2017 Fall

"Phase Transformation *in* Materials"

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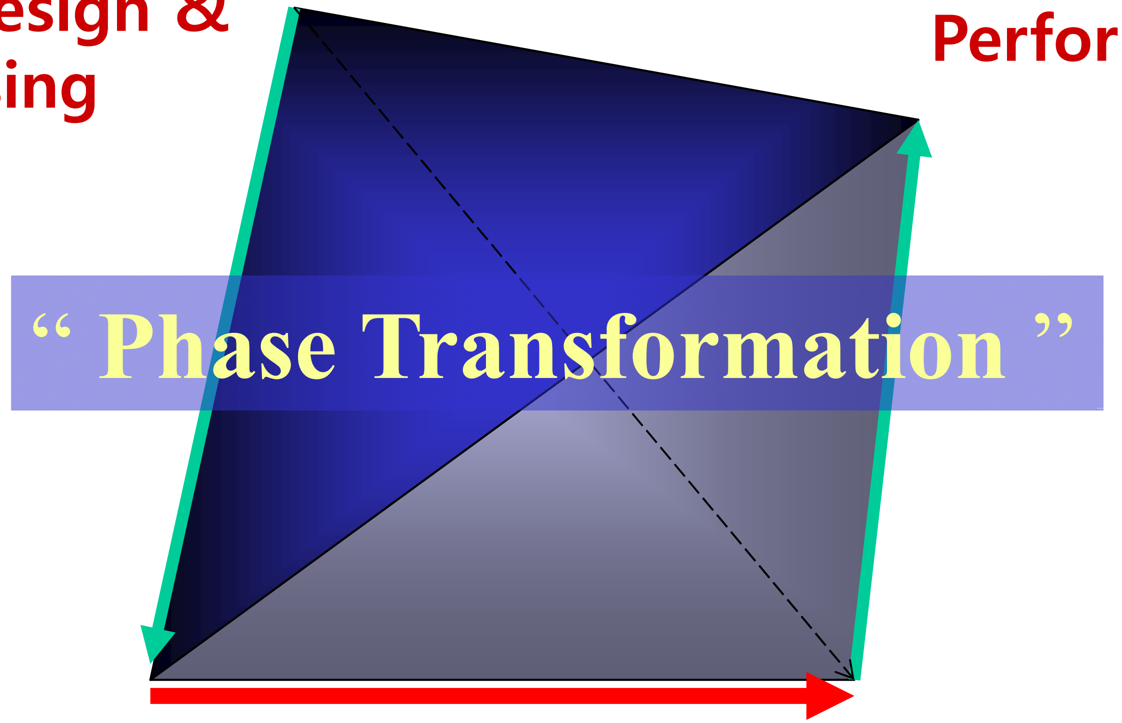
Contents for previous class

Microstructure-Properties Relationships



Alloy design & Processing

Performance

“ Phase Transformation ”

Microstructure

down to atomic scale

Properties

“Tailor-made Materials Design”

Contents for previous class

Contents of this course_Phase transformation

Background to understand phase transformation

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

Representative Phase transformation

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

Contents for today's class I

Chapter 1

Thermondynamics and Phase Diagrams

- Equilibrium

- Single component system

  Gibbs Free Energy
  as a Function of Temp. and Pressure

- Classification of phase transition

- Driving force for solidification

Q1: “thermodynamic equilibrium”?

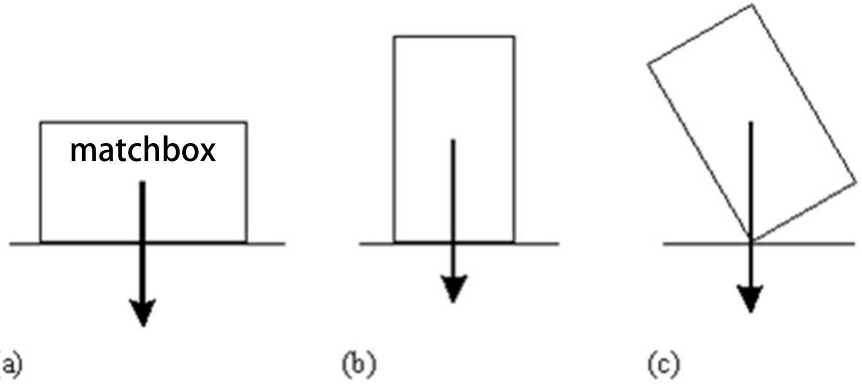
Lowest possible value of Gibb’s Free Energy

→ The main use of thermodynamics in metallurgy is to allow the prediction of whether an alloy is in equilibrium.

Chapter 1

Equilibrium

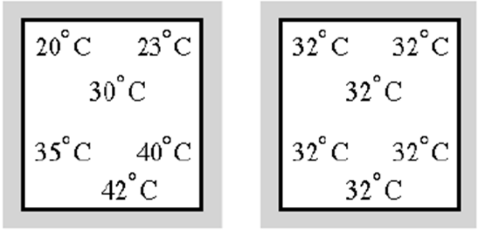
Mechanical equilibrium



: 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.

Relative Stability of a System ➡ Gibbs Free Energy

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

Useful when P is constrained during thermodynamic process.

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

Mixture of one or more phases

$$H = E + PV$$

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

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*

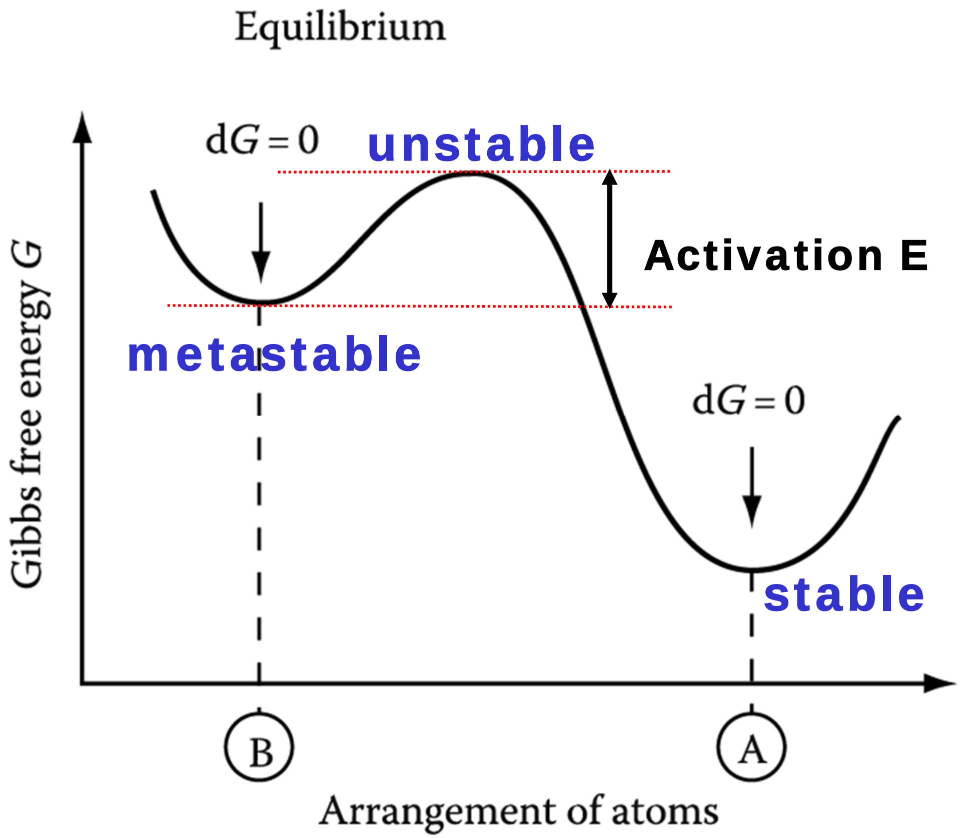
S : Entropy, The *Randomness* of the System

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?

Different elements or chemical compounds

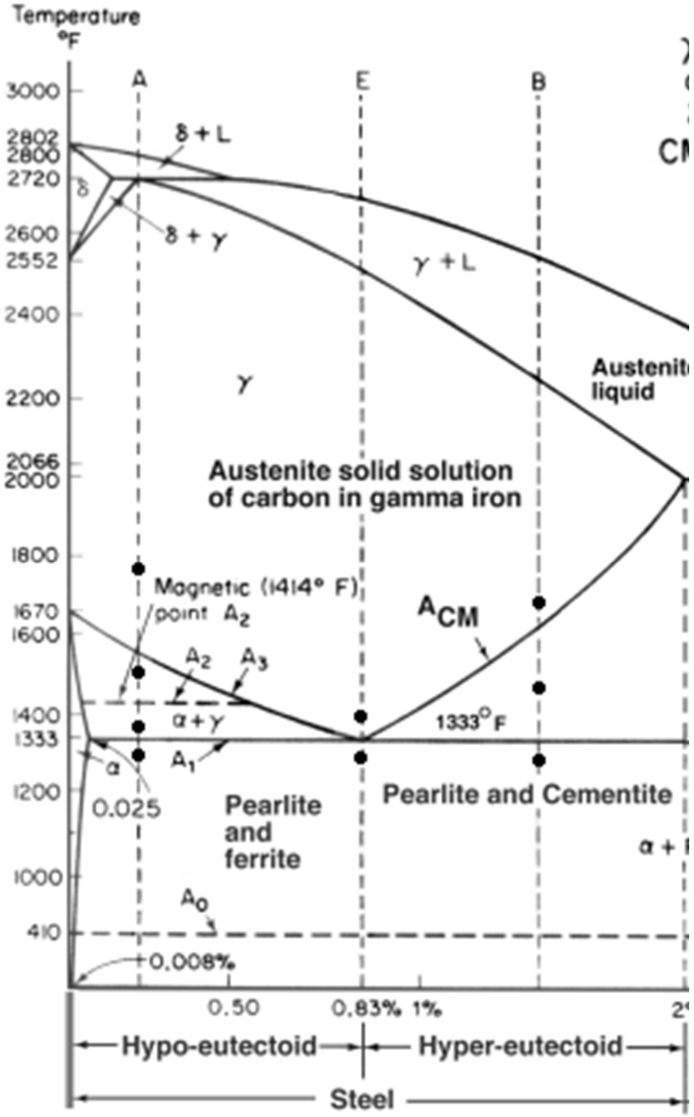
1.2 Single component system

One element (Al, Fe)

One type of molecule (H_2O)

- **Allotropic forms?**
- **How is phase stability measured?**

$$G = H - TS$$



Fe → **C**

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,

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

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,

$$H \equiv E + PV \longrightarrow \begin{aligned} dH &= dE + PdV + VdP \\ &= \delta Q - \delta w + PdV + VdP \\ &= \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \end{aligned}$$

$$\boxed{dE = \delta Q - P \cdot dV}$$

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

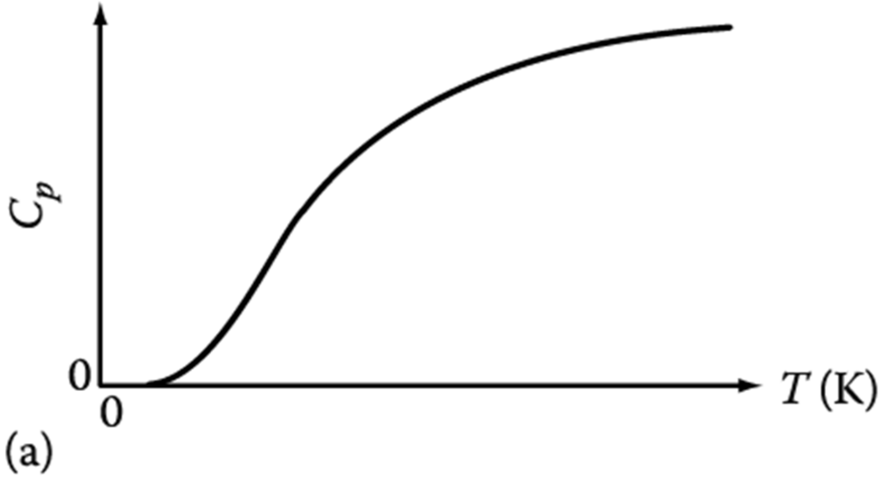
➡ $$\frac{dP}{dT} = 0 \text{ when } P \text{ is constant} \qquad \boxed{(\frac{dH}{dT})_P = (\frac{\delta Q}{dT})_P = C_P} \qquad \boxed{H = \int C_p dT}$$

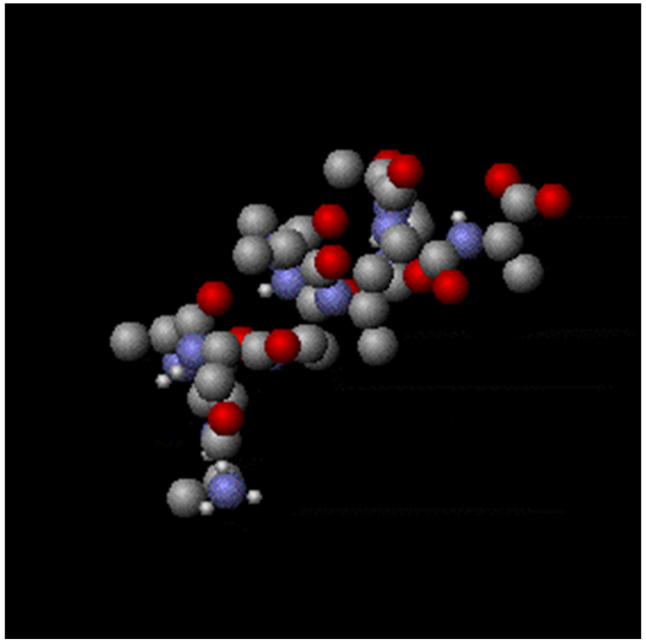
In alloy work one usually consider systems at constant pressure so that enthalpy changes are more important then energy changes.

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 *<u>internal degrees of freedom</u>* contributes to a substance's specific heat capacity and not to its temperature.

*** 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?

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

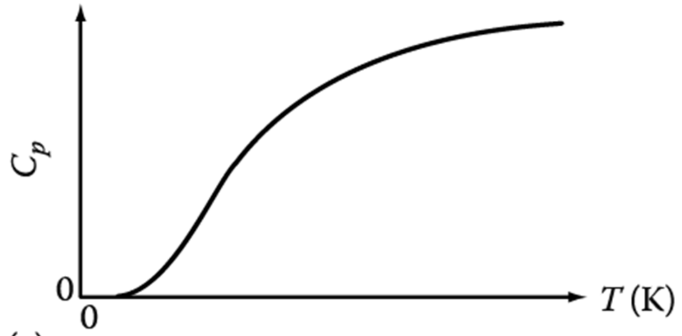
H = 0 at 298K for a pure element

in its most stable state.

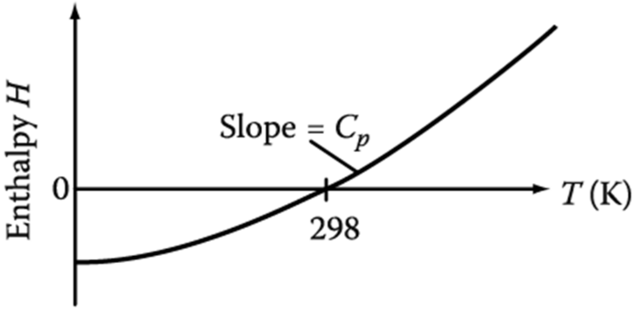
: When considering a phase transformation or a chemical reaction, the important thing is not the value of the thermodynamic function, but the amount of change.

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

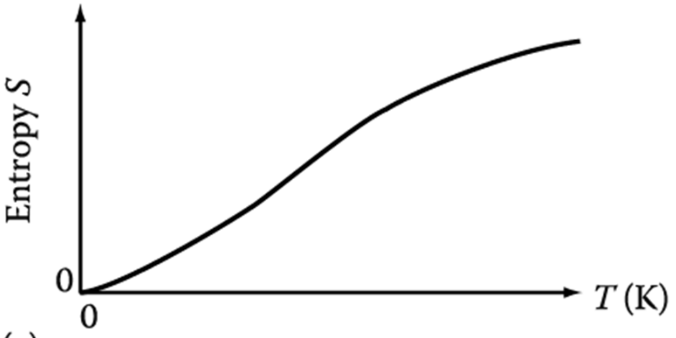
$$\textbf{S = ?} \quad \boxed{\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P} \quad \boxed{S = \int_{0}^{T} \frac{C_P}{T} dT}$$



(a)



(b)

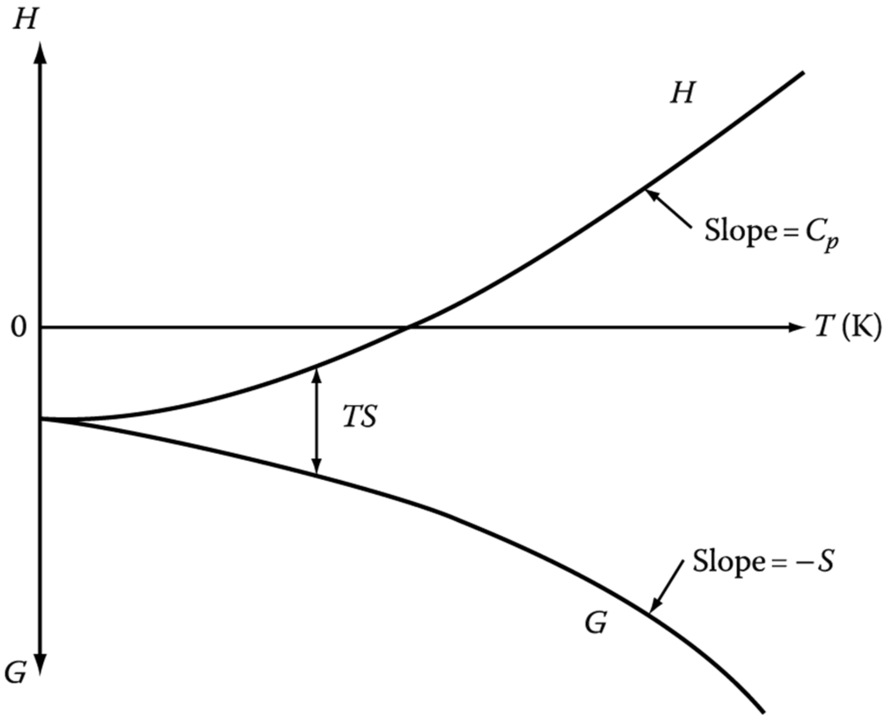


(c)

*** 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.



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

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

$$G = H - TS$$

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

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

$$= VdP - SdT$$

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

$$dG = VdP - SdT$$

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

*** 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.**

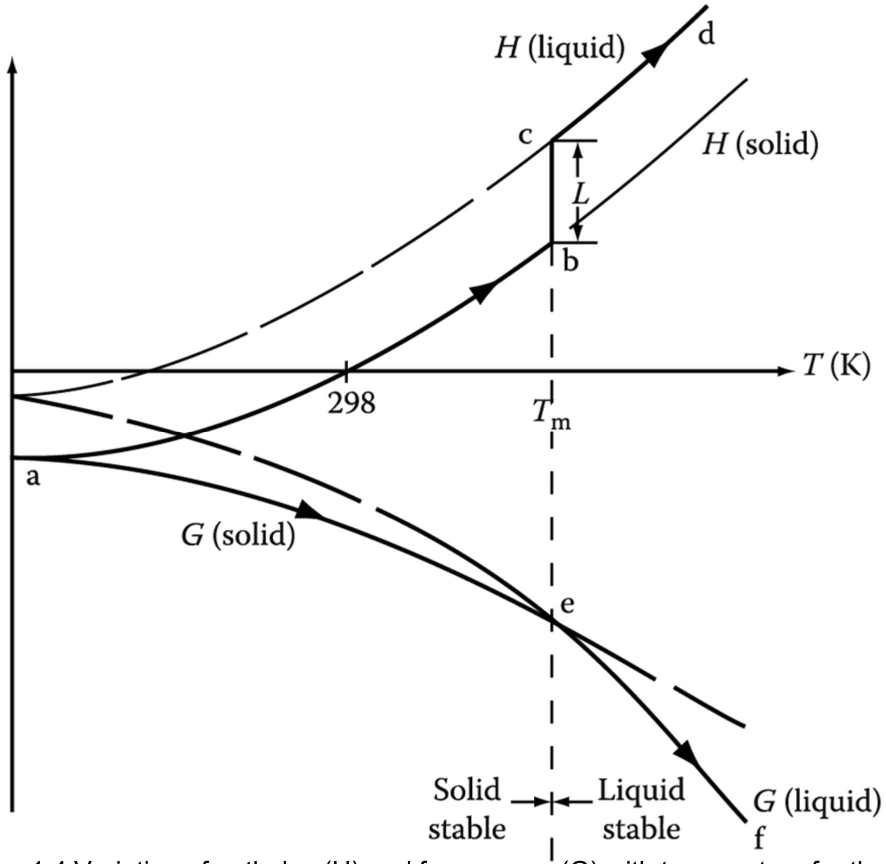


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting, Tm the Equilibrium melting temperature.

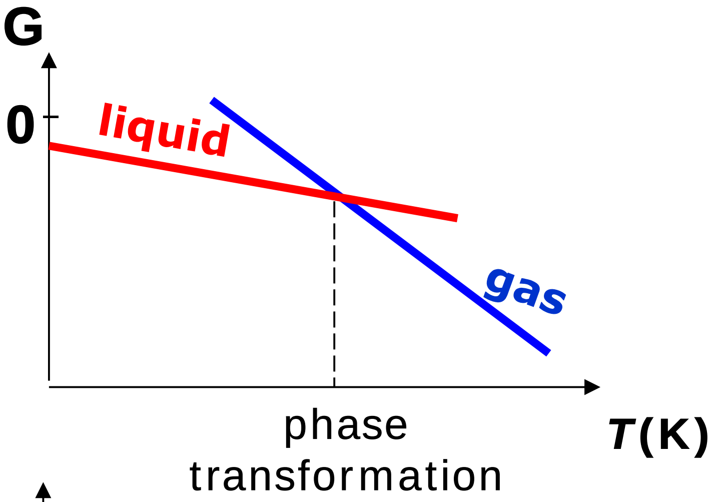
- **Which is larger, G^L or G^S at low T?**
- **$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)**

Considering P, T

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

$$dG = VdP - SdT$$

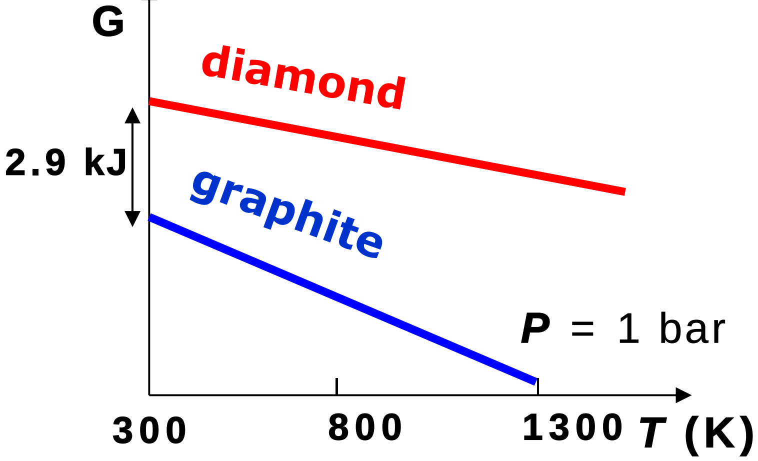
$$G(P,T) = G(P_0,T_0) + \int_{P0}^{P1} V(T_0,P)dP - \int_{T0}^{T1} S(P,T)dT$$



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

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

(applies to all coexistence curves)

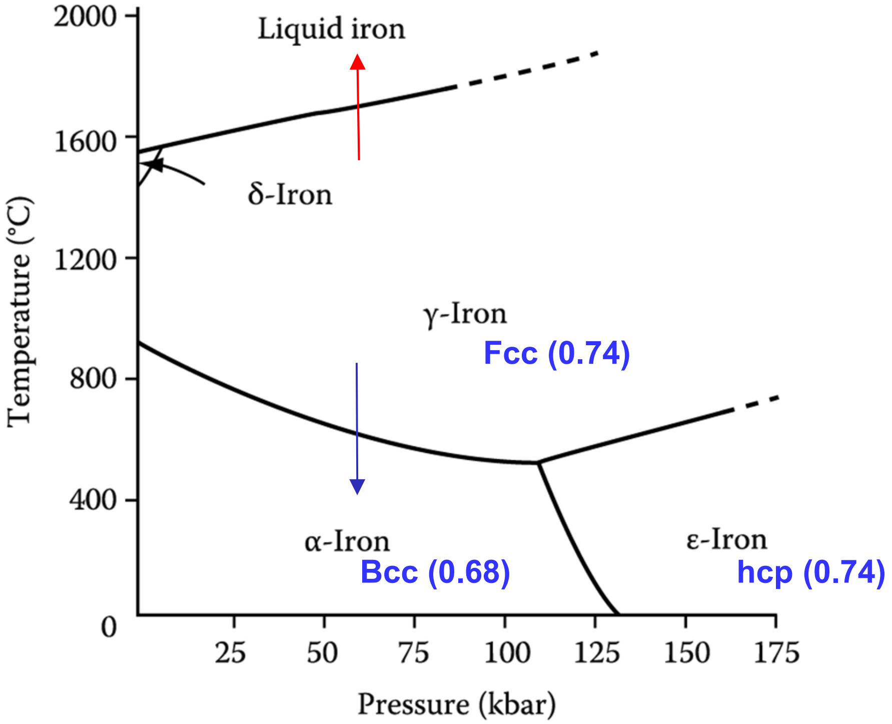


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

For, γ →liquid; ΔV (+), ΔH(+)

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

For, α→γ ; ΔV (-), ΔH(+)

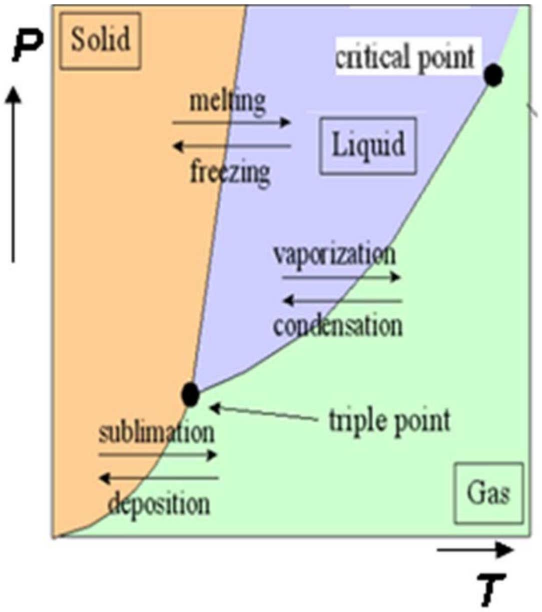
$$\left(\frac{dP}{dT}\right) = \frac{\Delta H}{T_{eq}\Delta V} < 0$$

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

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

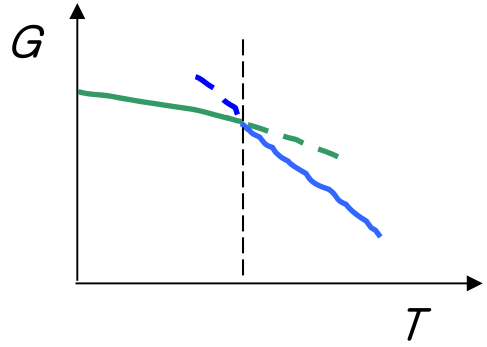
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

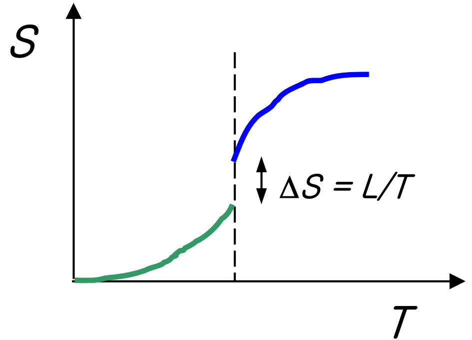
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

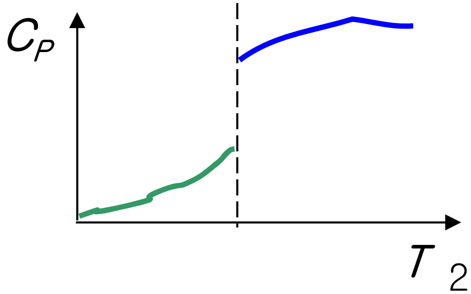
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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



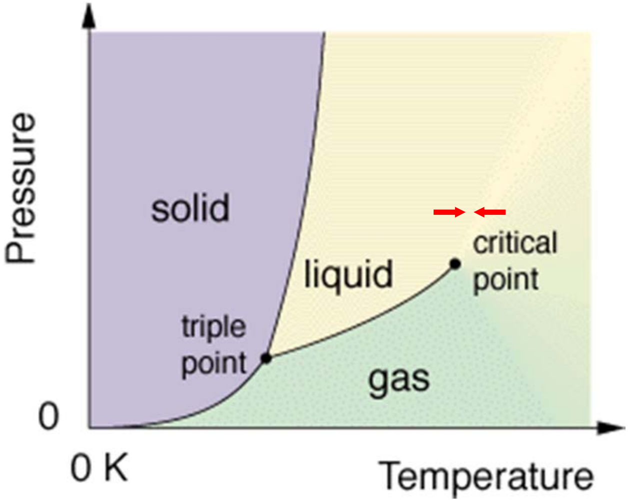


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$



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

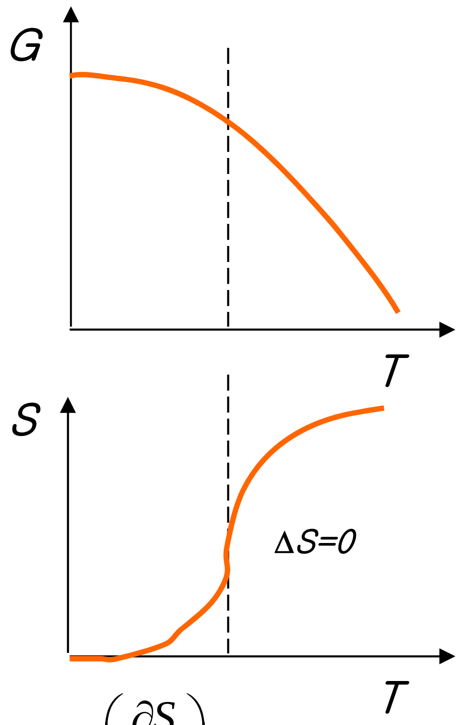
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

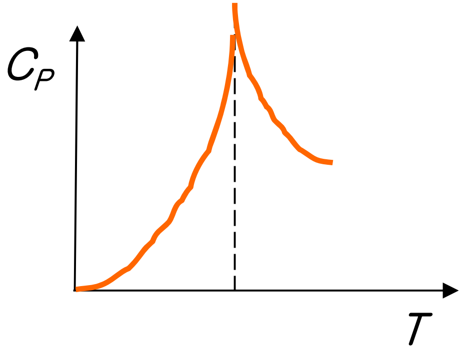
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

Second-order transition



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



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

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)

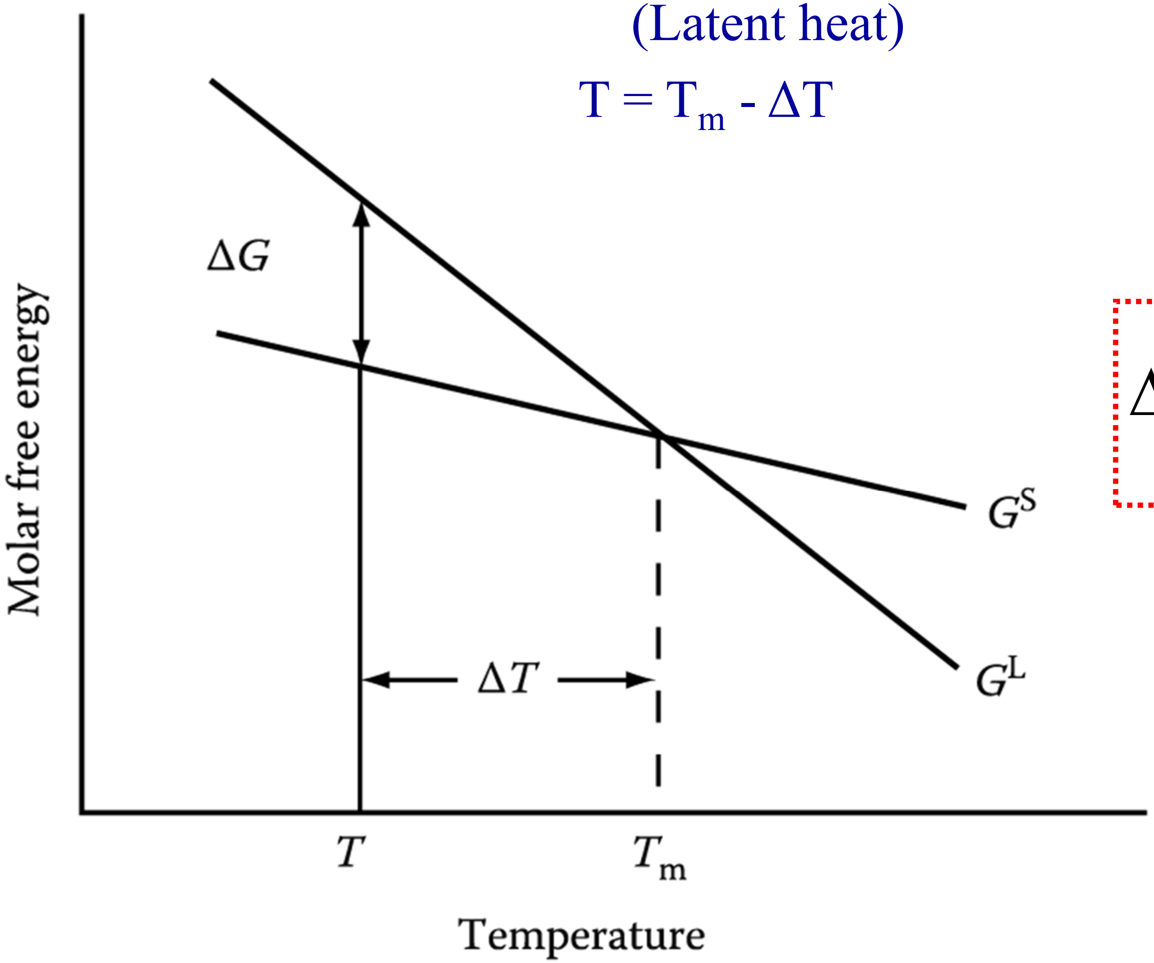
$T = T_m - \Delta T$

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

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

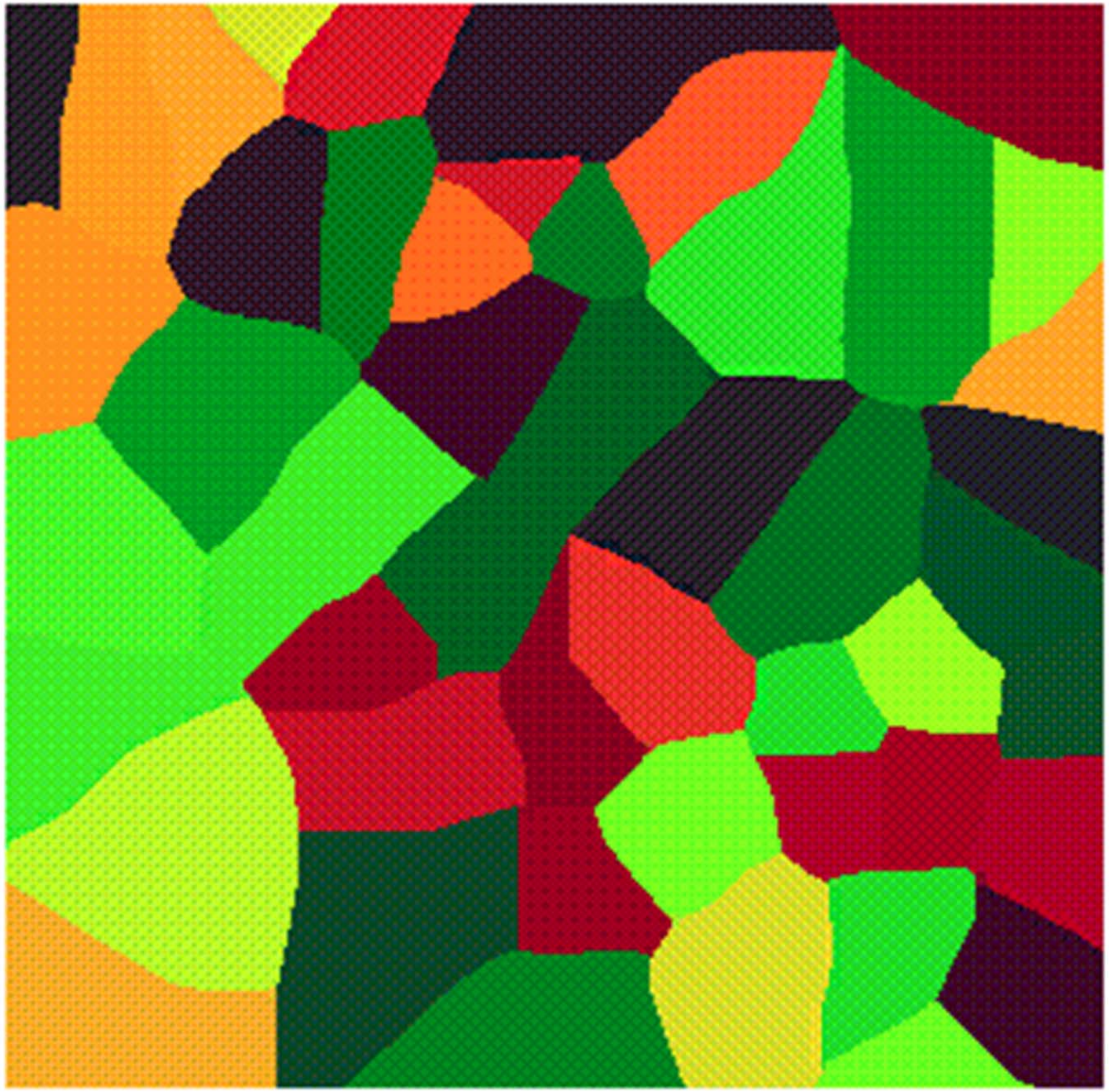
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

(eq. 1.17)



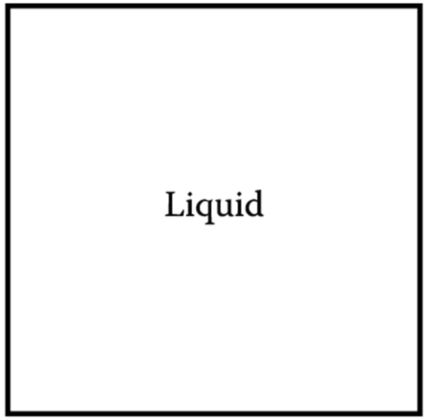
$$\boxed{\Delta G = \frac{L\Delta T}{T_m}}$$

4. Solidification: Liquid → Solid

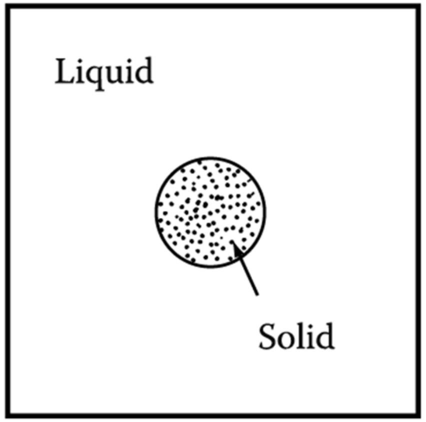


4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

4.1.1. Homogeneous Nucleation



(a) G_1



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

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

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

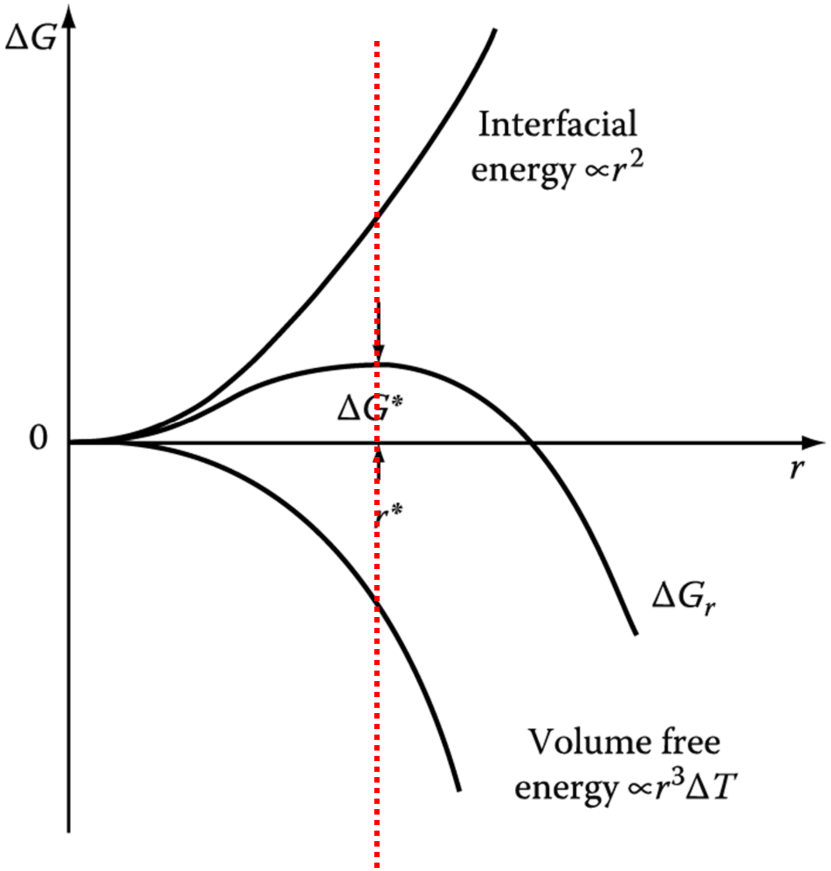
G_V^S, G_V^L **: free energies per unit volume**

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

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.

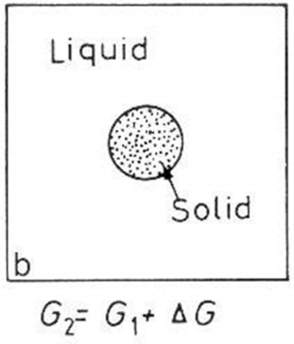
Why r^* is not defined by $\Delta G_r = 0$?

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

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

r^* **: critical nucleus size**

r* ⇒ dG=0



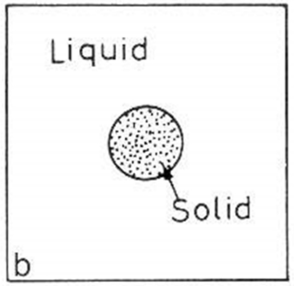
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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

1.2.3 Driving force for solidification

solidification

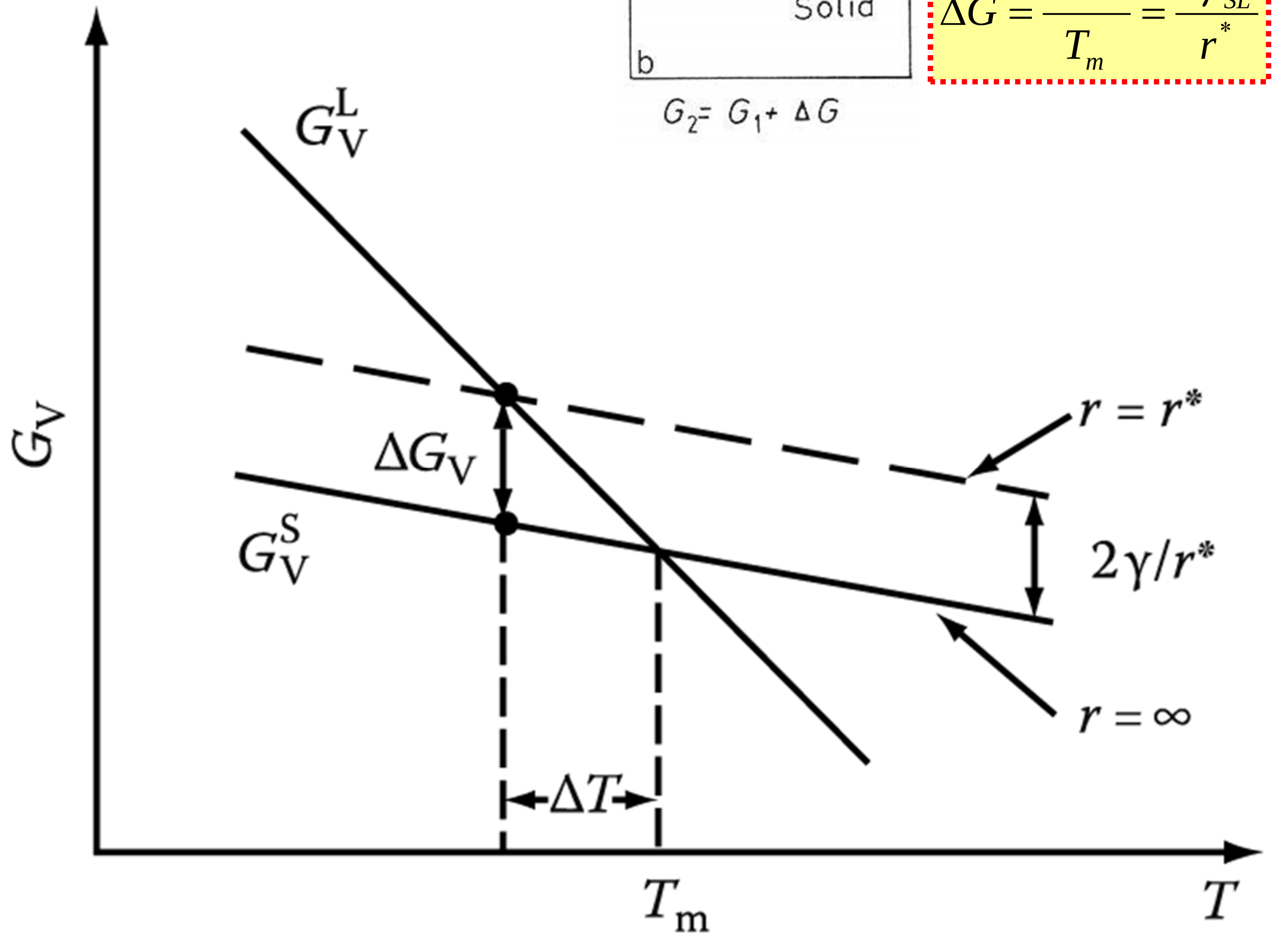
Liquid → **Solid**



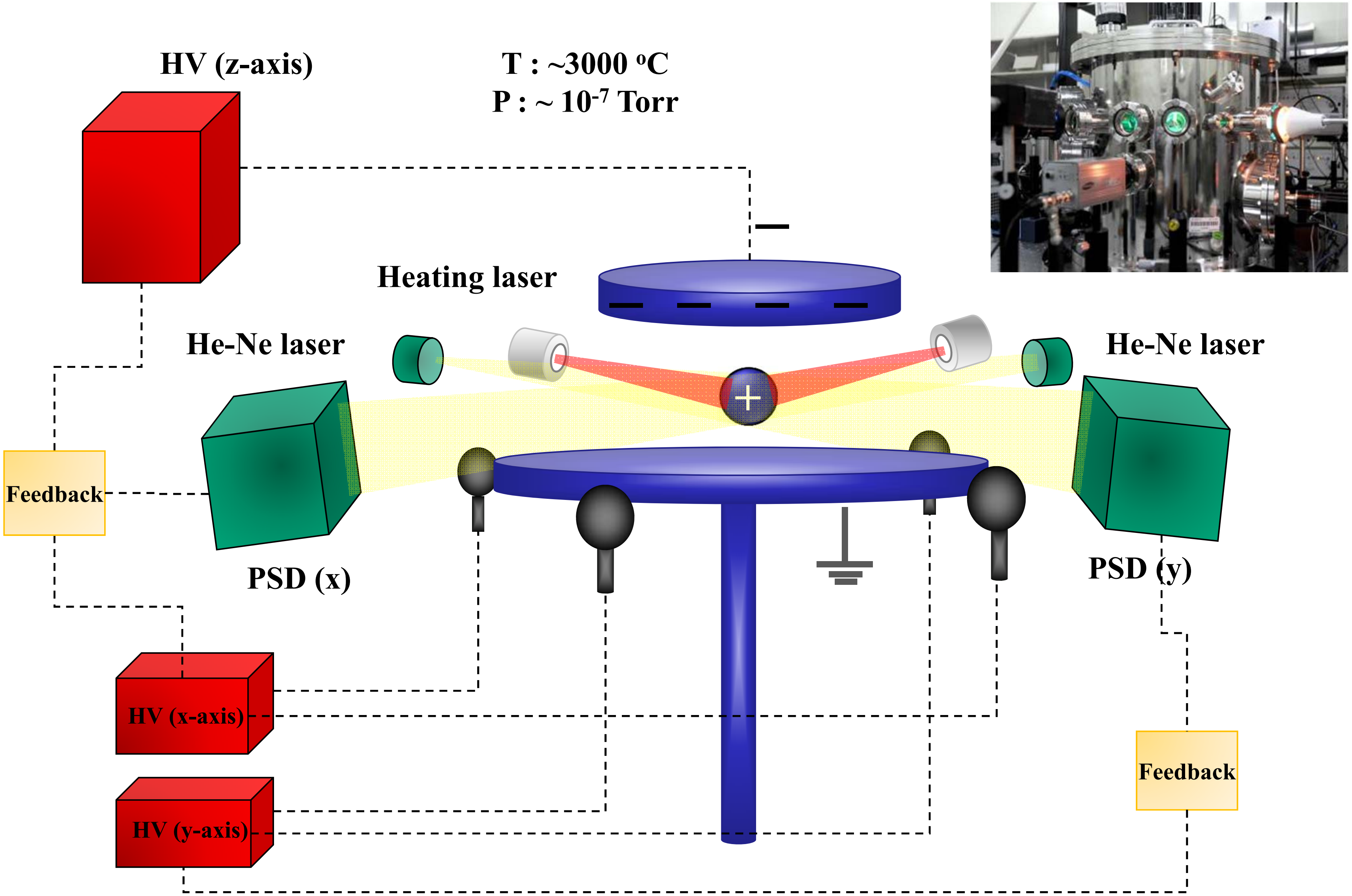
$G_2 = G_1 + \Delta G$

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

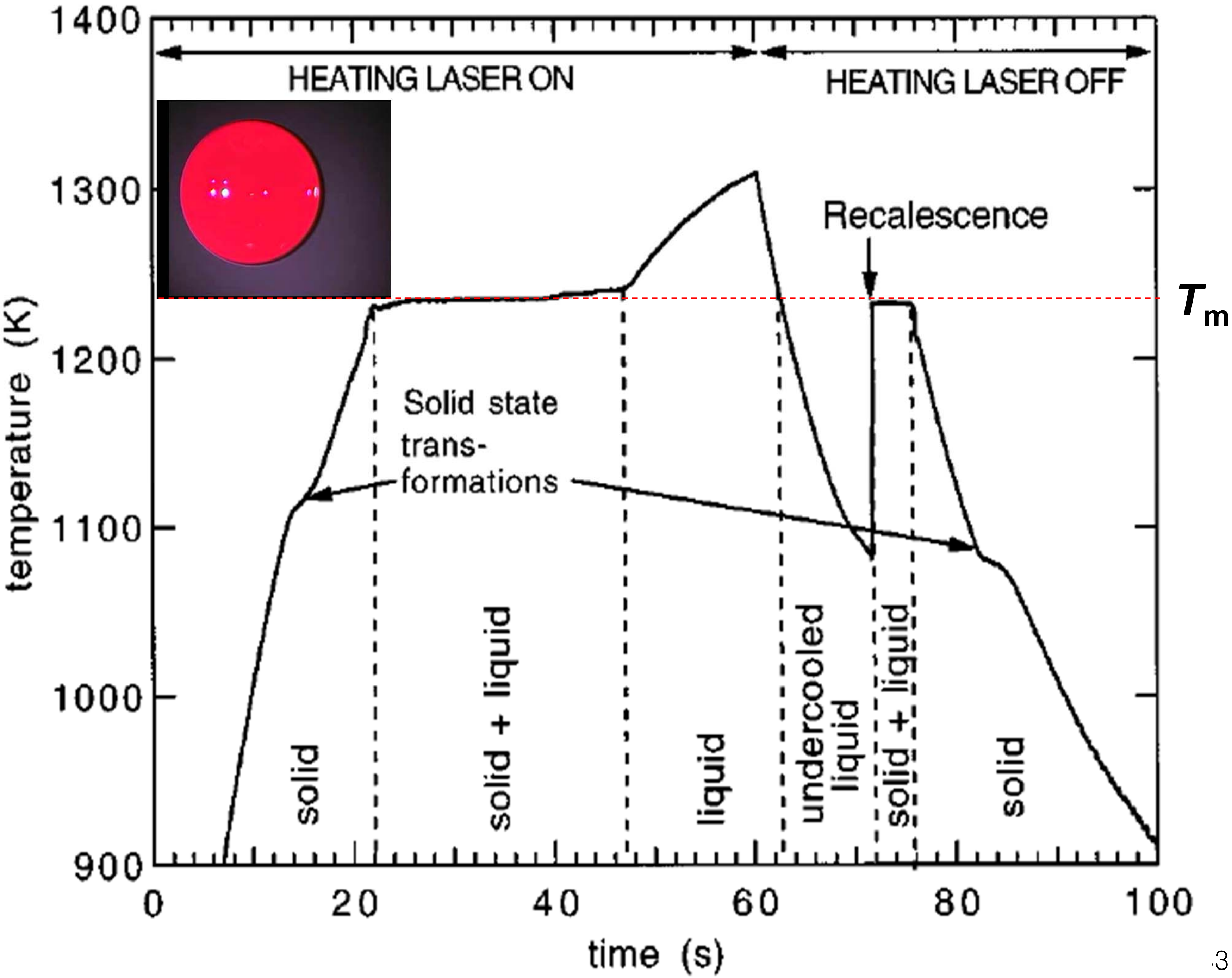
$$\boxed{\Delta G = \frac{L\Delta T}{T_m} = \frac{2\gamma_{SL}}{r^*}}$$



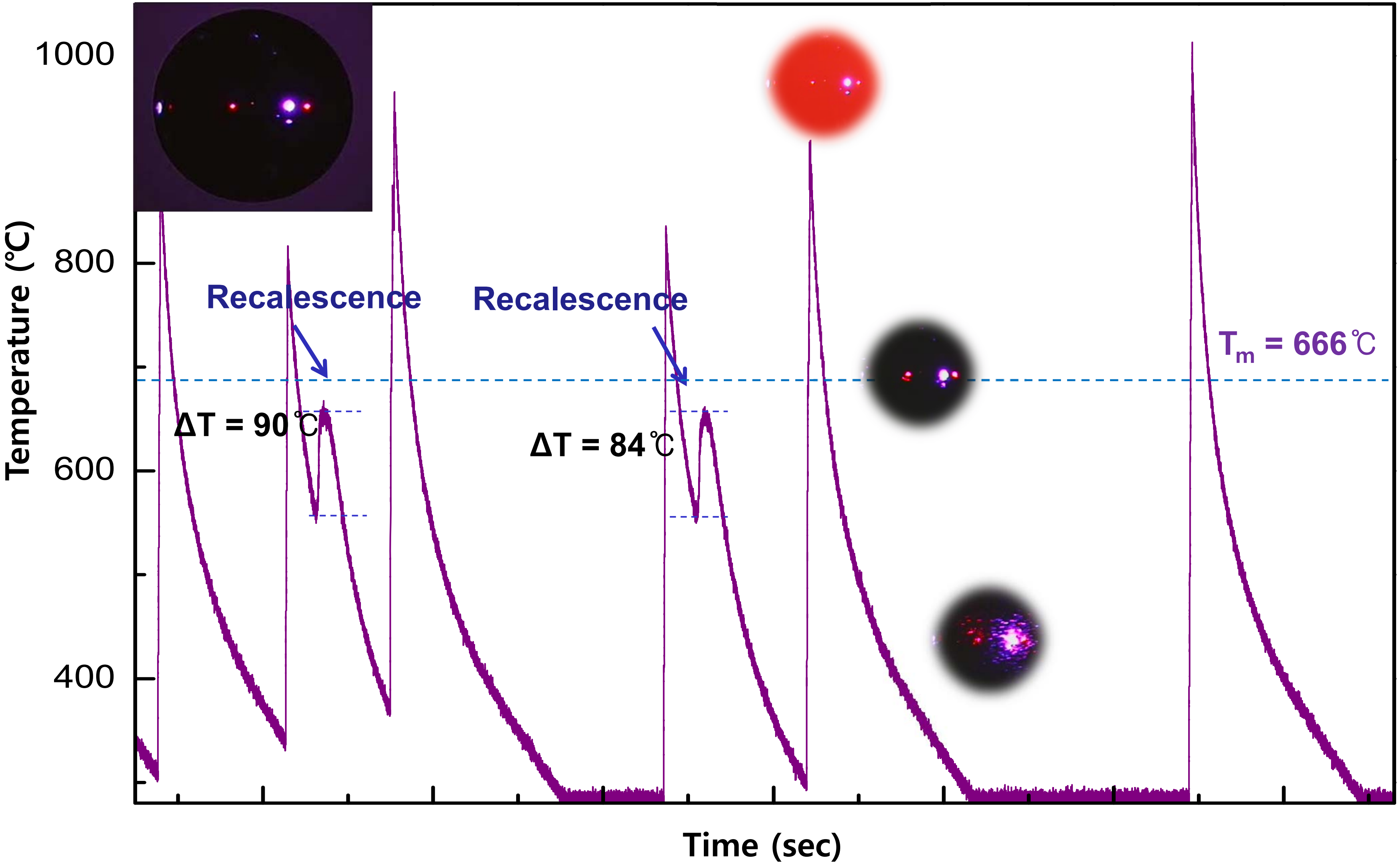
Electrostatic levitation in KRISS



KRISS material : Dr. G.W.Lee


HEATING LASER ON
HEATING LASER OFF
Recalescence
T_m
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

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



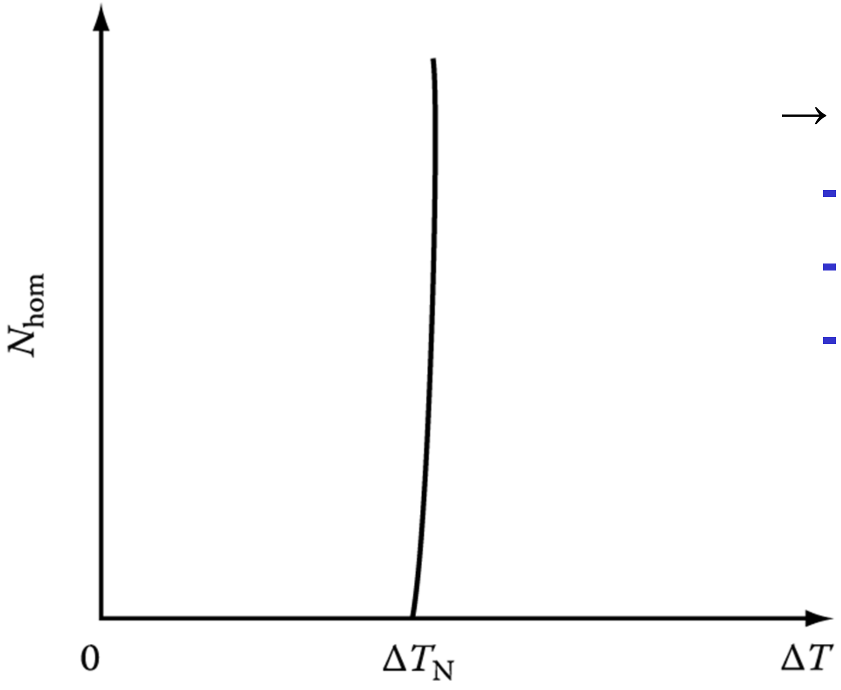
* The homogeneous nucleation rate - kinetics

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

: 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, ΔT_N~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

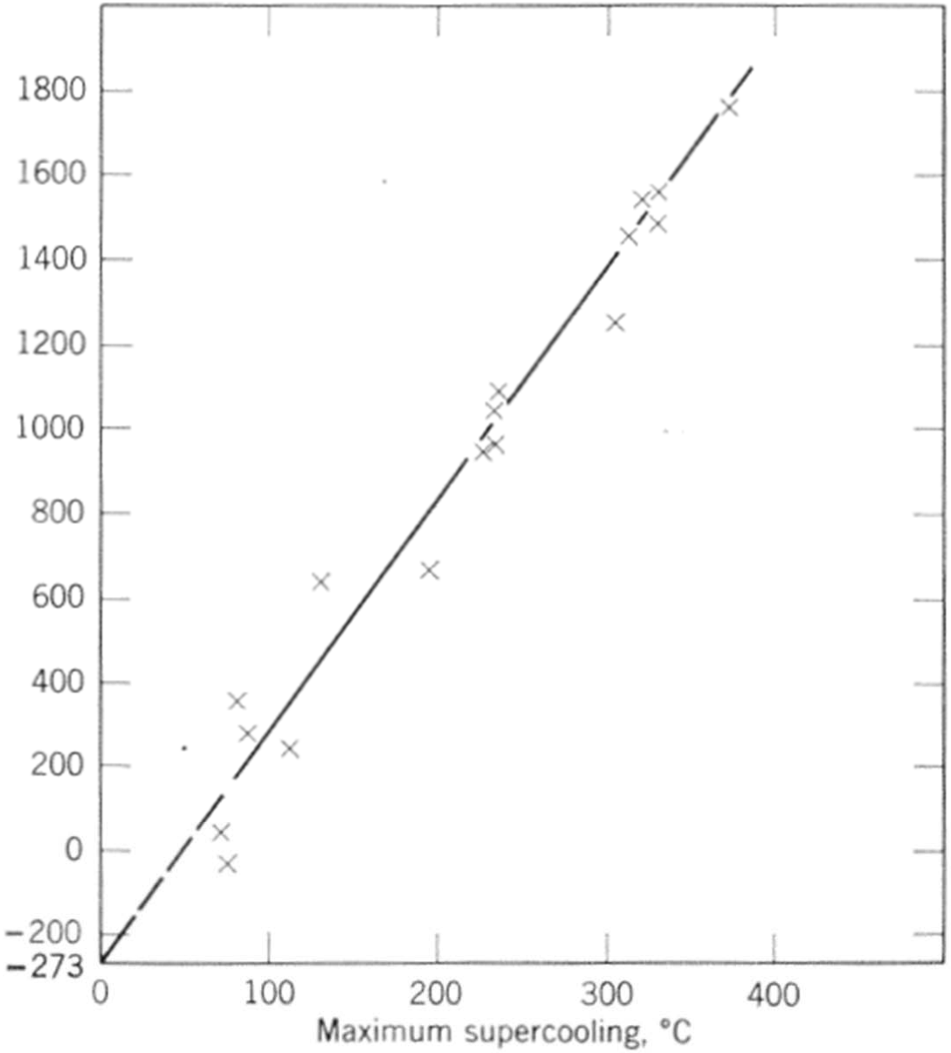


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

Solidification: Liquid → Solid

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

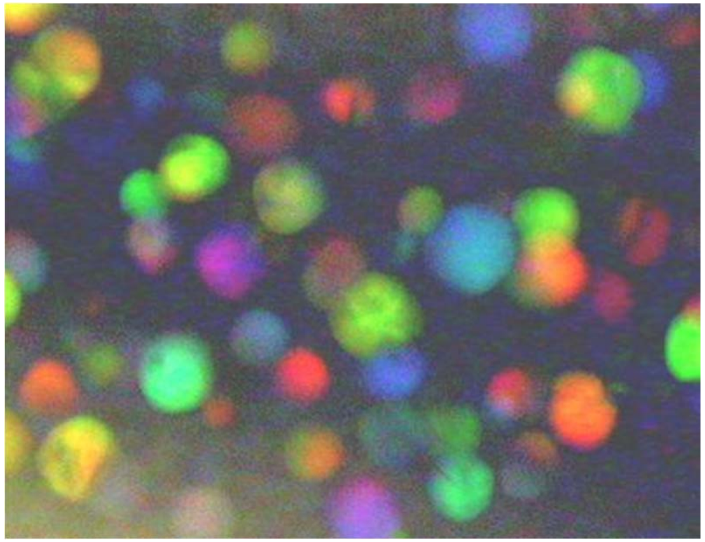
Nucleation in Pure Metals

T_m : $G_L = G_S$

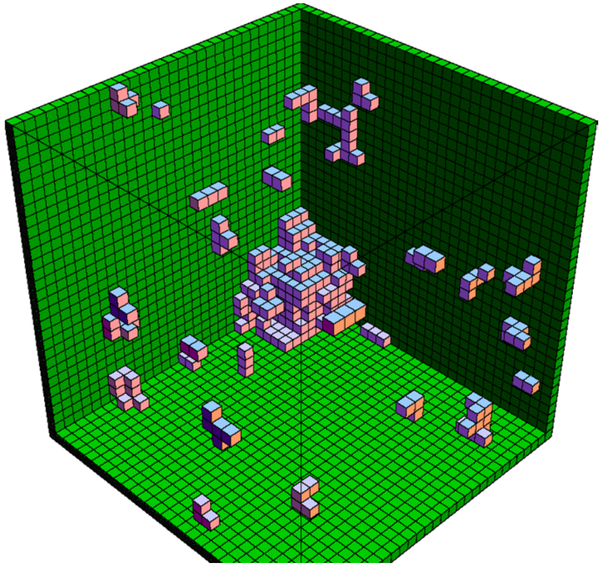
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

- Homogeneous nucleation



- Heterogeneous nucleation



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

* Driving force for melting

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

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

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

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

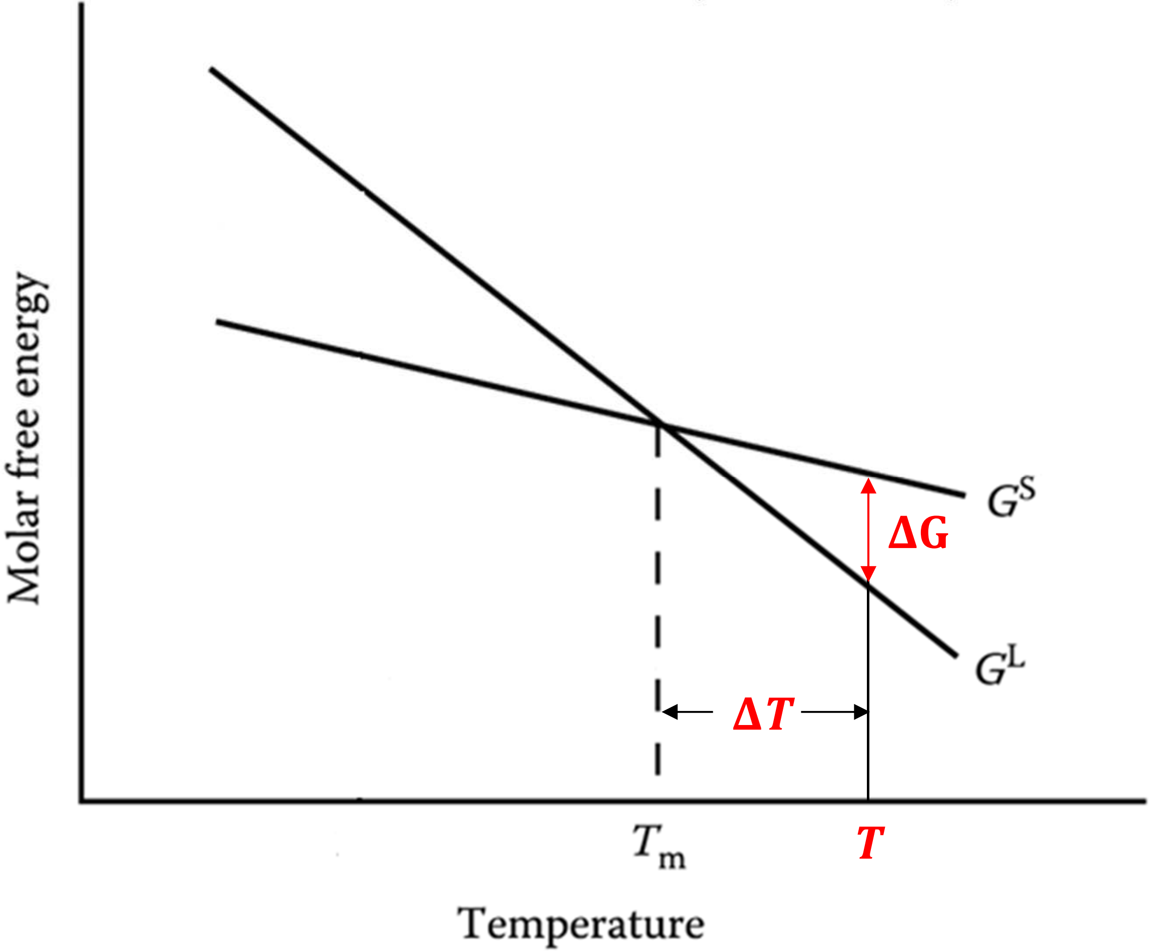
(Latent heat)

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

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

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

(eq. 1.17)



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

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.

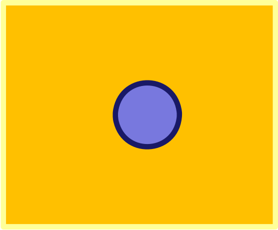
Why?

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

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

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

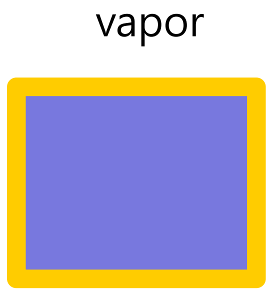
- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid



Contents for today's class

Chapter 1

Thermondynamics and Phase Diagrams

- **Equilibrium** $dG = 0$

Lowest possible value of G

No desire to change ad infinitum

Phase Transformation

$\Delta G = G_2 - G_1 < 0$

- **Single component system**

Gibbs Free Energy as a Function of Temp. and Pressure

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

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

Clausius-Clapeyron Relation

- **Classification of phase transition**

First order transition: CDD/Second order transition: CCD

- **Driving force for solidification** $\Delta G = \dfrac{L\Delta T}{T_m}$