2017 Spring

"Calculation and Applications Phase Equilibria"

Principles *of* Solidification

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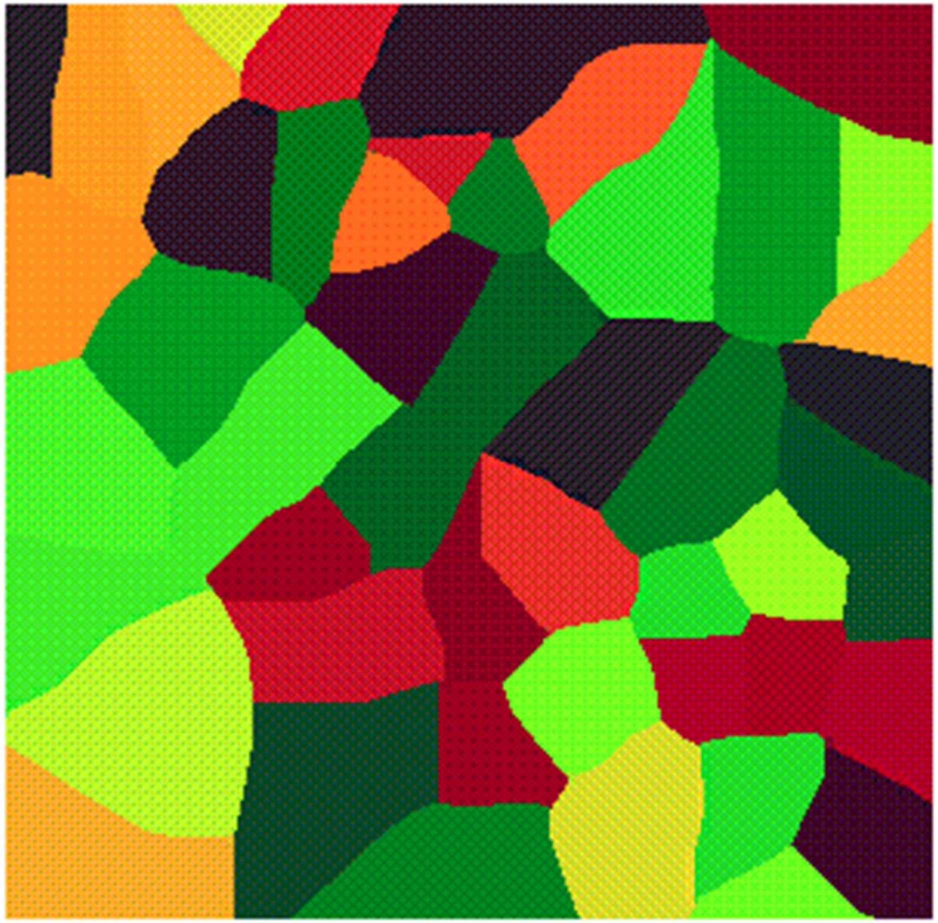
Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid ⟶ Solid



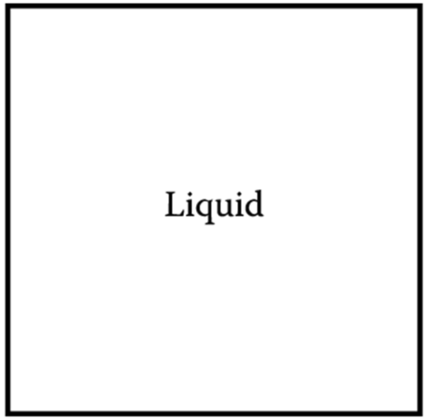
4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

Thermodynamic Transitions: Δ G = 0

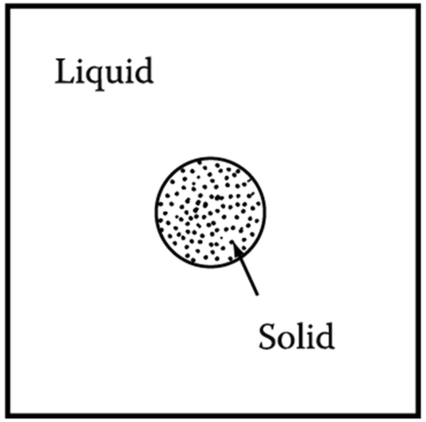
1) G_L versus G_S

2) Interfacial free energy

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

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

1) Homogeneous Nucleation

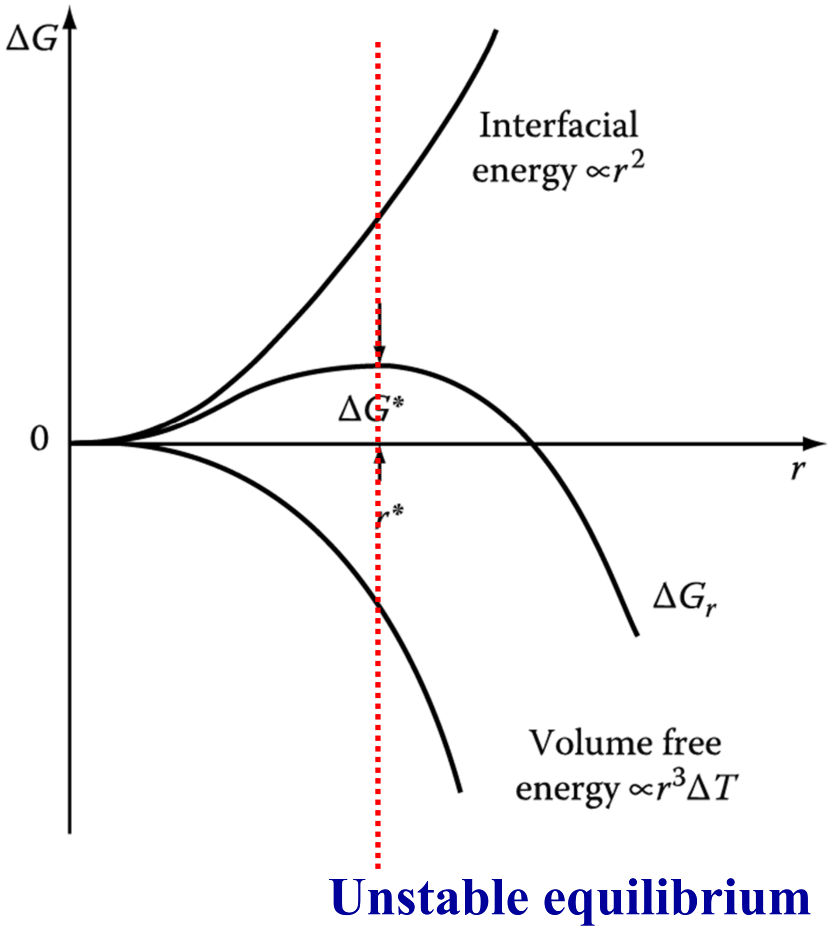


Fig. 4.2 The free energy change associated with homogeneous nucleation of a sphere of radius r.

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**

1.8 Themodynamic Criteria for Equilibrium (at T_m)

2) 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)

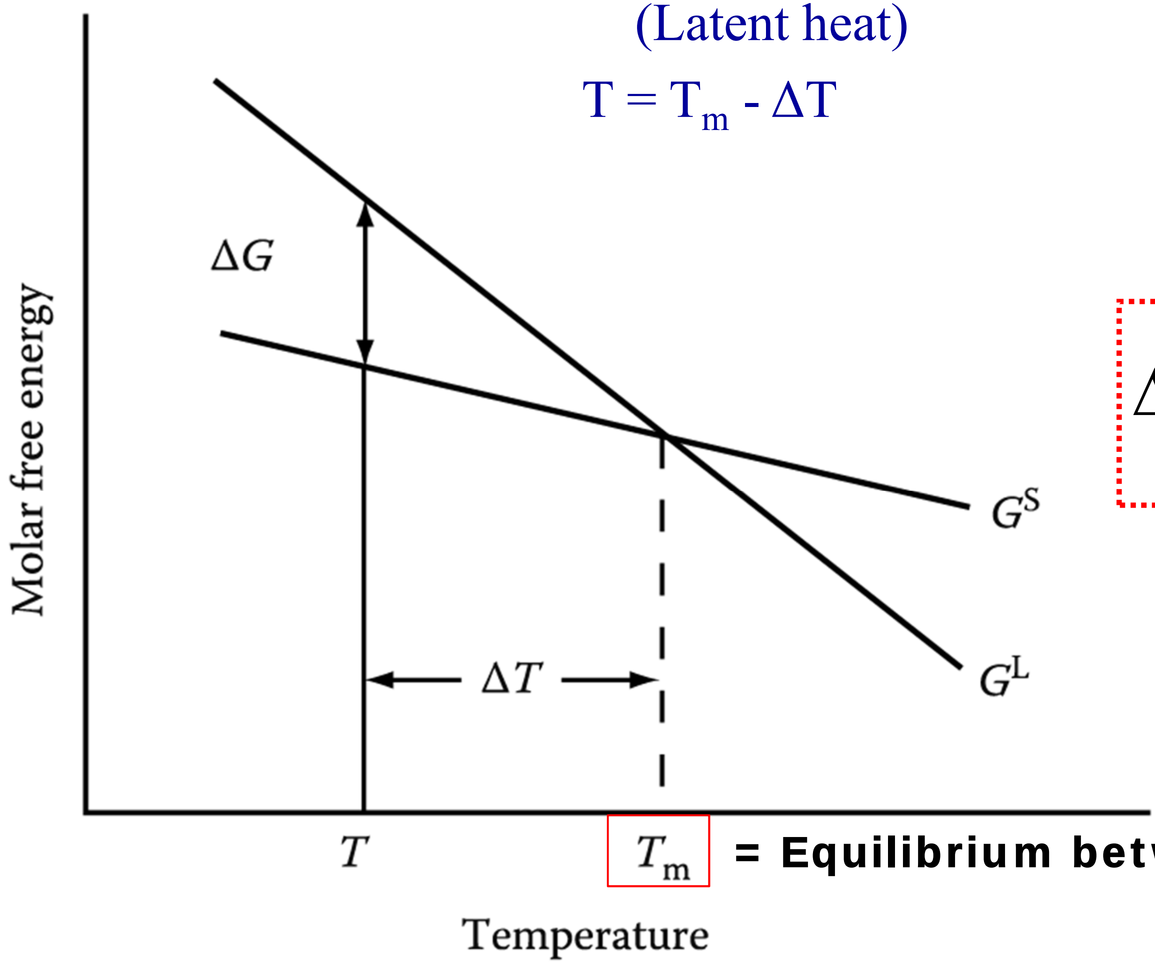
$T = T_m - \Delta T$

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

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

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

(eq. 1.17)



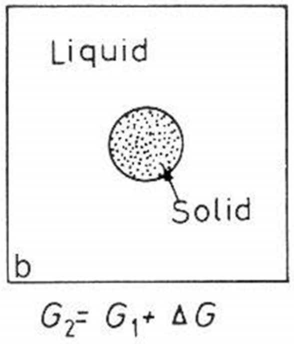
$$\Delta G = \frac{L\Delta T}{T_m}$$

T_m **= Equilibrium between Solid and Liquid**

2) Driving force for solidification

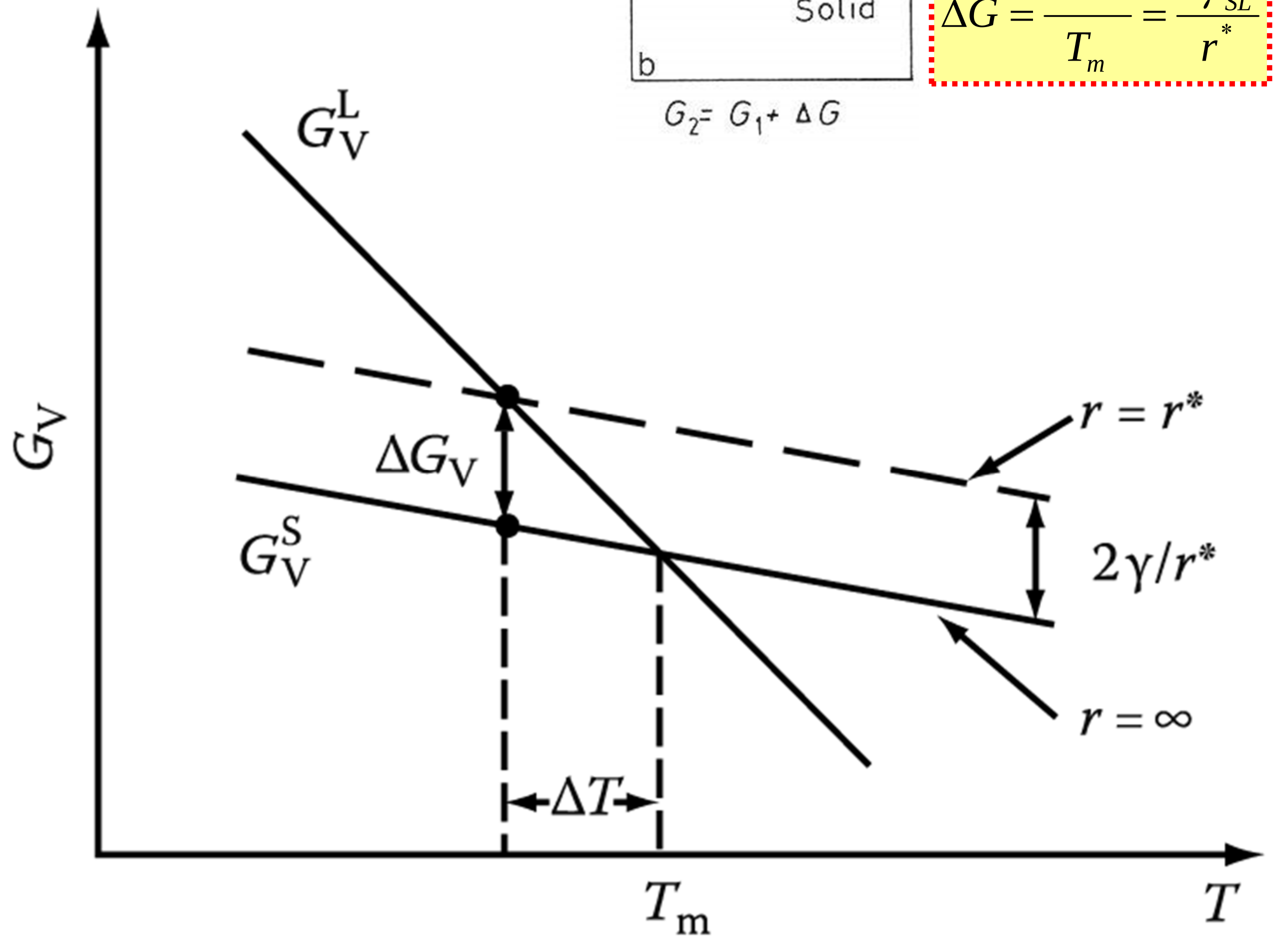
solidification

Liquid → **Solid**



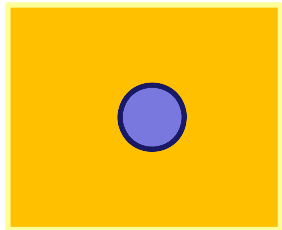
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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



Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

3) 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.

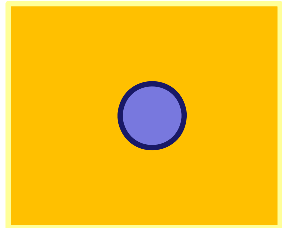
Why?

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

vapor

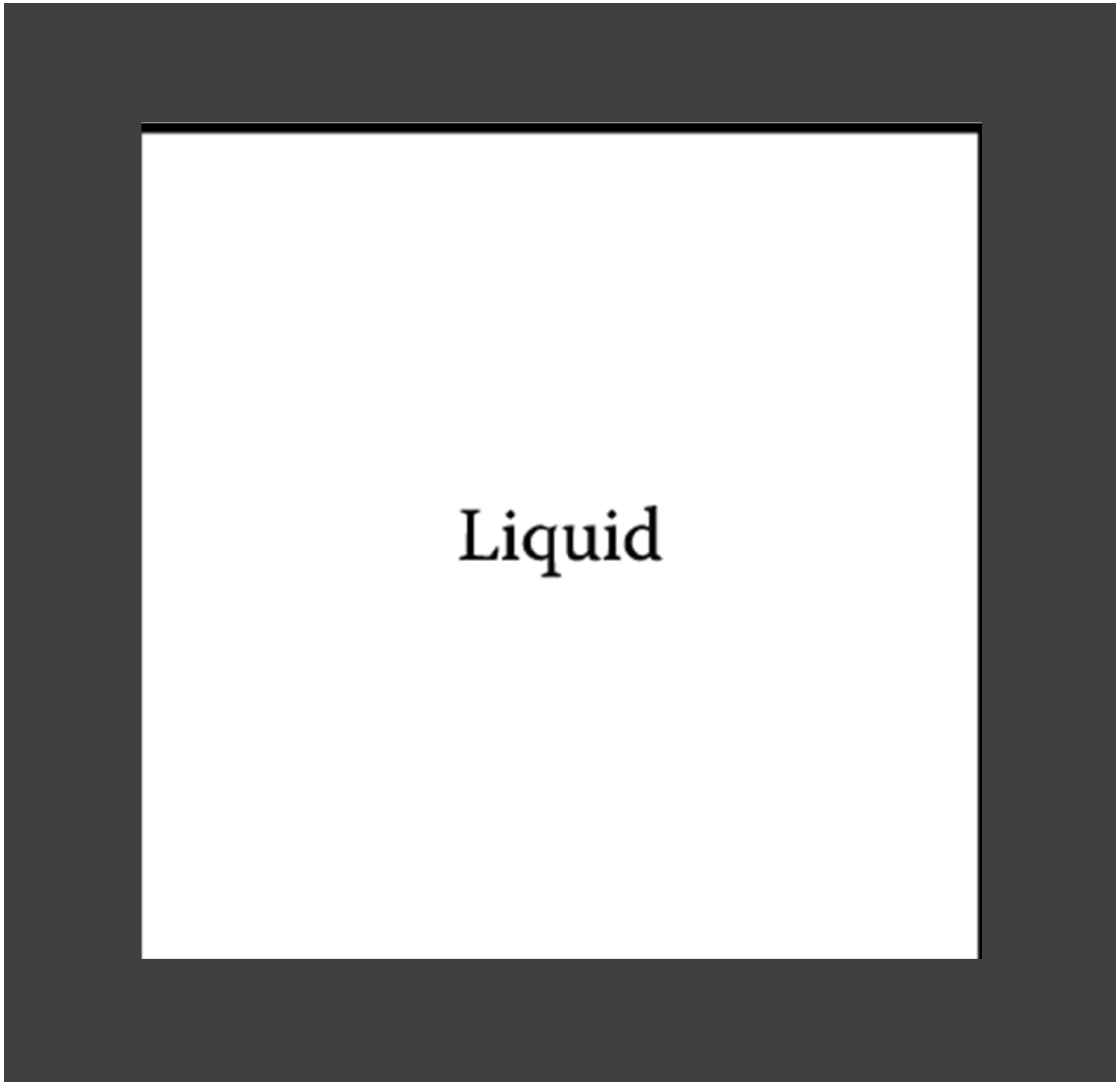
- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid

Incentive Homework 1:
Example of Superheating (PPT 3 pages)

2) Change of interfacial free energy → Heterogeneous Nucleation



Solidification: Liquid → Solid

- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / S(θ) wetting angle

- **Nucleation in Pure Metals**
- **Homogeneous Nucleation**

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

r* & ΔG* ↓ as ΔT ↑

$$N_{hom} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}$$

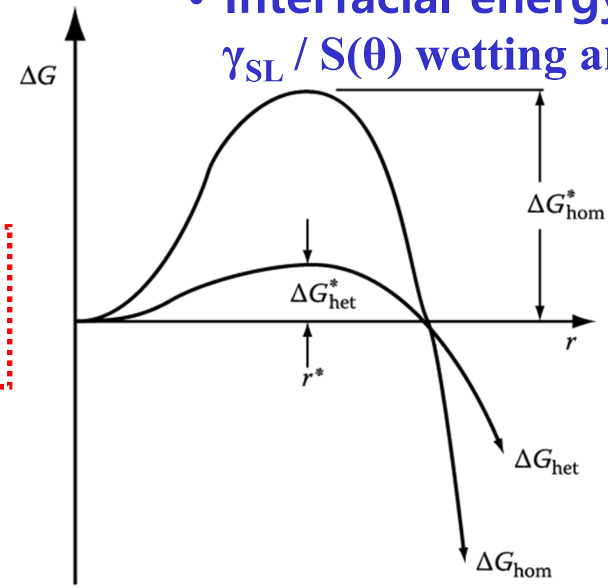
- **Heterogeneous Nucleation**

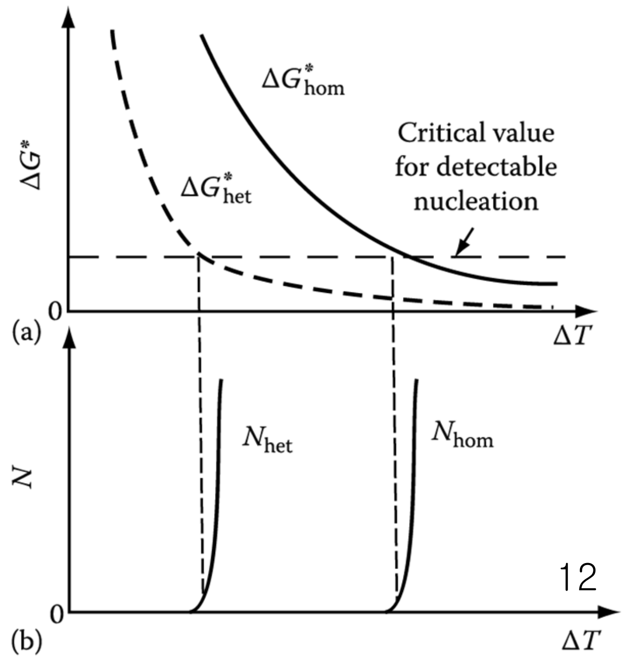
$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*$$

$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

- **Nucleation of melting**

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

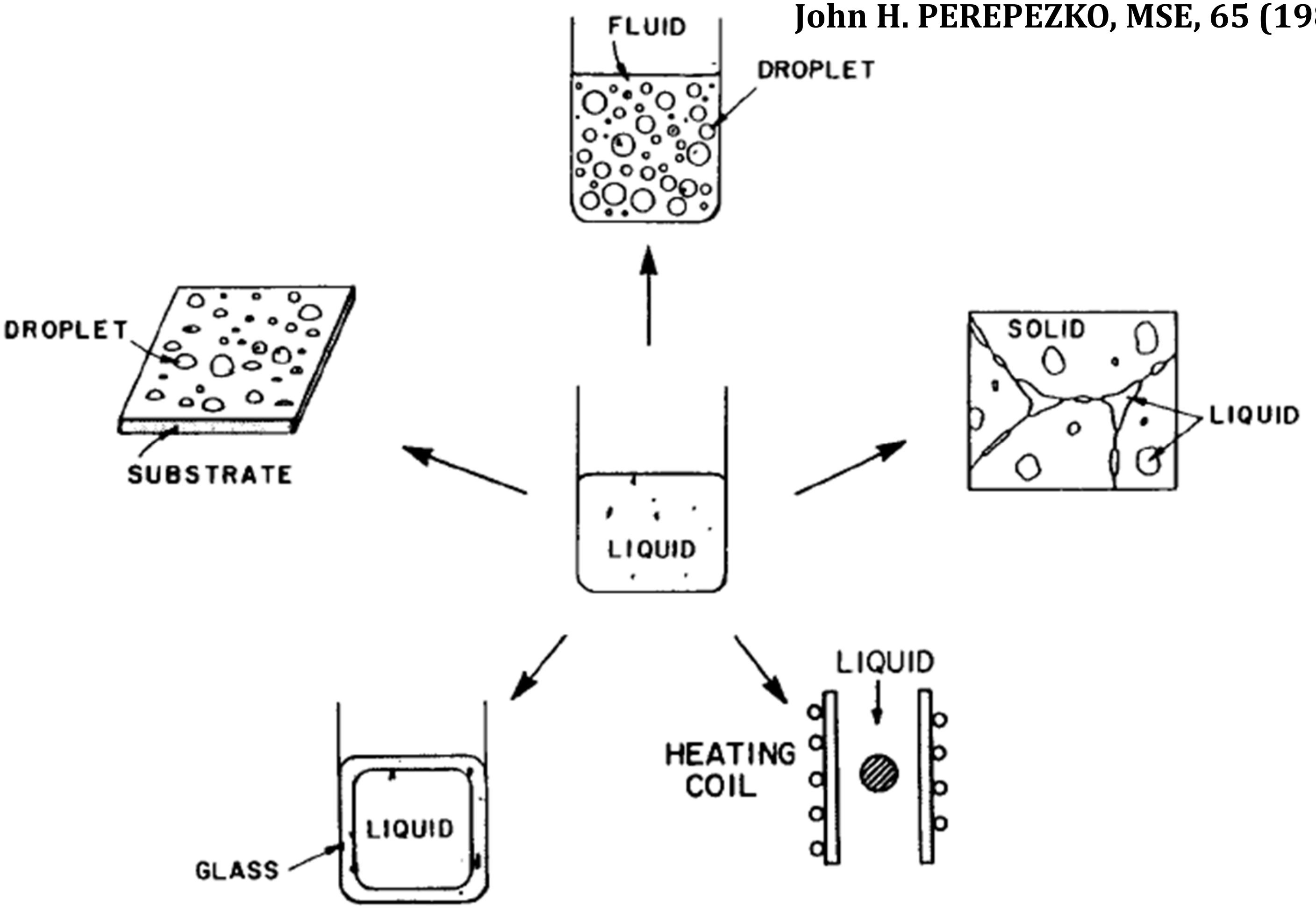




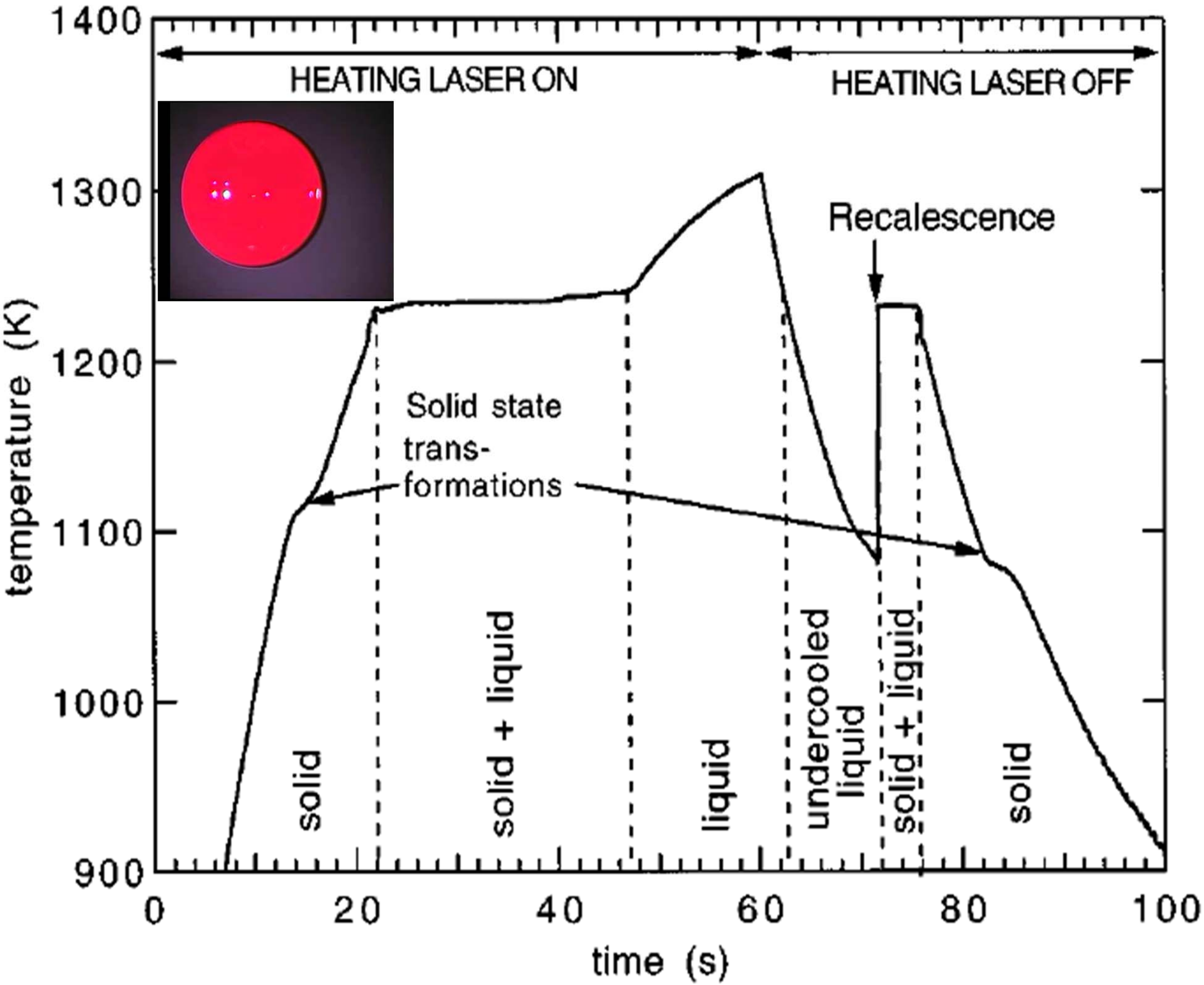
What is the meaning for the ΔT (undercooling) during solidification?

How to obtain large undercooling during cooling?

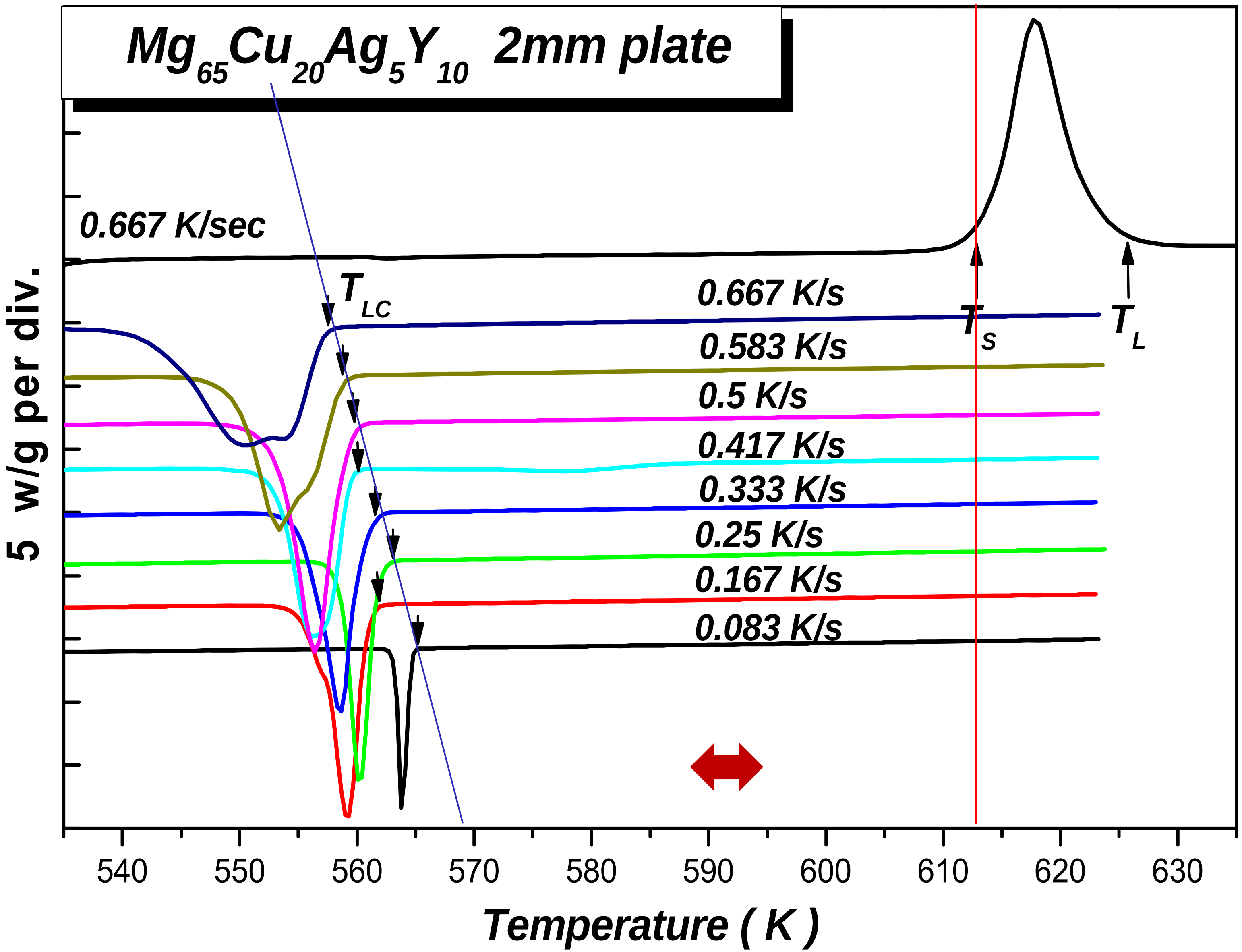
John H. PEREPEZKO, MSE, 65 (1984) 125-135



By dispersing a liquid into a large number of small droplets within a suitable medium, the catalytic effects of active nucleants may be restricted to a small fraction of the droplets so that many droplets will exhibit extensive undercooling.



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



$Mg_{65}Cu_{20}Ag_5Y_{10}$ 2mm plate
0.667 K/sec
T_{LC}
0.667 K/s
0.583 K/s
0.5 K/s
0.417 K/s
0.333 K/s
0.25 K/s
0.167 K/s
0.083 K/s
T_S
T_L
5 w/g per div.
540
550
560
570
580
590
600
610
620
630
Temperature (K)

TTT versus CCT

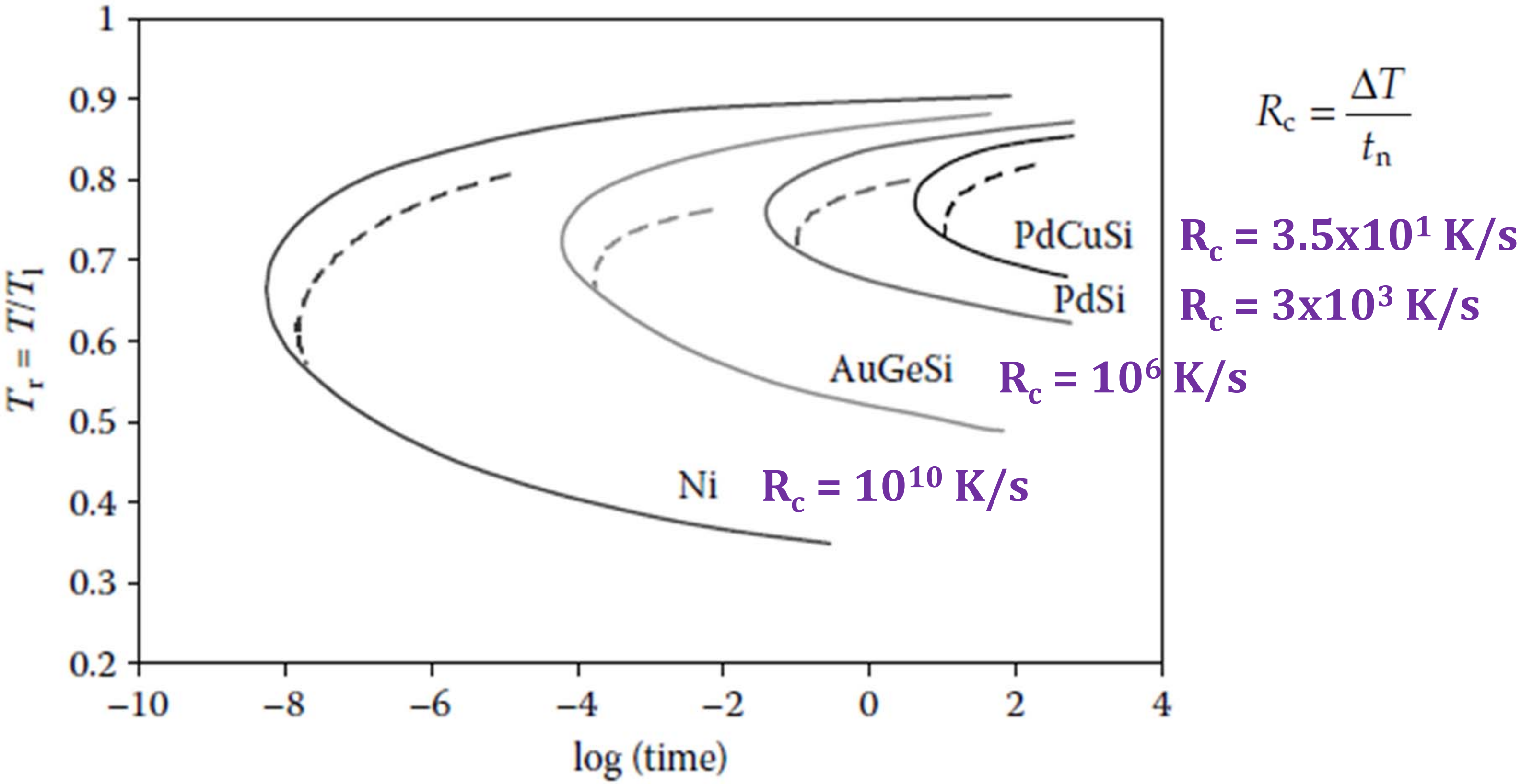
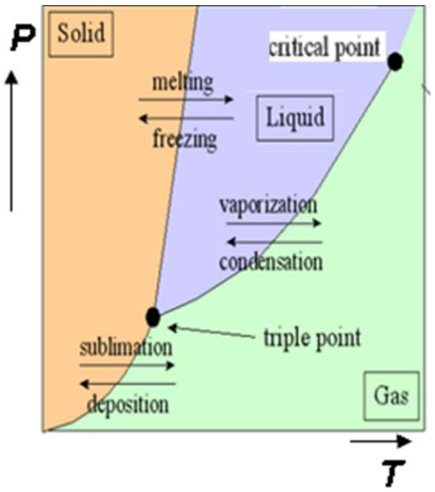


FIGURE
Time–temperature–transformation (*T–T–T*) curves (solid lines) and the corresponding continuous cooling transformation curves (dashed lines) for the formation of a small volume fraction for pure metal Ni, and $Au_{78}Ge_{14}Si_8$, $Pd_{82}Si_{18}$, and $Pd_{78}Cu_6Si_{16}$ alloys.

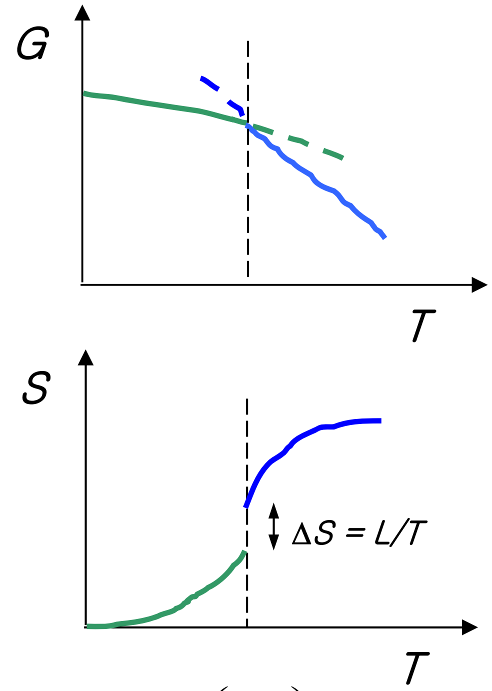
T_{rg} 1/4 1/2 2/3

How to classify thermodynamic transition?



The First-Order Transitions

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

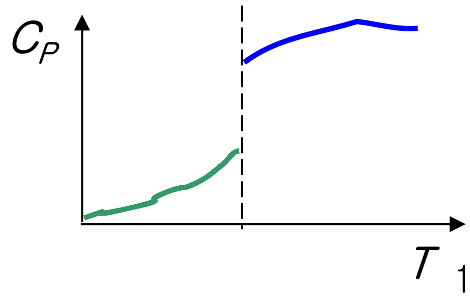
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

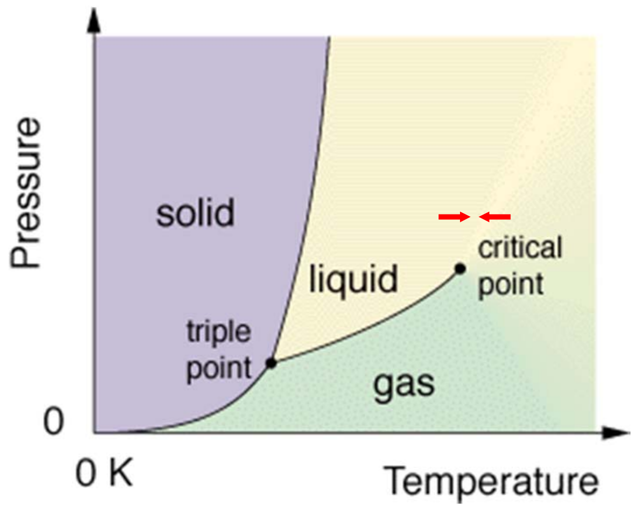
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Heat capacity at constant P or V — **Coefficient of Thermal expansion** — **Compressibility at constant T or S**

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

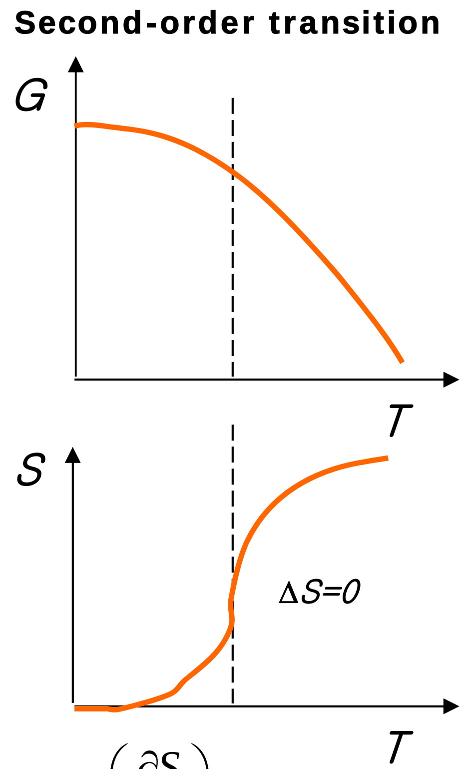


  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

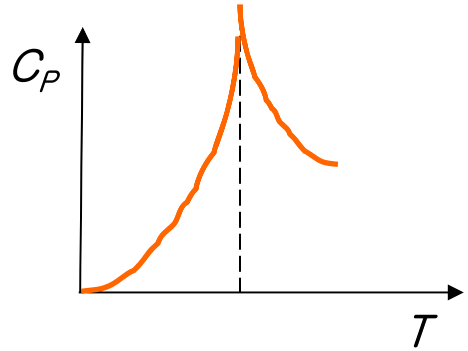


The Second Order Transition

No Latent heat
Continuous entropy



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



- 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

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

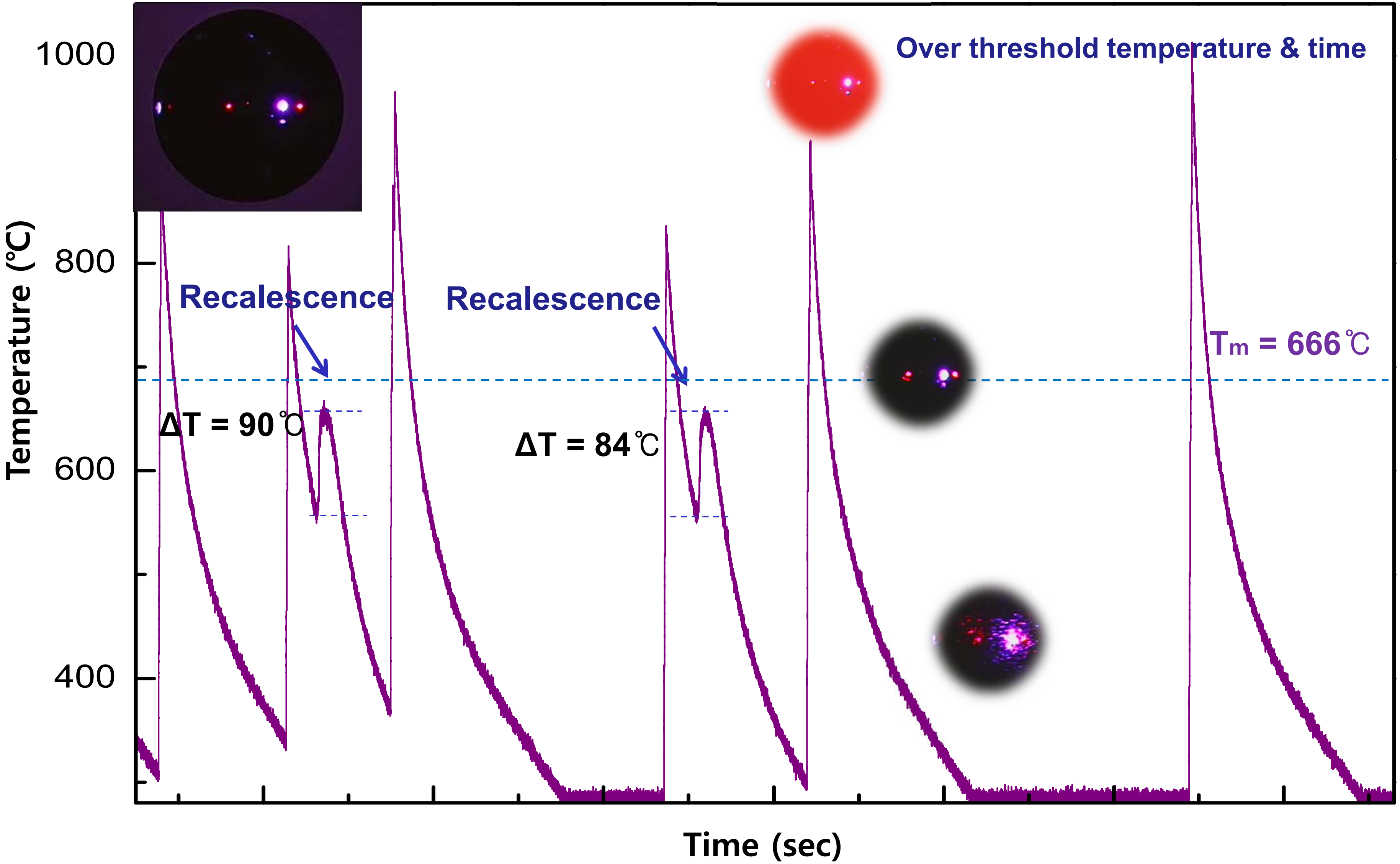
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

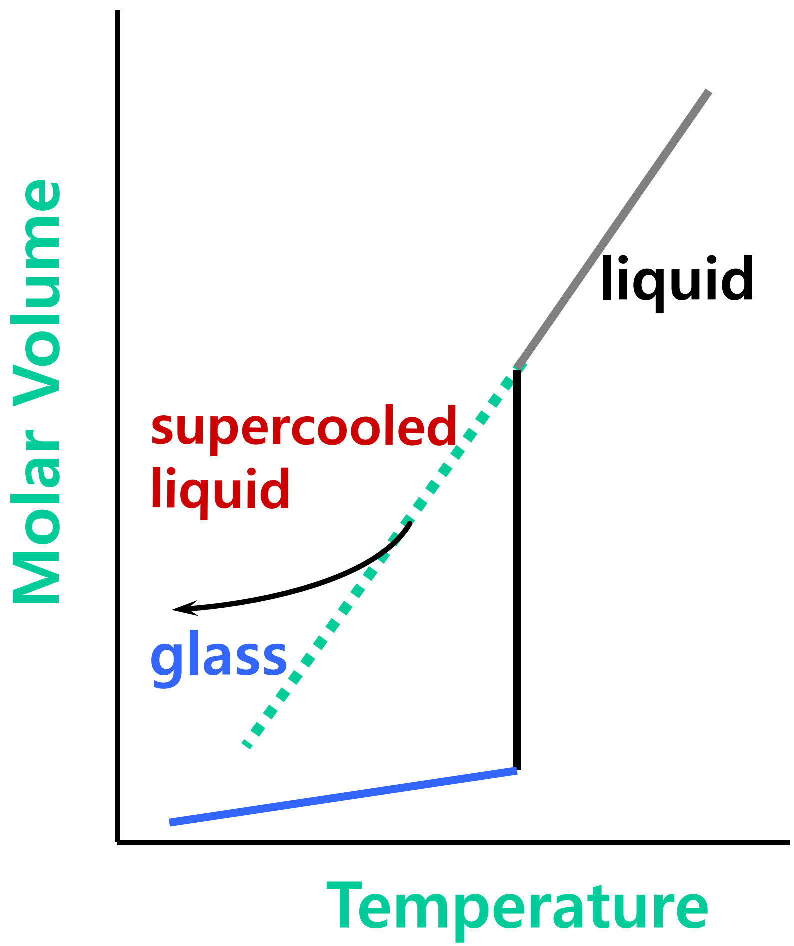
How to obtain kinetic transition?

Cyclic Cooling Curves of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (VIT 1)

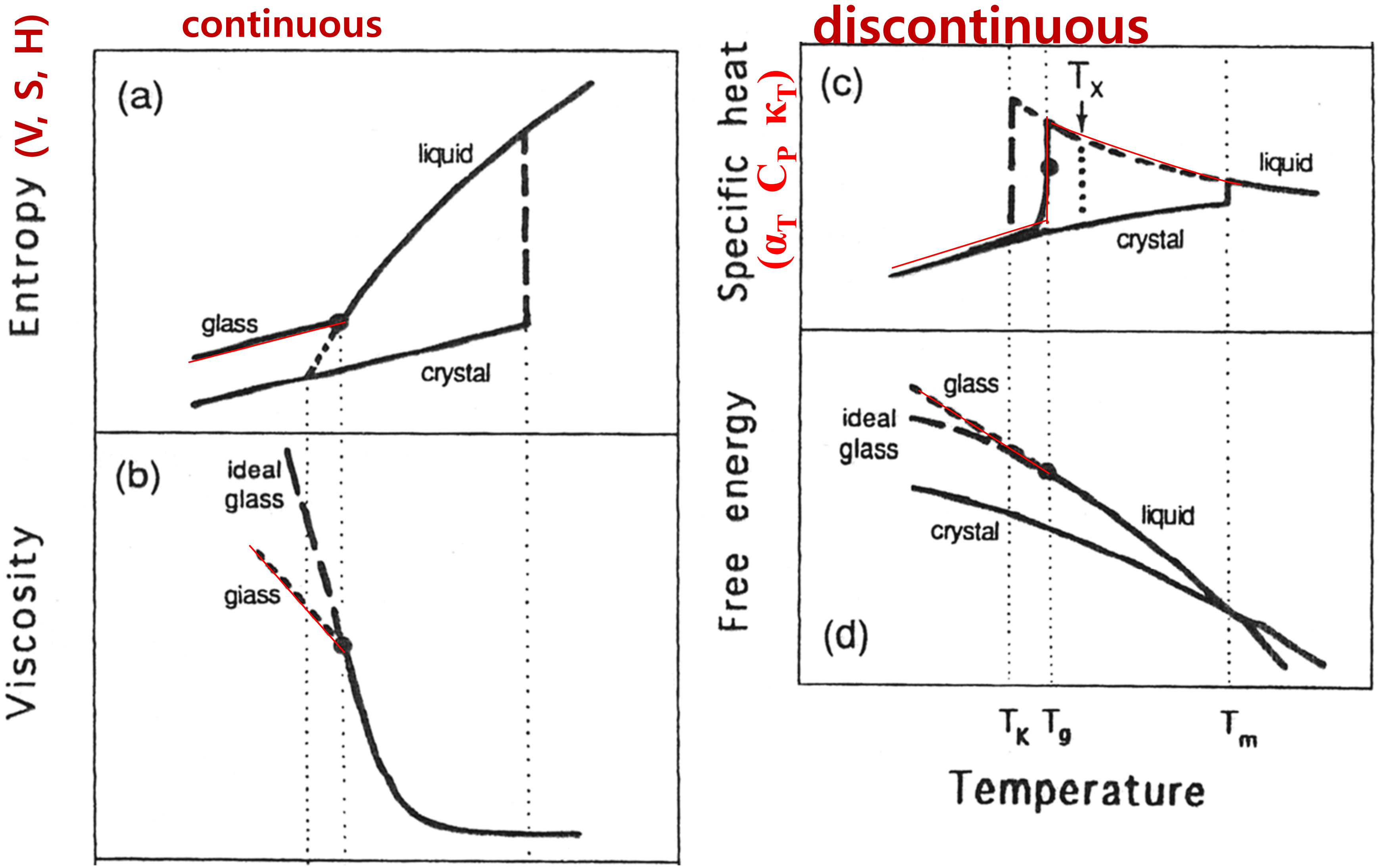


Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - (1)"Internal" time scale controlled by the viscosity (bonding) of the liquid for atom/molecule arrangement
  - (2) "External" timescale controlled by the cooling rate of the liquid



Glass transition
(1) ≈ (2)



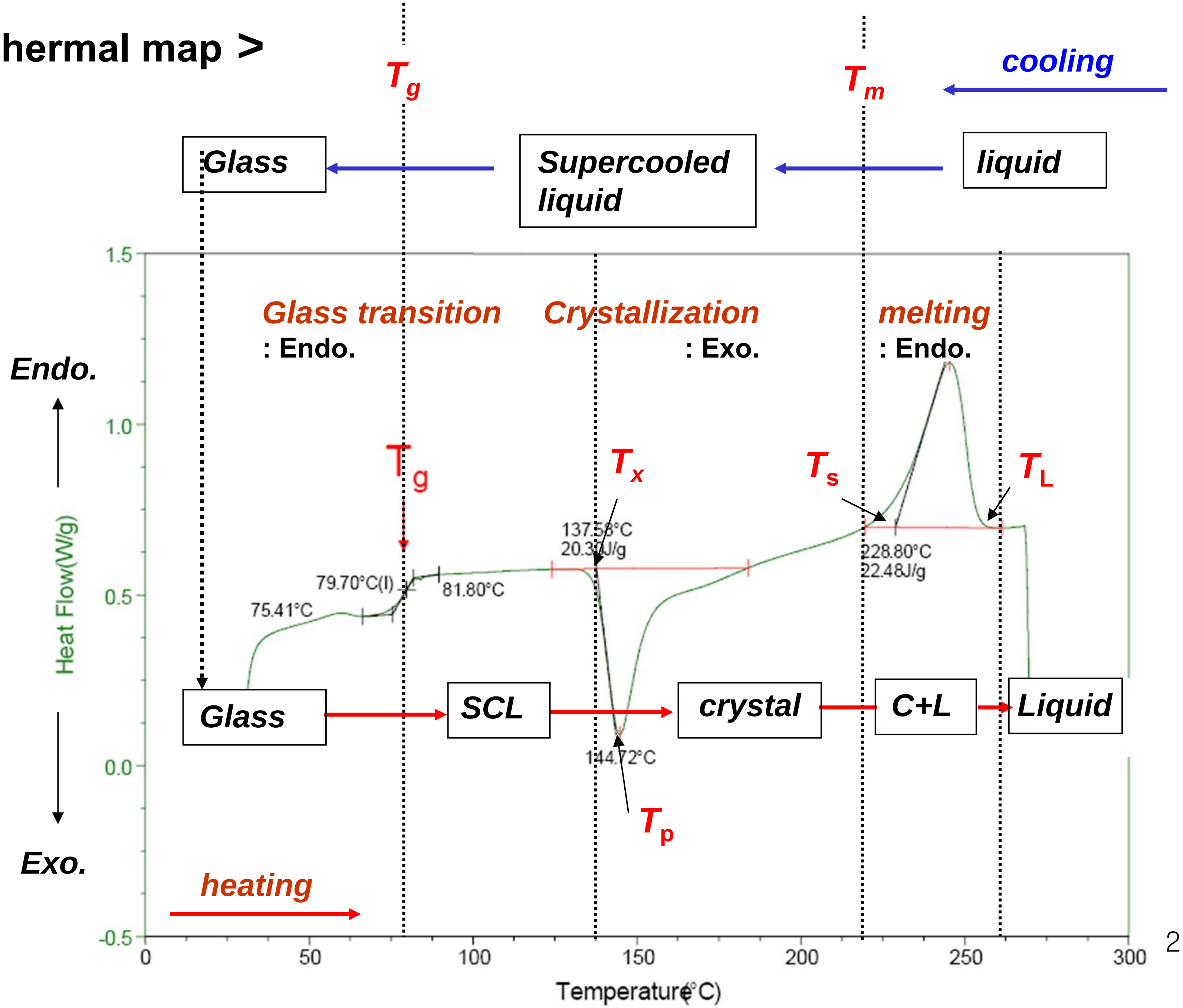
Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

Glass transition is kinetic Transitions

< Thermal map >



Tg
Tm
cooling
Glass
Supercooled liquid
liquid
Glass transition
: Endo.
Crystallization
: Exo.
melting
: Endo.
Endo.
Exo.
Heat Flow(W/g)
Tg
Tx
Ts
TL
Tp
79.70°C(I)
75.41°C
81.80°C
137.58°C
20.37J/g
228.80°C
22.48J/g
144.72°C
Glass
SCL
crystal
C+L
Liquid
heating
1.5
1.0
0.5
0.0
-0.5
0
50
100
150
200
250
300
Temperature(°C)