2016 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

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Q1: Theories for the glass transition

Theories for the glass transition

A. Thermodynamic phase transition

- **Glass transition**

H , V , S : continuous **C_p α_T K_T : discontinuous**

→ **by thermodynamic origin, 2nd order transition**

→ **In fact, it appears on some evidences that the glass transition is not a simple second-order phase transition.**

$$R = \frac{\Delta\kappa_T \Delta C_P}{TV(\Delta\alpha_T)^2} \neq 1$$

B. Entropy

- **Heat capacity** → **dramatic change at T_g**
- **Description of glass transition by entropy (Kauzmann)**

$$\boxed{S = \int C_P d\ln T}$$

→ **The slow cooling rate, the lower T_g** → **T_K or T_g^0**

→ **Measurement of Kauzmann temp. is almost impossible.**

(∵ very slow cooling rate →longer relaxation time →crystallization)

Theories for the glass transition

C. Relaxation behavior

Below glass transition: frozen-in liquid

→ **glass transition is observed when the experimental time scale (1) becomes comparable with the time scale for atom/molecule arrangement (2)**

→ **If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass**

(A concept of glass transition based on kinetic view point)

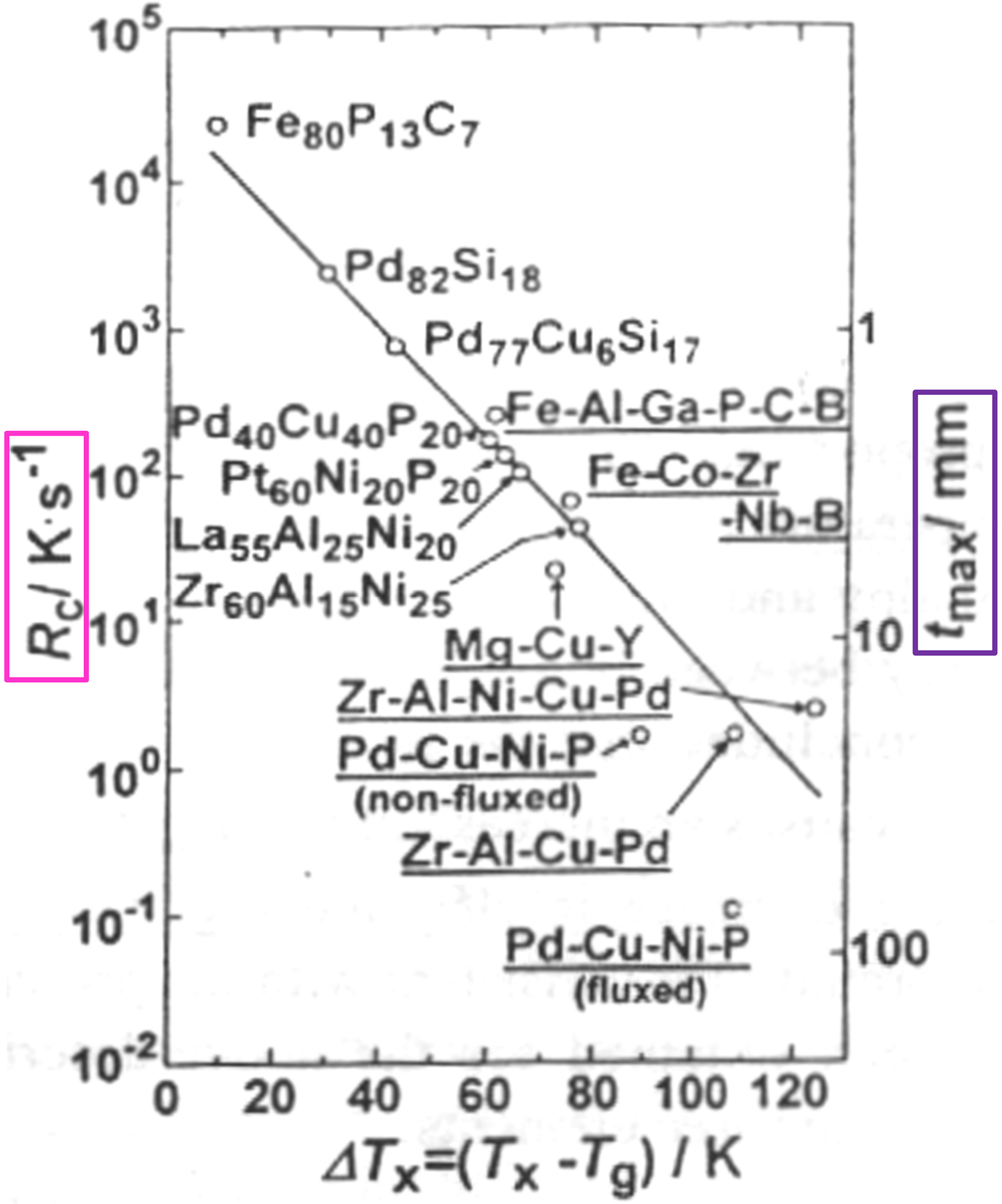
: property of liquid-like structure suddenly changes to that of solid-like structure

d. viscosity

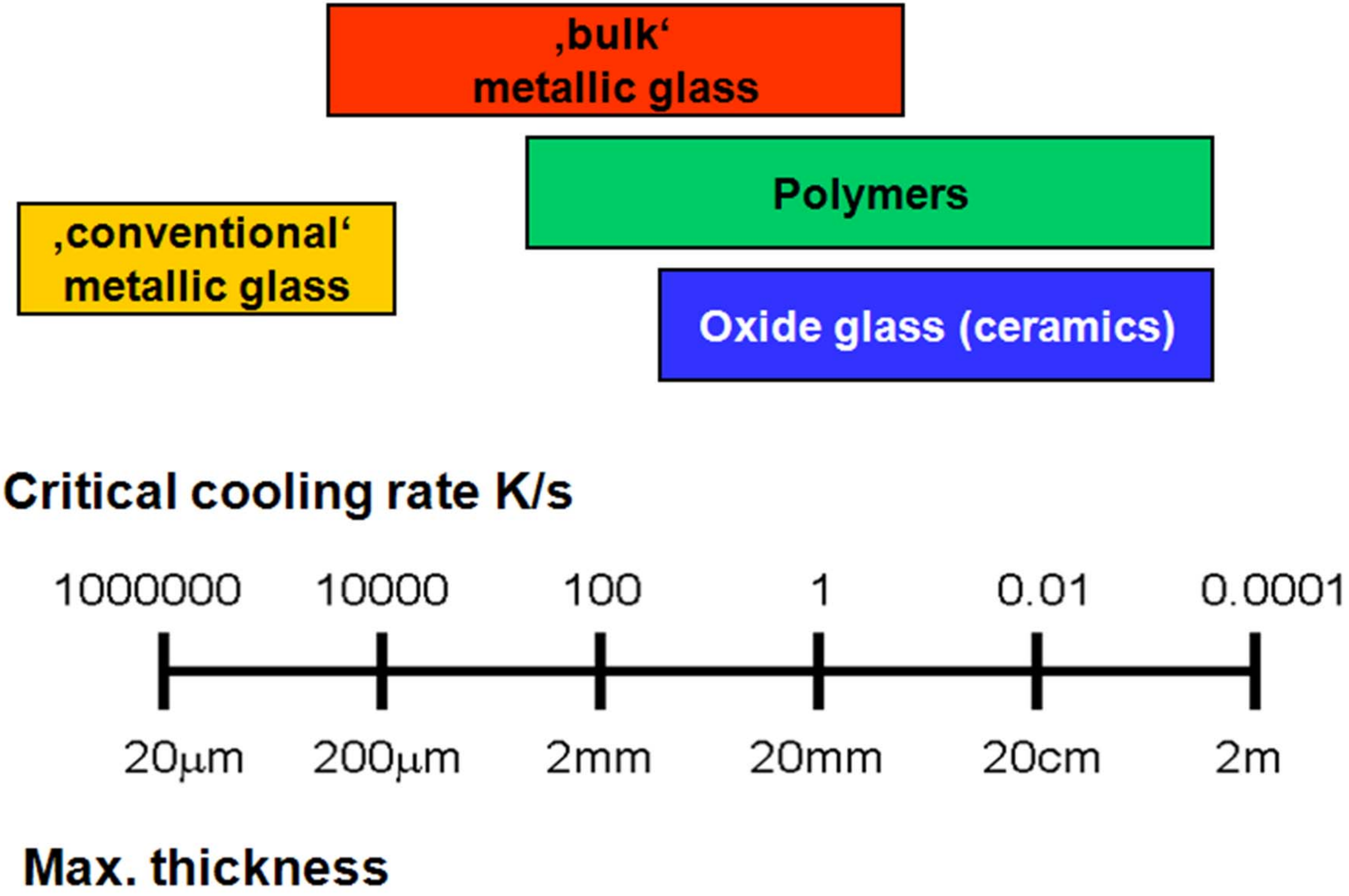
- **Viscosity (10^{15} centiPoise= $10^{12\text{-}13}$ Pa s) at T_g**
- **most glass forming liquid exhibit high viscosity.**
- **In glass transition region, viscosity suddenly changes. (fragile glass)**
  → **Fragility concept: Strong vs Fragile**
- **Viscous flow** → **Several atomistic model**
  - **absolute rate model**
  - **free volume model**
  - **excess entropy model**

Q2: Glass formation

Critical cooling rate is inversely proportional to the diameter of ingot.



Critical cooling rates and thicknesses for different materials



‚bulk‘
metallic glass

Polymers

‚conventional‘
metallic glass

Oxide glass (ceramics)

Critical cooling rate K/s

1000000 10000 100 1 0.01 0.0001

20µm 200µm 2mm 20mm 20cm 2m

Max. thickness

Critical Cooling Rates for Various Liquids

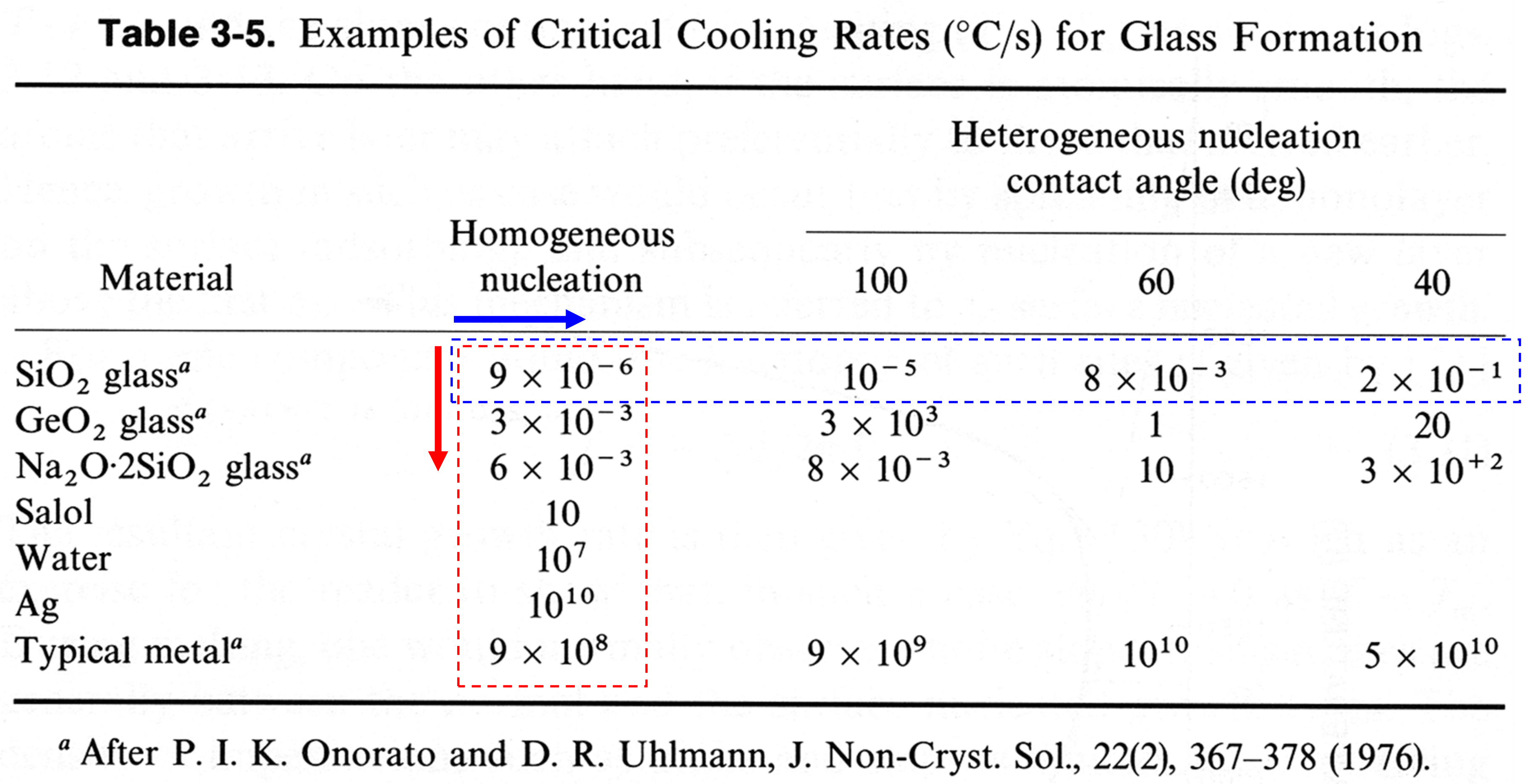


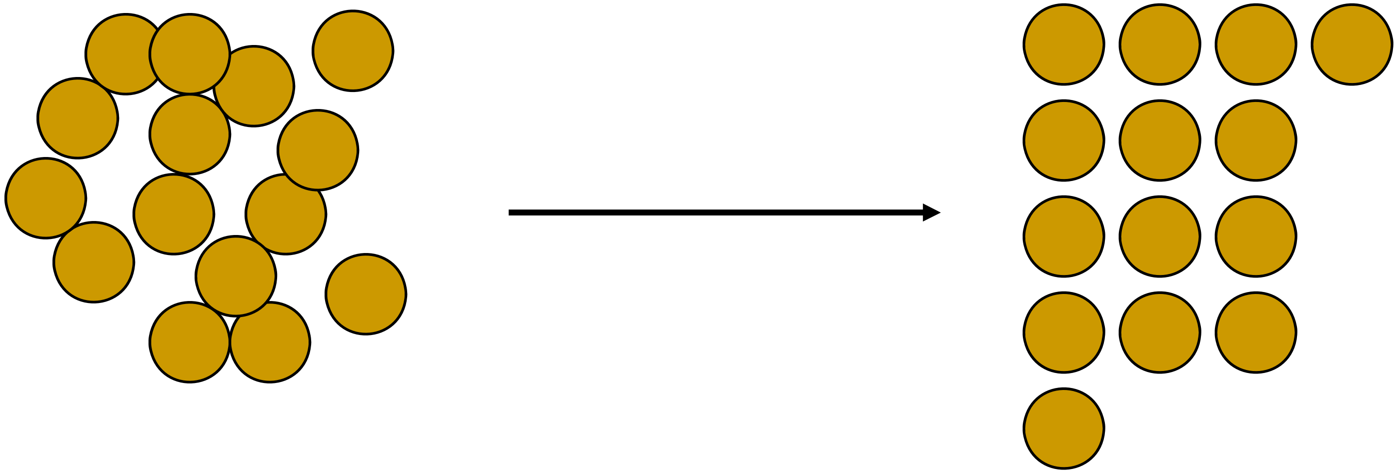
Table 3-5. Examples of Critical Cooling Rates (°C/s) for Glass Formation

Material	Homogeneous nucleation	Heterogeneous nucleation contact angle (deg)		
		100	60	40
SiO_2 glass[a]	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO_2 glass[a]	3×10^{-3}	3×10^{3}	1	20
$Na_2O{\cdot}2SiO_2$ glass[a]	6×10^{-3}	8×10^{-3}	10	$3 \times 10^{+2}$
Salol	10			
Water	10^{7}			
Ag	10^{10}			
Typical metal[a]	9×10^{8}	9×10^{9}	10^{10}	5×10^{10}

[a] After P. I. K. Onorato and D. R. Uhlmann, J. Non-Cryst. Sol., 22(2), 367–378 (1976).

Nucleation and Growth Rates Control R_c

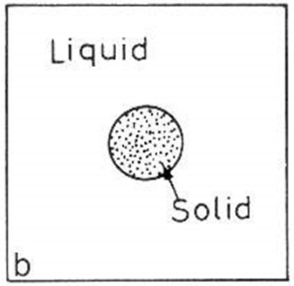
- Nucleation, the first step…
- First process is for microscopic clusters (nuclei) of atoms or ions to form
  - Nuclei possess the beginnings of the structure of the crystal
  - Only limited diffusion is necessary
  - Thermodynamic driving force for crystallization must be present



1.2.3 Driving force for solidification

solidification

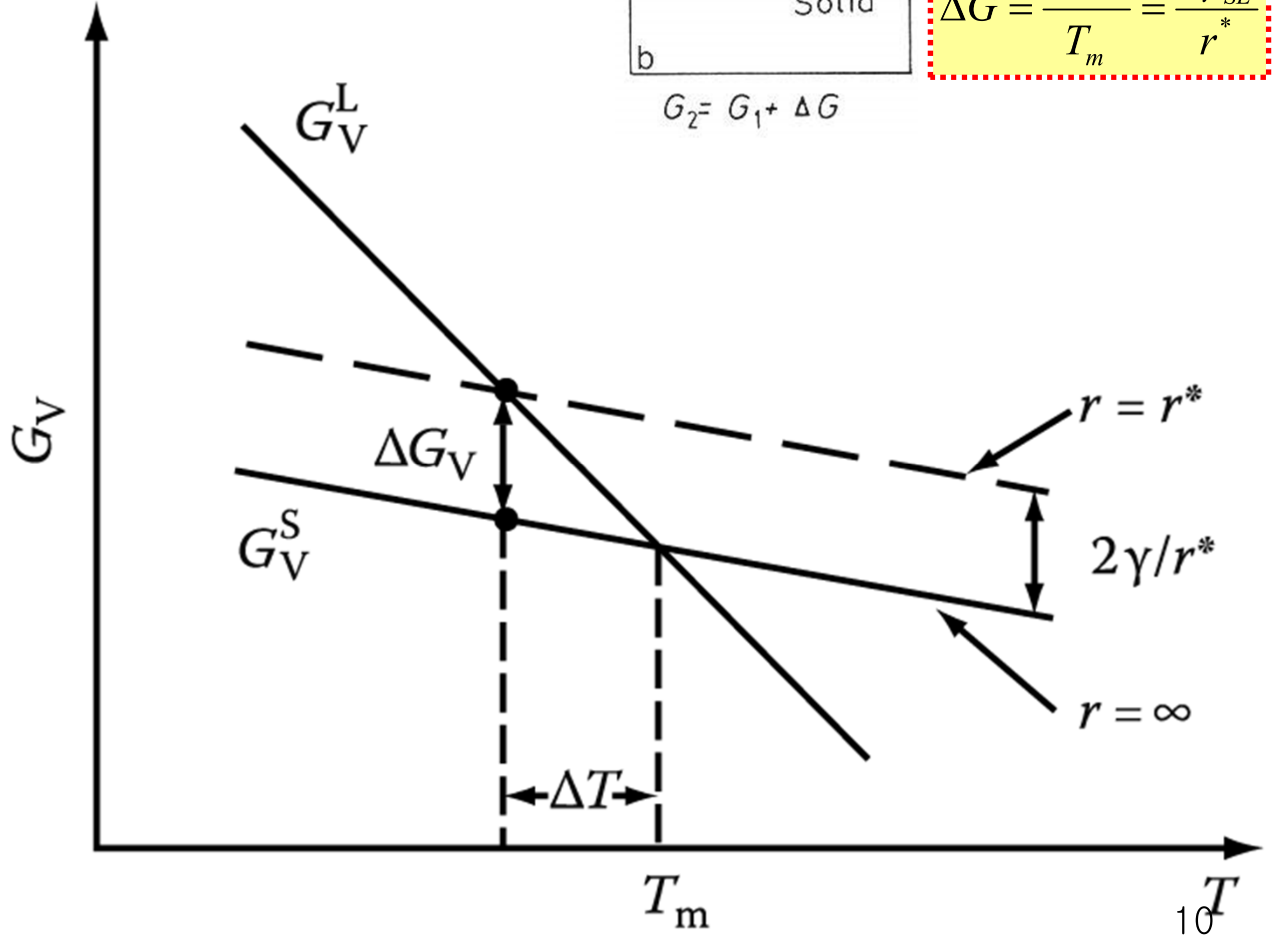
Liquid → Solid



$G_2 = G_1 + \Delta G$

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

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



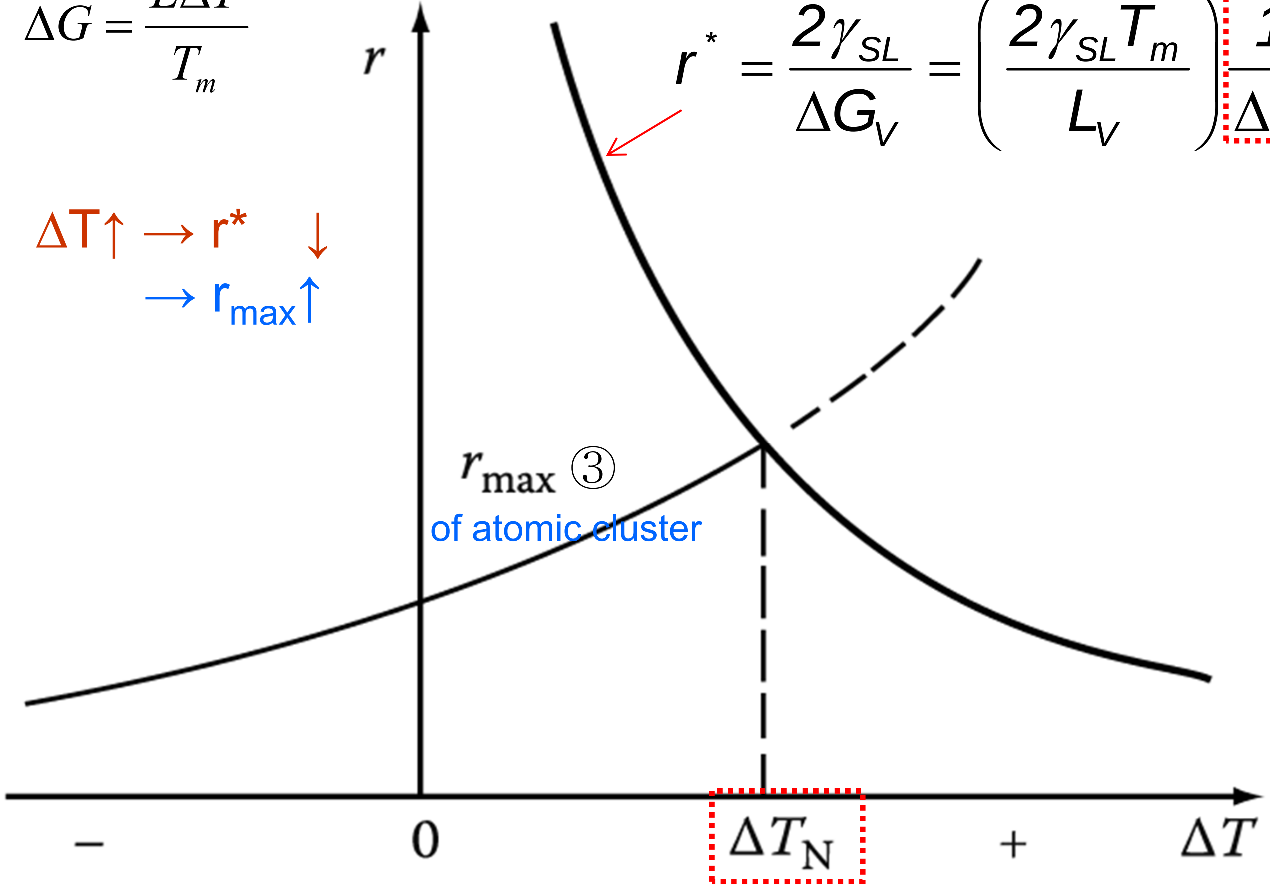
The creation of a critical nucleus ~ thermally activated process

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

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL}T_m}{L_V}\right)\boxed{\frac{1}{\Delta T}}$$

ΔT↑ → r* ↓

→ r_{max}↑



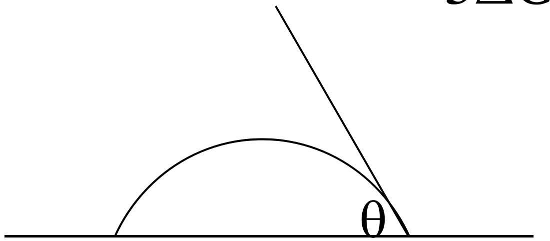
ΔT_N is the critical undercooling for homogeneous nucleation.

Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

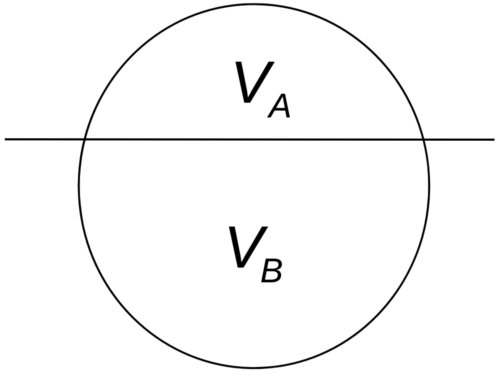
The number of clusters with r^* at $\Delta T < \Delta T_N$ is negligible.

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot\frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



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



$$\Delta G_{sub}^{*} = \Delta G_{homo}^{*}\left(\frac{2-3\cos\theta+\cos^3\theta}{4}\right)$$

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

How about the nucleation at the crevice or at the edge?

Growth of crystals from nuclei

- Growth processes then enlarge existing nuclei
- Smallest nuclei often redissolve
- Larger nuclei can get larger
- Thermodynamics favors the formation of larger nuclei

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

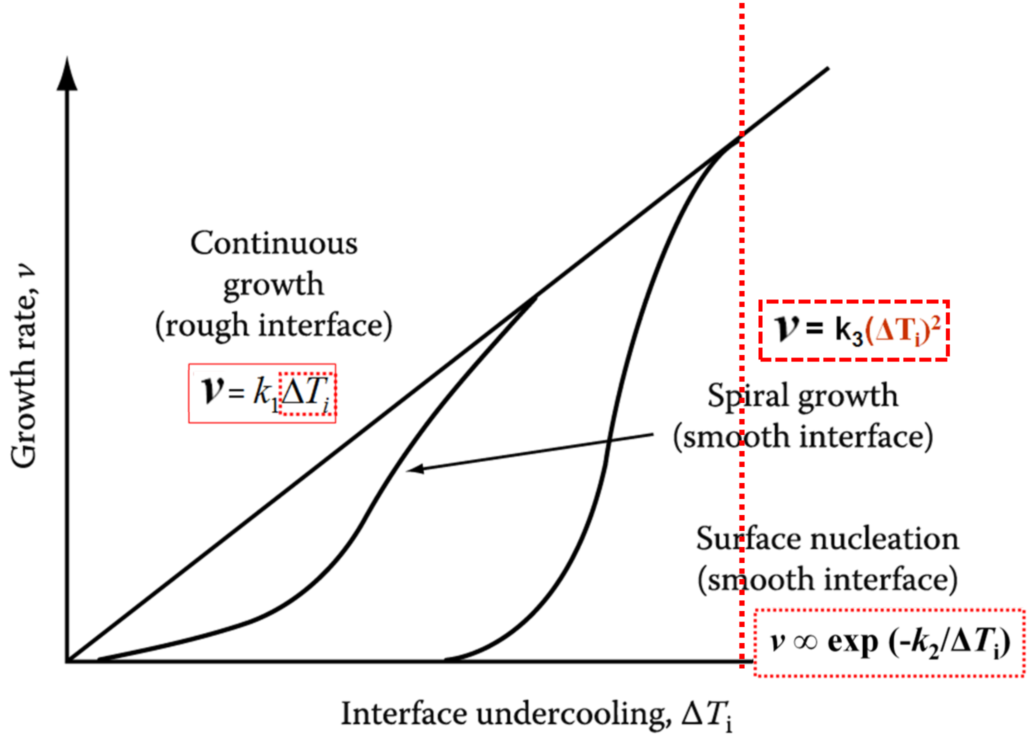
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ⟷ Large ΔT → cellular/dendritic growth

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

→ kinetic roughening

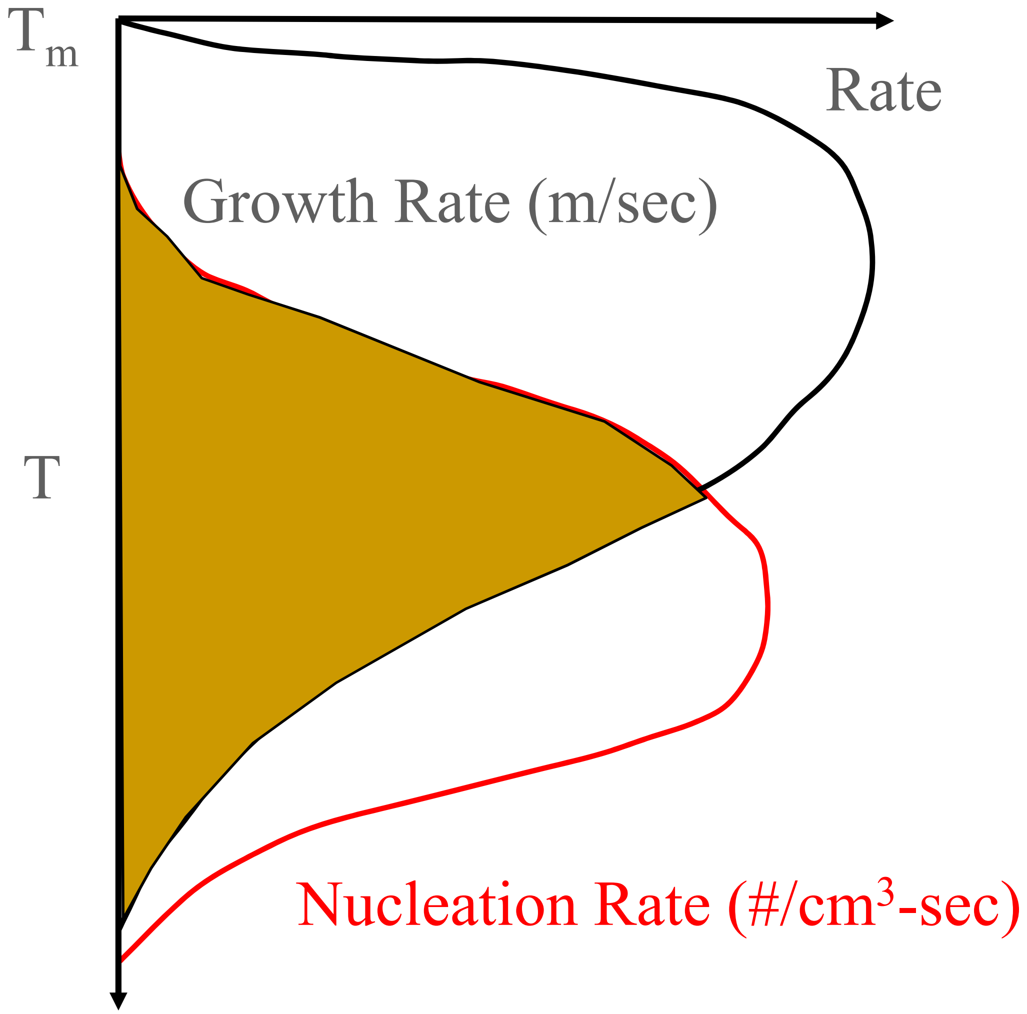


Nucleation and Growth Control R_c

- Poor glass formers:
  - Liquids which quickly form large numbers of nuclei close to T_m
  - That grow very quickly

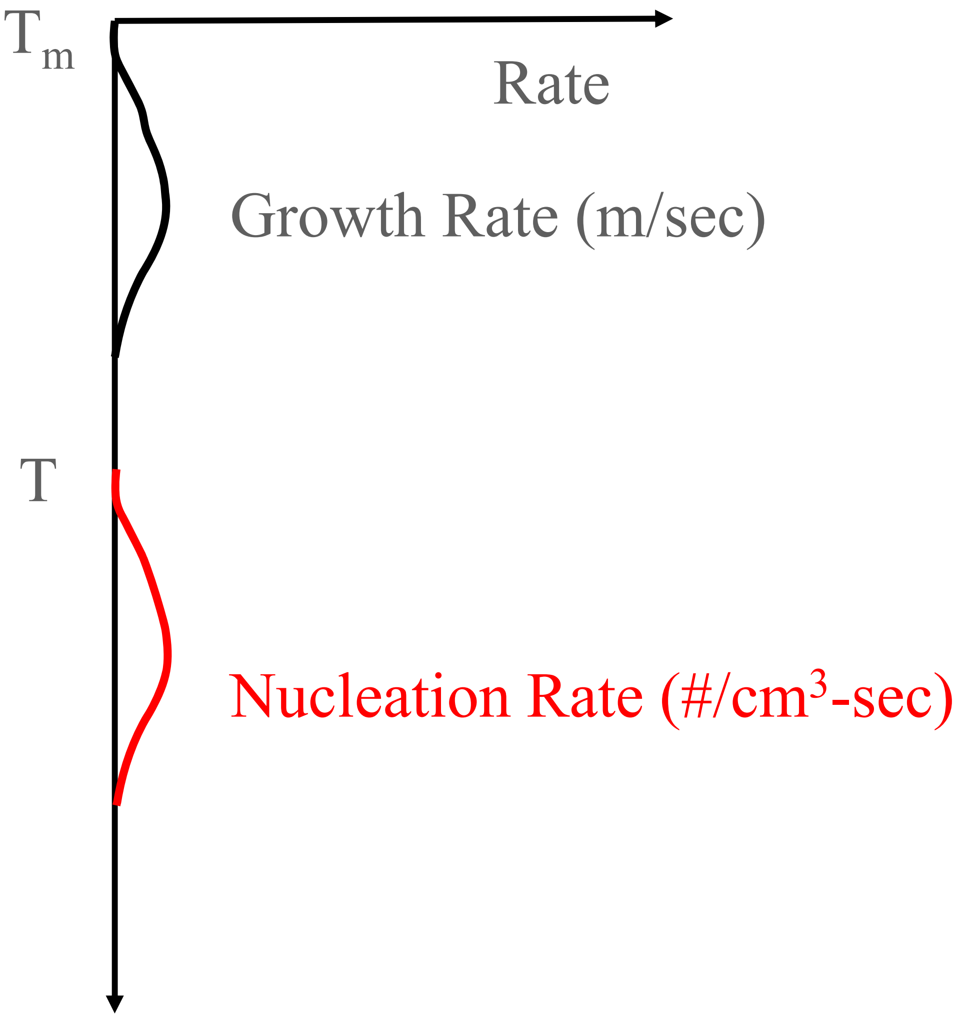
- Good glass formers
  - Liquids that are sluggish to form nuclei even far below T_m
  - That grow very slowly

Nucleation and Growth Rates – Poor Glass Formers



- Strong overlap of growth and nucleation rates
- Nucleation rate is high
- Growth rate is high
- Both are high at the same temperature

Nucleation and Growth Rates – Good Glass Formers



- No overlap of growth and nucleation rates
- Nucleation rate is small
- Growth rate is small
- At any one temperature one of the two is zero

Q3: Classical Nucleation Theory–TTT diagram

Nucleation Rate Theory

- Rate at which atoms or ions in the liquid organize into microscopic crystals, nuclei

- I = number of nuclei formed per unit time per unit volume of liquid

- Nucleation Rate (I) $\propto$ number density of atoms x
  fastest motion possible x
  thermodynamic probability of formation x
  diffusion probability

Nucleation Rate Theory

$$I = \underbrace{n}_{\text{Number density}}\underbrace{\nu}_{\text{Fastest motion}}\underbrace{\exp(-NW^{*}/RT)}_{\text{Thermodynamic probability}}\underbrace{\exp(-\Delta E_D/RT)}_{\text{Diffusion probability}}$$

n = number density of atoms, molecules, or formula units per unit volume

= ρ N/Atomic, molecular, formula weight

ν = vibration frequency ~ 10^{13} sec^{-1}

N = Avogadro's number

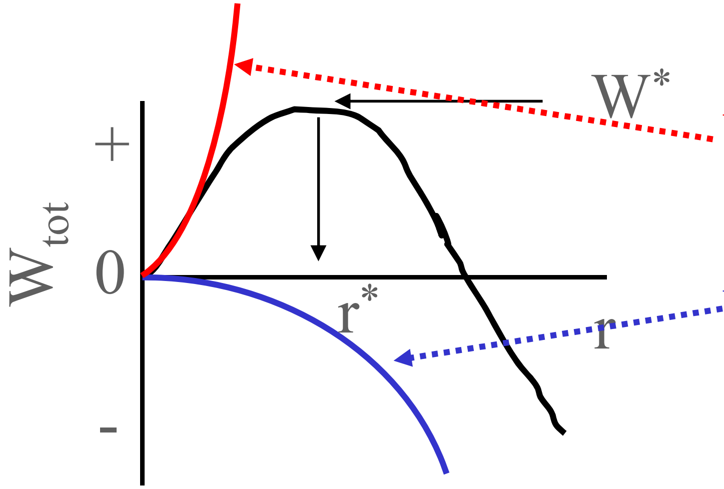
= 6.023×10^{23} atoms/mole

W^{*} = thermodynamic energy barrier to form nuclei

ΔE_D = diffusion energy barrier to form nuclei

~ viscosity activation energy

Nucleation Rate – Thermodynamic barrier W*



$W_S = 4\pi r^2\sigma,$ surface

σ is the surface energy

$W_B = 4/3\pi r^3 \Delta G_{crsyt}(T),$ bulk

$\Delta G_{cryst}(T)$, the Gibb's Free-Energy

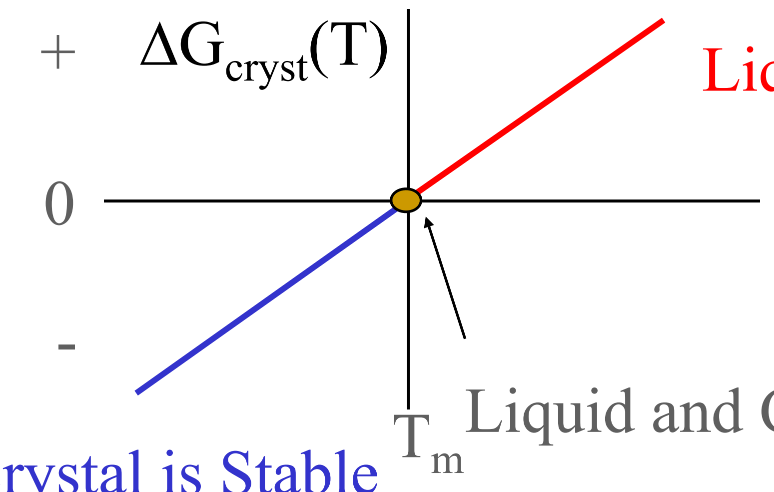
of Cryst. per unit volume, V_m

$$W_{tot} = W_S + W_B$$

- At r^*, $(\partial W(r)/ \partial r)_{r=r^*} = 0$
- $r^* = - 2\sigma/ \Delta G_{cryst}(T)$
- $W(r^*) \equiv W^* = 16\pi\, \sigma^3/3(\Delta G_{cryst}(T))^2$

Nucleation Rate I(T)

- $I = n\nu\exp(-N\ 16\pi\ \sigma^3/3(\Delta G_{crsyt}(T))^2\ /RT)\exp(-\Delta E_D/RT)$
- $\Delta G_{cryst}(T) = \Delta H_{cryst}(T_m)(1 - T/T_m)/V_m \equiv \Delta H_{cryst}(T_m)(\Delta T_m/T_m)$



Liquid is Stable

Liquid and Crystal are in equilibrium

Crystal is Stable

Approx. for σ:

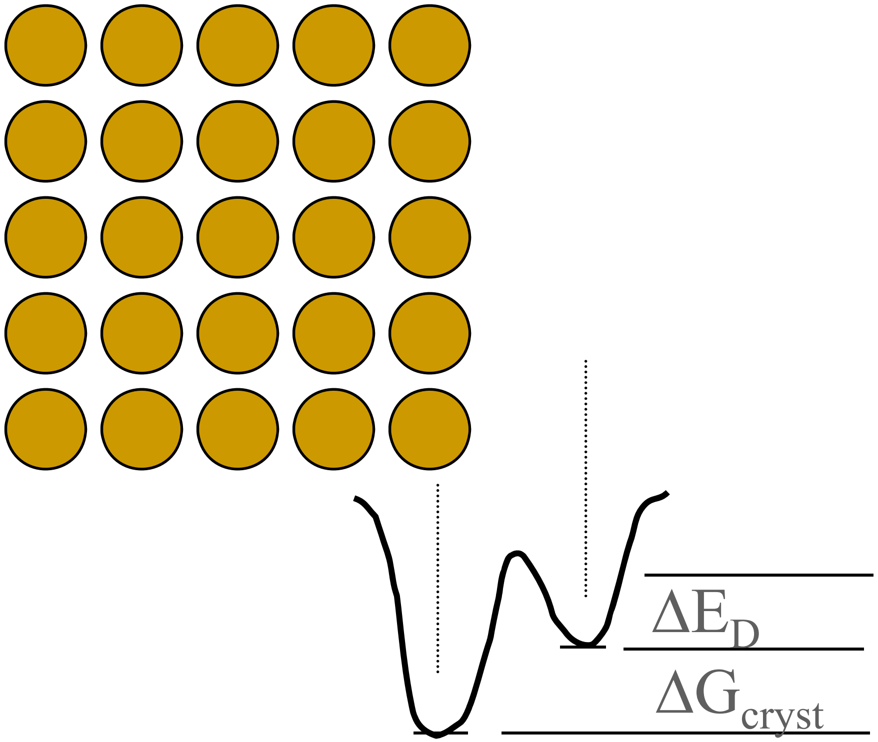
$\sigma \sim 1/3\Delta H_{melt}/N^{1/3}V_m^{2/3}$

note $\Delta H_{melt} = -\Delta H_{cryst}$

$$I = n\nu\exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

Growth Rates - $\mu(T)$

- Crystal growth requires
  - Diffusion to the nuclei surface
  - Crystallization onto the exposed crystal lattice



$$\nu_{l\rightarrow c} = \nu \exp(-\Delta E_D/RT)$$
$$\nu_{c\rightarrow l} = \nu \exp(-(\Delta E_D - \Delta G_{cryst})/RT)$$

$$\nu_{net} = \nu_{l\rightarrow c} - \nu_{c\rightarrow l} =$$

$$\nu \exp(-\Delta E_D/RT) -$$
$$\nu \exp(-(\Delta E_D - \Delta G_{cryst})/RT)$$

$$\mu = a\,\nu_{net} = a\,\nu \exp(-\Delta E_D/RT) \times$$
$$(1 - \exp(\Delta G_{cryst})/RT)$$

Growth Rates - μ(T)

Diffusion coefficient, D

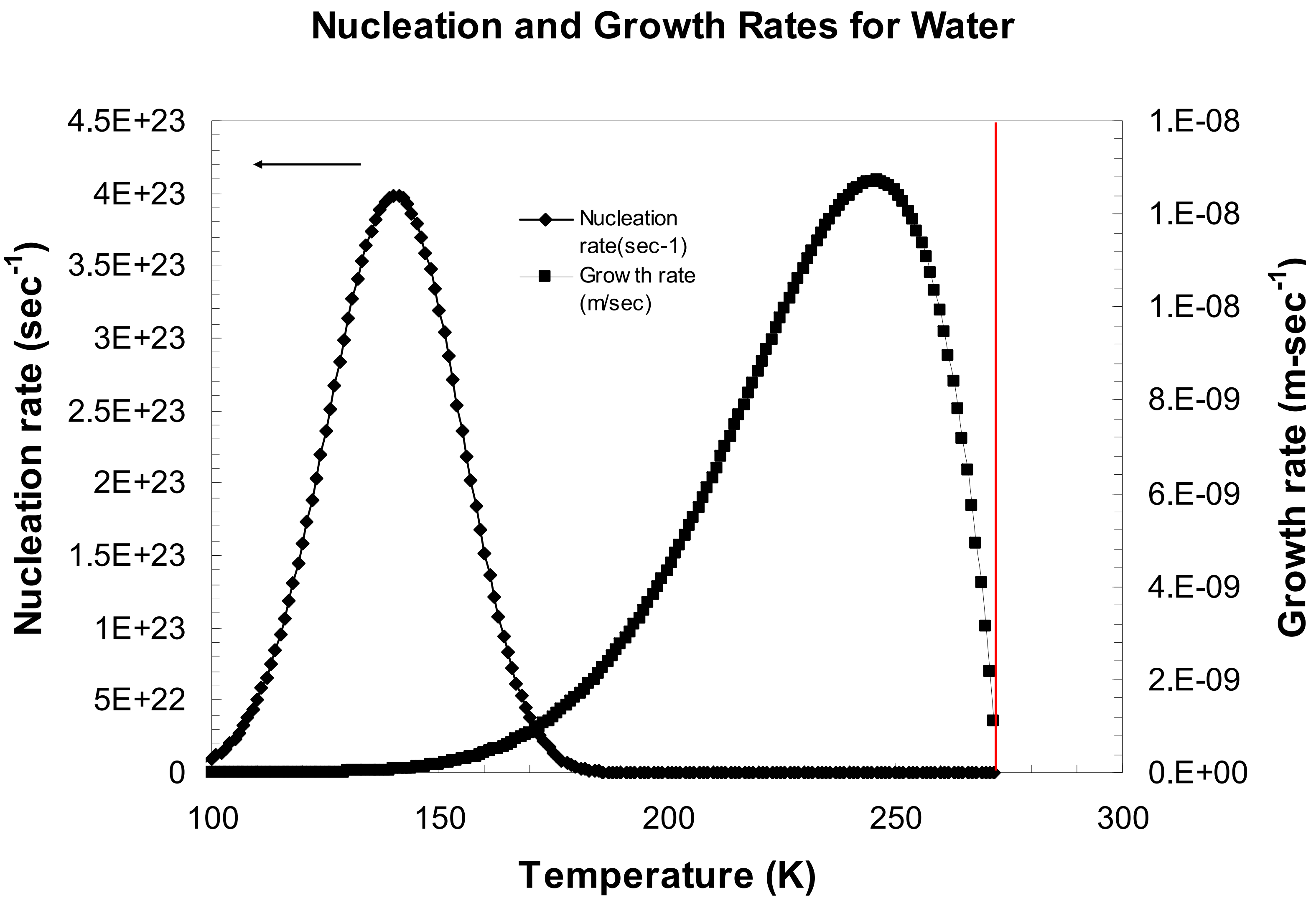
$$D(T) = a^2 \nu \exp\left[\frac{-\Delta E_D}{RT}\right] = \left(\frac{fRT}{3N\pi a\,\eta(T)}\right)$$

Stokes-Einstein relation between D and η

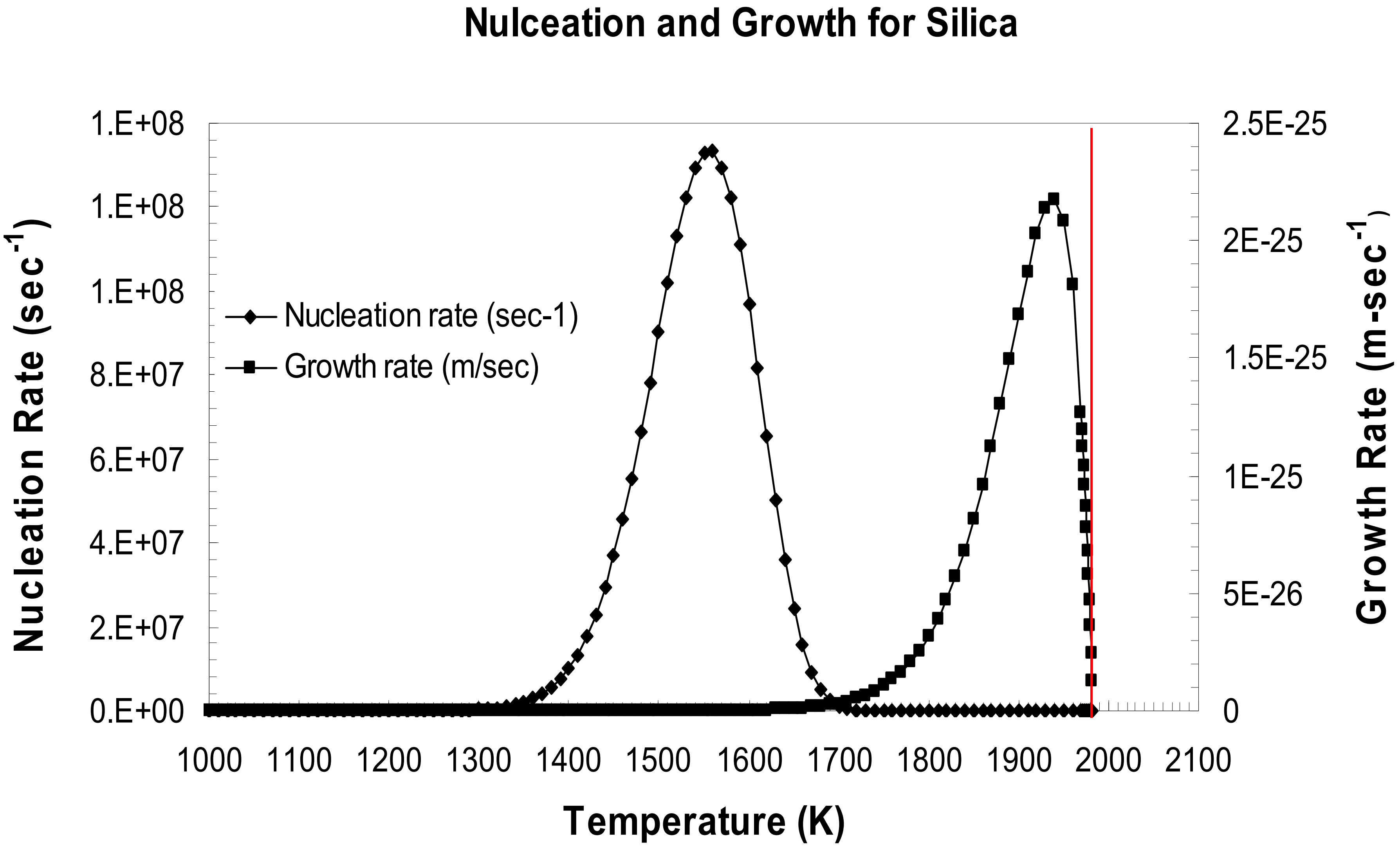
Hence:

$$\boxed{\mu(T) = \left(\frac{fRT}{3N\pi a^2 \eta(T)}\right)\left(1 - \exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)}$$

Nucleation and Growth Rates



Nucleation and Growth Rates



Time–Temperature–Transformation Curves (TTT)

- How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?

- $f(t,T) \sim \pi \underline{I(T)} \underline{\mu(T)^3} t^4/3$

where *f* is the fractional volume of crystals formed, typically taken to be 10^{-6}, a barely observable crystal volume.

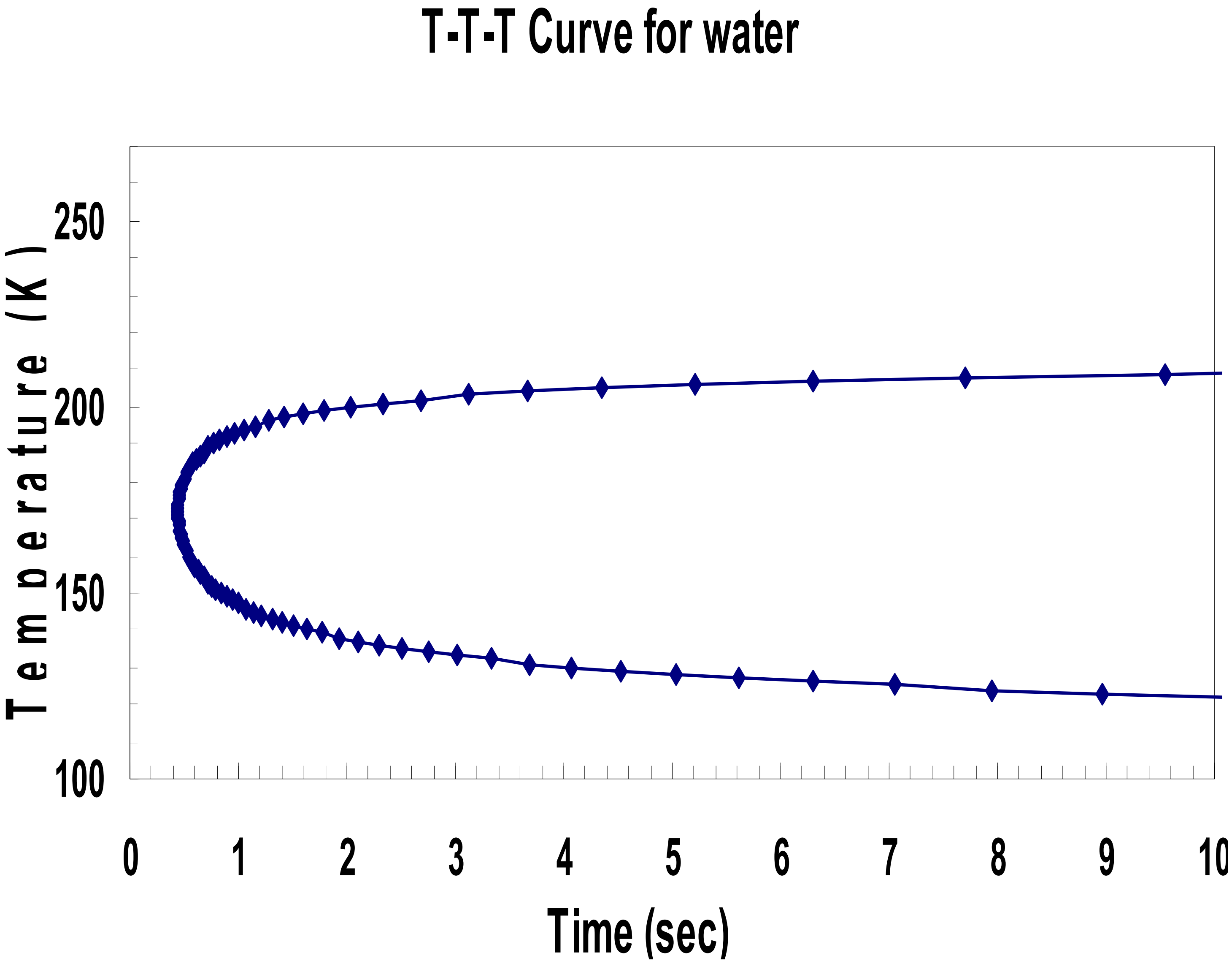
Nucleation rates

$$I = n\nu \exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

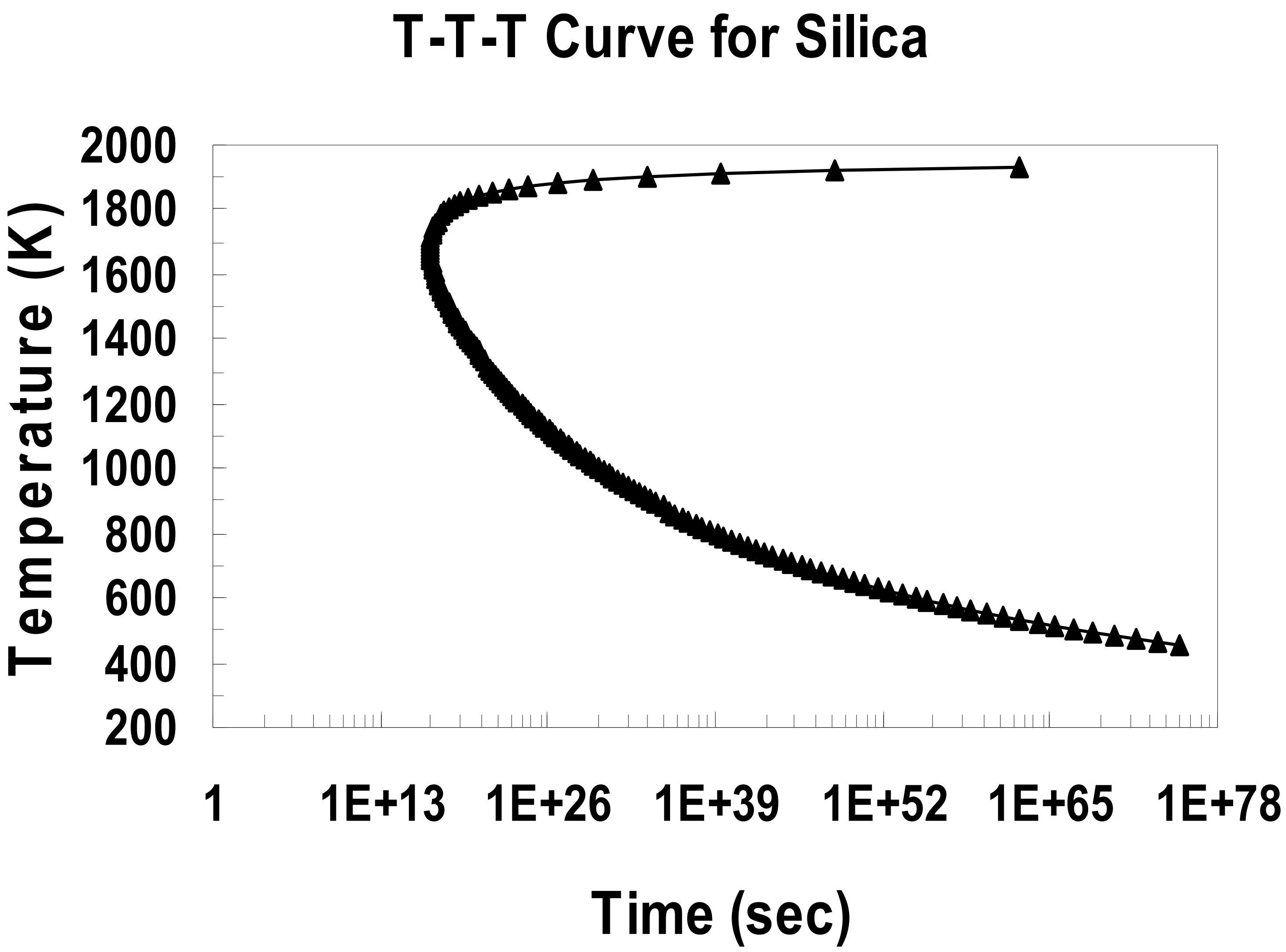
Growth rates

$$\mu(T) = \left(\frac{fRT}{3N\pi a^2\eta(T)}\right)\left(1-\exp\left[\left(\frac{\Delta H_m}{RT}\right)\left(\frac{\Delta T}{T_m}\right)\right]\right)$$

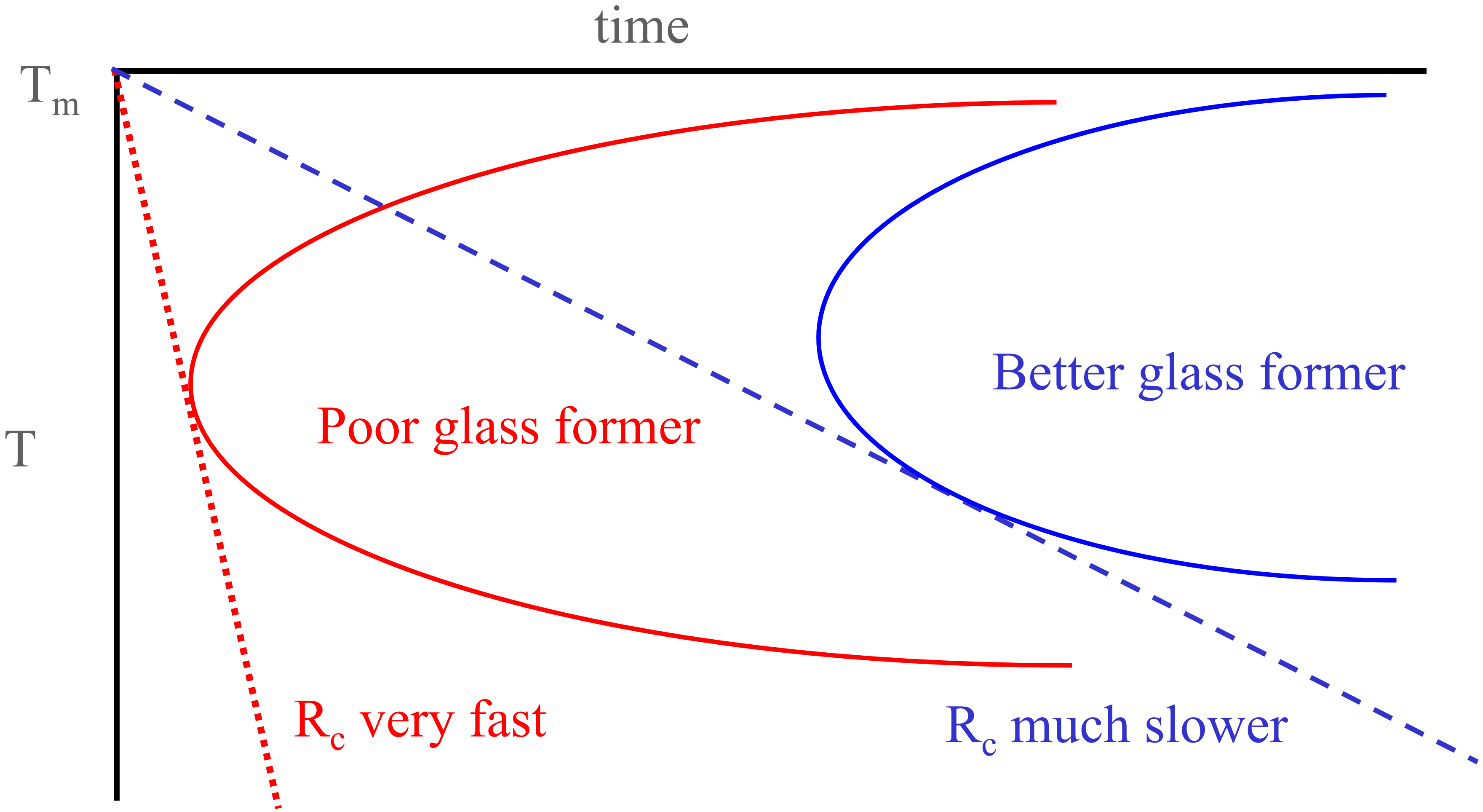
Time Transformation Curves for Water

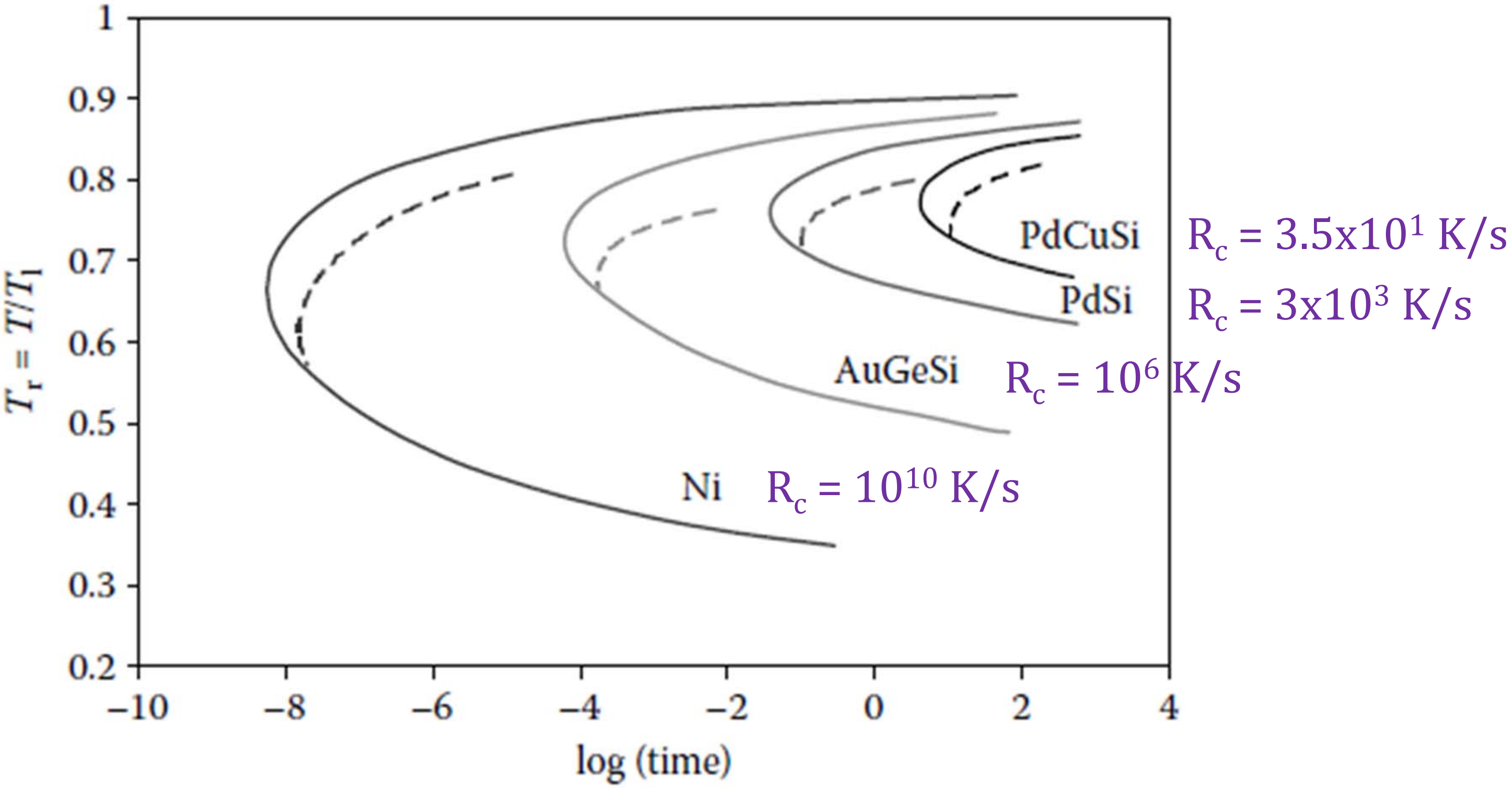


Time Transformation Curves for Silica



TTT curves and the critical cooling rate, R_c





$R_c = 3.5 \times 10^1$ K/s

$R_c = 3 \times 10^3$ K/s

$R_c = 10^6$ K/s

$R_c = 10^{10}$ K/s

FIGURE 2.3
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

Q4: Overall Transformation Kinetics–TTT diagram

“Johnson-Mehl-Avrami Equation”

5.4 Overall Transformation Kinetics – TTT Diagram

If isothermal transformation,

The fraction of Transformation as a function of Time and Temperature

$\rightarrow \; f(t,T)$

Plot f vs log t.

- isothermal transformation
- f ~ volume fraction of β at any time; 0~1

Plot the fraction of transformation (1%, 99%) in T-log t coordinate.

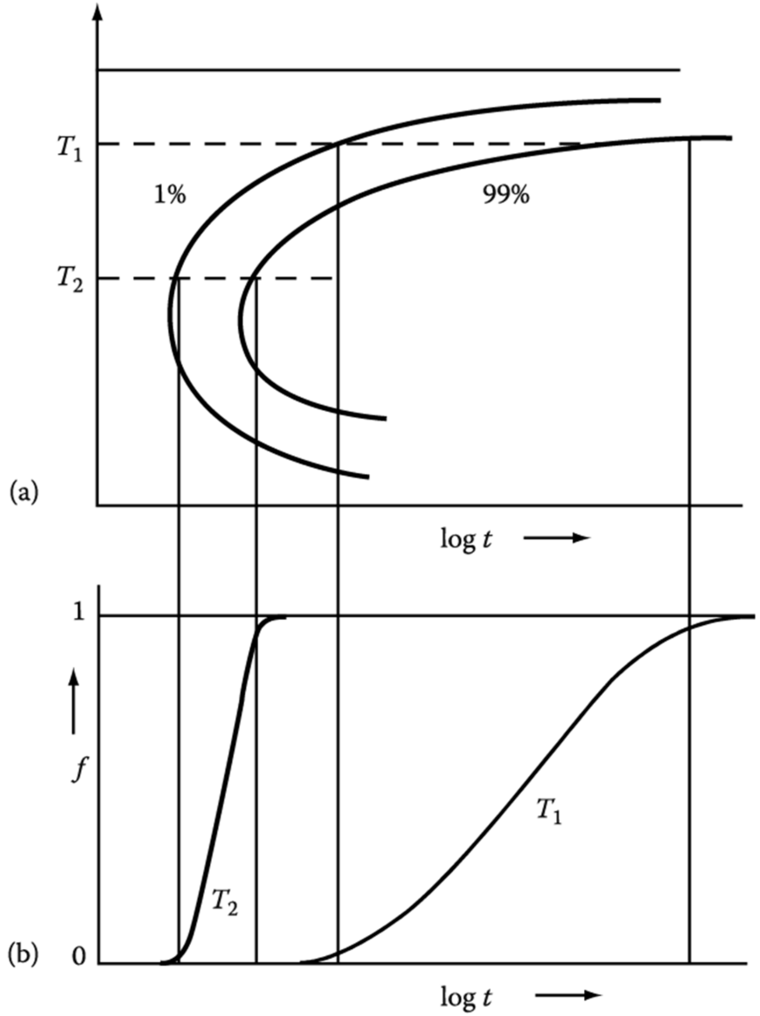
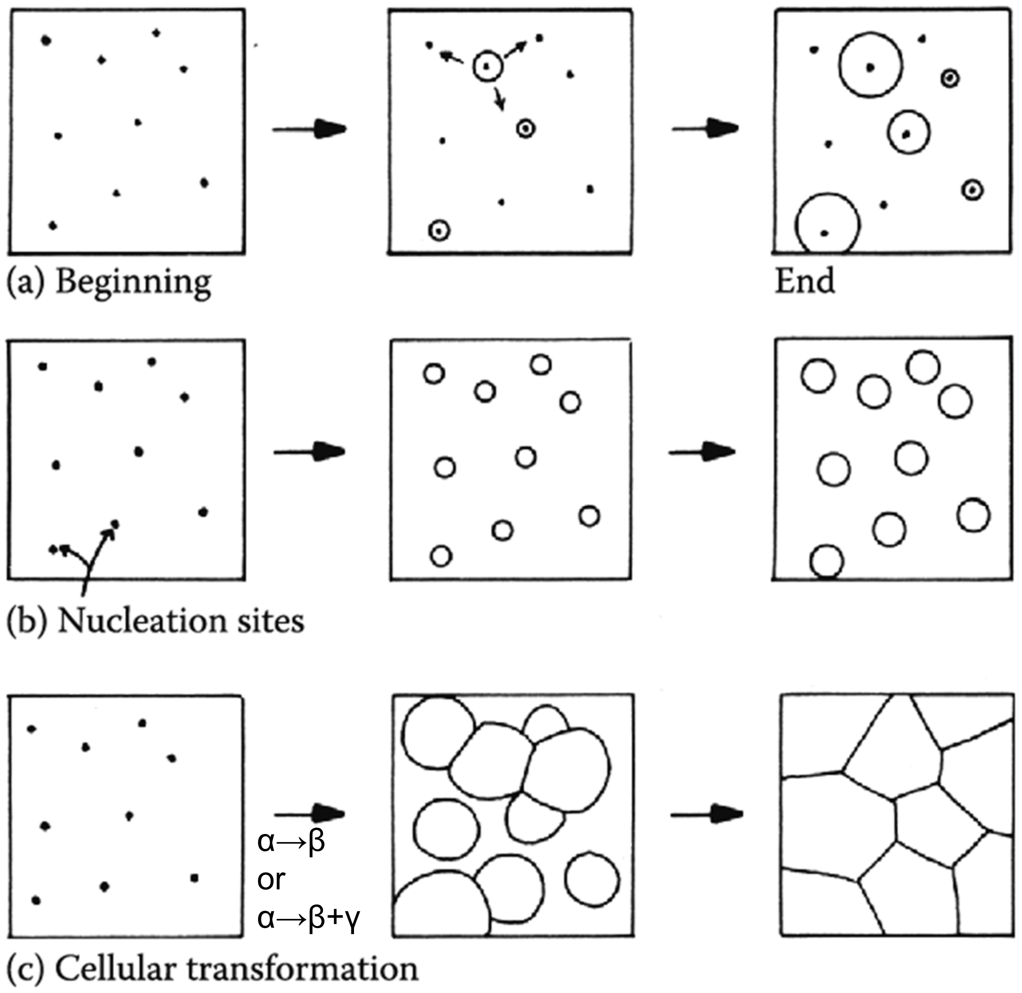


Fig. 5.23 The percentage transformation versus time for different transformation temperatures.

Influence factors for f(t,T): nucleation rate, growth rate, density and distribution of nucleation sites, impingement of adjacent cells

Example,

Three Transformation Types



Wide range of particle sizes

Fig. 5.24 (a) Nucleation at a constant rate during the whole transformation.
(b) Site saturation – all nucleation occurs at the beginning of transformation.
(c) A cellular transformation.

(a) continuous nucleation

Metastable α phase with many nucleation sites by quenching to T_t

→ f depends on the *nucleation rate and the growth rate.*

(b) all nuclei present at t = 0

→ f depends on the *number of nucleation sites and the growth rate.*

(c) All of the parent phase is consumed by the transformation product.

Transformation terminate by the impingement of adjacent cells growing with a constant velocity.

→ pearlite, cellular ppt, massive transformation, recrystallization

α → β

Transformation Kinetics

- Avrami proposed that for a three-dimensional nucleation and growth process kinetic law

$$f = 1 - \exp\left(-kt^{n}\right)$$

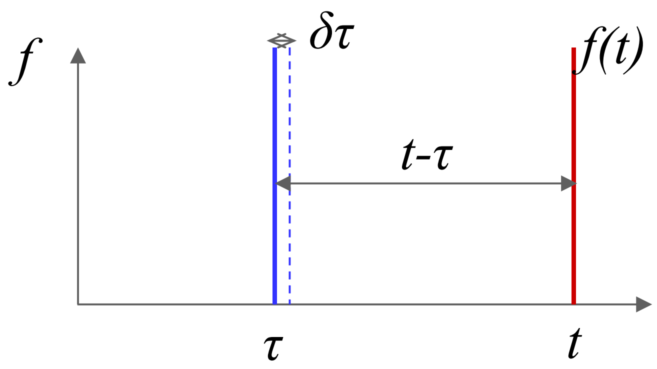
Johnson-Mehl-Avrami equation

f : volume fraction transformed $= \dfrac{\text{Volume of new phase}}{\text{Volume of specimen}}$

- Assumption :
  - √ reaction produces by nucleation and growth
  - √ nucleation occurs randomly throughout specimen
  - √ reaction product grows rapidly until impingement

Constant Nucleation Rate Conditions

- **Nucleation rate (*I*) is constant.**
- **Growth rate (v) is constant.**
- **No compositional change**



$$df_e = \frac{\begin{pmatrix}\text{Vol. of one particle nucleated} \\ \text{during } d\tau \text{ measured at time t}\end{pmatrix} \times \begin{pmatrix}\text{number of nuclei} \\ \text{formed during } d\tau\end{pmatrix}}{\text{Volume of specimen}}$$

$$df_e = \frac{\frac{4}{3}\pi\left[v(t-\tau)\right]^3 \times \left(IV_0 d\tau\right)}{V_0}$$

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\,(vt)^3$$

$$V' = \frac{4}{3}\pi v^3 (t-\tau)^3$$

$$f_e(t) = \int_o^t I \cdot \frac{4}{3}\pi\left[v(t-\tau)\right]^3 d\tau$$

$$= I \cdot \frac{4}{3}\pi v^3 \left[-\frac{1}{4}(t-\tau)^4\right]_0^t = \boxed{\frac{1}{3}\pi I v^3 t^4}$$

- do not consider impingement & repeated nucleation
- only true for $f \ll 1$

As time passes the β cells will eventually impinge on one another and the rate of transformation will decrease again.

Constant Nucleation Rate Conditions

- consider impingement + repeated nucleation effects

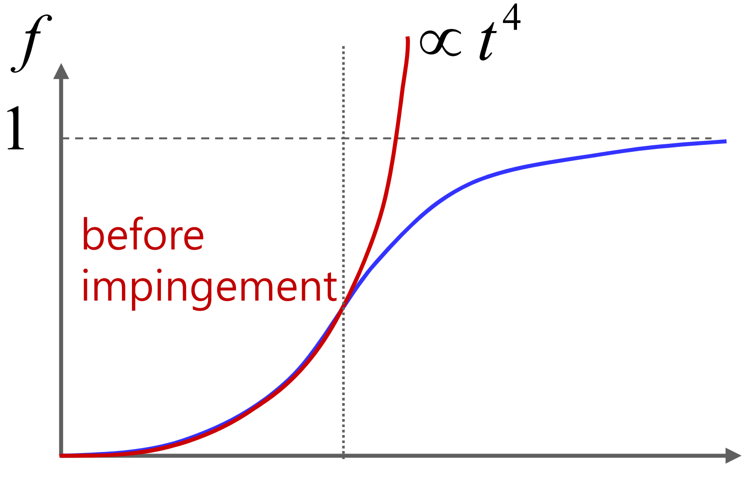
$$df = (1-f)\,df_e \qquad \longrightarrow \qquad df_e = \frac{df}{1-f}$$

$$f_e = -\ln(1-f)$$

$$f(t) = 1-\exp(-f_e(t)) = 1-\exp\left(-\frac{\pi}{3}Iv^3t^4\right)$$

* Short time:
1-exp(z)~Z (z ≪1)

* Long time:
t→∞, $f \to 1$



Johnson-Mehl-Avrami Equation

$$f = 1-\exp(-kt^n)$$

k: T sensitive $f(I, v)$ $\qquad -\frac{\pi}{3}Iv^3$

n: 1 ~ 4 (depend on nucleation mecnanism)

Growth controlled. **Nucleation-controlled.**

If no change of nucleation mechanism during phase transformation, n is not related to T.

i.e. 50% transform

Exp (-0.7) = 0.5

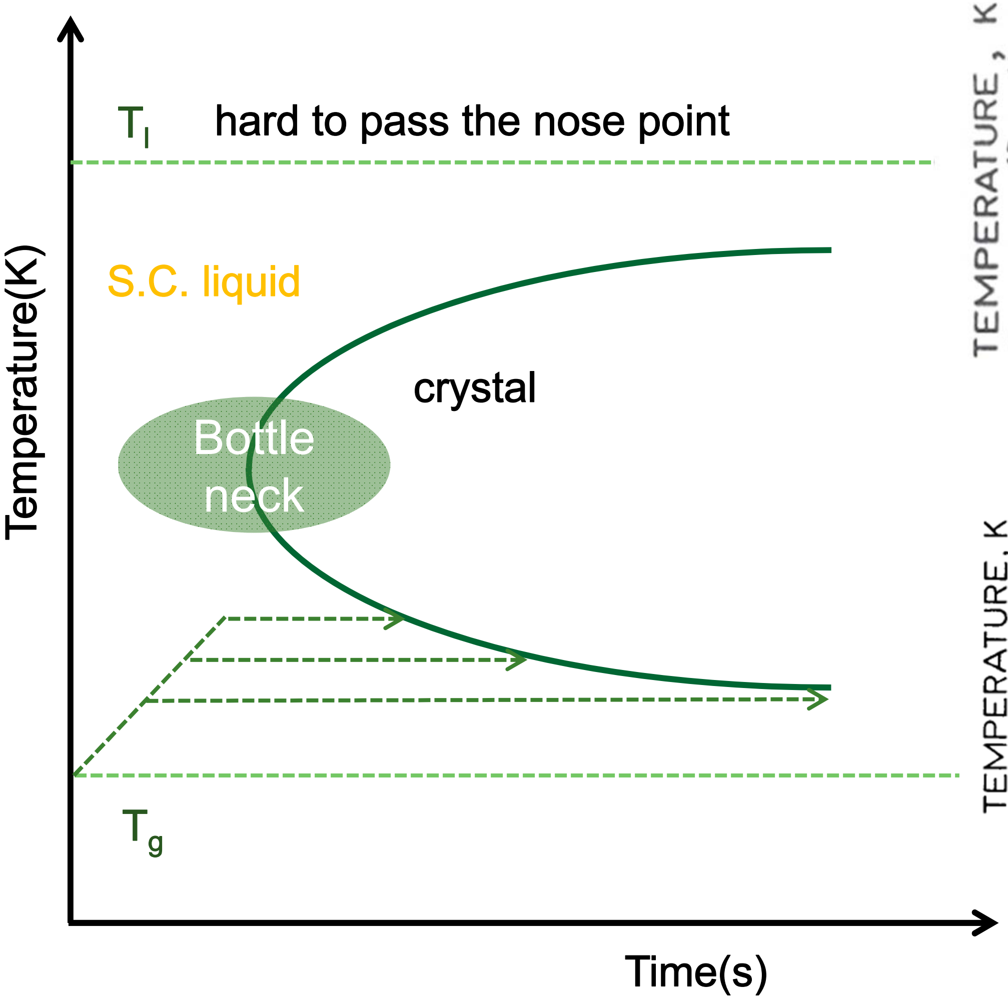
$$kt_{0.5}^n = 0.7 \qquad t_{0.5} = \frac{0.7}{k^{1/n}} \quad \xRightarrow{\frac{\pi}{3}Iv^3} \quad t_{0.5} = \frac{0.9}{N^{1/4}v^{3/4}}$$

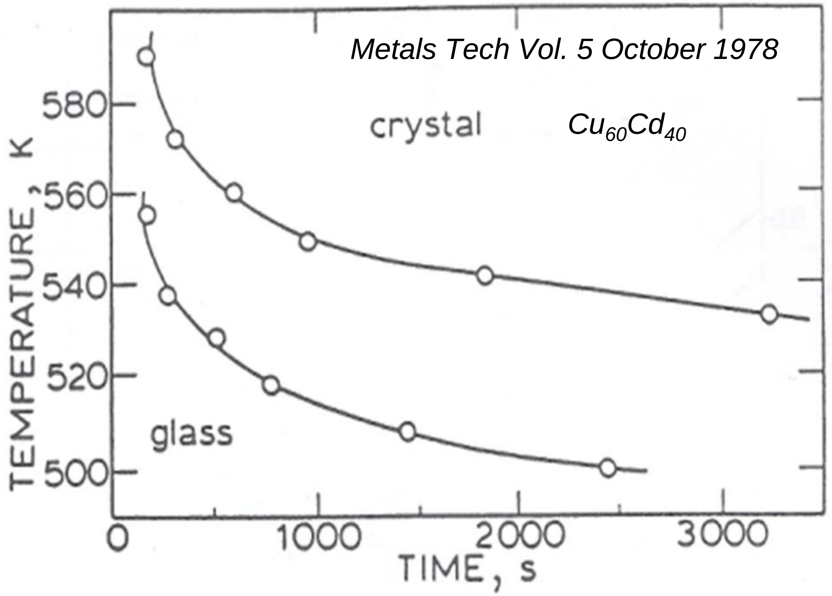
Rapid transformations are associated with (large values of k), or (rapid nucleation and growth rates)

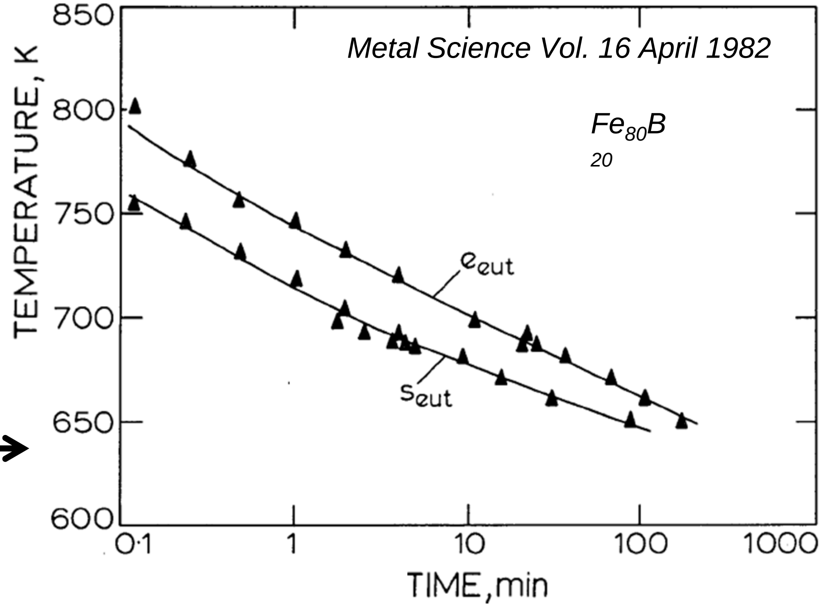
Q5: Measurement of TTT diagram

Measurement of TTT Diagram during Heating by DSC/DTA

Measuring lower part of TTT diagram

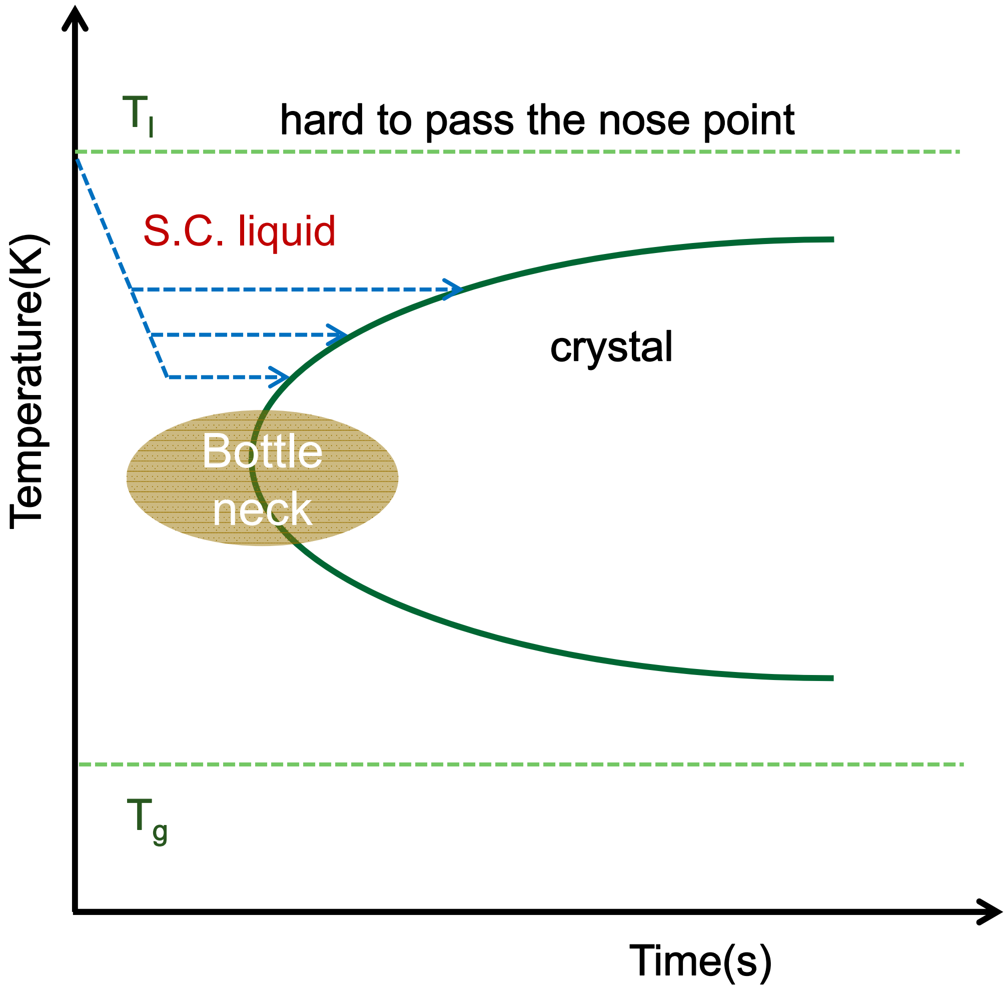



Metals Tech Vol. 5 October 1978

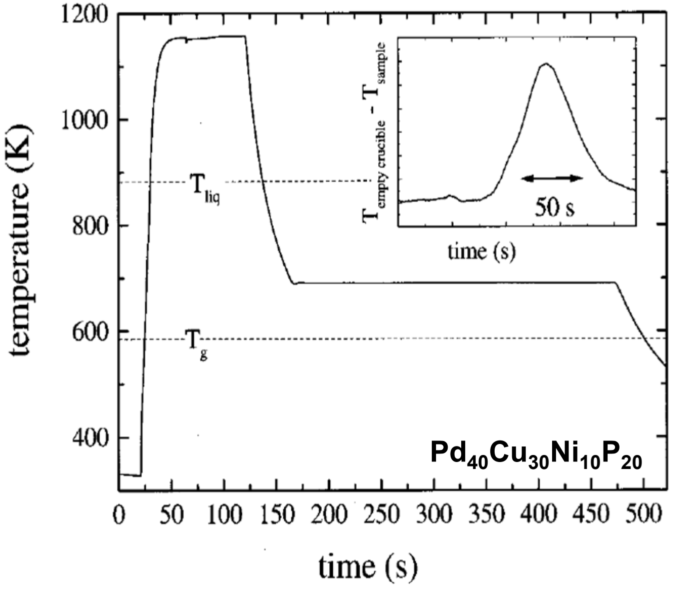

Metal Science Vol. 16 April 1982

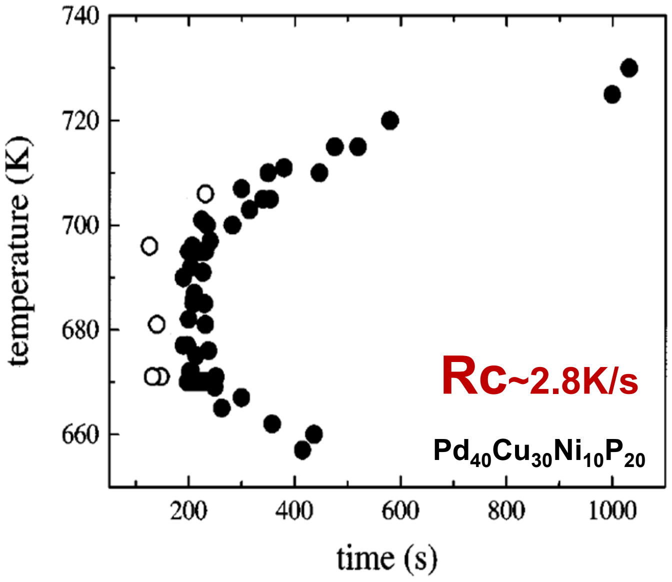
Measurement of TTT Diagram during Heating by DSC/DTA

Measuring upper part of TTT diagram



Appl. Phys. Lett., vol. 77, No. 8, 32 August 2000





Calculation of Time-Temperature-Transformation Diagram

Nucleation Rate

$$I = n\nu\exp(-NW^*/RT)\exp(-\Delta E_D/RT)$$

W^*: thermodynamic energy barrier to form nuclei

$$W^* = 16\pi\sigma^3/3(\Delta G_{cryst}(T))^2$$

$$I = n\ \nu\ \exp(-16\pi\sigma^3/3(\Delta G_{cryst}(T))^2/RT)\ \exp(-\Delta E_D/RT)$$

Growth rate

$$\mu = a\nu\exp(-\ \Delta E_D/RT)\ \mathrm{x}\ (1 - \exp(\Delta G_{cryst})/RT)$$

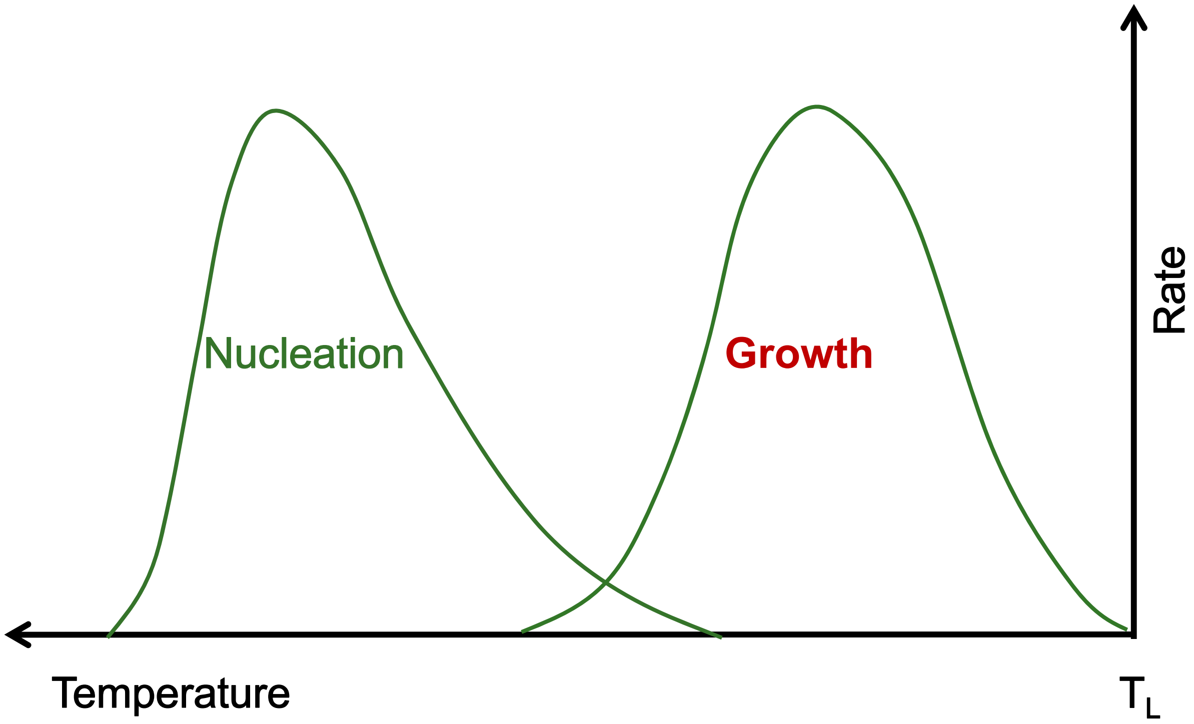
D : diffusion coefficient

E_D :diffusion energy barrier to form nuclei

$$D(T)= a^2\nu\exp(-\ \Delta E_D/RT) =fRT/3N\pi a^2\eta(T))$$

Stokes-Einstein relation between D and η

$$\mu(T)= (fRT/3N\pi a^2\eta(T))\ (1 - \exp(\Delta G_{cryst})/RT)$$



Calculation of Time-Temperature-Transformation Diagram

Nucleation Rate

$I = n\nu\exp(-NW^*/RT)\exp(-\Delta E_D/RT)$

W*: thermodynamic energy barrier to form nuclei

$W^* = 16\pi\sigma^3/3(\Delta G_{cryst}(T))^2$

$I = n\,\nu\,\exp(-16\pi\sigma^3/3(\Delta G_{cryst}(T))^2/RT)\,\exp(-\Delta E_D/RT)$

Growth rate

$\mu = a\nu\exp(-\Delta E_D/RT) \times (1 - \exp(\Delta G_{cryst})/RT)$

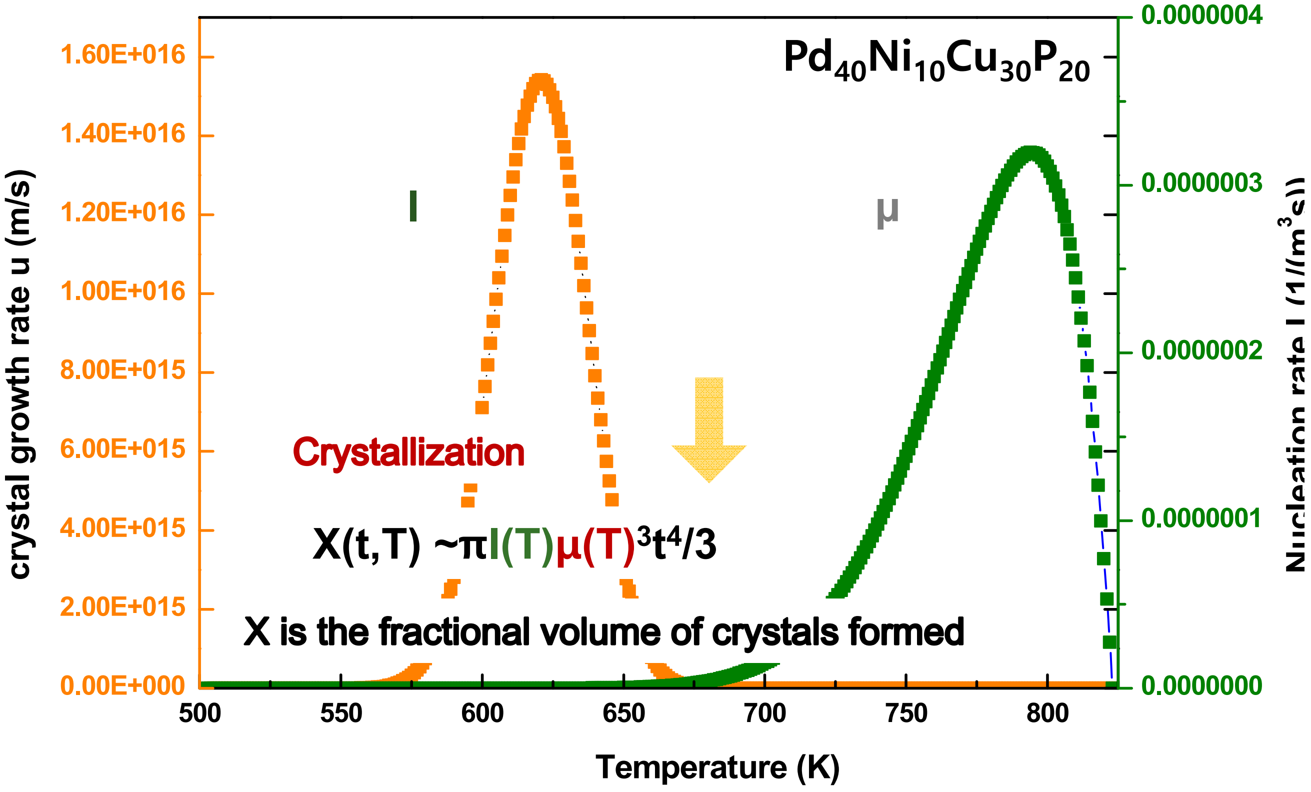
D : diffusion coefficient

E_D :diffusion energy barrier to form nuclei

$D(T) = a^2\nu\exp(-\Delta E_D/RT) = fRT/3N\pi a^2\eta(T))$

Stokes-Einstein relation between D and η

$\mu(T) = (fRT/3N\pi a^2\eta(T))\,(1 - \exp(\Delta G_{cryst})/RT)$



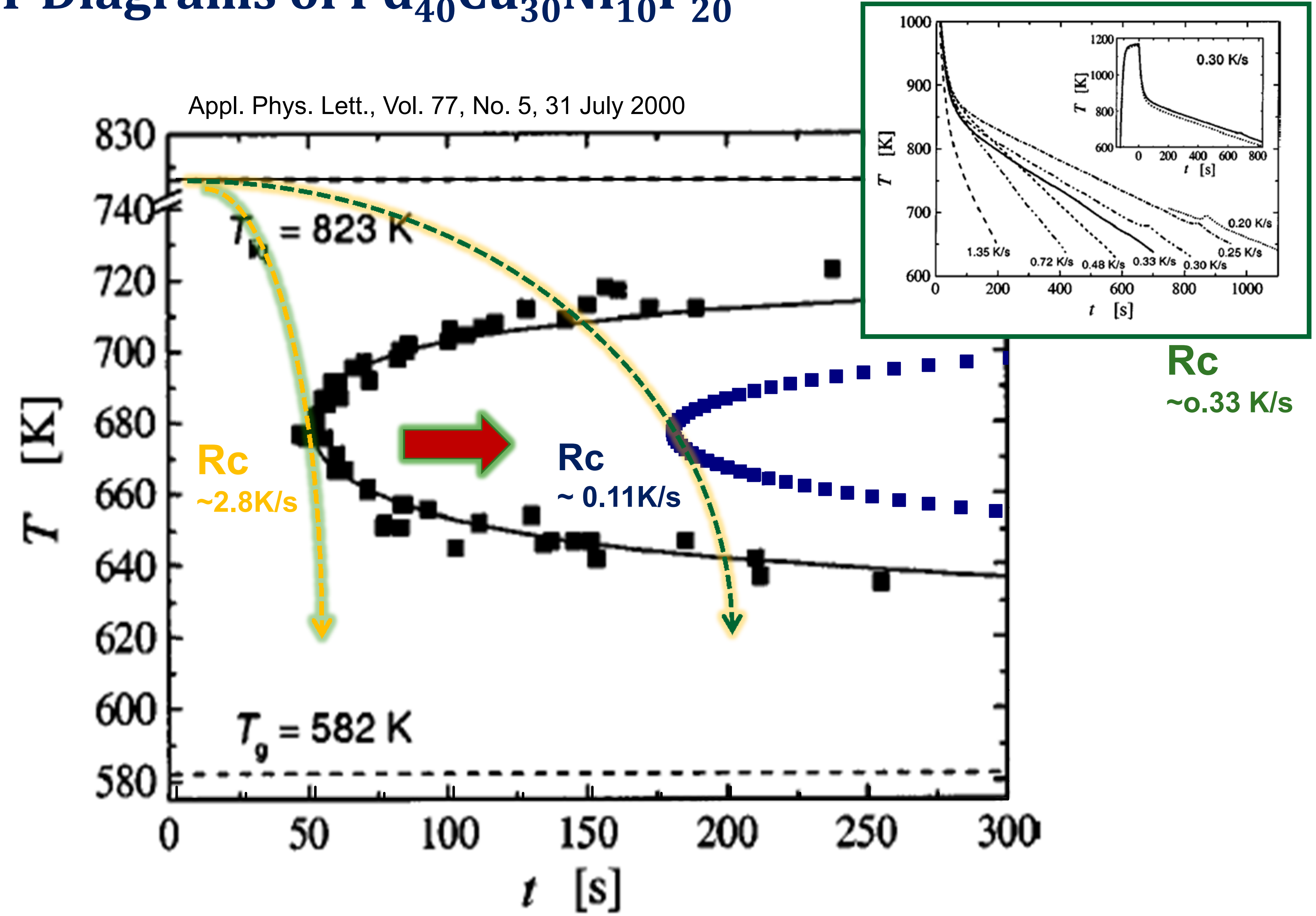
Crystallization

$X(t,T) \sim \pi I(T)\mu(T)^3 t^4/3$

X is the fractional volume of crystals formed

TTT Diagrams of $Pd_{40}Cu_{30}Ni_{10}P_{20}$

Appl. Phys. Lett., Vol. 77, No. 5, 31 July 2000



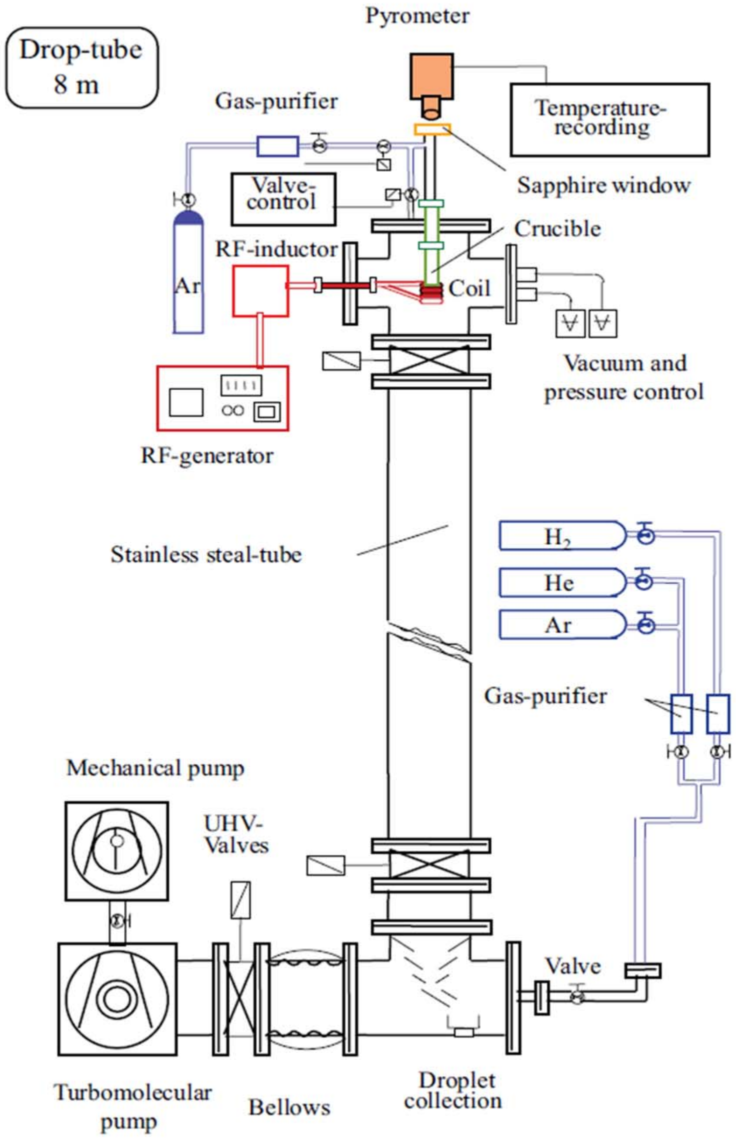
Rc
~2.8K/s

Rc
~ 0.11K/s

Rc
~o.33 K/s

Measurement of TTT Diagram by Drop Tube Technique

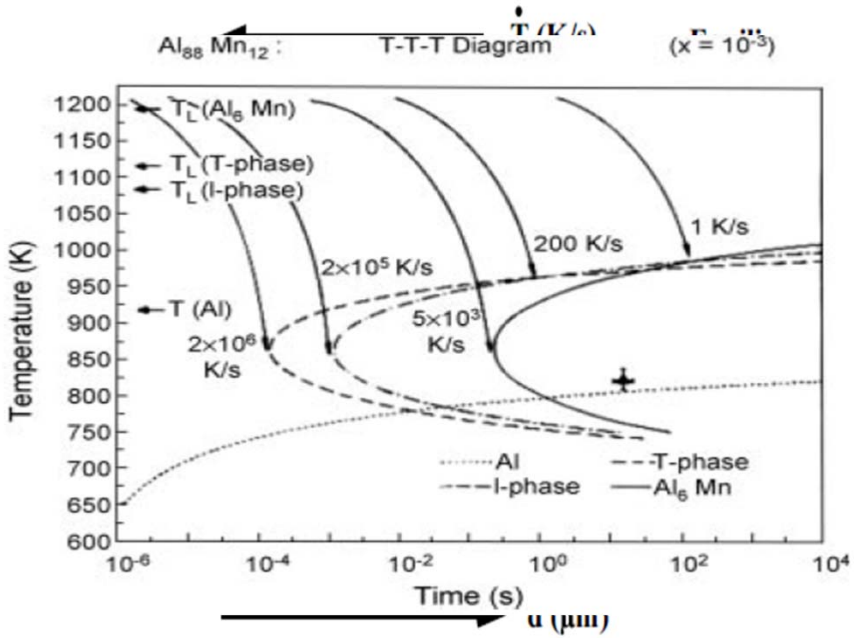
Solidification of containerless undercooled Melts, edited by Dieter M. Herlach and Douglas M. Matson, 2012, p.1-7



- Schematic view of DLR drop tube

Drop tube technique

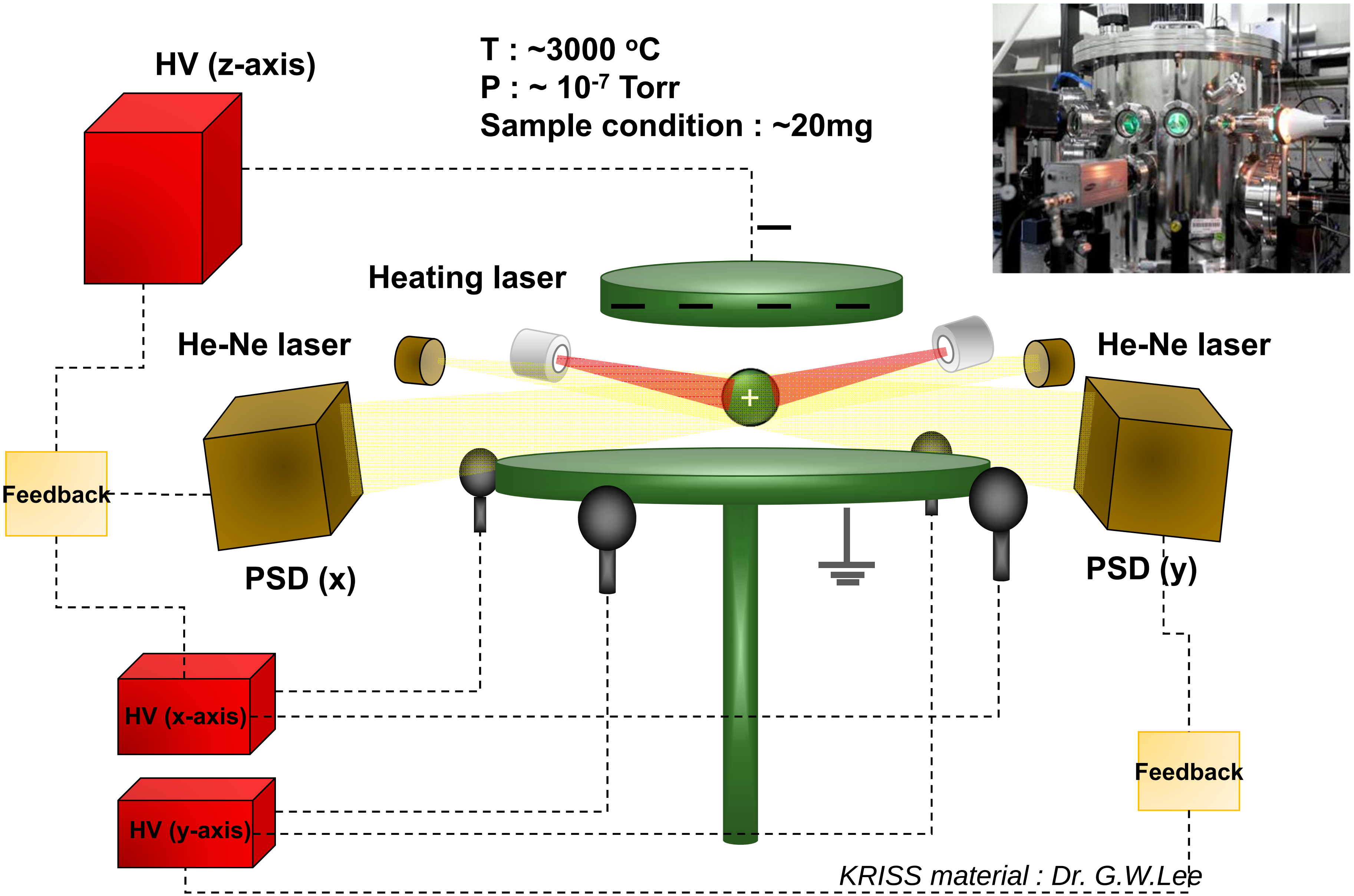
- rapid cooling of small particles
  by dispersion of the melt
- reduction of heterogeneous nucleation
  by containerless processing



- TTT diagrams of the various phases involved in the solidification of undercooled droplets of $Al_{88}Mn_{12}$

Phase mixture in droplets of $Al_{88}Mn_{12}$ alloy as a function of droplet diameter

Electrostatic Levitation in KRISS

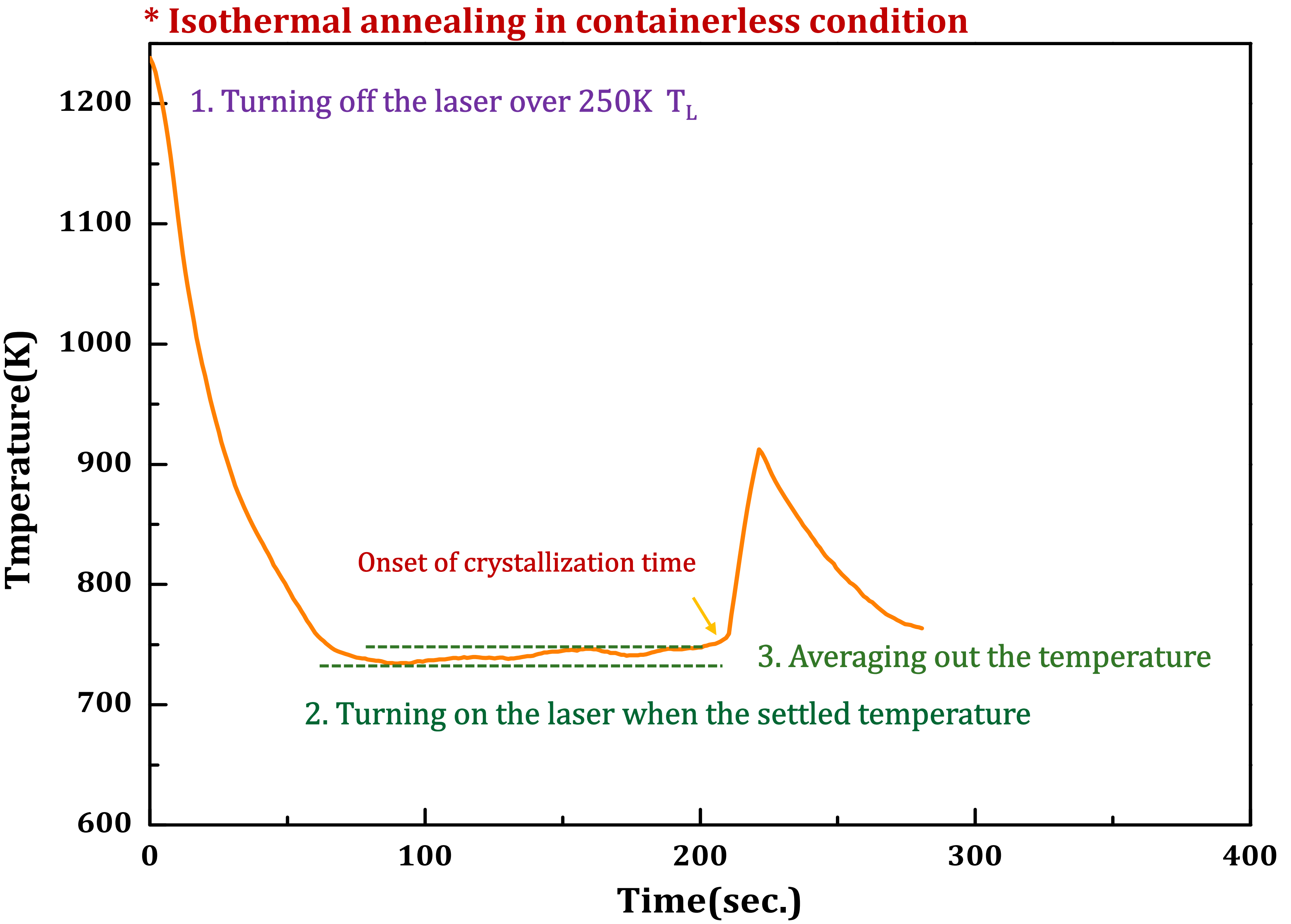


T : ~3000 °C
P : ~ 10^{-7} Torr
Sample condition : ~20mg

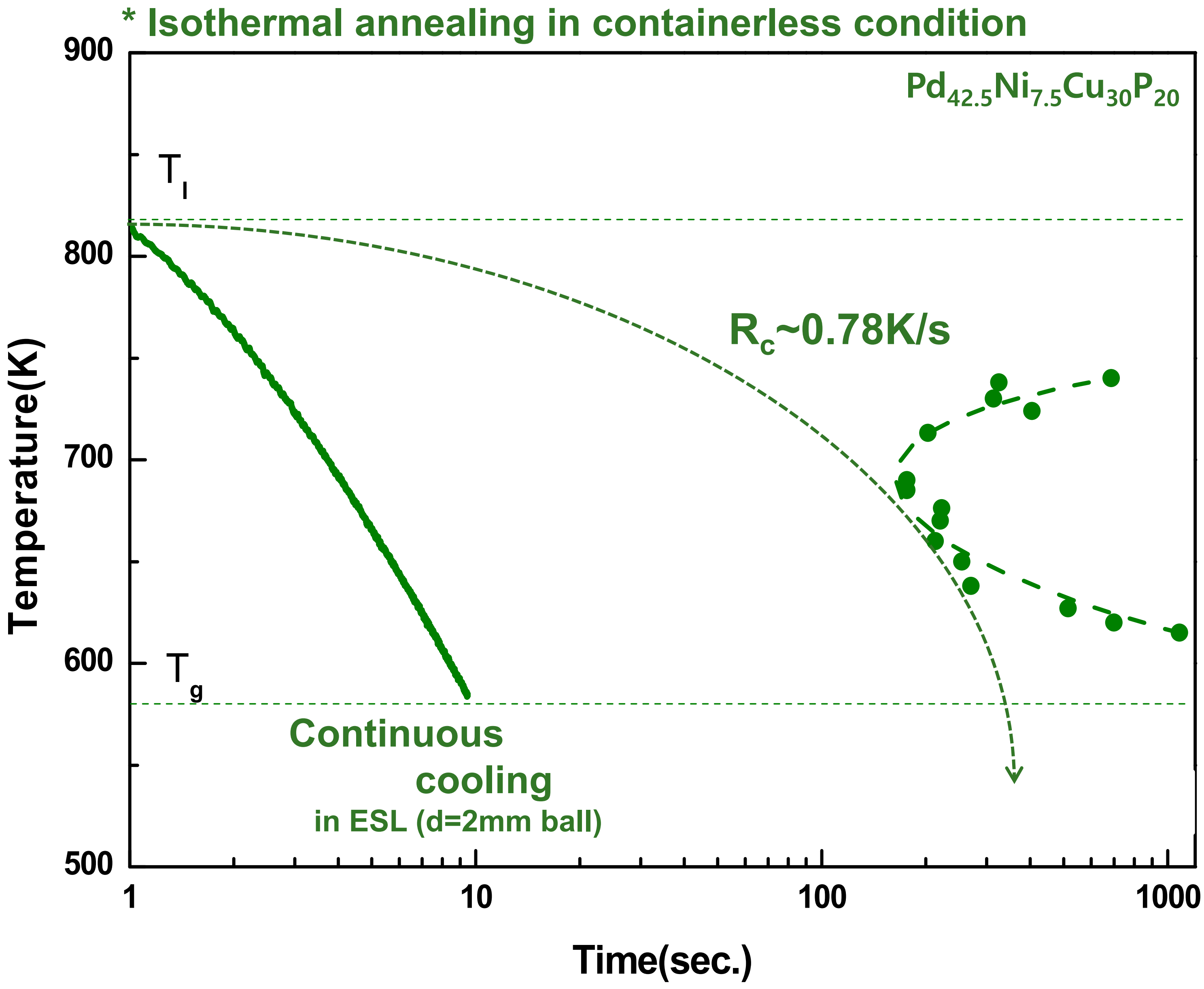
KRISS material : Dr. G.W.Lee

Electrostatic Levitation in KRISS

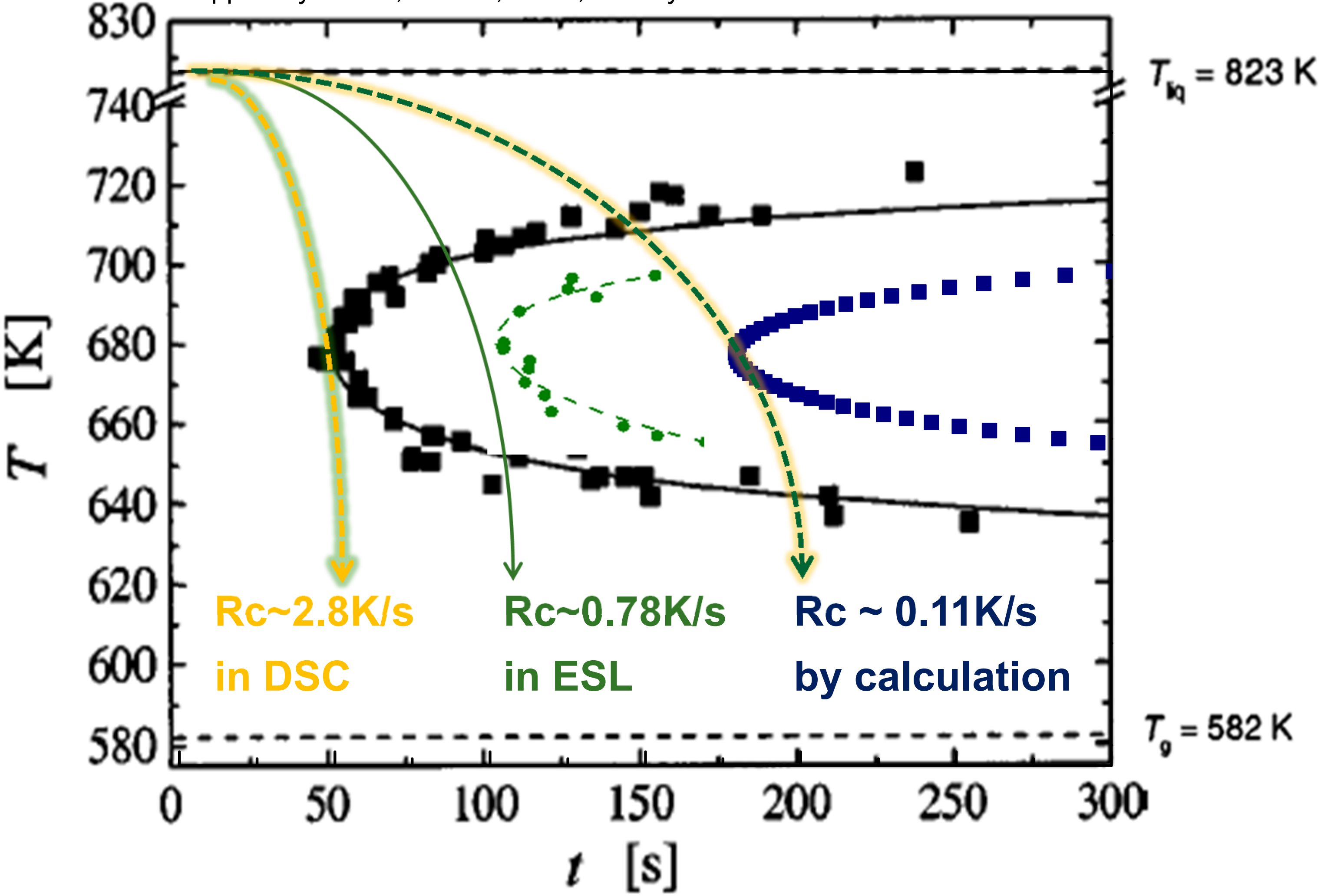
Measurement of TTT Diagram by ESL Technique



TTT Diagram of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



TTT Diagram of $Pd_{40}Cu_{30}Ni_{10}P_{20}$



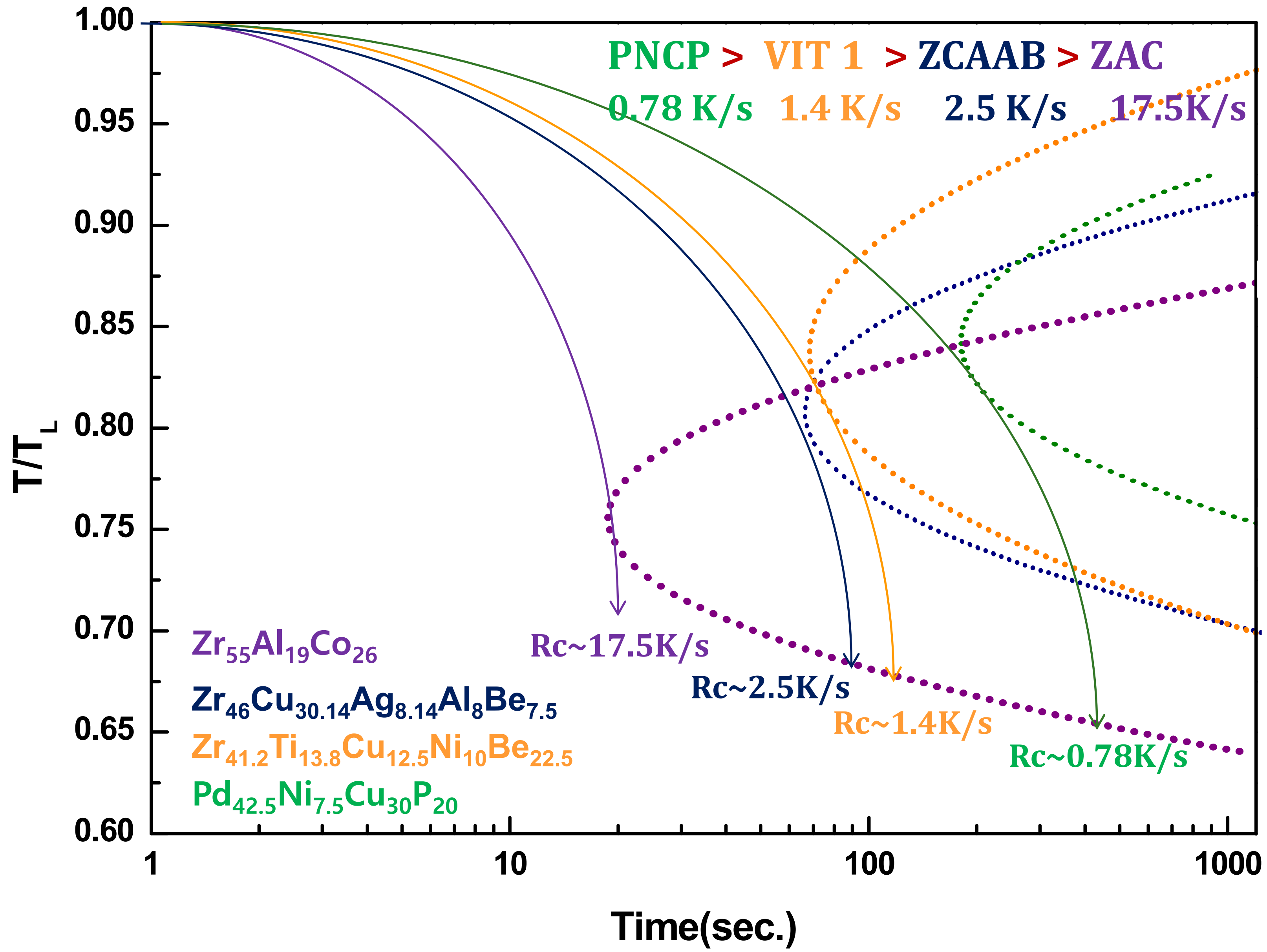
Appl. Phys. Lett., Vol. 77, No. 5, 31 July 2000

Rc~2.8K/s
in DSC

Rc~0.78K/s
in ESL

Rc ~ 0.11K/s
by calculation

Comparison of TTT Diagrams : ZAC > ZCAAB > VIT1 > PNCP



* Time-Temperature-Transformation diagrams

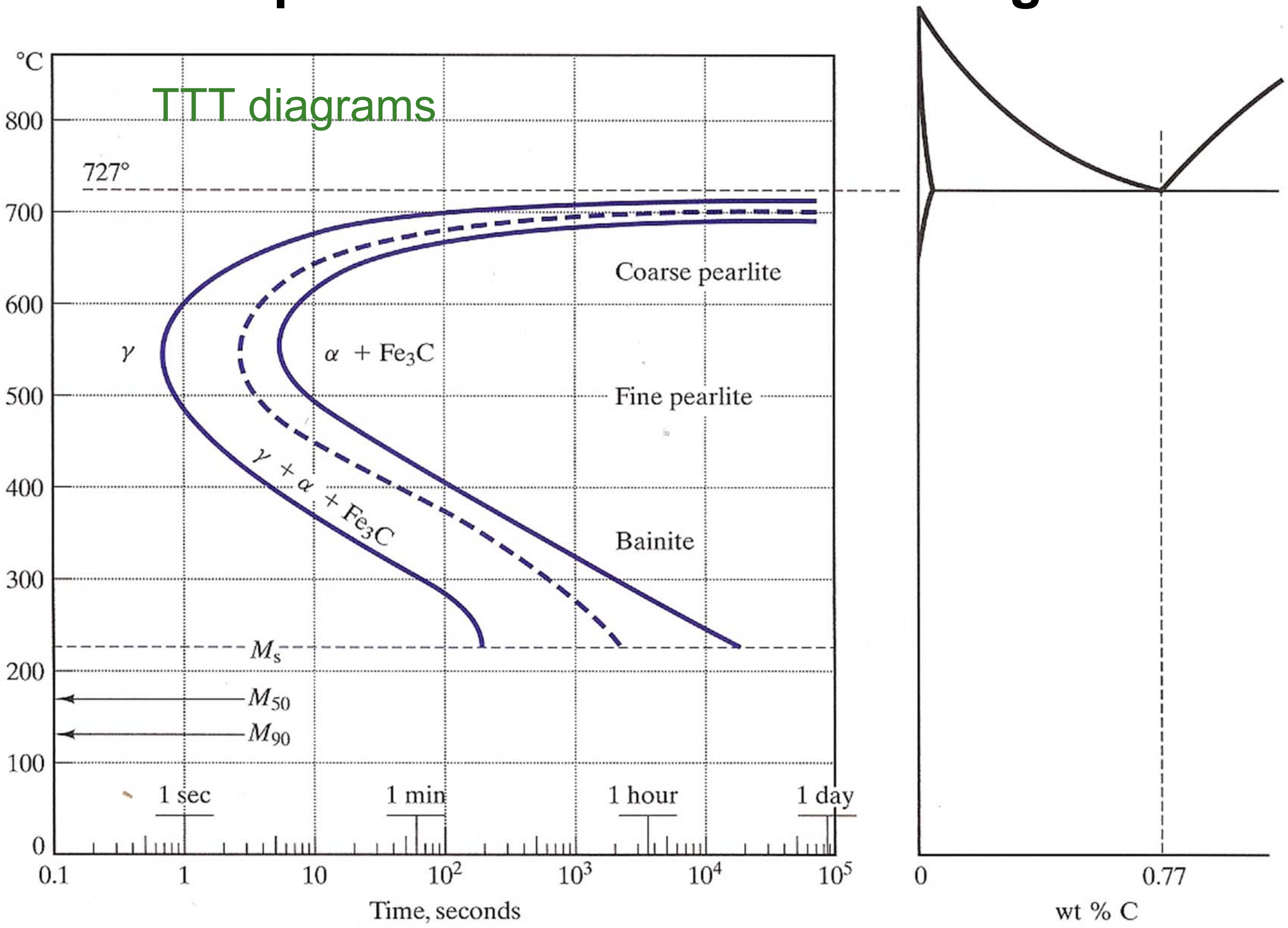
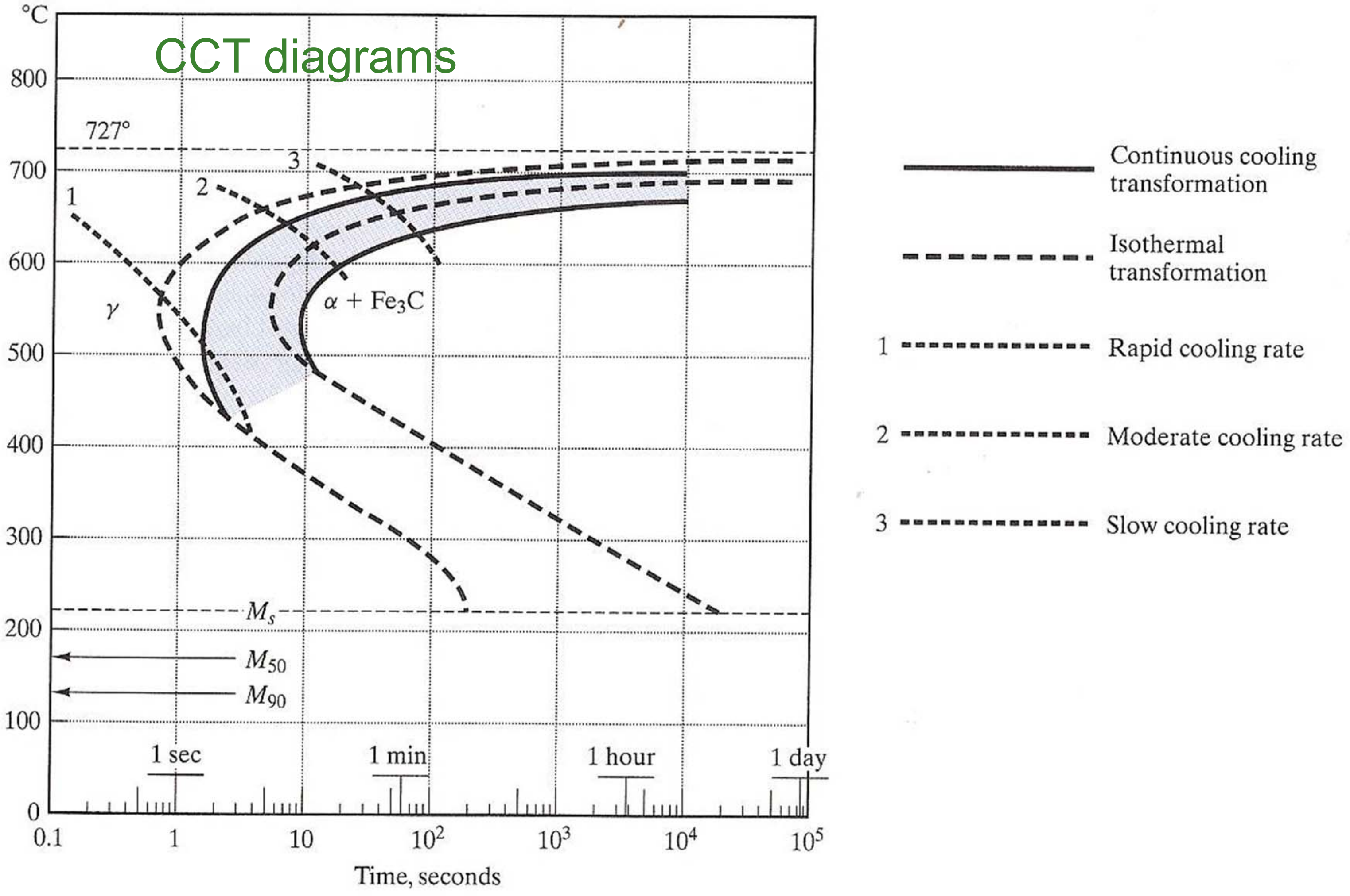


FIGURE 10.11 *A more complete TTT diagram for eutectoid steel than was given in Figure 10.7. The various stages of the time-independent (or diffusionless) martensitic transformation are shown as horizontal lines.* M_s *represents the start,* M_{50} *represents 50% transformation, and* M_{90} *represents 90% transformation. One hundred percent transformation to martensite is not complete until a final temperature (*M_f*) of −46°C.*

* Continuous Cooling Transformation diagrams



CCT diagrams

FIGURE 10.14 *A continuous cooling transformation (CCT) diagram is shown superimposed on the isothermal transformation diagram of Figure 10.11. The general effect of continuous cooling is to shift the transformation curves downward and toward the right. (After* Atlas of Isothermal Transformation and Cooling Transformation Diagrams, *American Society for Metals, Metals Park, OH, 1977.)*