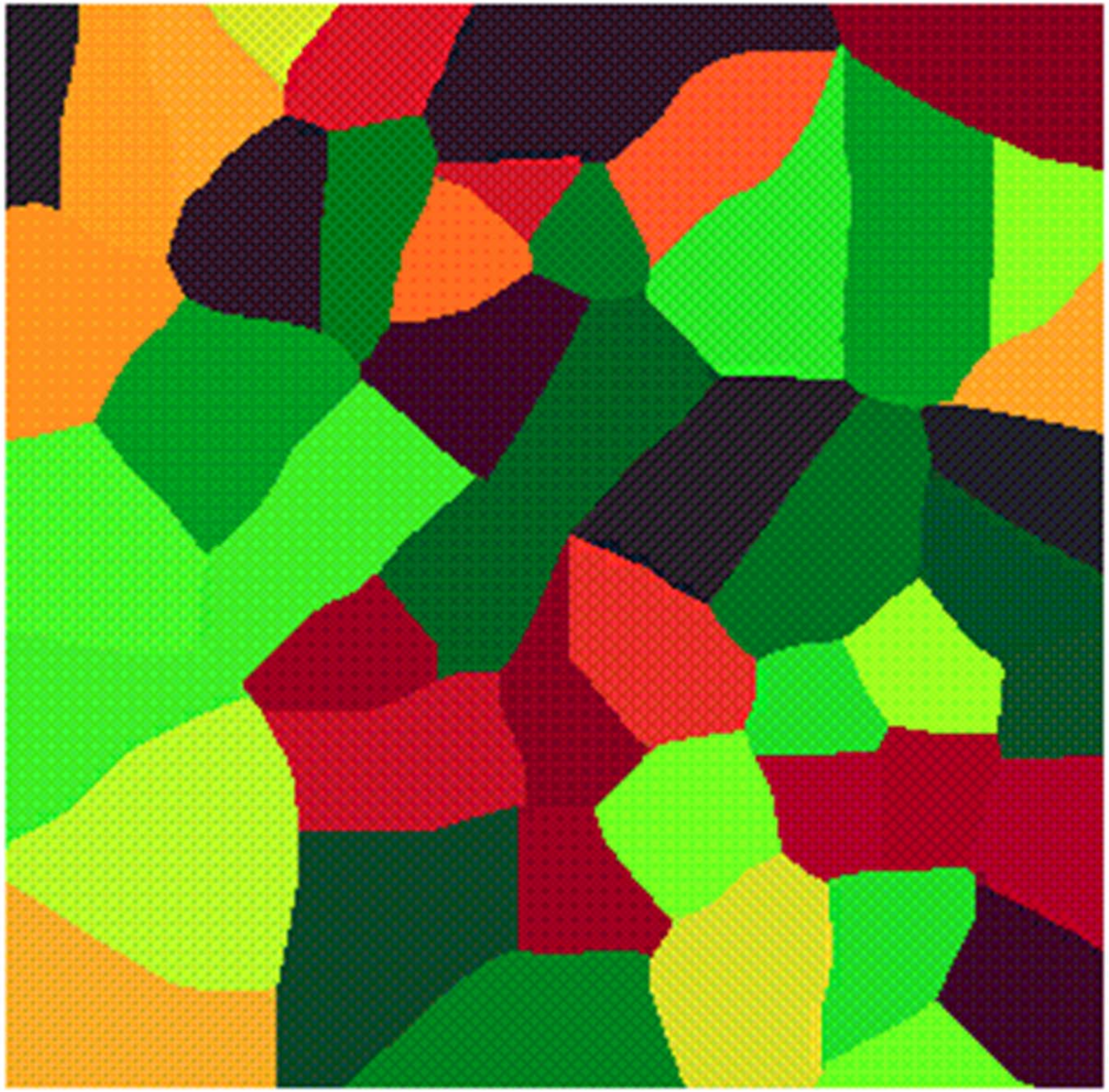


Solid state physics v47, 1 (1994)



Supercooling

4. Solidification: Liquid ⟶ Solid



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

4.1.1. Homogeneous Nucleation

(a) G_1

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

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

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

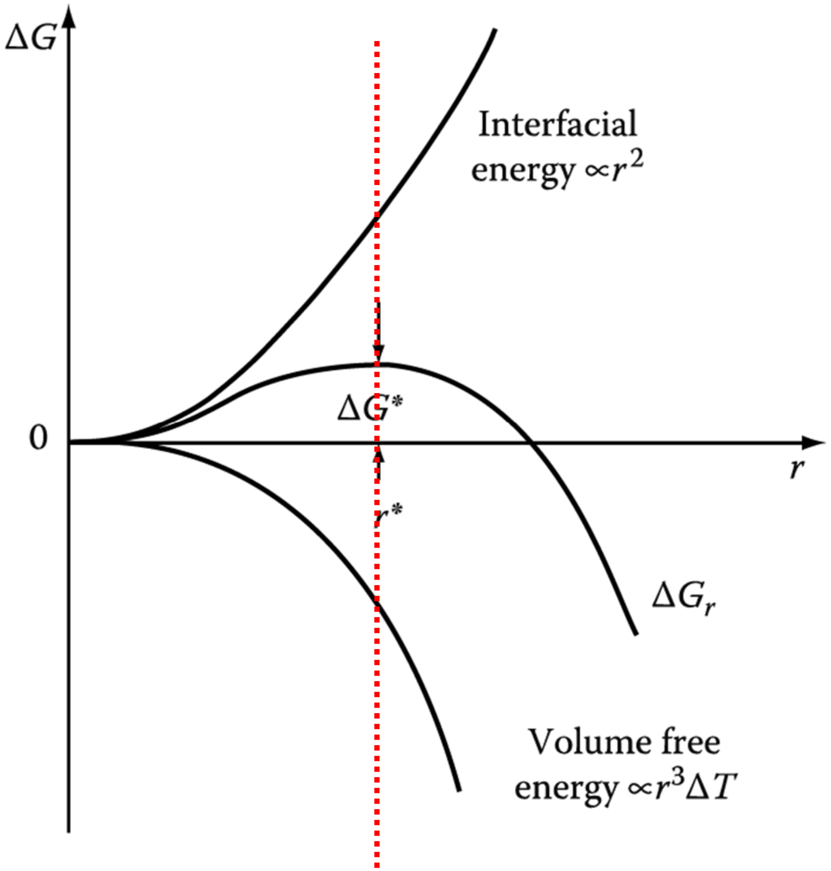
G_V^S, G_V^L **: free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

4.1.1. Homogeneous Nucleation



Unstable equilibrium

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

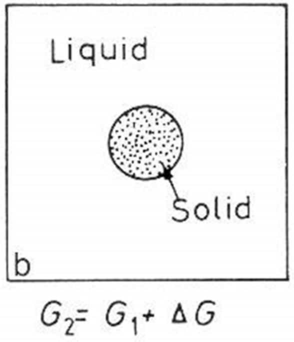
Why r^* is not defined by $\Delta G_r = 0$?

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

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

r^* **: critical nucleus size**

r* ⇨ **dG=0**

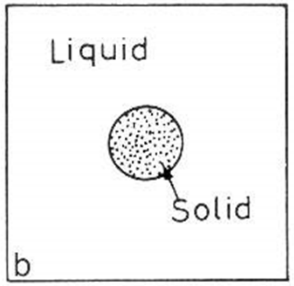


$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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

1.2.3 Driving force for solidification

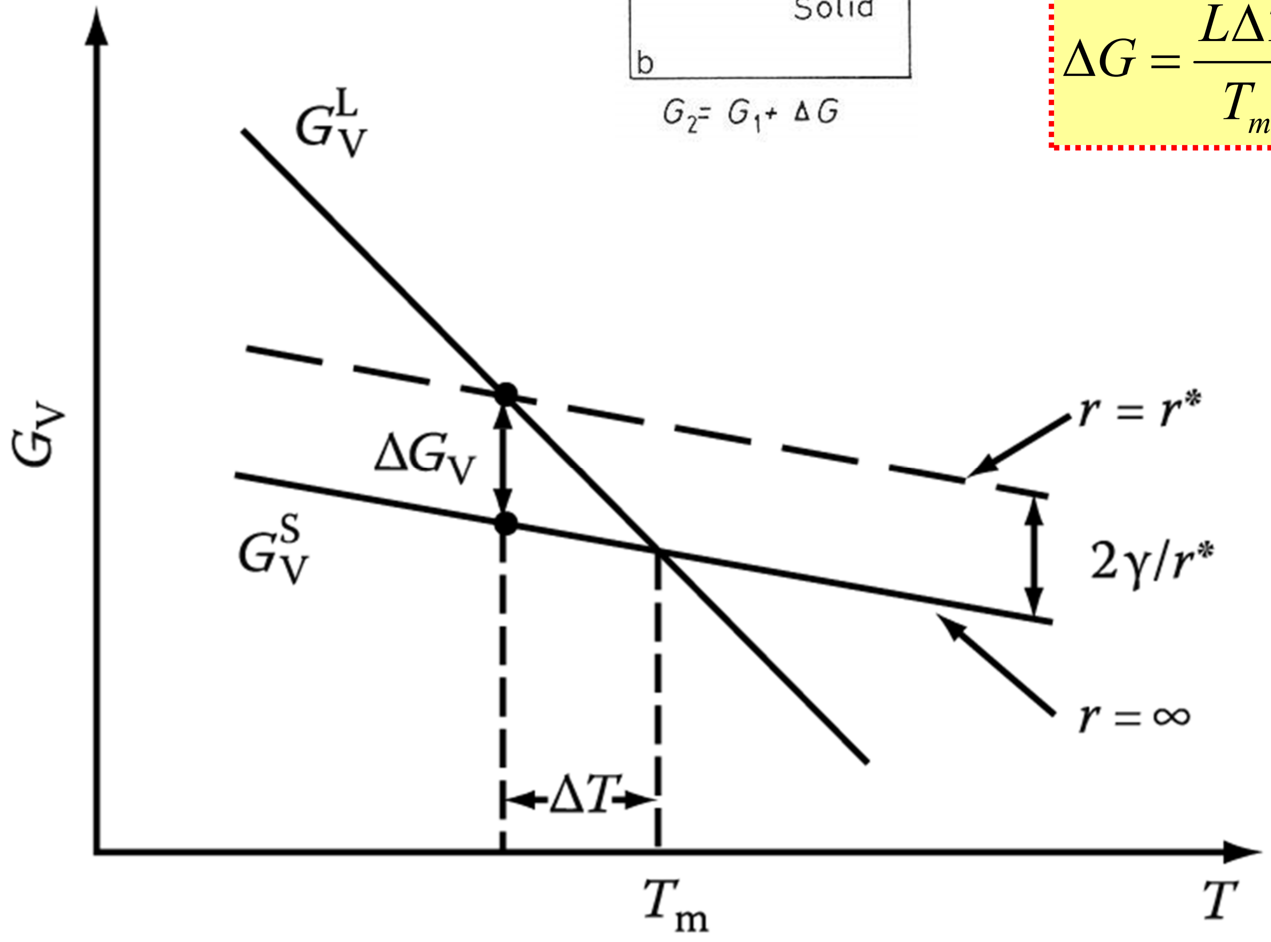
Liquid $\xrightarrow{\text{solidification}}$ **Solid**



$G_2 = G_1 + \Delta G$

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

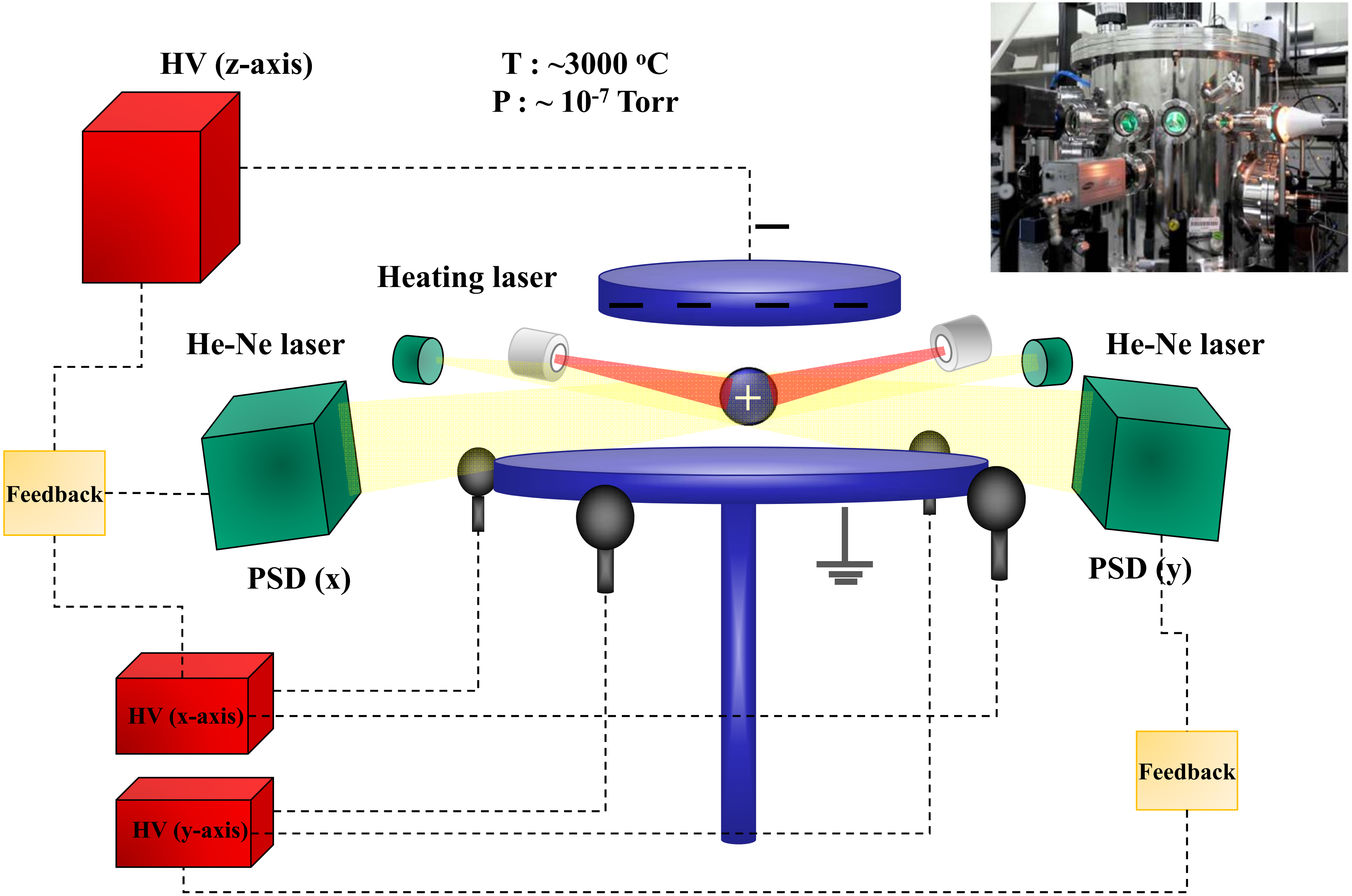
$$\Delta G = \frac{L\Delta T}{T_m} = \frac{2\gamma_{SL}}{r^*}$$



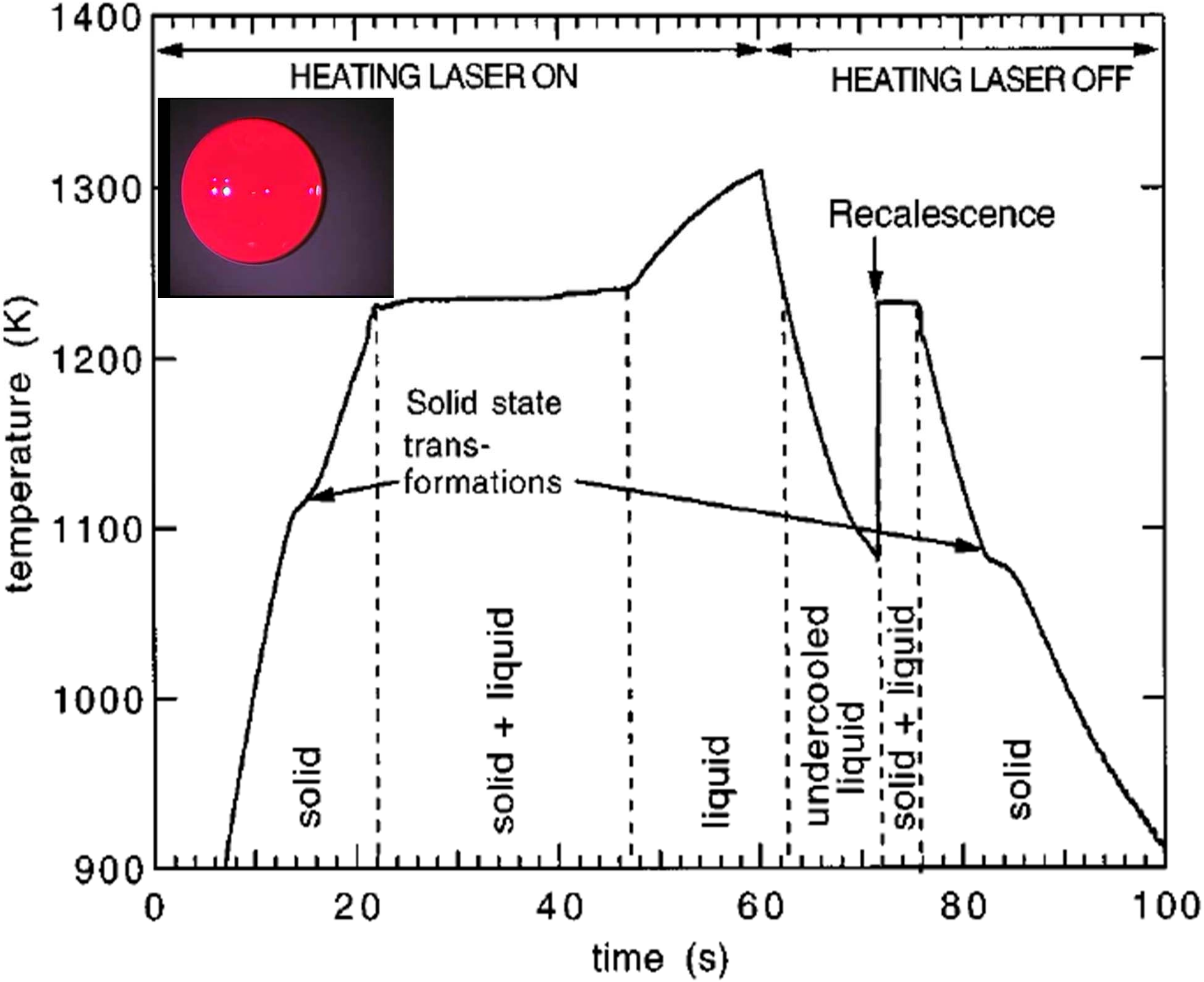
Electrostatic levitation in KRISS

T : ~3000 °C

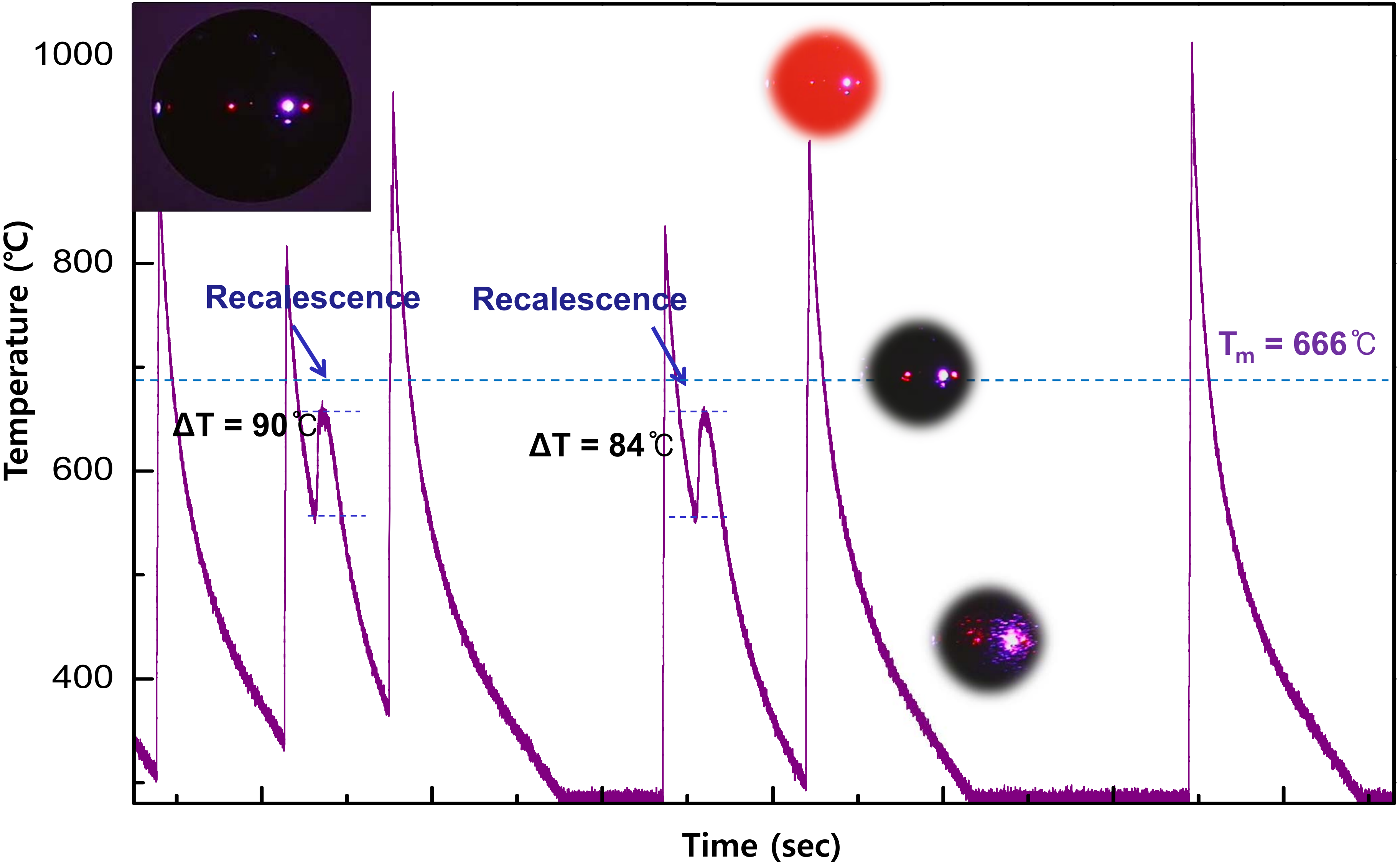
P : ~ 10^{-7} Torr



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)
1400
1300
1200
1100
1000
900
time (s)
0
20
40
60
80
100

Cyclic cooling curves of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$



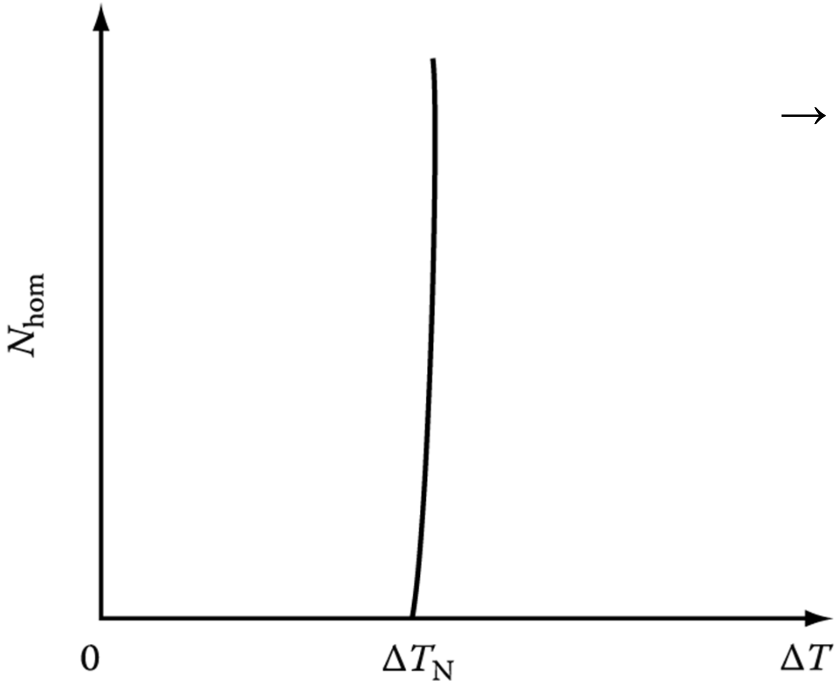
* The homogeneous nucleation rate - kinetics

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

: insensitive to Temp.

How do we define nucleation temperature, ΔT_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. ~200K)

The homogeneous nucleation rate as a function of undercooling ΔT.

ΔT_N is the critical undercooling for homogeneous nucleation.

* Relationship between Maximum Supercoolings and T_m

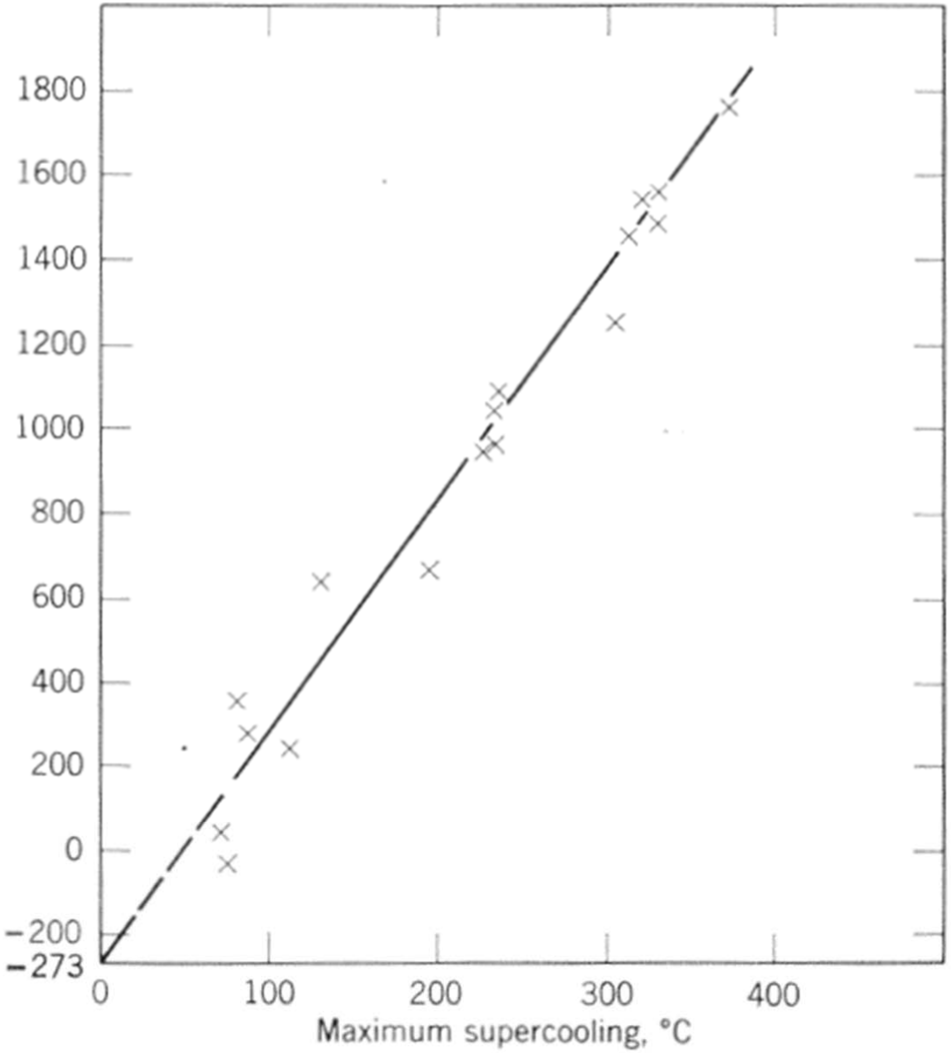


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

Solidification: Liquid $\longrightarrow$ Solid

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

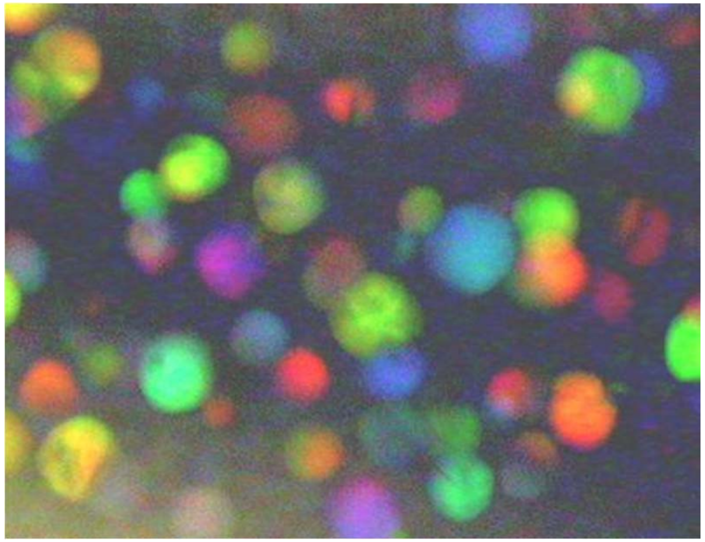
Nucleation in Pure Metals

T_m : $G_L = G_S$

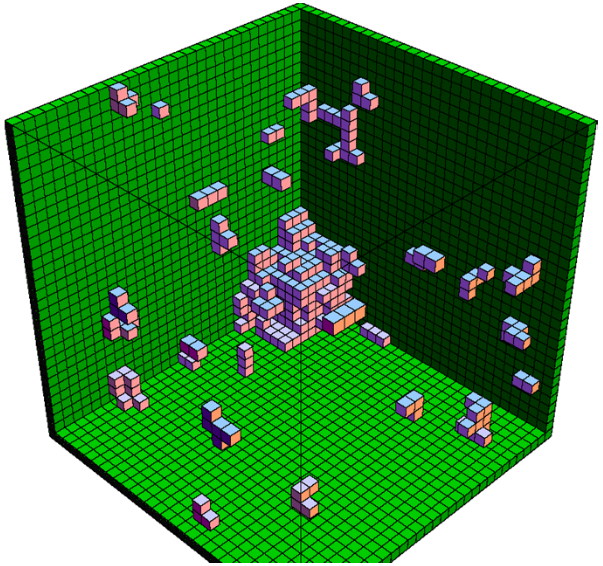
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

- Homogeneous nucleation



- Heterogeneous nucleation



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

* Driving force for melting

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

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

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

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

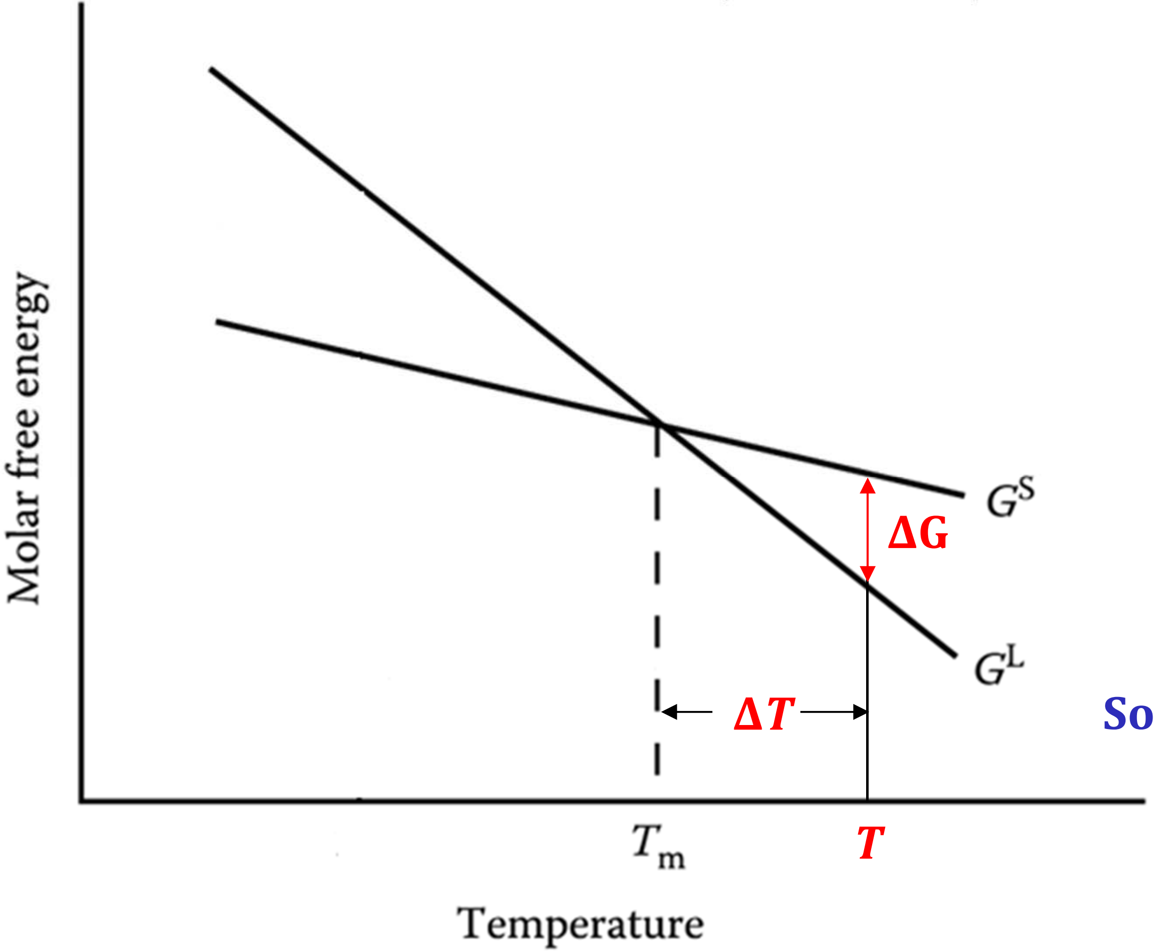
(Latent heat)

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

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

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

(eq. 1.17)



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

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.

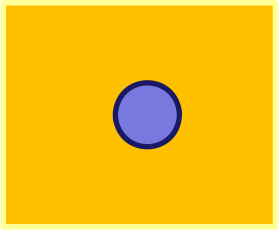
Why?

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$ **(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!

vapor

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid

Contents for today's class

CHAPTER 1 Introductory Thermondynamics

- **Equilibrium** $\boxed{dG = 0}$

Lowest possible value of G
No desire to change ad infinitum

- **Single component system**

Gibbs Free Energy as a Function of Temp. and Pressure

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \quad \left(\frac{\partial G}{\partial P}\right)_T = V} \qquad \boxed{\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}}$$

Clausius-Clapeyron Relation

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

- **Classification of phase transition**

First order transition: CDD/Second order transition: CCD

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

Driving force for solidification $\boxed{\Delta G = \frac{L\Delta T}{T_m}}$