2015 Fall

"Phase Transformation *in* Materials"

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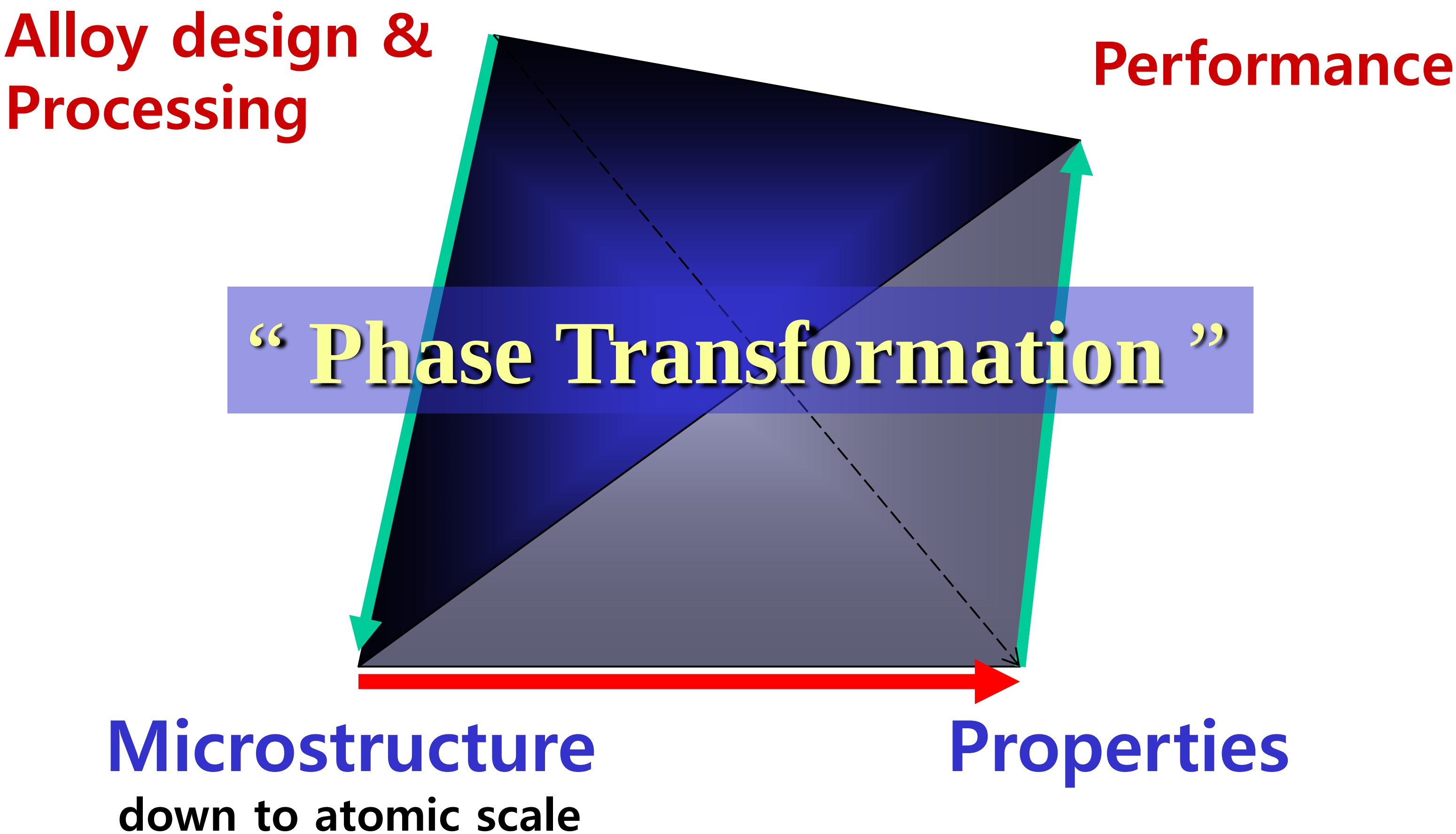
Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

Microstructure-Properties Relationships



“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 $\rightarrow$ Solid
- (Ch5) Diffusional Transformations in Solid: Solid $\rightarrow$ Solid
- (Ch6) Diffusionless Transformations: Solid $\rightarrow$ Solid

Contents for today's class

Chapter 1

Thermondynamics and Phase Diagrams

- Equilibrium

- Single component system

  Gibbs Free Energy
  as a Function of Temp. and Pressure

- Classification of phase transition

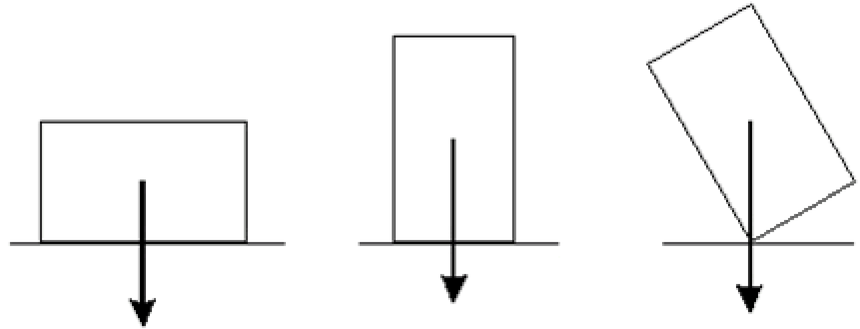
- Driving force for solidification

Q1: “thermodynamic equilibrium”?

Lowest possible value of Gibb’s Free Energy

Equilibrium

Mechanical equilibrium

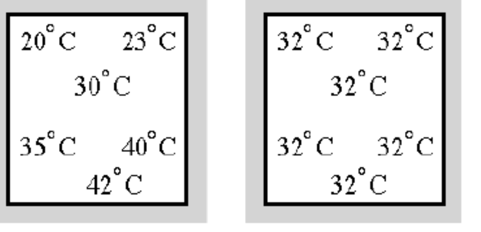


(a) (b) (c)

: 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.

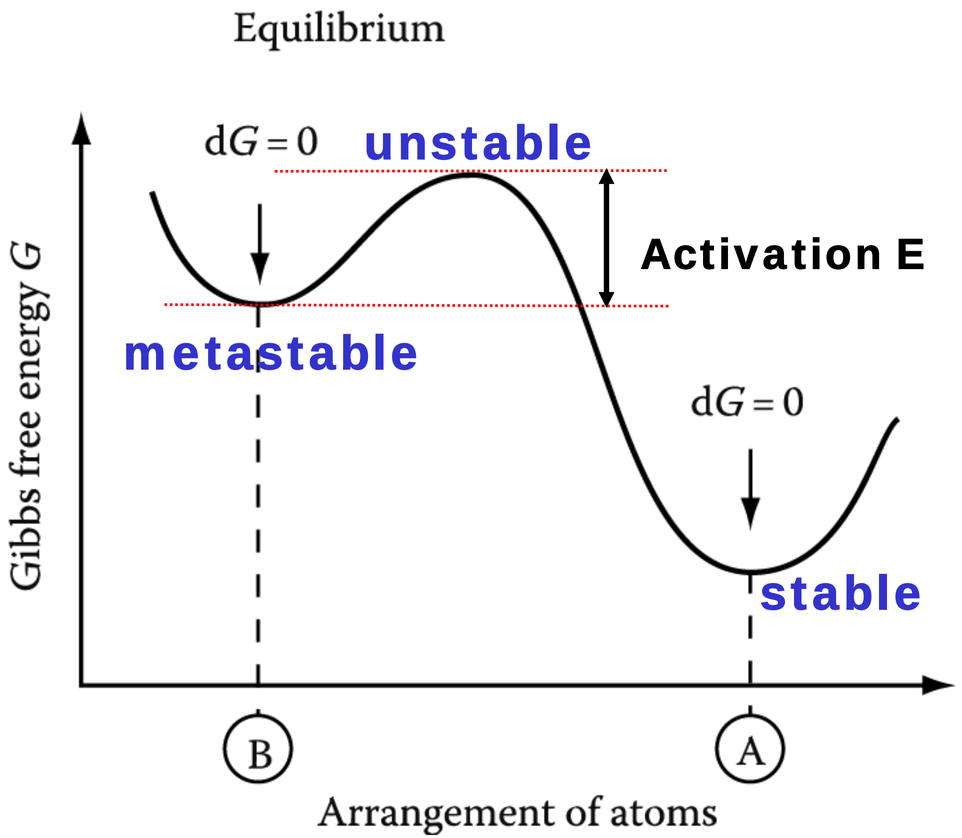
Thermodynamic equilibrium

: the system is under mechanical, thermal and chemical equilibrium

Equilibrium

$$\boxed{dG = 0}$$

Lowest possible value of Gibb's Free Energy
No desire to change ad infinitum



Phase Transformation

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

Relative Stability of a System ➡ <u>Gibbs Free Energy</u>

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

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

<u>Kinetic Energy :</u>

Atomic Vibration (Solid, Liquid)

Translational and Rotational Energy in liquid and gas.

<u>Potential Energy :</u> Interactions or Bonds between the atoms within the system

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

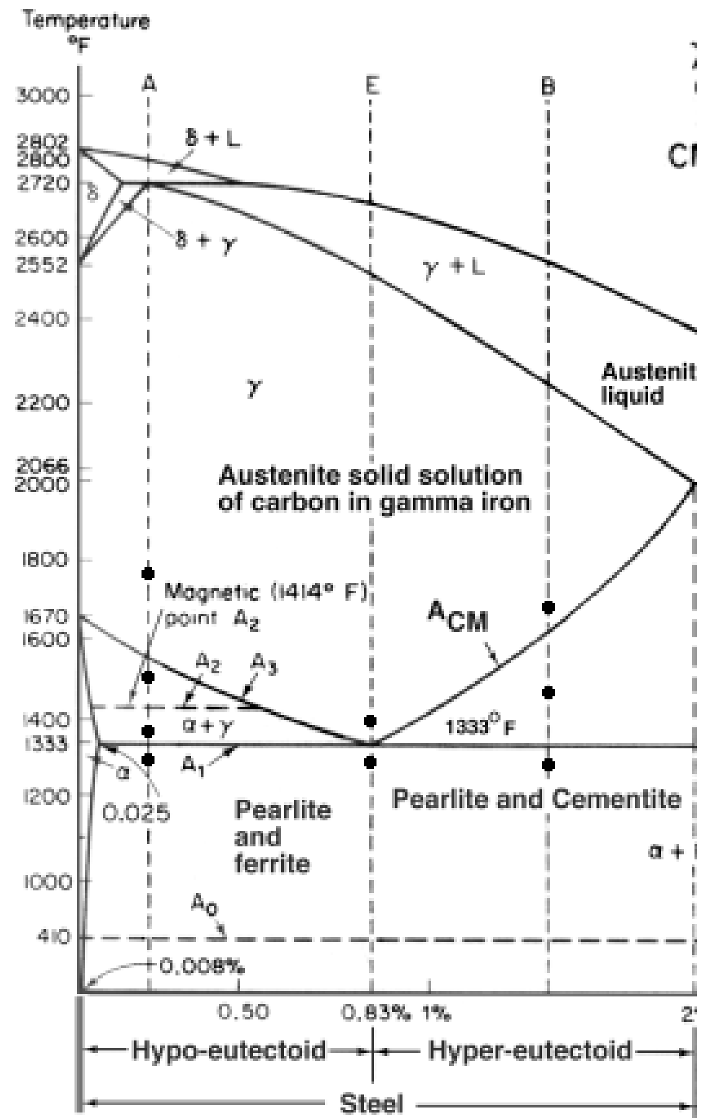
S* : *Entropy, The *Randomness* of the System

Q2: What is single component system?

1.2 Single component system

One element (Al, Fe)

One type of molecule (H_2O)



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,

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

실험적으로 V 를 일정하게 하는 것 (Cv)이 어렵기 때문에 V 보다 P를 일정하게 유지하는 것 (Cp)이 편함 → pressure ex) 1 atm,

When pressure is constant,

$$H \equiv E + PV$$

$$\begin{aligned} dH &= dE + PdV + VdP \\ &= \delta Q - \delta w + PdV + VdP \\ &= \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \end{aligned}$$

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

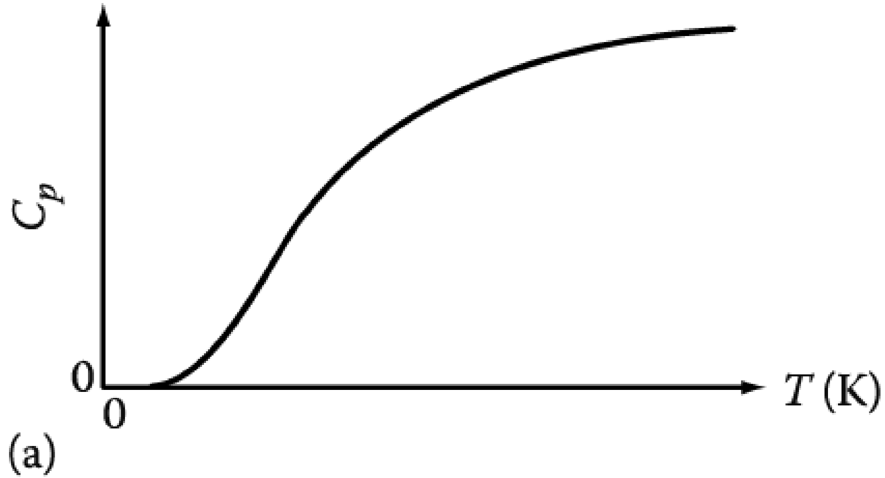
$$\frac{dP}{dT} = 0 \quad \text{when } P \text{ is constant}$$

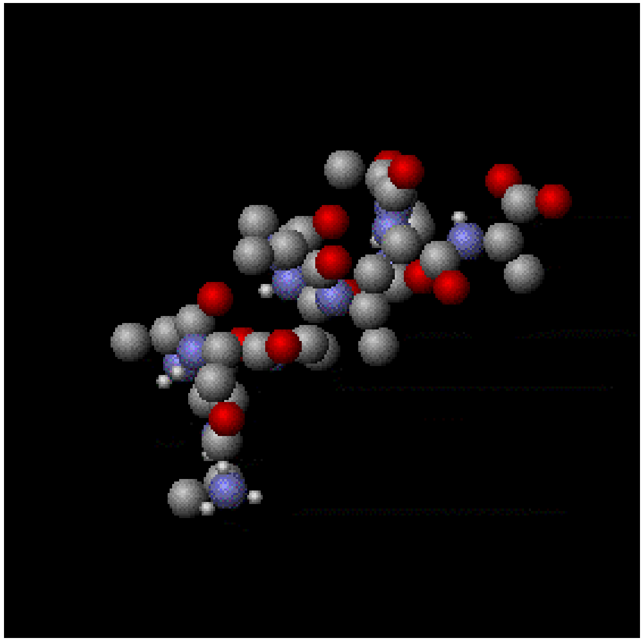
$$\boxed{\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P} \qquad \boxed{H = \int C_p dT}$$

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.

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.

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.

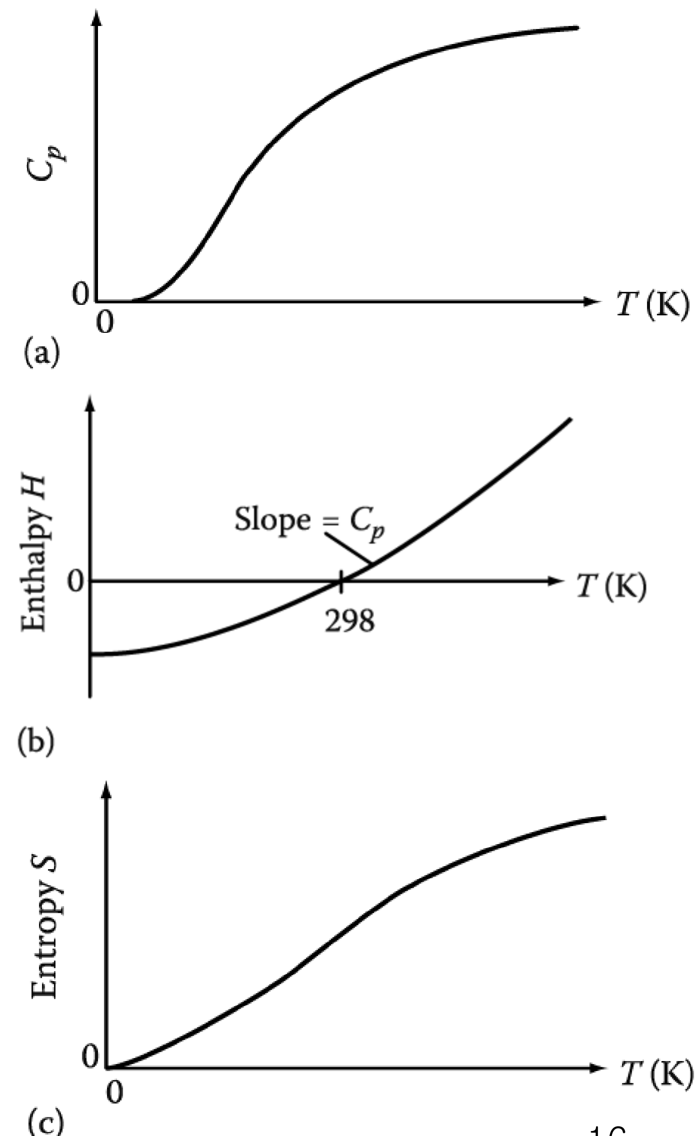
: 상변태 또는 화학반응을 고려할 때 중요한 것은 열역학적 함수 값이 아니고그 변화량이다.

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

S = ?

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

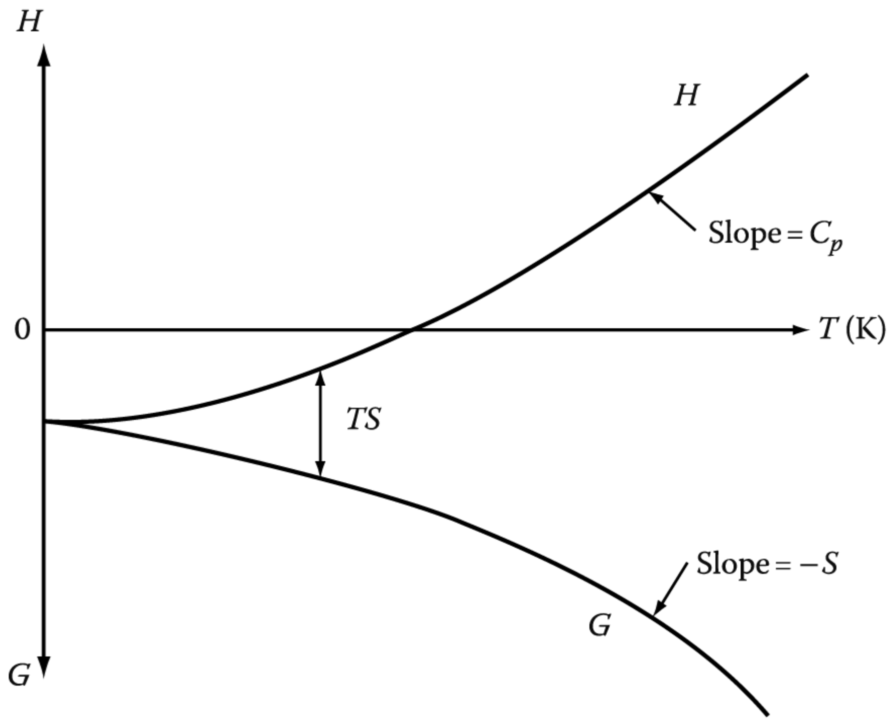
$$\boxed{S = \int_{0}^{T} \frac{C_P}{T} dT}$$



*** 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.



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

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

$$G = H - TS$$

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

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

$$= VdP - SdT$$

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

$$dG = VdP - SdT$$

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

*** 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.

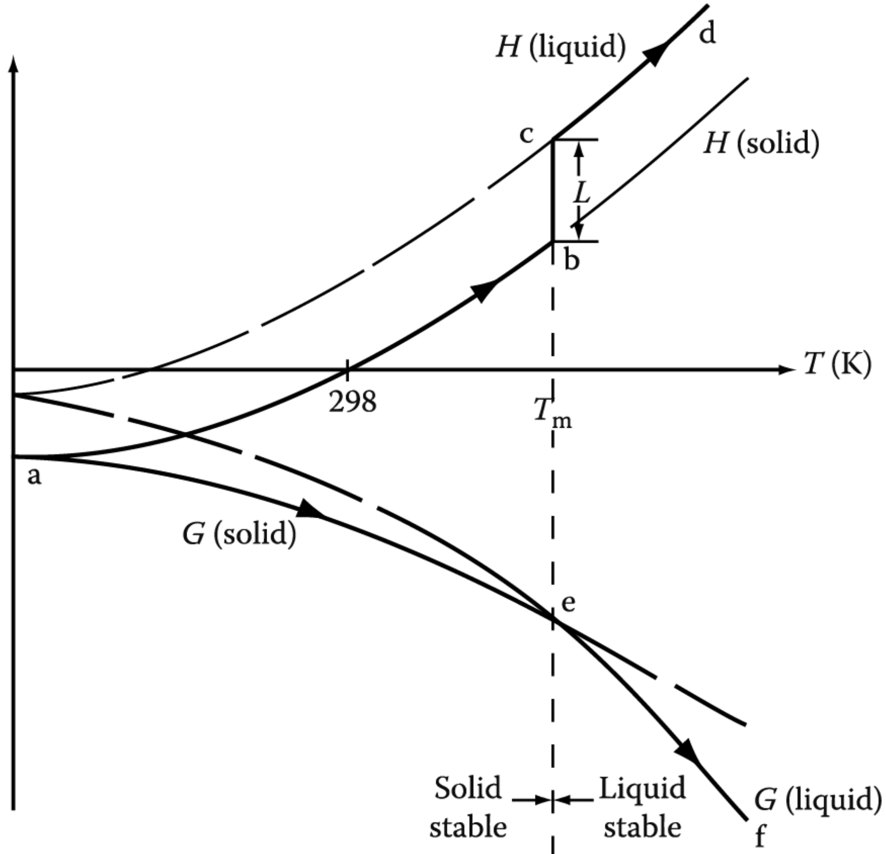


Fig. 1.4 Variation of enthalpy (H) and free energy (G) with temperature for the Solid and liquid phases of a pure metal. L is the latent heat of melting, Tm the Equilibrium melting temperature.

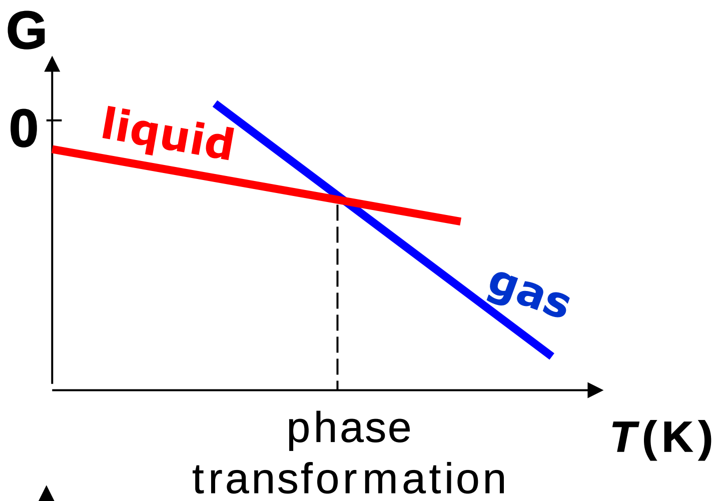
- **Which is larger, G^L or G^S at low T?**
- **$G^L > G^S$ (at low Temp) and $G^S > G^L$ (at high Temp)**

Considering P, T

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

$$dG = VdP - SdT$$

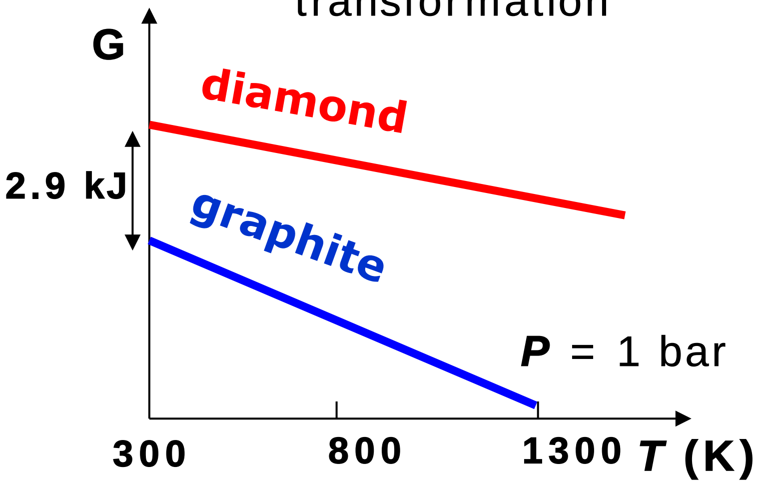
$$G(P,T) = G(P_0, T_0) + \int_{P0}^{P1} V(T_0, P)dP - \int_{T0}^{T1} S(P,T)dT$$



S(water) = 70 J/K

S(vapor) = 189 J/K

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



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

Q7: What is the role of pressure on equilibrium?

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

(applies to all coexistence curves)

1.2.2 Pressure Effects

Different molar volume 을 가진 두 상이 평형을 이룰 때 만일 압력이 변한다면 평형온도 T 또한 압력에 따라 변해야 한다.

If α & β phase are equilibrium,

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

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

At equilibrium,

$$dG^{\alpha} = dG^{\beta}$$

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

여기서 $\Delta S = \dfrac{\Delta H}{T_{eq}}$ 이므로

*** *Clausius-Clapeyron Relation* :**

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

(applies to all coexistence curves)

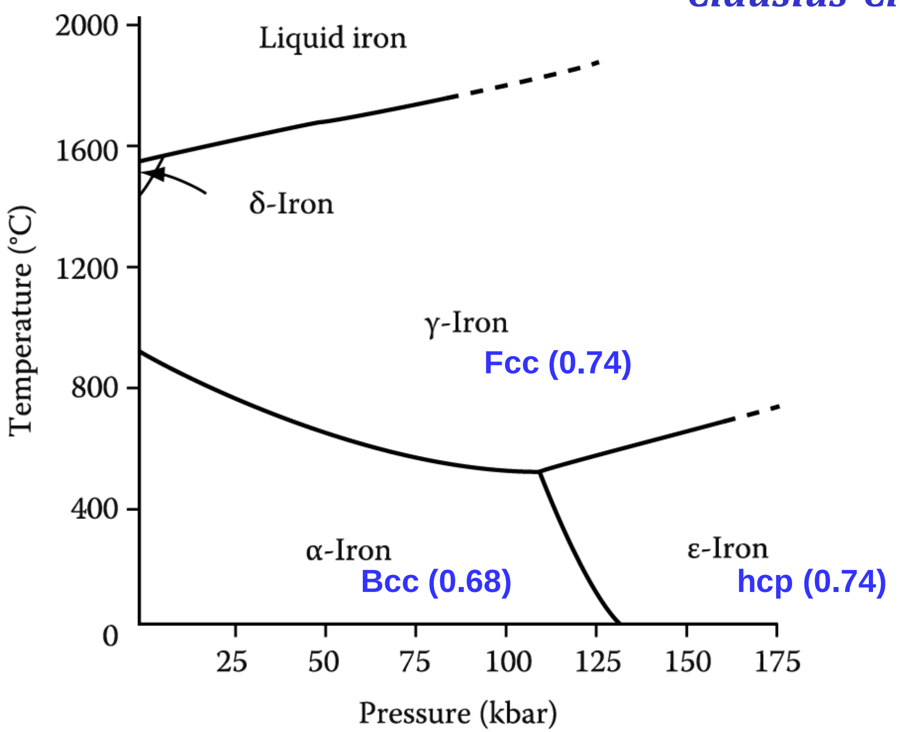


Fig. 1.5 Effect of pressure on the equilibrium phase diagram for pure iron

For, γ →liquid; ΔV (+), ΔH(+)

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

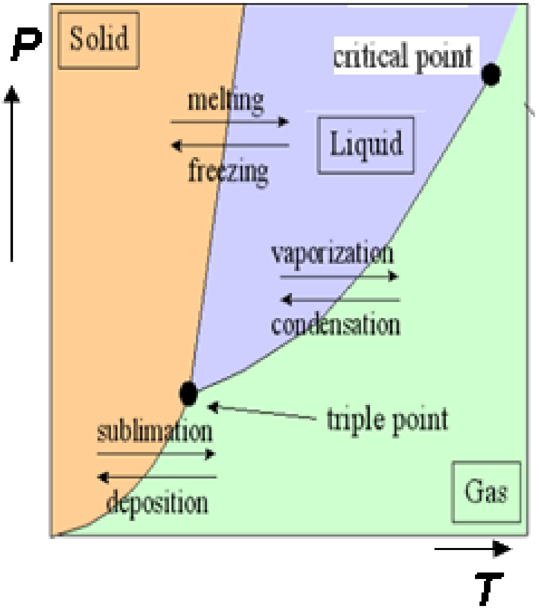
For, α→γ ; ΔV (-), ΔH(+)

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

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

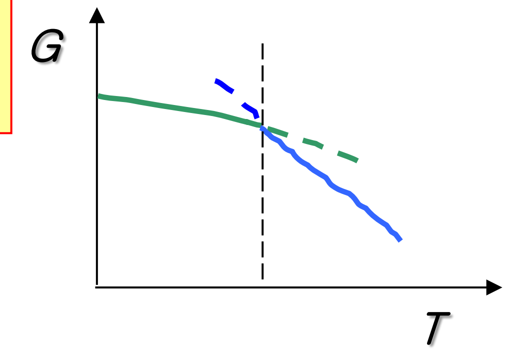
Q8: How to classify phase transition?

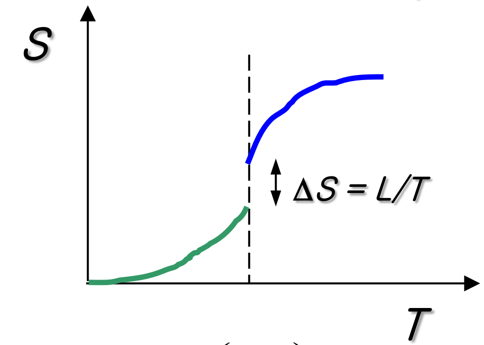
“First order transition” vs “Second order transition”



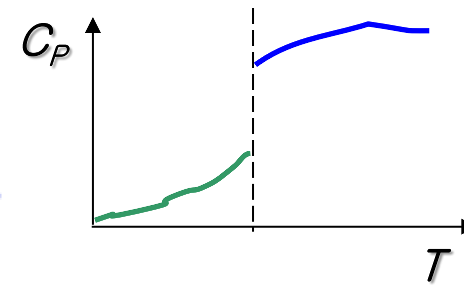
The First-Order Transition

Latent heat
Energy barrier
Discontinuous entropy, heat capacity





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



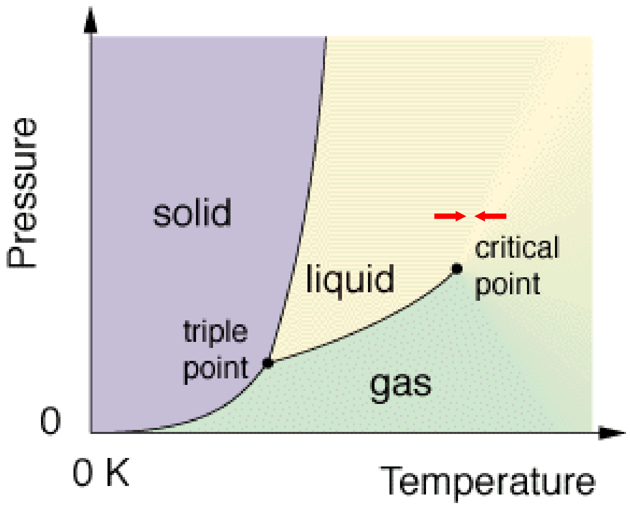
- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

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

  - 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

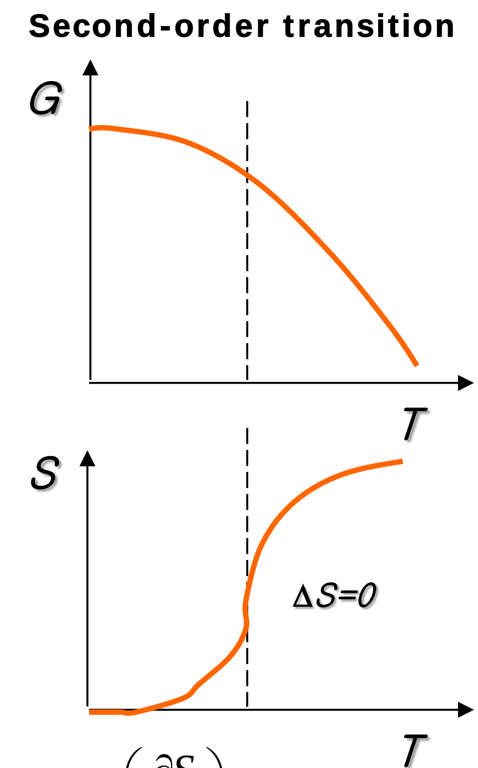
- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

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

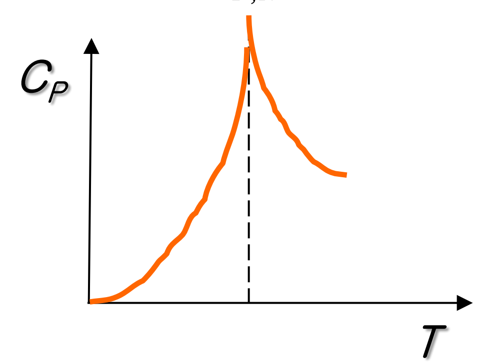
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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



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



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)

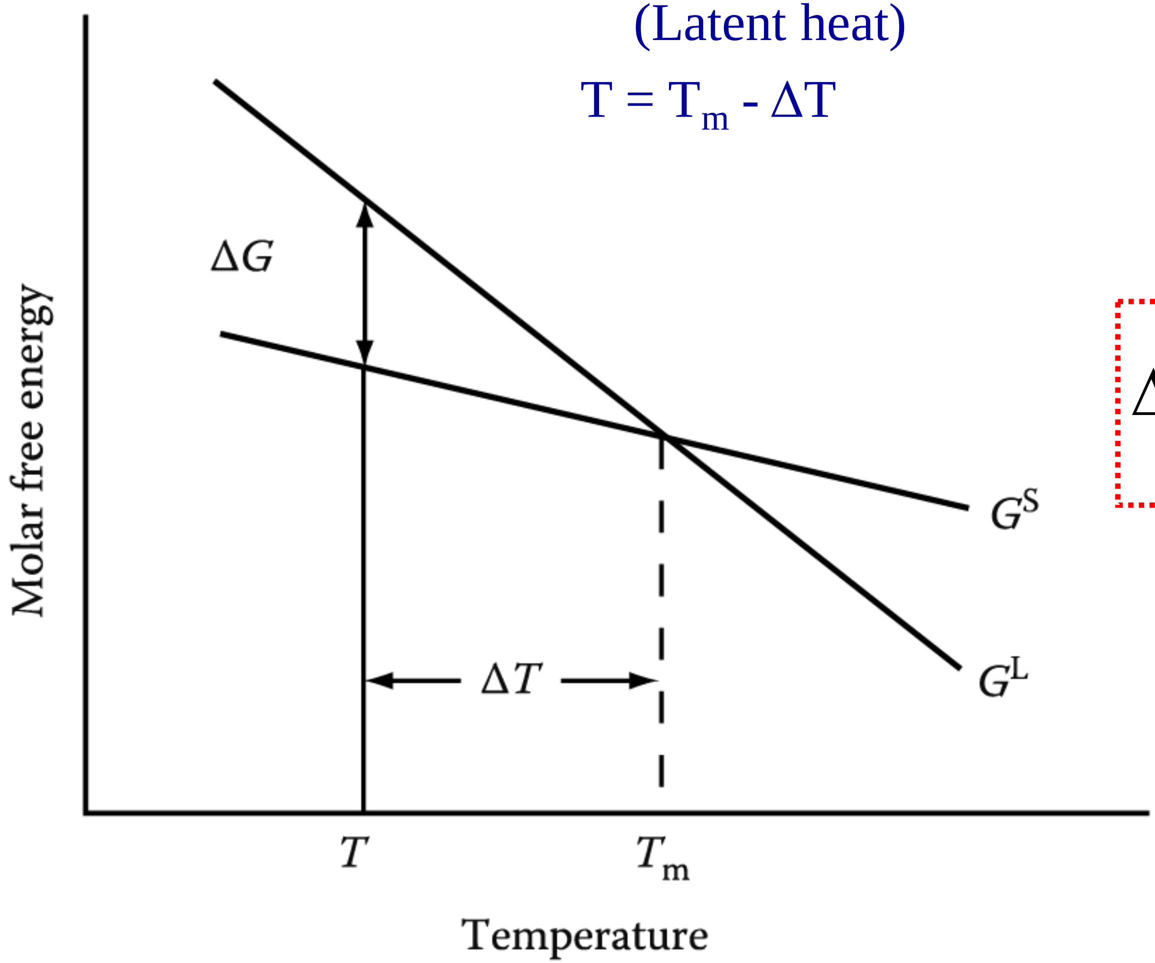
$T = T_m - \Delta T$

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

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

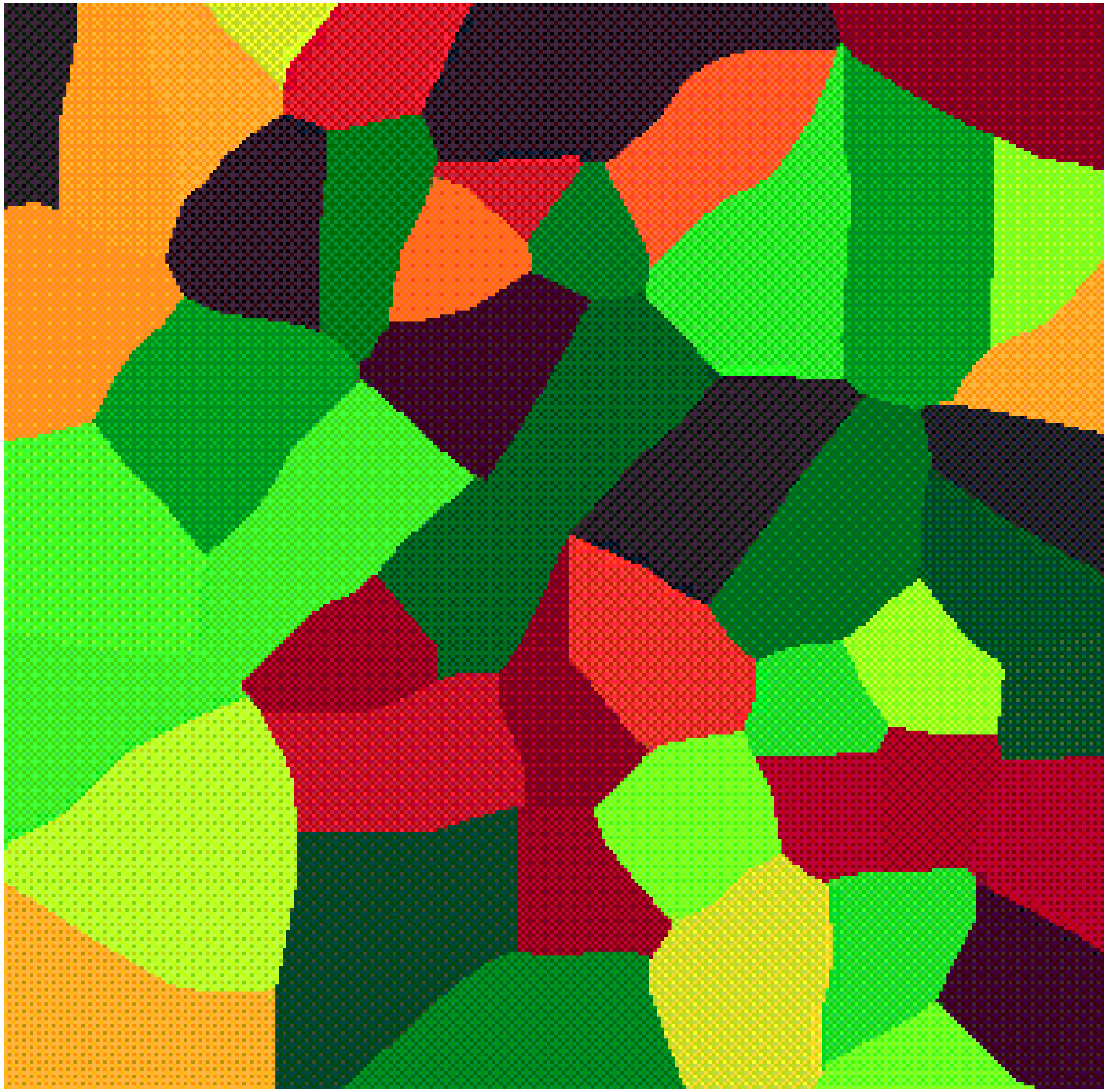
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

(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) $G_2 = G_1 + \Delta G$

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

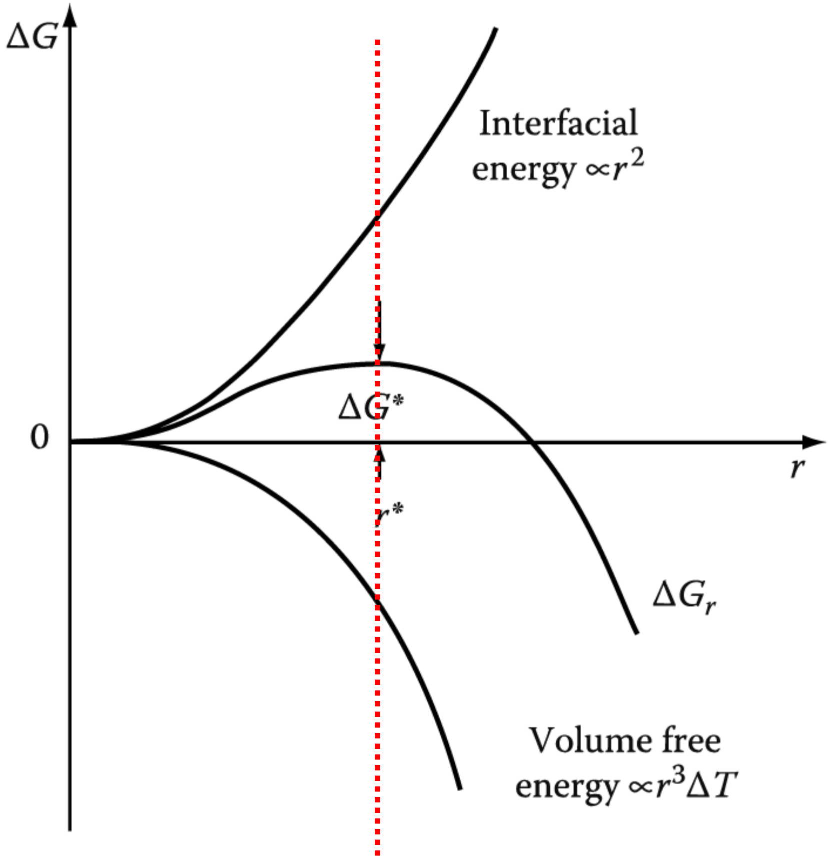
$G_V^S,\ G_V^L$ **: free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

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)**

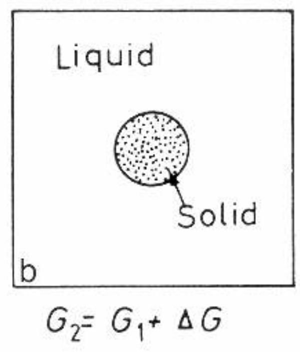
r > r* : stable **(lower free E by increase size)**

r* **: critical nucleus size**

r* ⇨ **dG=0**

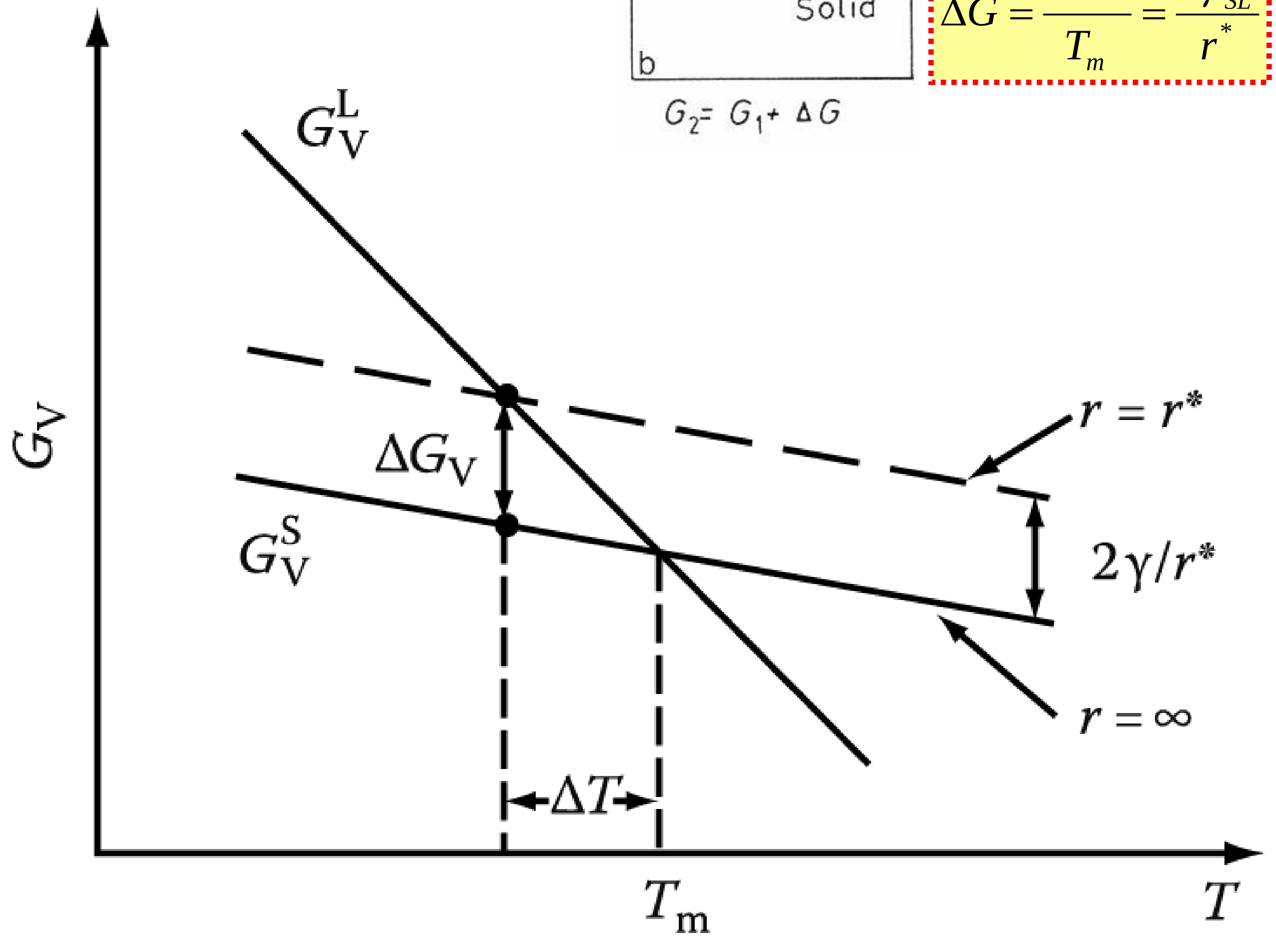
1.2.3 Driving force for solidification

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

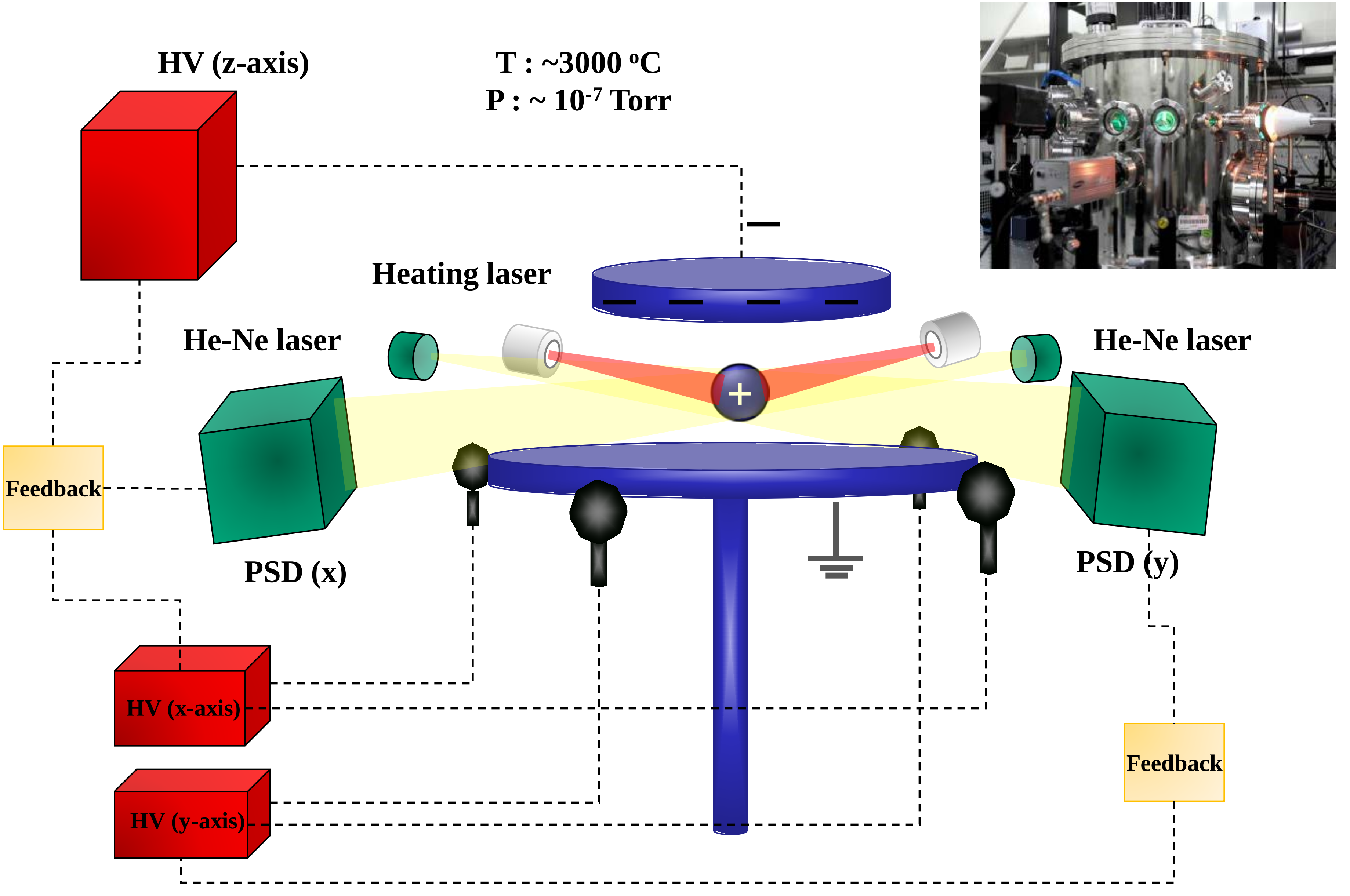


$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

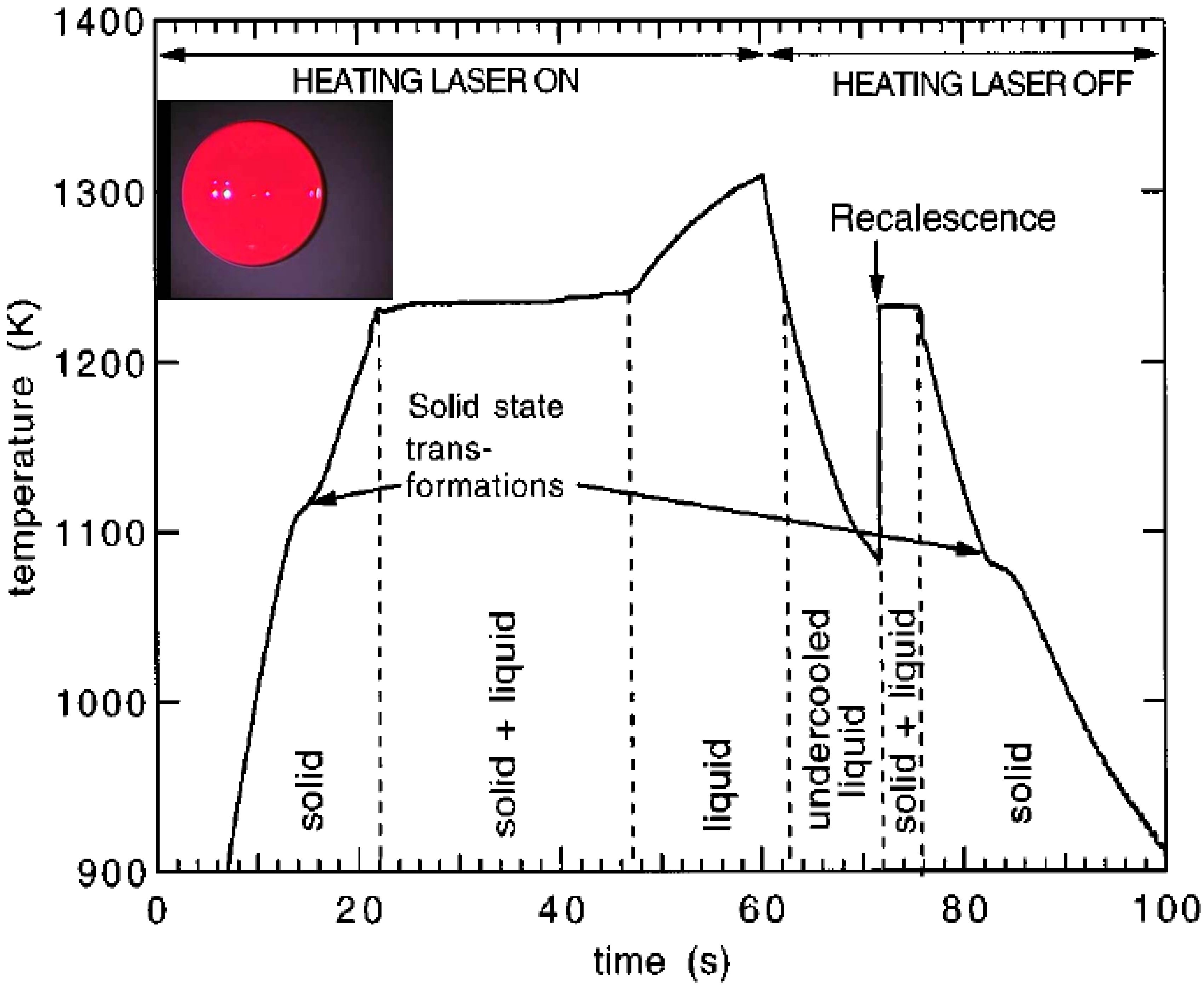
$$\Delta G = \frac{L\Delta T}{T_m} = \frac{2\gamma_{SL}}{r^*}$$



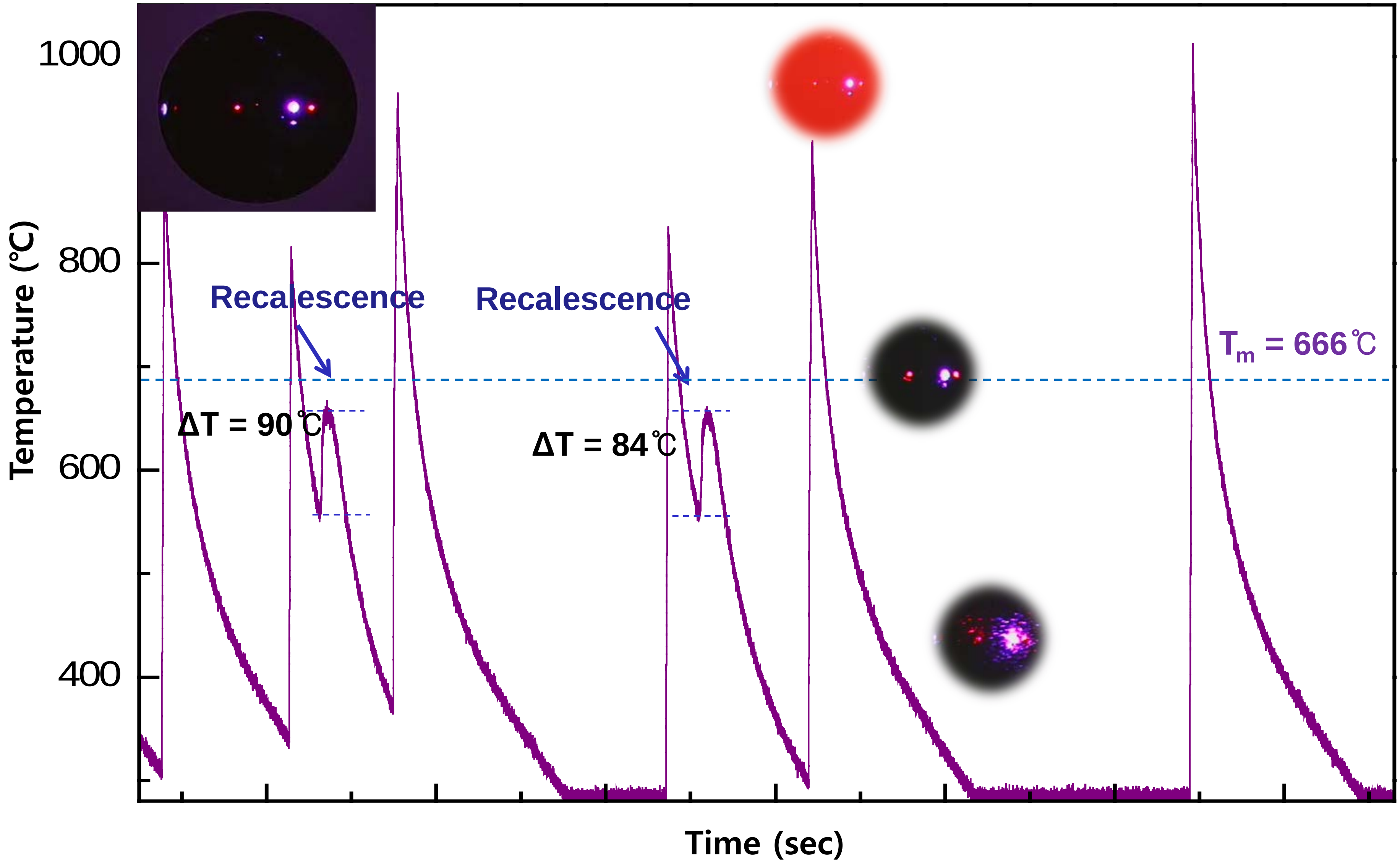
Electrostatic levitation in KRISS



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

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



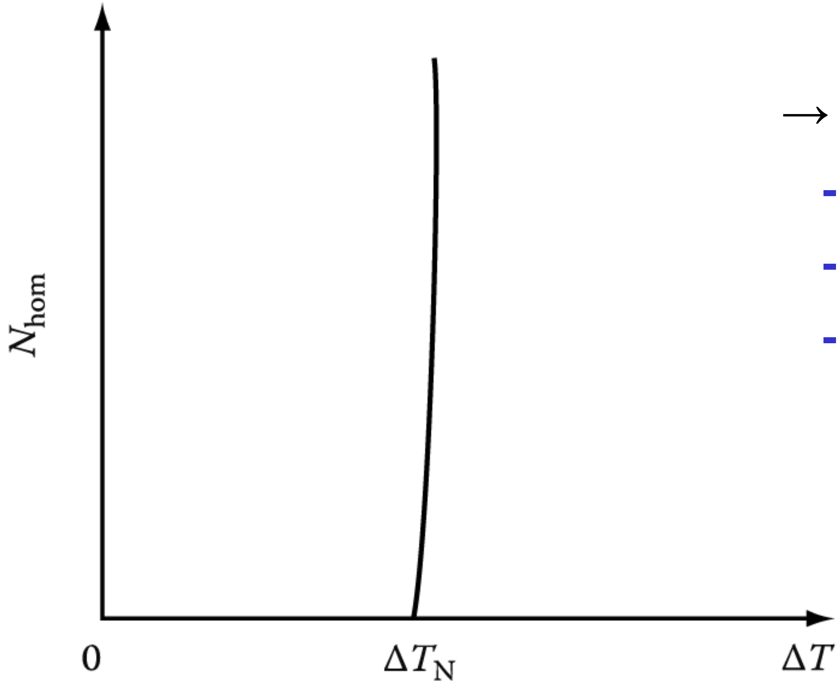
* The homogeneous nucleation rate - kinetics

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

: insensitive to Temp.

How do we define nucleation temperature, ΔT_N ?

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



→ **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

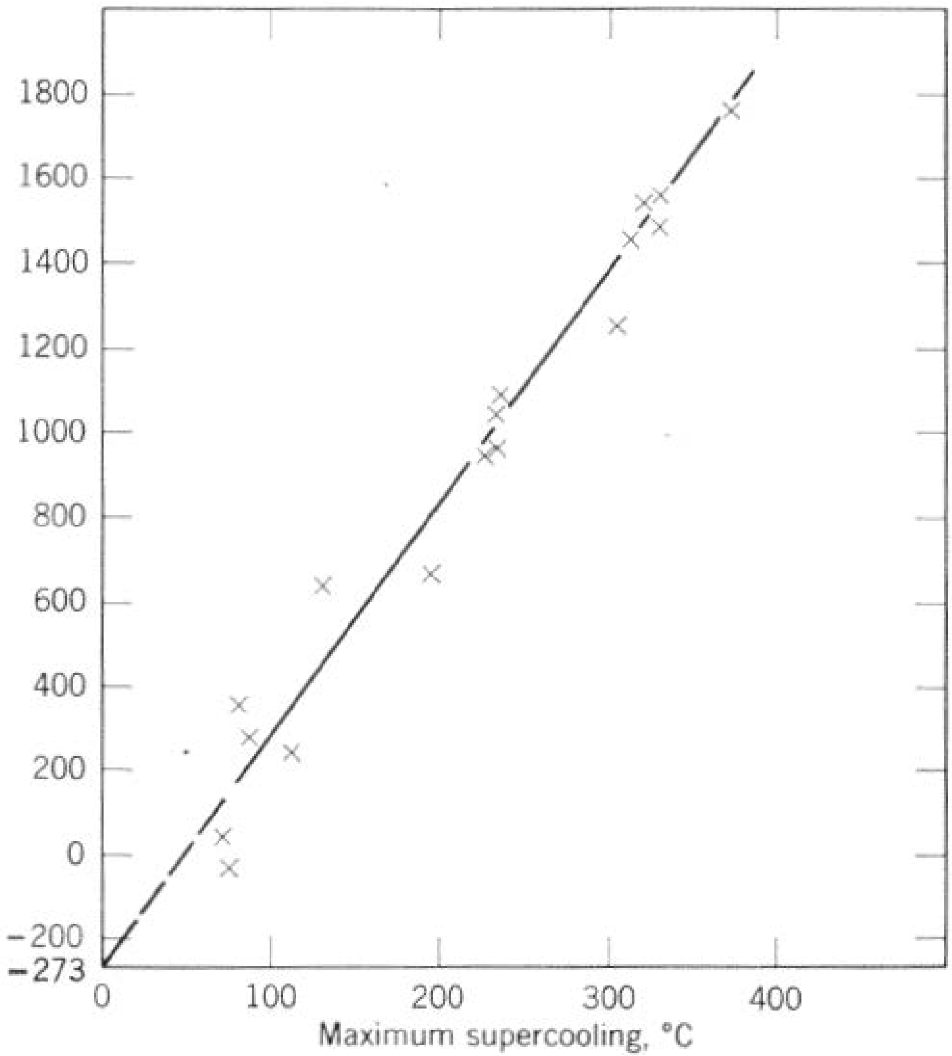


Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

Solidification: Liquid → Solid

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

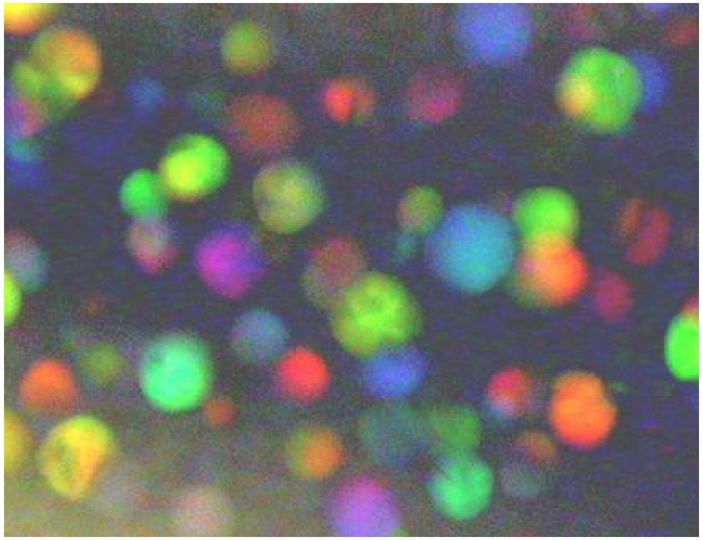
Nucleation in Pure Metals

T_m : $G_L = G_S$

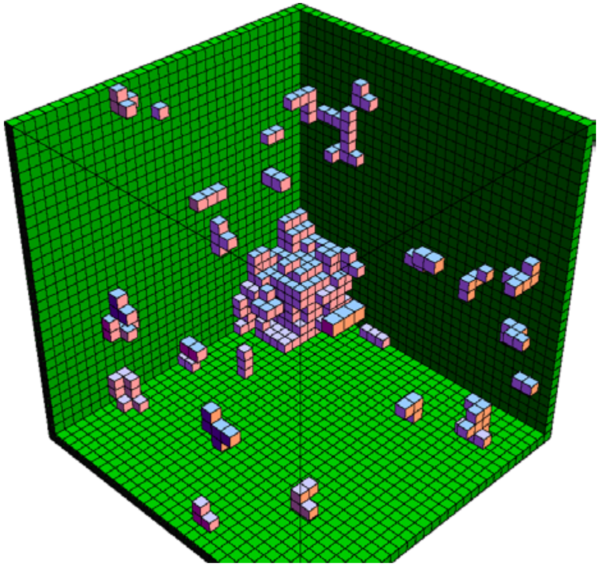
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

- Homogeneous nucleation



- Heterogeneous nucleation



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

* Driving force for melting

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

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

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

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

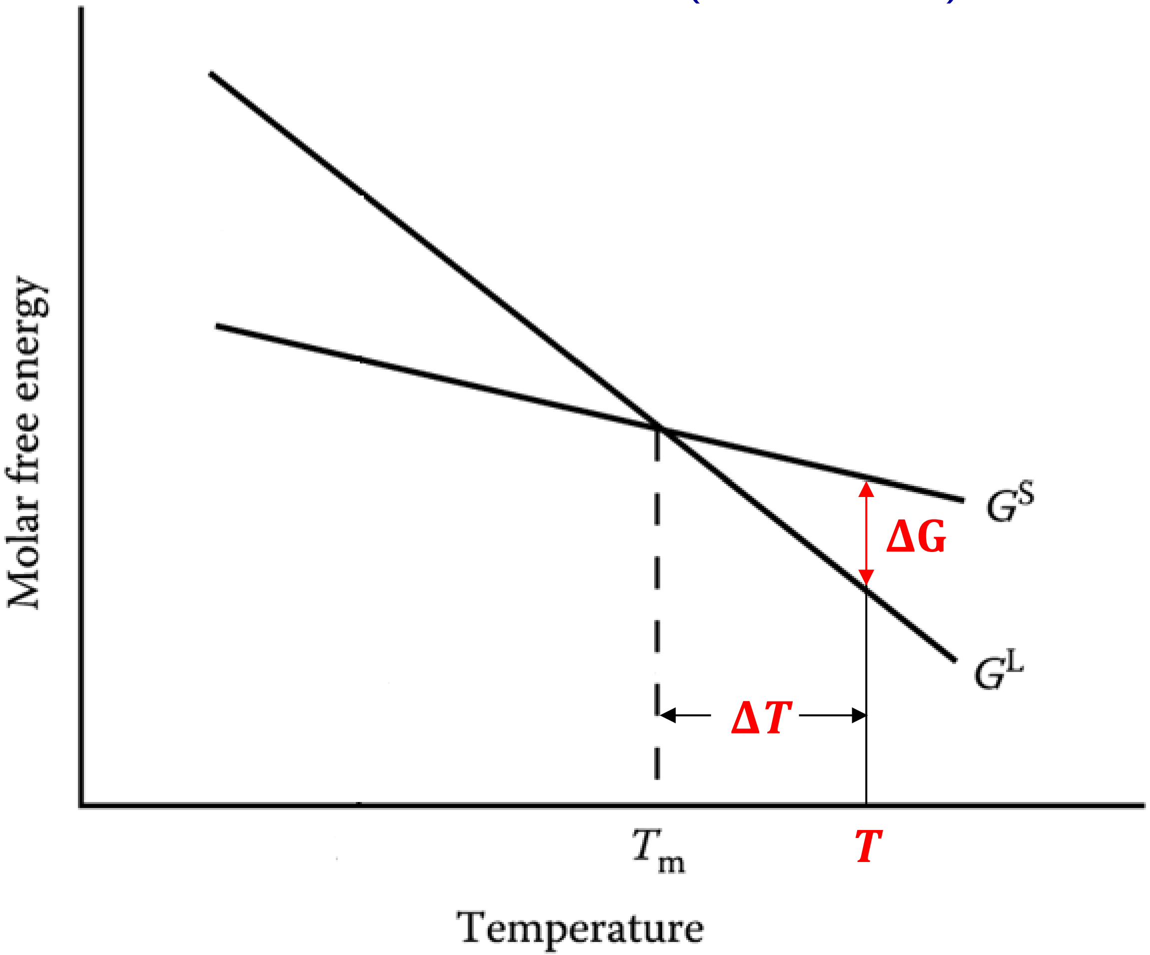
(Latent heat)

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

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

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

(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.

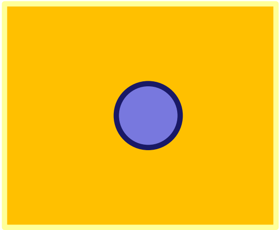
Why?

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

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

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid T_m Undercooled Liquid Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

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

vapor

Melting: Liquid ← Solid

Contents for today's class

Chapter 1

Thermodynamics and Phase Diagrams

- Equilibrium

$$dG = 0$$

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

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