2018 Fall

Advanced Solidification

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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: "Principles of Solidification",
BRUCE CHALMERS, John & Sons, Inc (1964)

References: 1) "Solidification Processing," MERTON C. FLEMINGS,
McGraw-Hill Book Company, INC (1974)
2) "Fundamentals of Solidification," W. KURZ,
TRANS TECH PUBLICATION (1984)
3) "Solidification and Casting," G.J. DAVIES,
JOHN WILEY & SONS (1973)

Additional reading materials will be provided.

Course Goals

This course provides a critical review of the state of knowledge and understanding of <u>the process of solidification</u>, defined for this purpose as <u>the discontinuous change of state from liquid to crystalline solid</u>. In particular, this course is intended to provide an understanding of the physical processes that relate to solidification and to show how these processes combine to produce the phenomena observed in practical situations. An essential aim of many solidification processes is to obtain optimum properties in the resultant material. This course can provide a working knowledge of how the solidification principles can be utilized to produce structures with improved mechanical or physical properties, which then can be used to solve problems involving materials and process design. By the end of the semester, you will be able to understand key concepts, experimental techniques, and open questions in the solidification phenomena of various materials.

Contents in 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**

Schedule

week 1 Brief introduction : the relevant thermodynamic laws, properties, and relationships

week 2 Solidification as an Atomic Process I

week 3 Solidification as an Atomic Process II

week 4 Nucleation I

week 5 Nucleation II

week 6 Microscopic Heat Flow Consideration I

week 7 Microscopic Heat Flow Consideration II

week 8 Reduction of Solute during solidification I

week 9 Reduction of Solute during solidification II

week 10 Polyphase Solidification I

week 11 Polyphase Solidification II

week 12 Macroscopic Heat Flow and Fluid Flow I

week 13 Macroscopic Heat Flow and Fluid Flow II

week 14 The Structure of Cast Metals I

week 15 The Structure of Cast Metals II

Components of Your Grade:

1) Exams (midterm: 30% + final: 35%)

There will be two exams, each of which will take 2-3 hours. I will not use class time for the exams and instead will reserve separate time slots. The exams will be conceptual and difficult.

2) Reports and 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) Quizzes (15%) and Attendance (5%)

There will be a few short quizzes between the major exams. These will take place in class, at the beginning of class and will last for 20 minutes.

Remarks: The weight of each grade component may change up to 5% depending on the student’s achievement.

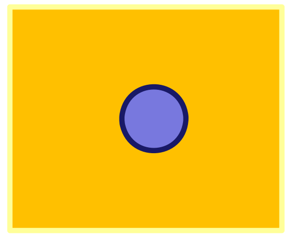
Policies and Procedures

- ***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 **Thursday**, nothing thereafter.
- ***If you wish, you may work together on homework assignments. BUT, you must hand in your own work, in <u>your own words.</u>***
- **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.

Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid

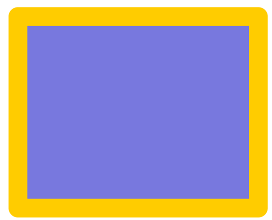


<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

No superheating required!

vapor



- Interfacial energy ⇨ No ΔT_N

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

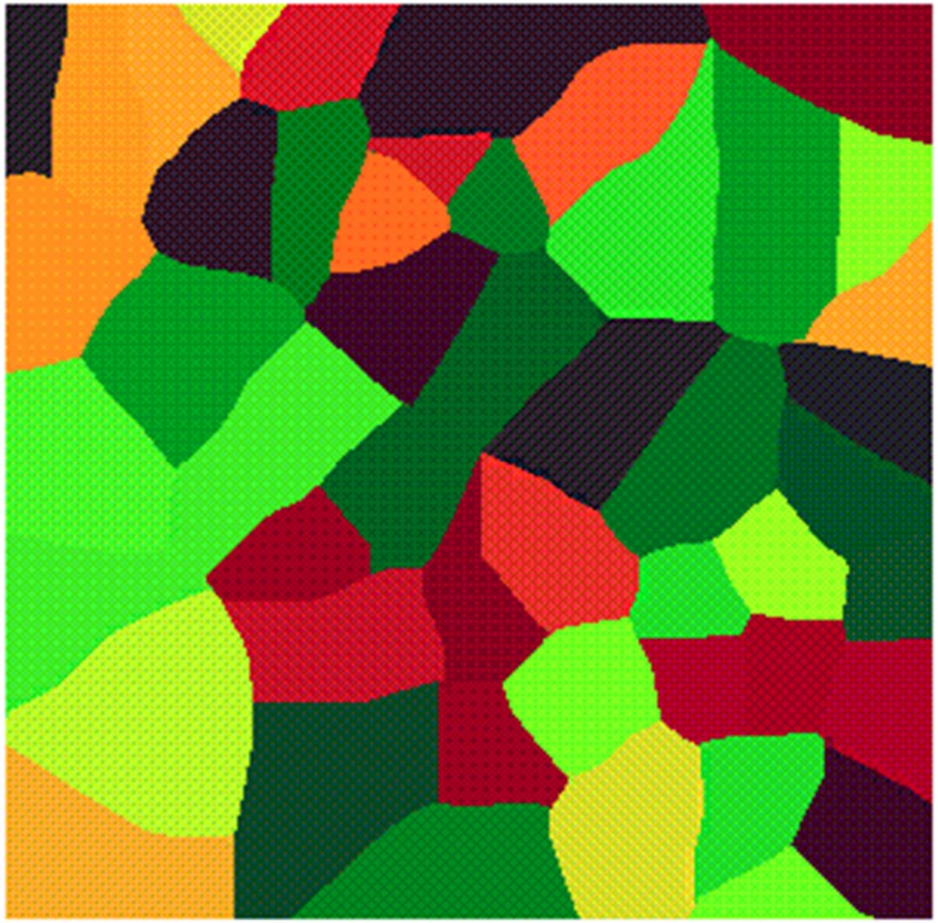
Melting: Liquid ← Solid

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

Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



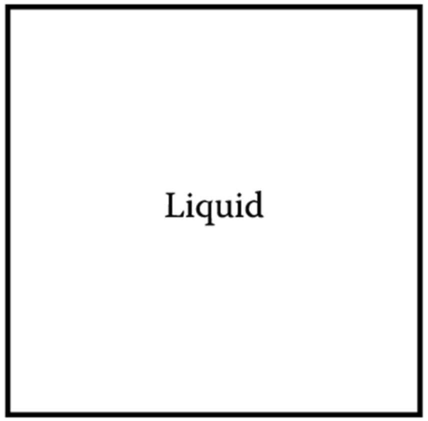
4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

Thermodynamic Transitions: $\Delta G = 0$

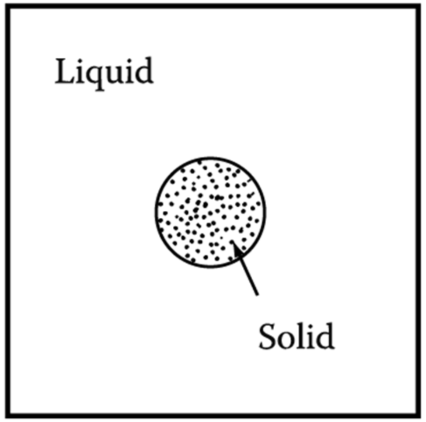
1) G_L versus G_S

2) Interfacial free energy

1) Homogeneous Nucleation



(a) G_1



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

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

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

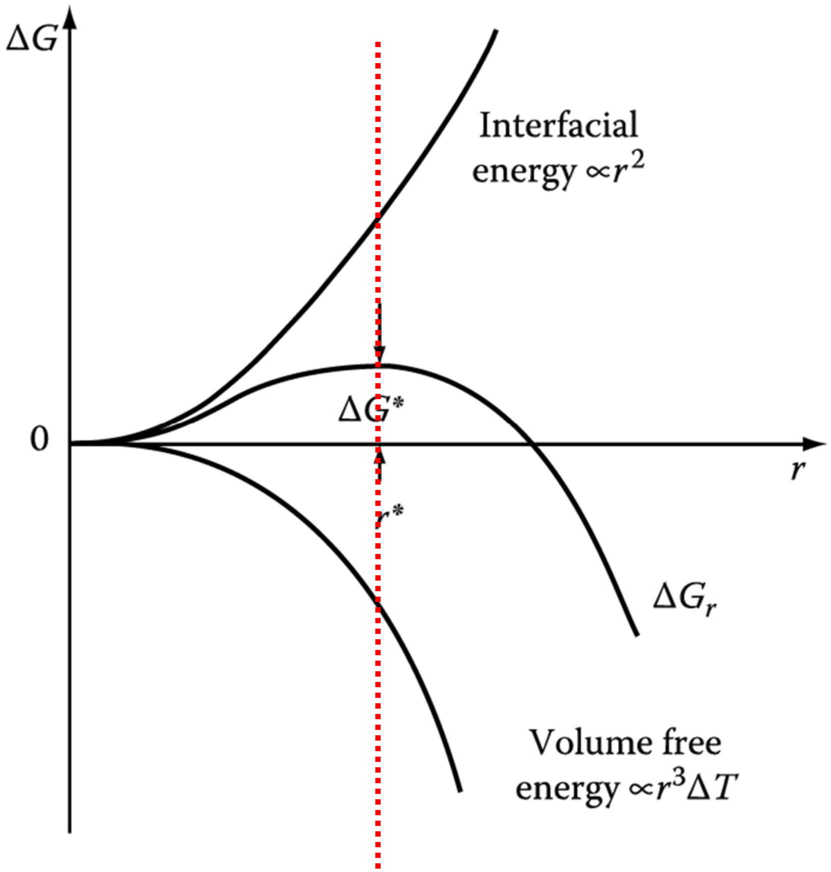
G_V^S, G_V^L **: free energies per unit volume**

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

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



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**

1.8 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)

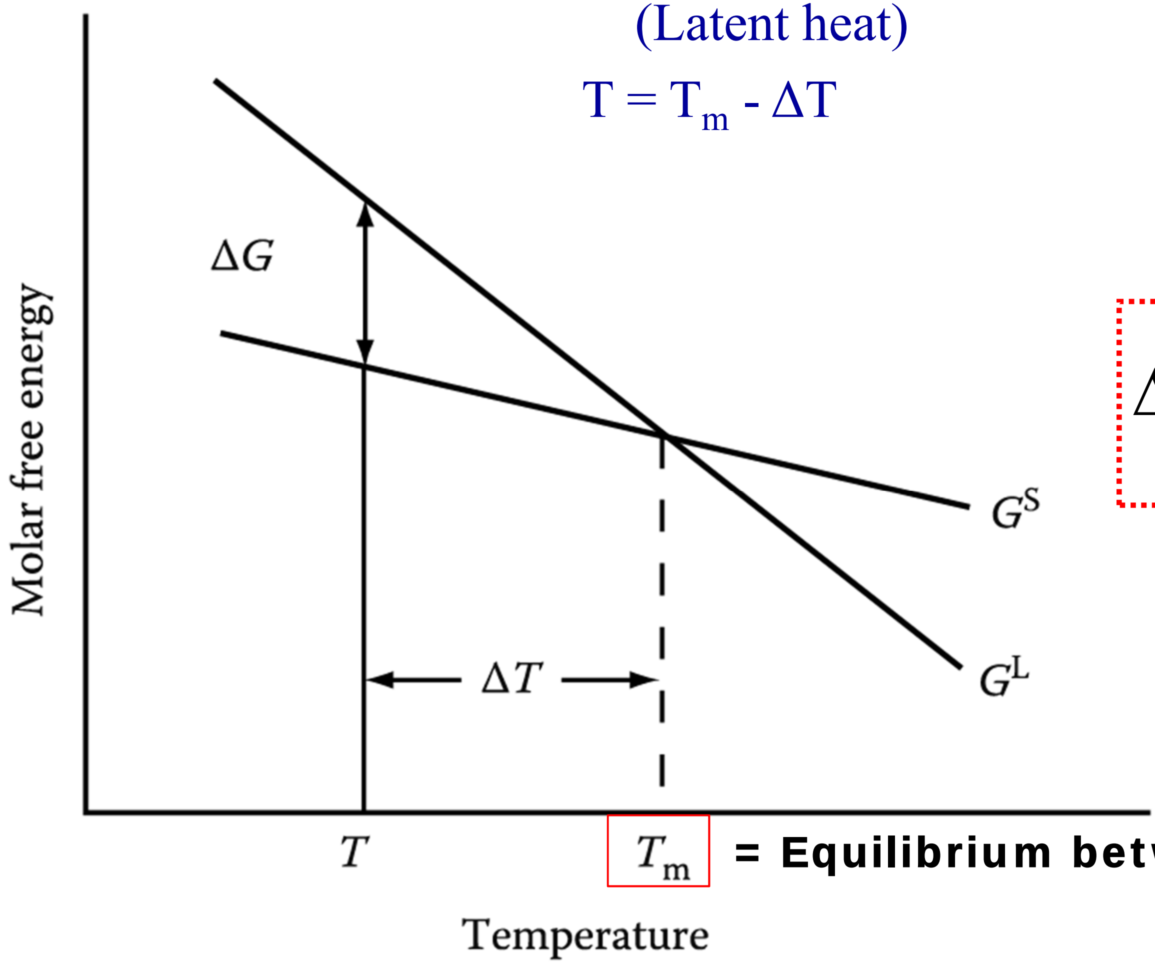
$T = T_m - \Delta T$

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

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

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

(eq. 1.17)



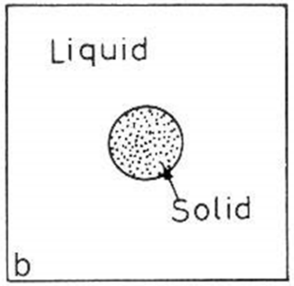
$$\Delta G = \frac{L\Delta T}{T_m}$$

T_m = **Equilibrium between Solid and Liquid**

2) Driving force for solidification

solidification

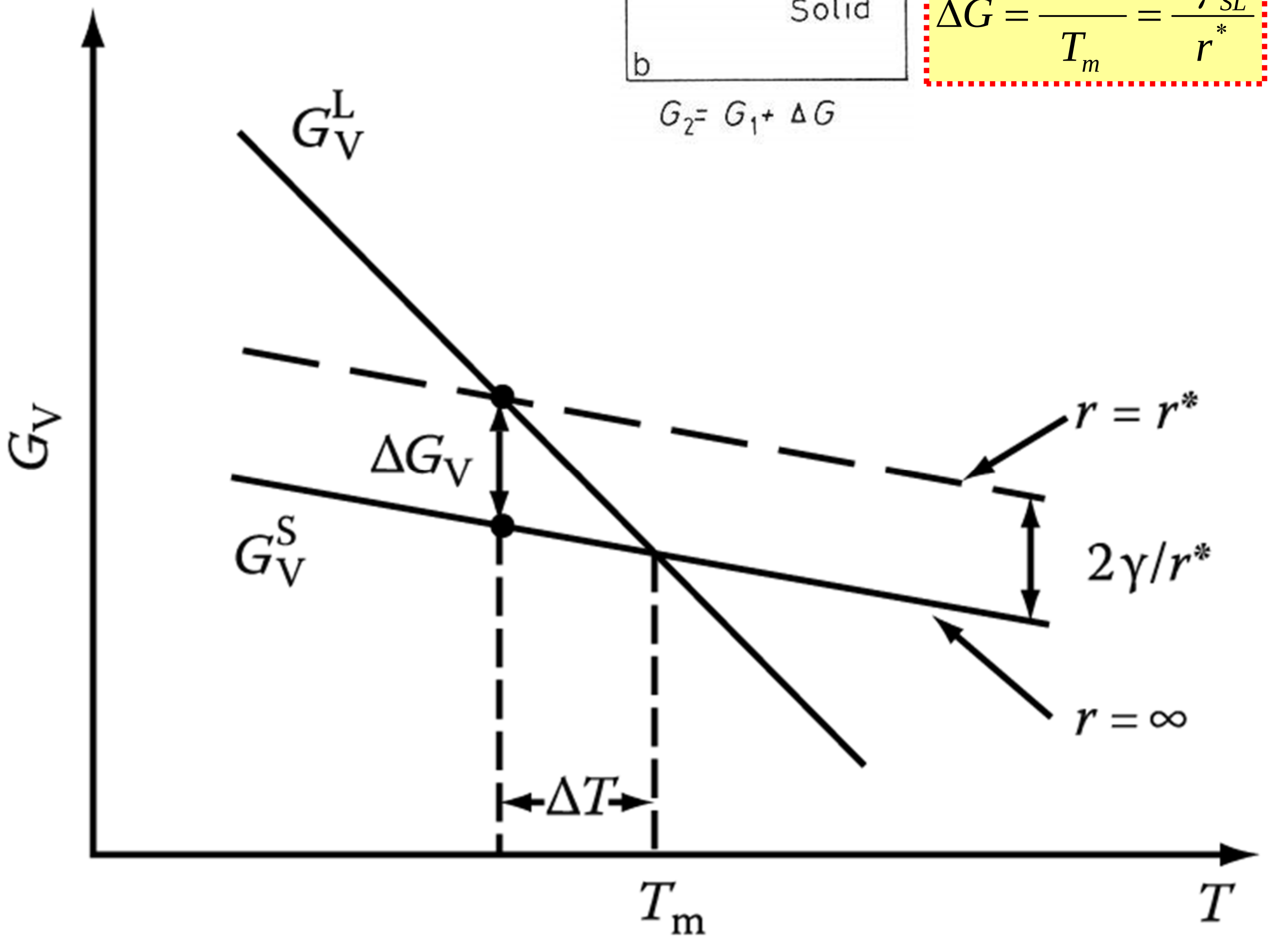
Liquid → **Solid**



$G_2 = G_1 + \Delta G$

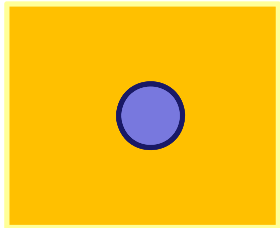
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

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



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.

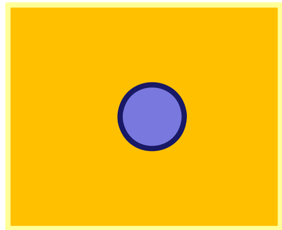
Why?

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

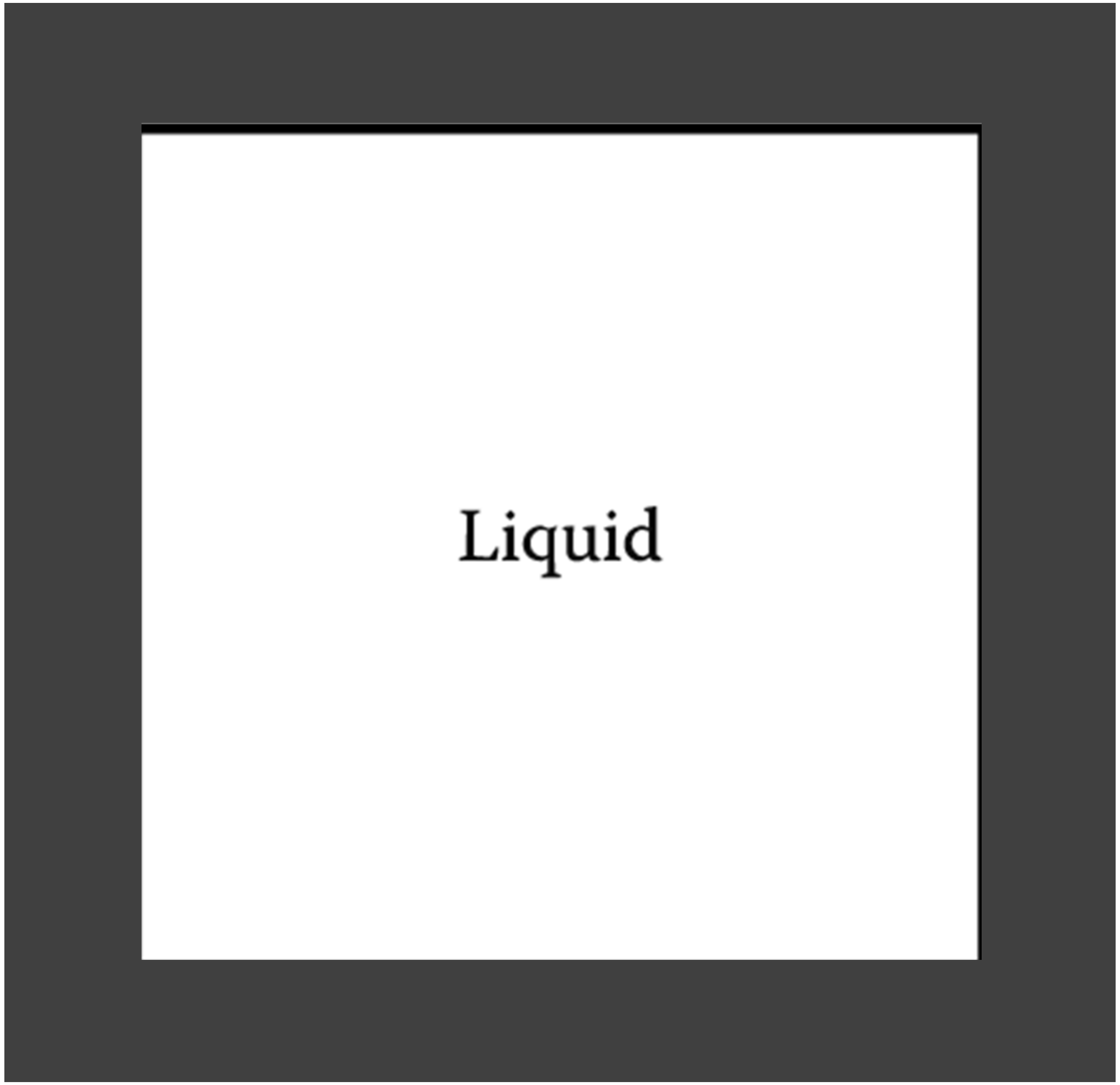
- Interfacial energy ⇨ No ΔT_N

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

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 ↑

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

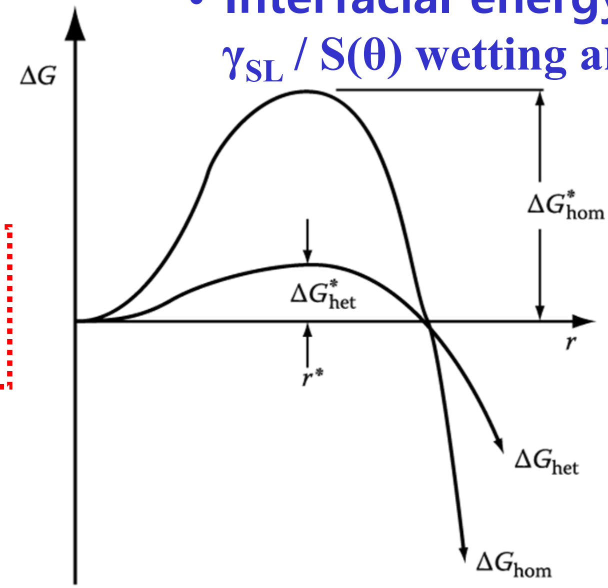
- **Heterogeneous Nucleation**

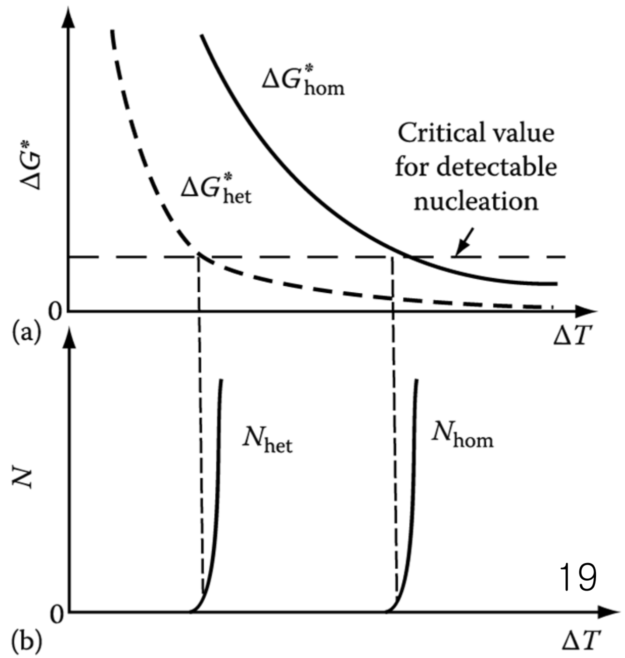
$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*$$

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

- **Nucleation of melting**

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

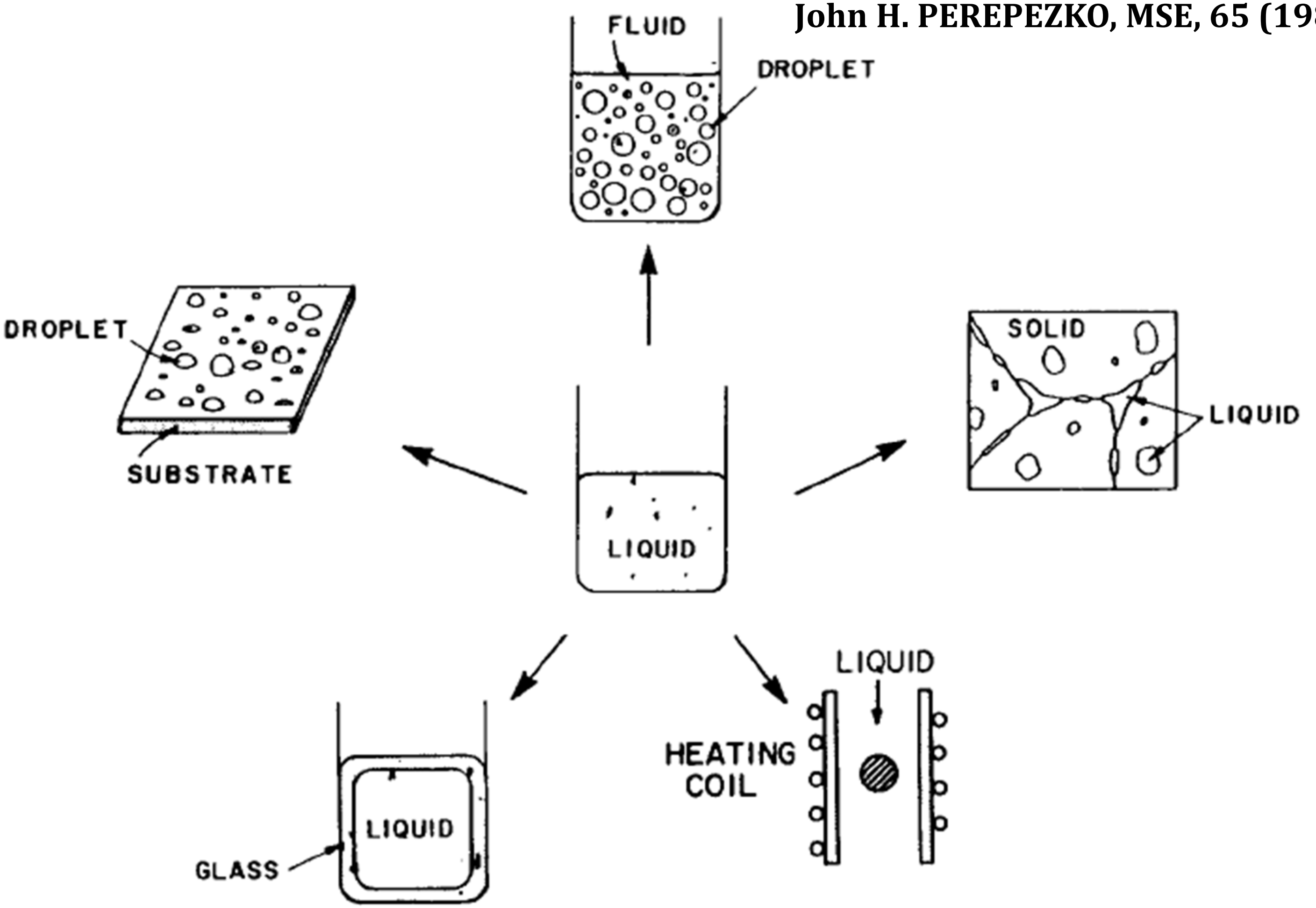




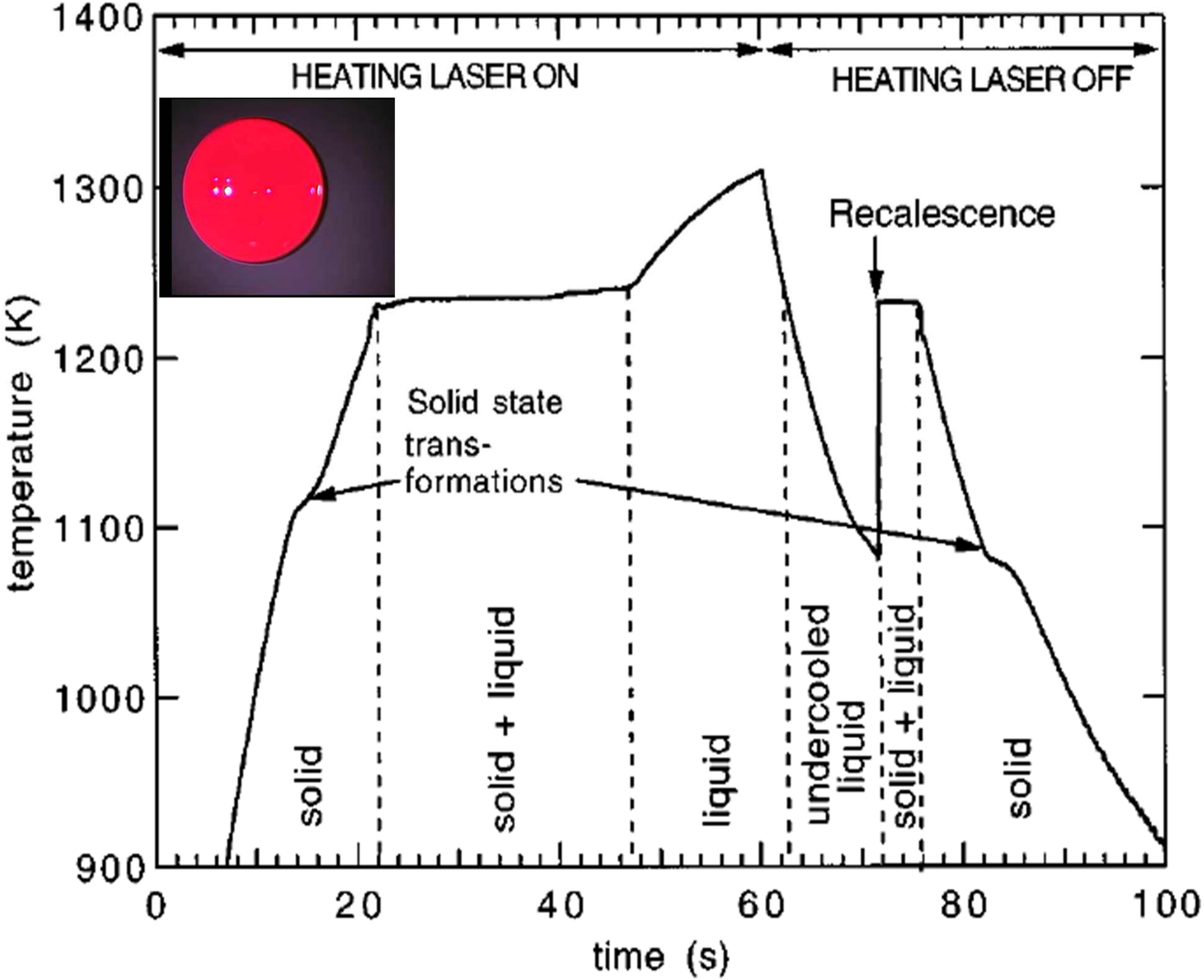
What is the meaning for the ΔT (undercooling) during solidification?

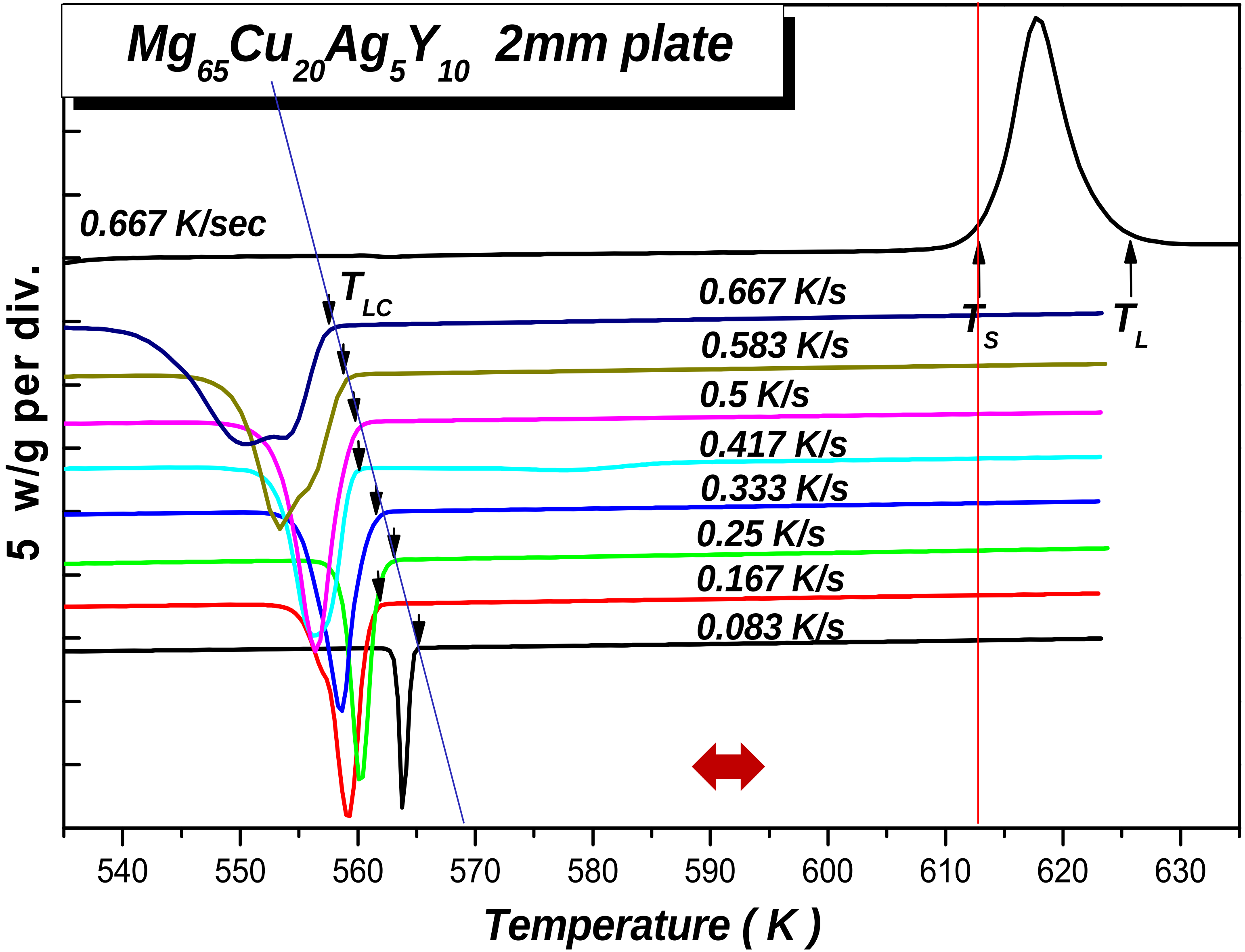
How to obtain large undercooling during cooling?

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

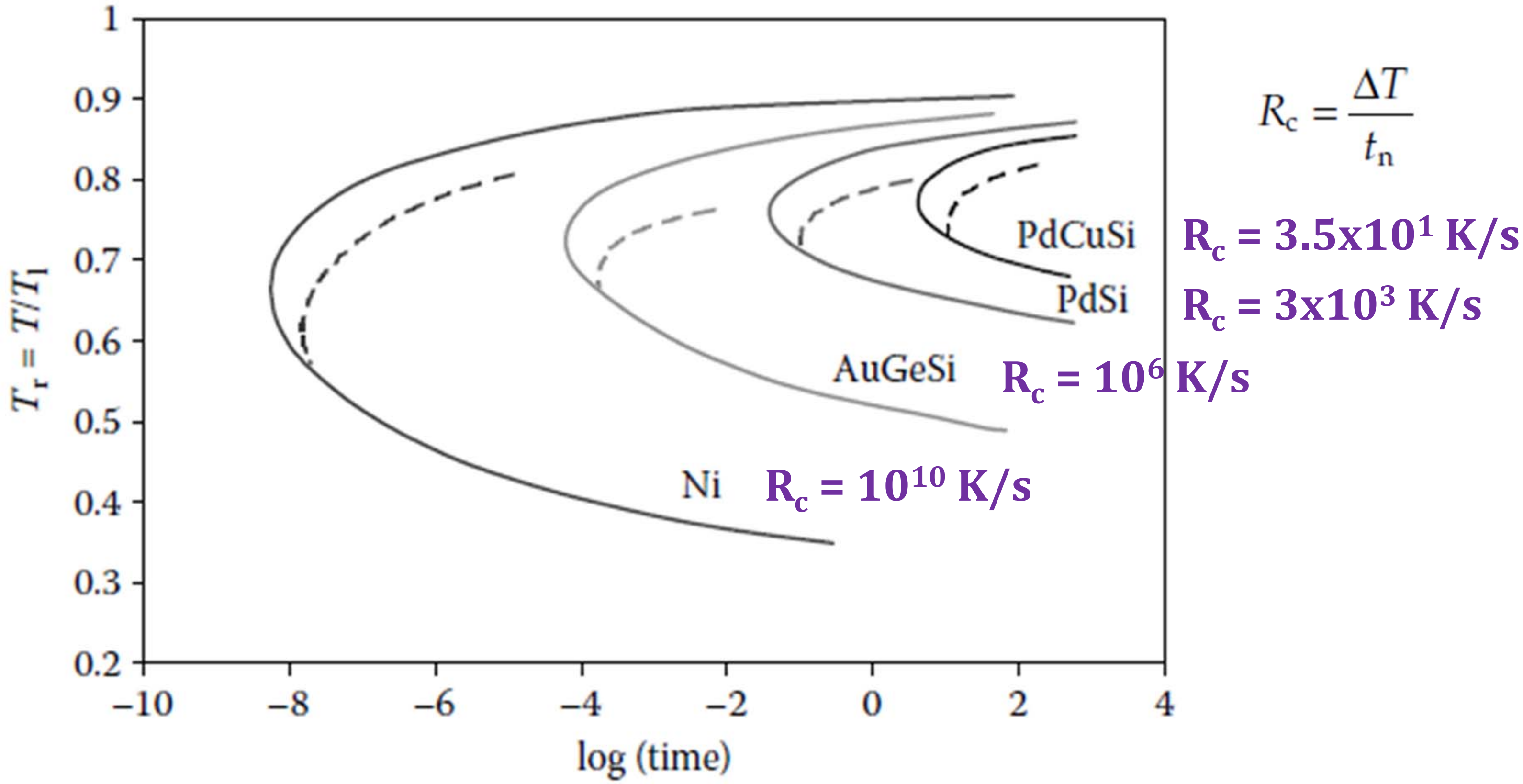


By dispersing a liquid into a large number of small droplets within a suitable medium, the catalytic effects of active nucleants may be restricted to a small fraction of the droplets so that many droplets will exhibit extensive undercooling.


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


Mg65Cu20Ag5Y10 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

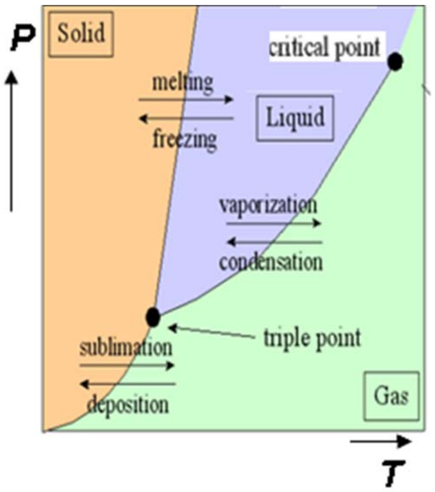


$$R_c = \frac{\Delta T}{t_n}$$

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.

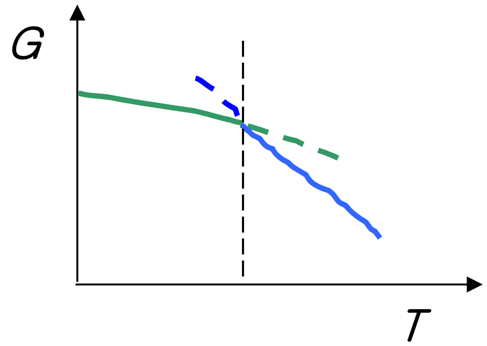
T_{rg}	Ni	$Au_{78}Ge_{14}Si_8$	$Pd_{82}Si_{18}$	$Pd_{78}Cu_6Si_{16}$
		1/4	1/2	2/3

How to classify thermodynamic transition?



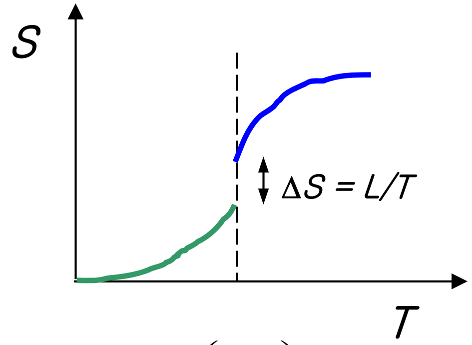
The First-Order Transitions

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

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

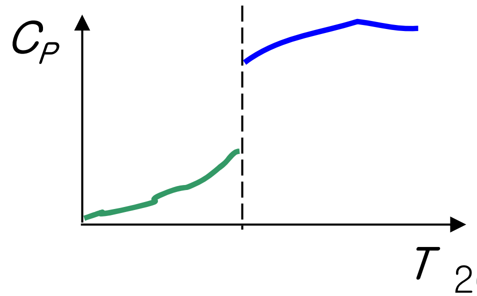


  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

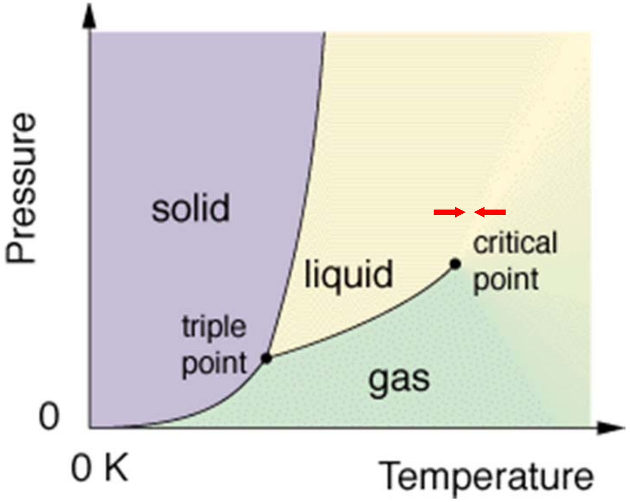
Heat capacity at constant P or V | **Coefficient of Thermal expansion** | **Compressibility at constant T or S**

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



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

The Second Order Transition



No Latent heat
Continuous entropy

- 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

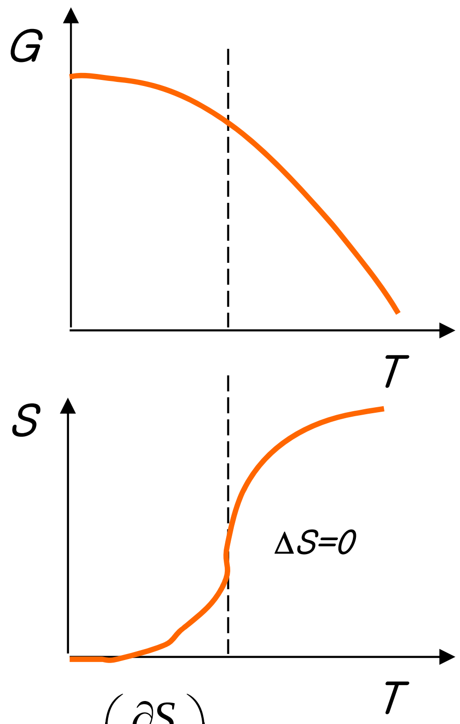
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

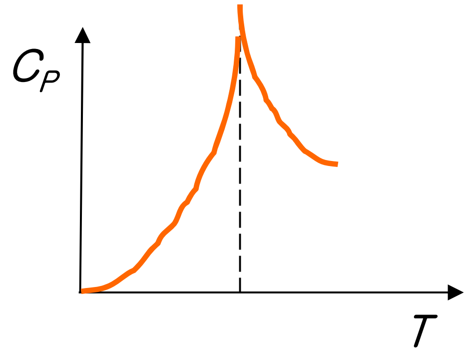
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

Second-order transition

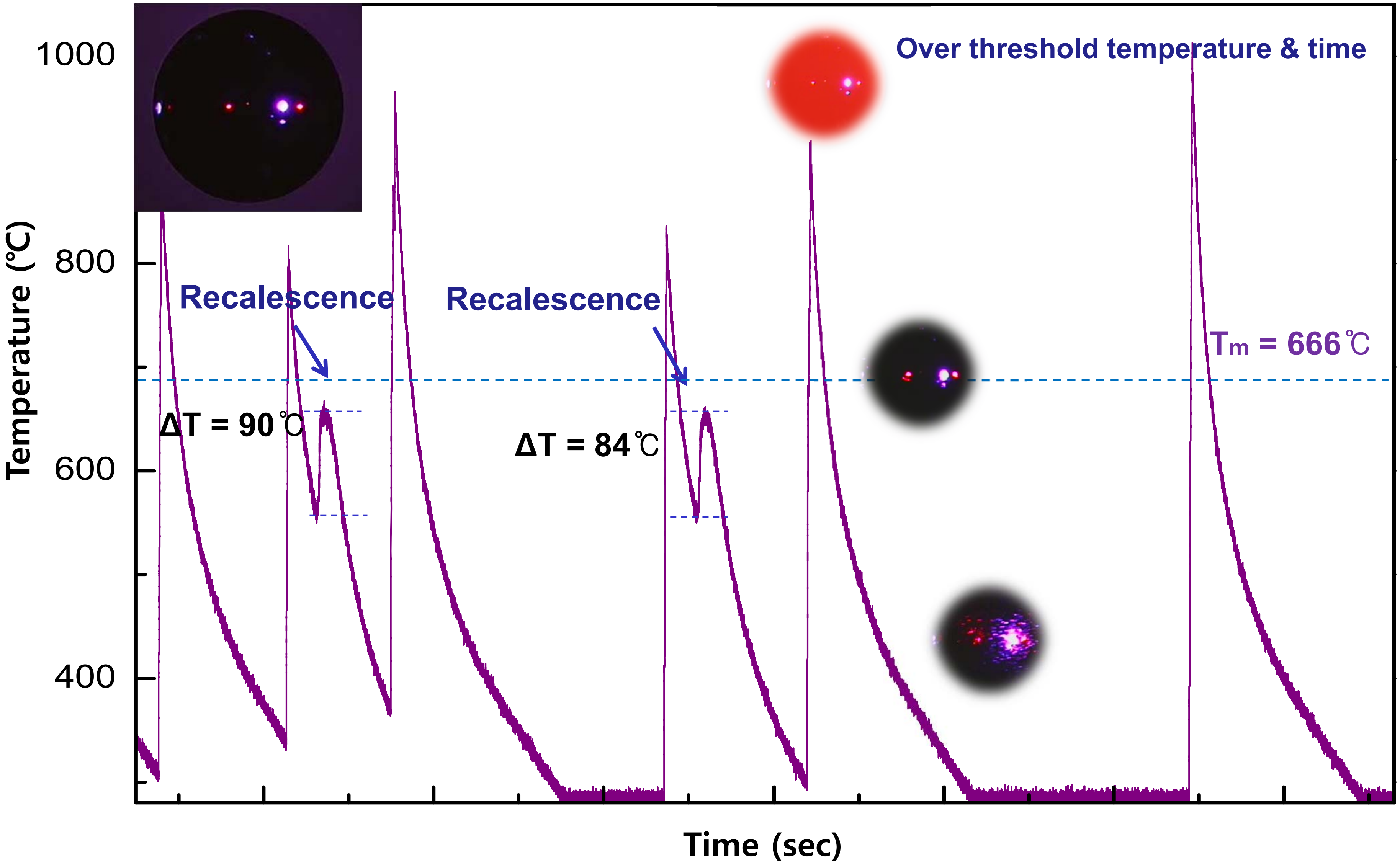


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \rightarrow \infty$$



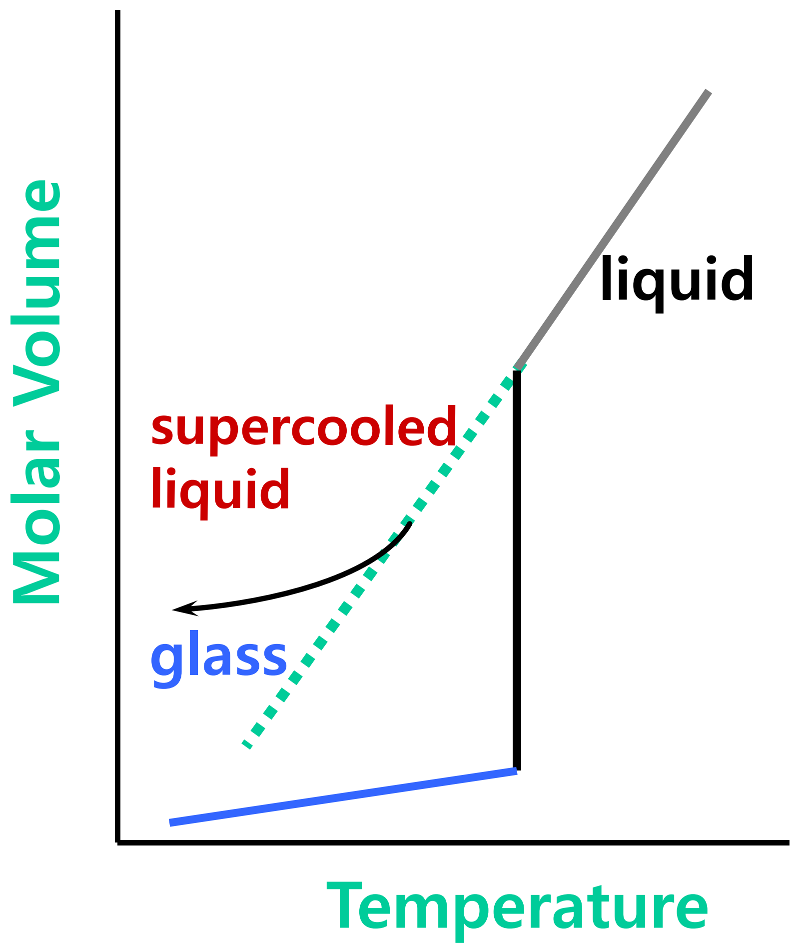
How to obtain kinetic transition?

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

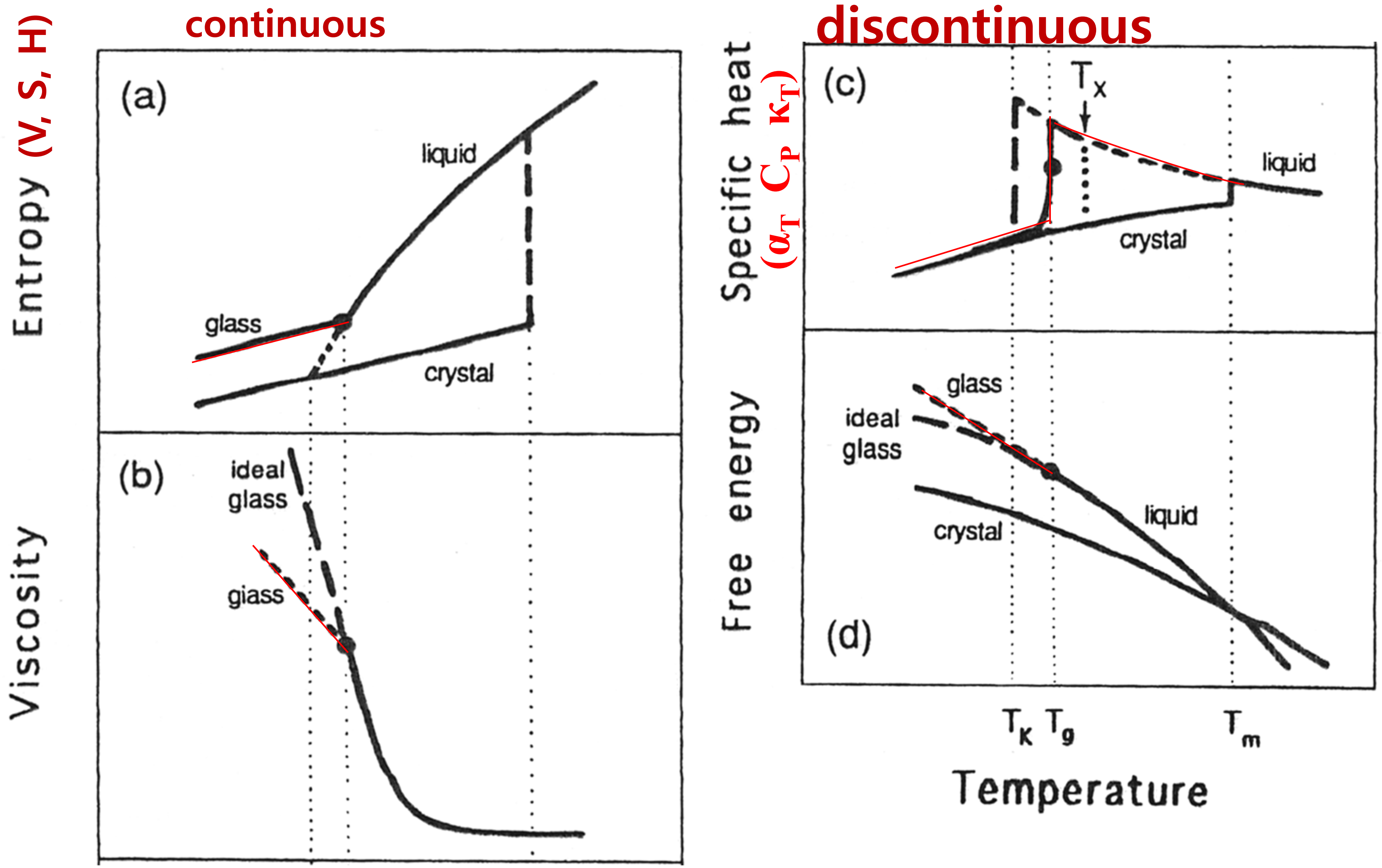


Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that <u>makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure</u>
- 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)



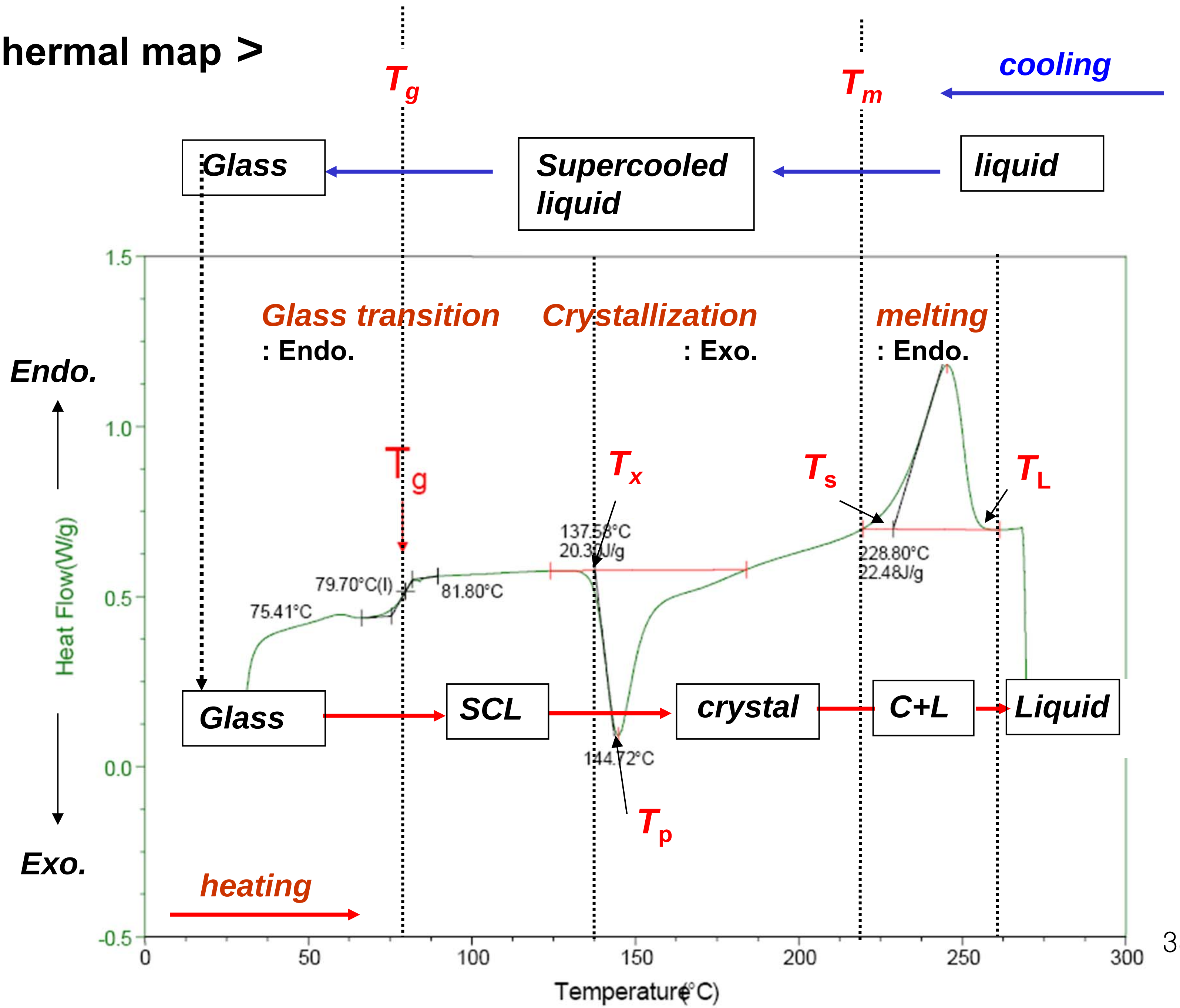
Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Chapter 1 Introduction of Solidification

Melting and Crystallization are Thermodynamic Transitions

Glass transition is kinetic Transitions

< Thermal map >



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