2019 Fall

"Advanced Physical Metallurgy"
- Non-equilibrium Solidification -

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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)**

$$S = \int C_P d\ln T$$

→ **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**

Fragility

- **Fragility ~ ability of the liquid to withstand changes in medium range order with temp.**

   ~ extensively use to figure out liquid dynamics and glass properties
   corresponding to "frozen" liquid state

< Classification of glass >

Strong network glass : Arrhenius behavior
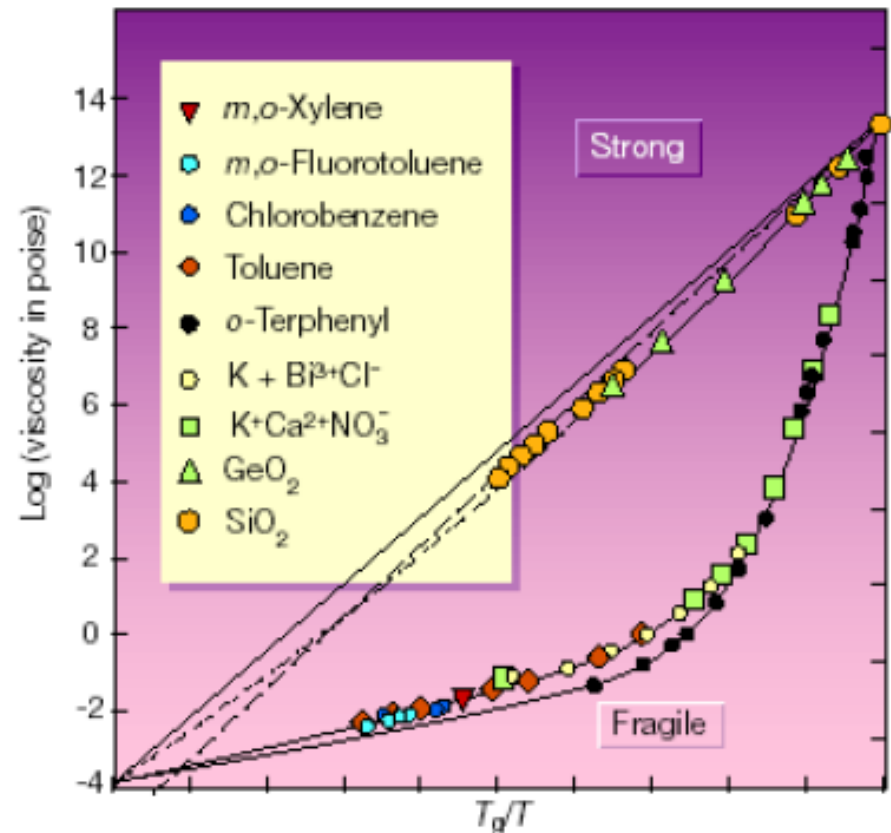
⇕

$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

Fragile network glass : Vogel-Fulcher relation

$$\eta = \eta_0 \exp[\frac{B}{T-T_0}]$$

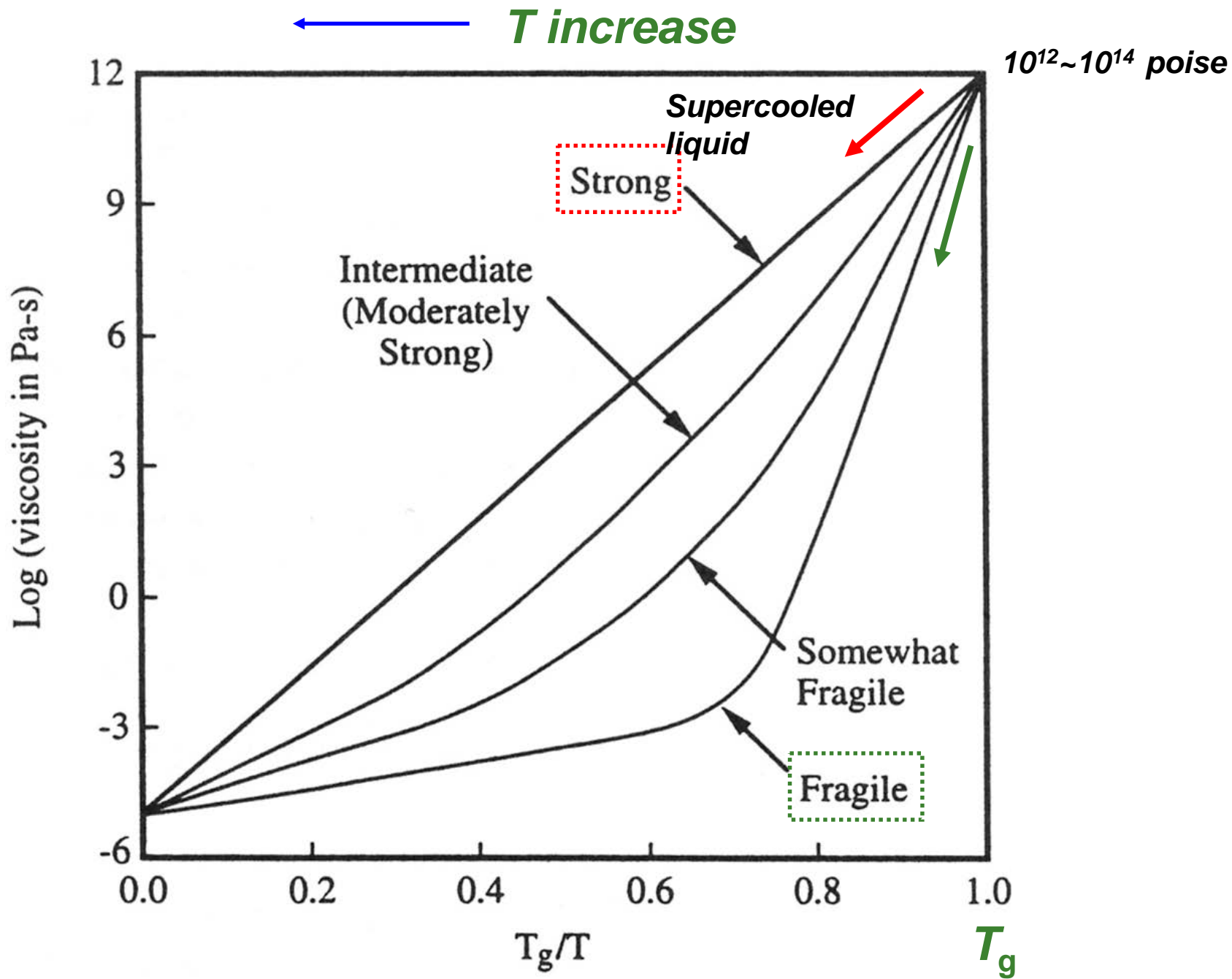**< Quantification of Fragility >**

$$m = \frac{d\log\eta(T)}{d(T_{g,n}/T)}\bigg|_{T=T_{g,n}} = \frac{d\log\tau(T)}{d(T_g/T)}\bigg|_{T=T_g}$$

Angell-plot (Uhlmann)

Log (viscosity in poise)

- ▼ m,o-Xylene
- ◉ m,o-Fluorotoluene
- ● Chlorobenzene
- ⬤ Toluene
- ● o-Terphenyl
- ◌ K + Bi^{3+}Cl$^-$
- ▢ K$^+$Ca^{2+}NO$_3^-$
- △ GeO$_2$
- ⬤ SiO$_2$

Strong

Fragile

T_g/T
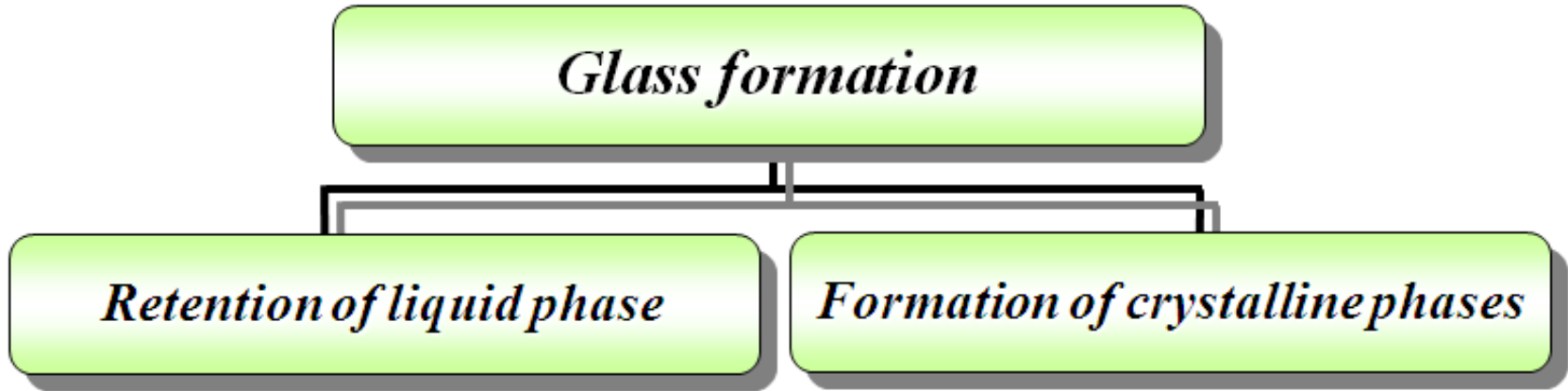
Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g

Q2: Glass formation

Glass formation

Retention of liquid phase | **Formation of crystalline phases**

Glass Formation results when

Liquids are cooled to below T_m (T_L) sufficiently fast to avoid crystallization.

Nucleation of crystalline seeds are avoided

Growth of Nuclei into crystallites (crystals) is avoided

Liquid is "frustrated" by internal structure that hinders both events

➡ "Glass Formation"

Critical cooling rate is inversely proportional to the diameter of ingot.
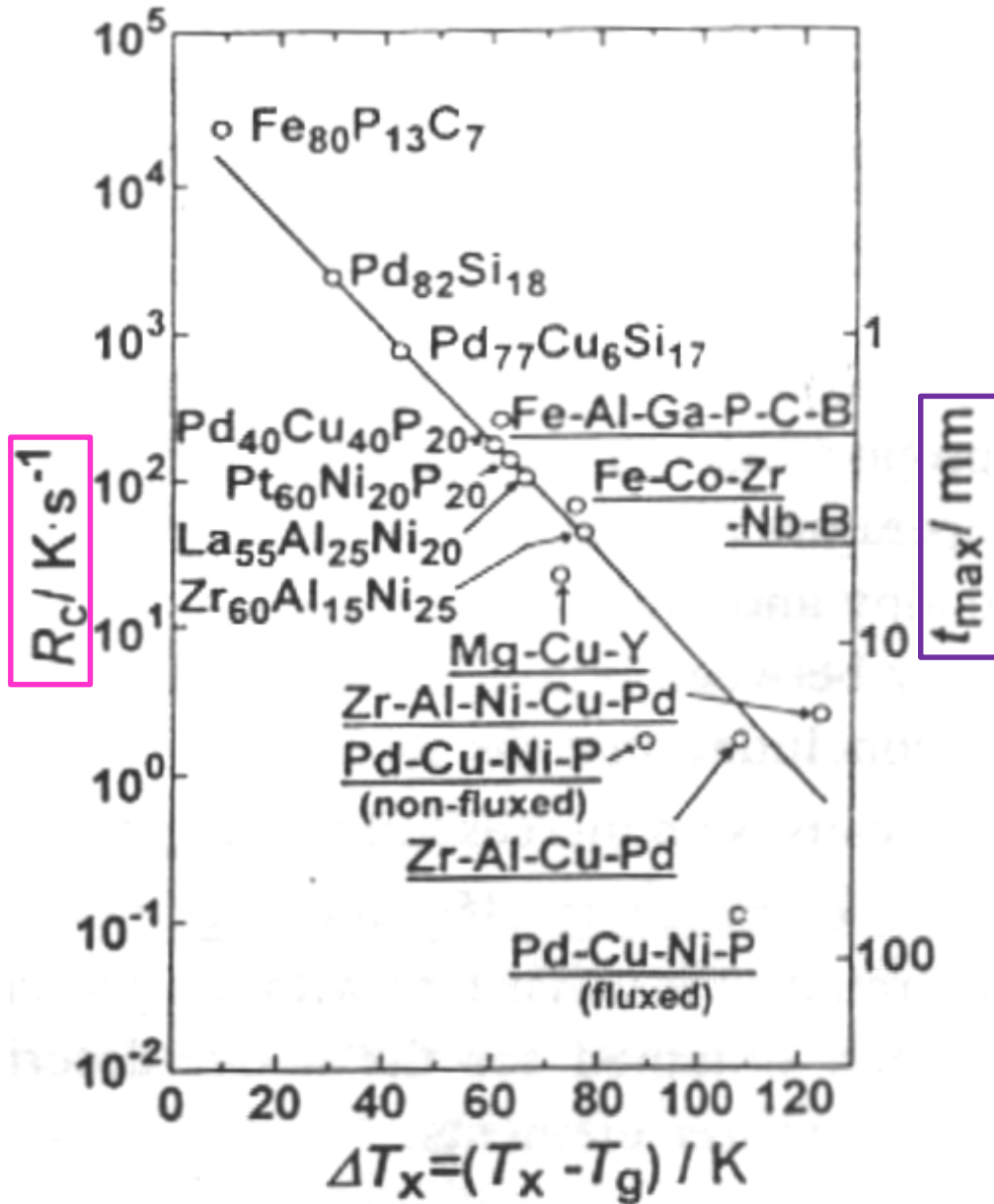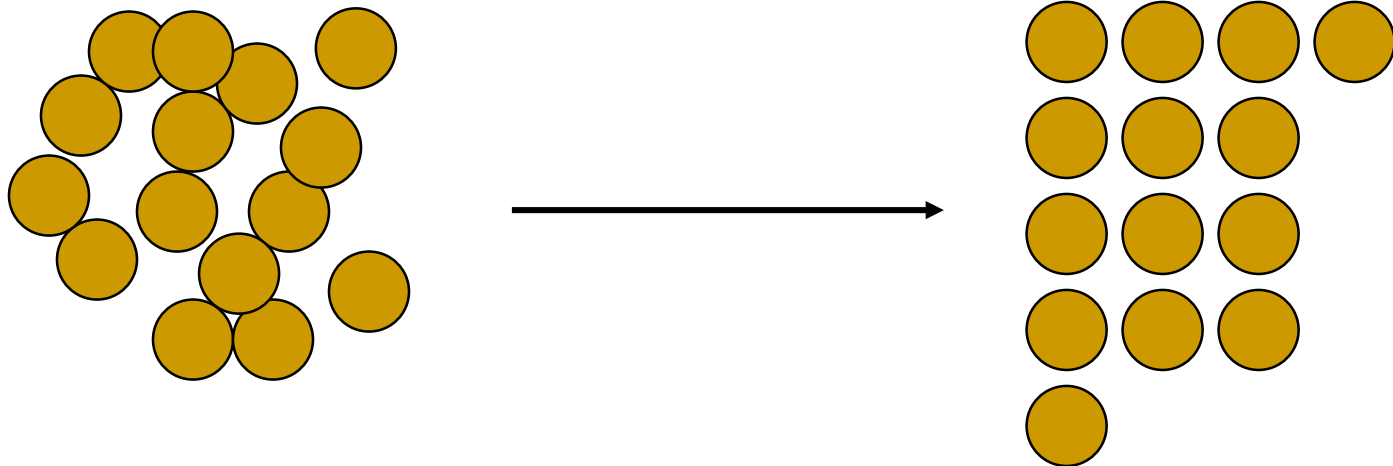
Critical Cooling Rates for Various Liquids

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

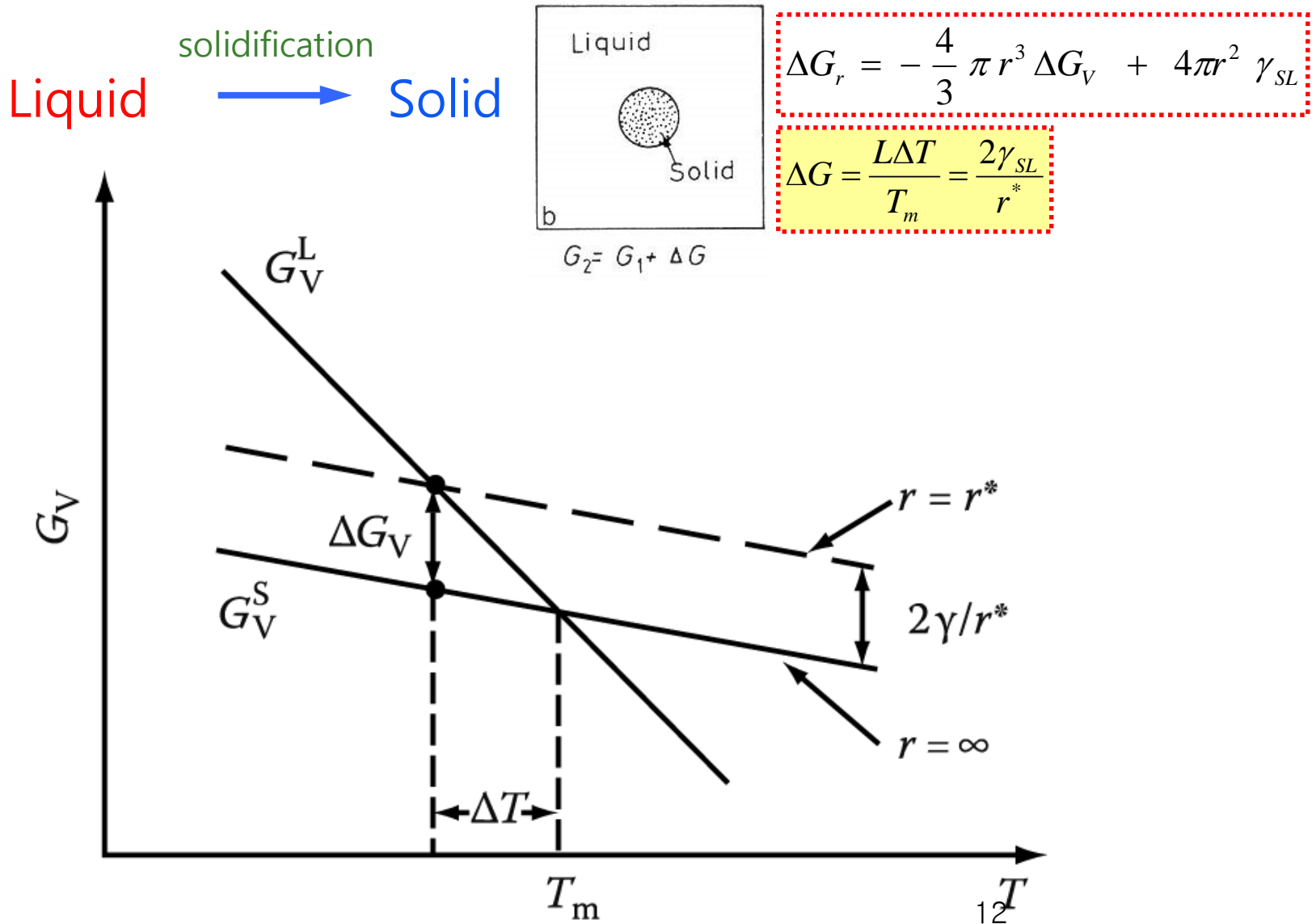| Material	Homogeneous nucleation	Heterogeneous nucleation contact angle (deg)		
		100	60	40
SiO_2 glass[a]	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO_2 glass[a]	3×10^{-3}	3×10^3	1	20
$Na_2O \cdot 2SiO_2$ glass[a]	6×10^{-3}	8×10^{-3}	10	$3 \times 10^{+2}$
Salol	10			
Water	10^7			
Ag	10^{10}			
Typical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

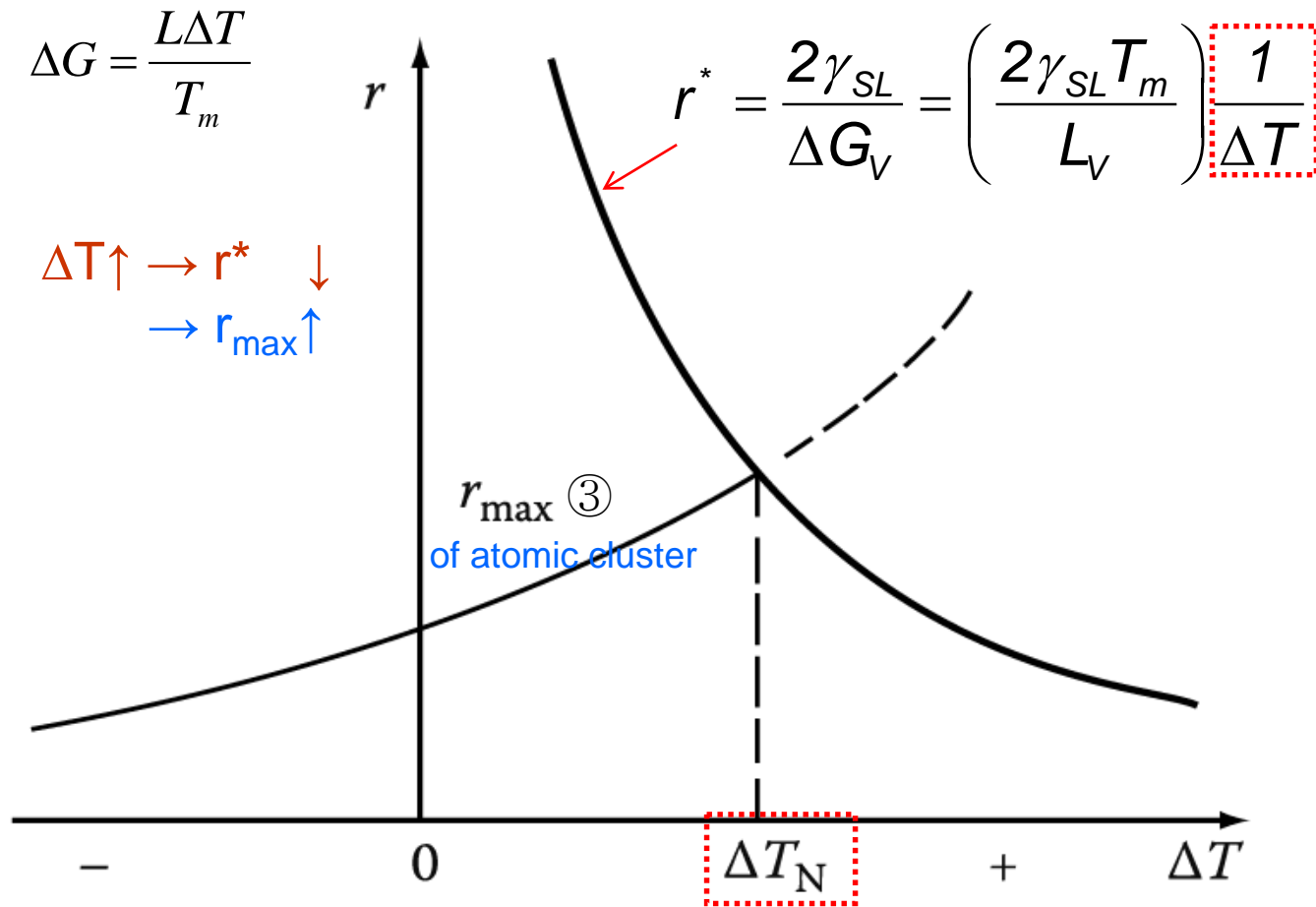- Nucleation, the first step…

- 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 $\longrightarrow$ Solid

Liquid

Solid

b

$G_2 = G_1 + \Delta G$

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

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

G_V^L

G_V^S

ΔG_V

$r = r^*$

$2\gamma/r^*$

$r = \infty$

G_V

ΔT

T_m

T

The creation of a critical nucleus ~ thermally activated process

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

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

$\Delta T\uparrow \rightarrow r^* \quad \downarrow$

$\rightarrow r_{max}\uparrow$

r_{max} ③
of atomic cluster

ΔT_N is the critical undercooling for homogeneous nucleation.

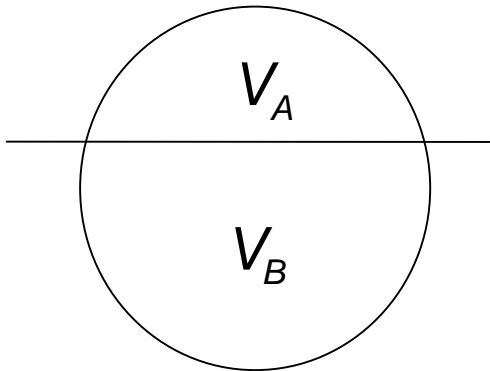Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

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

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Barrier of Heterogeneous Nucleation

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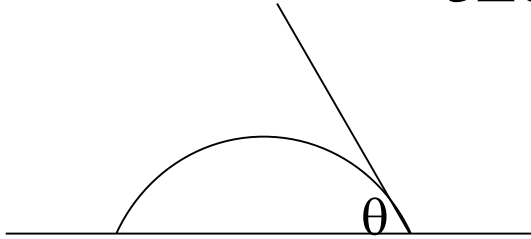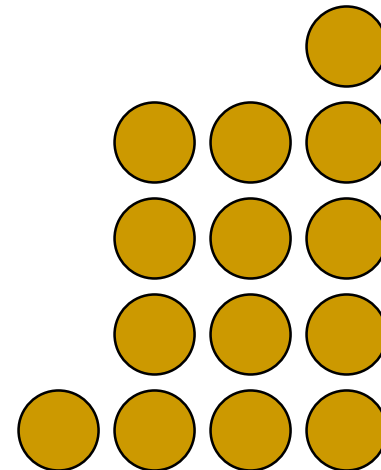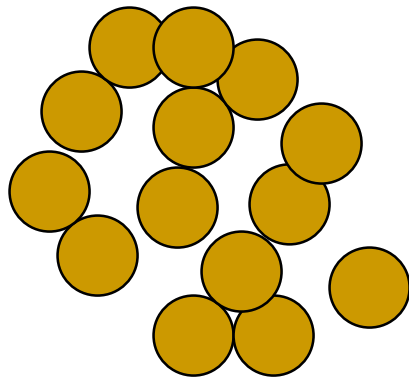
$$\Delta G_{het}^* = S(\theta)\Delta G_{hom}^*$$

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

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

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

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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

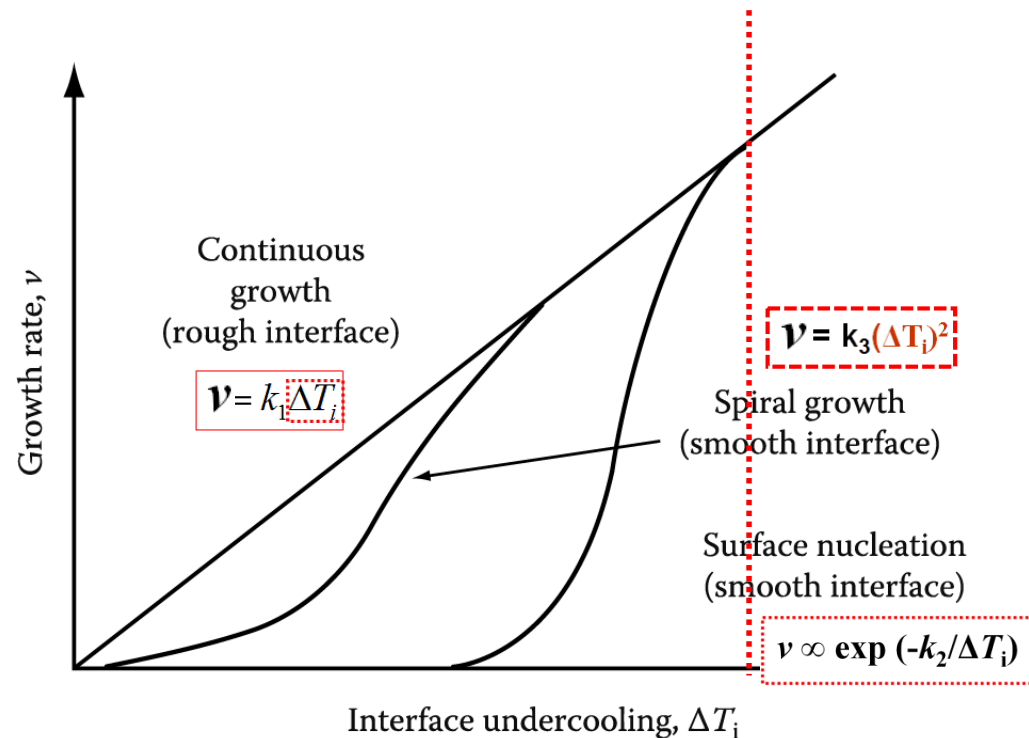Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

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

Continuous growth (rough interface)

$\boldsymbol{v} = k_1 \Delta T_i$

$\boldsymbol{v} = k_3(\Delta T_i)^2$

Spiral growth (smooth interface)

Surface nucleation (smooth interface)

$v \propto \exp(-k_2/\Delta T_i)$

Growth rate, v

Interface undercooling, ΔT_i

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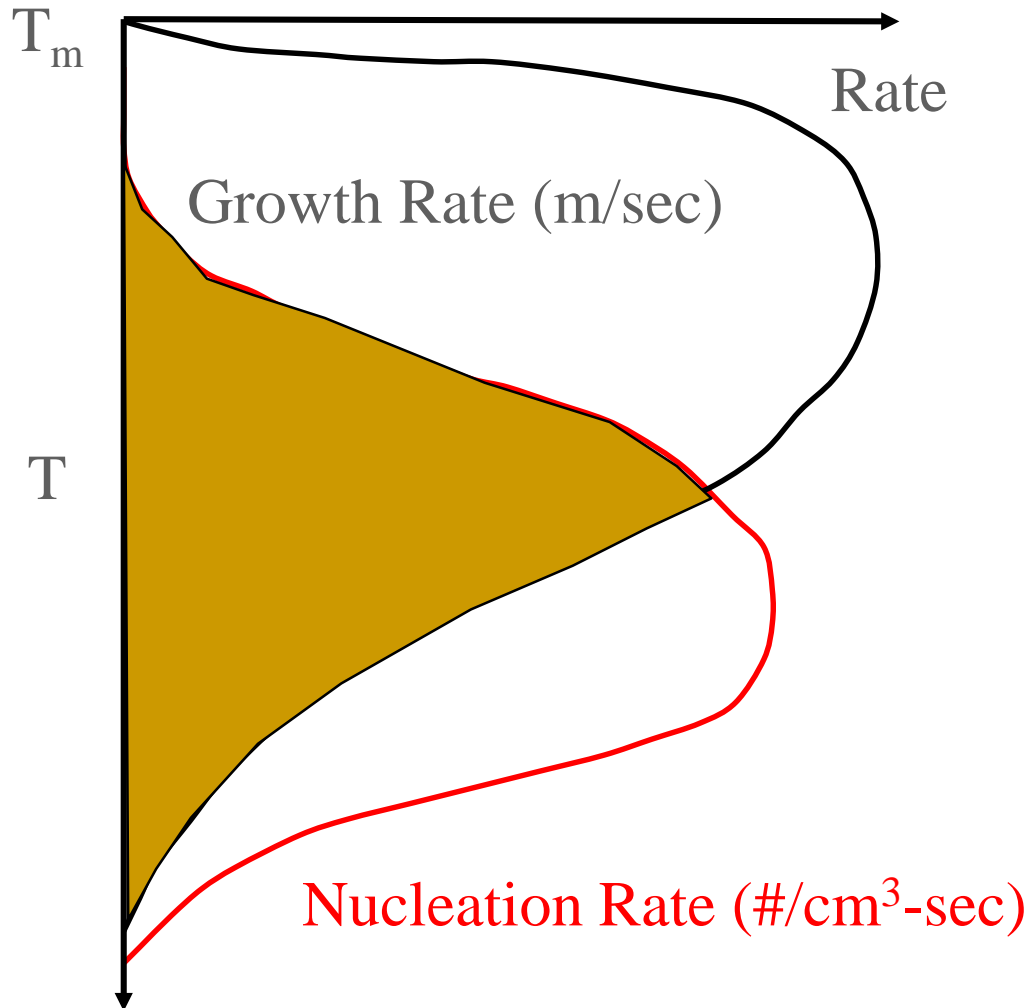
- **Strong overlap of growth and nucleation rates**
- Nucleation rate is high
- Growth rate is high
- Both are high at the same temperature

Nucleation and Growth Rates – Good Glass Formers

Rate

T_m

Growth Rate (m/sec)

T

Nucleation Rate (#/cm^3-sec)
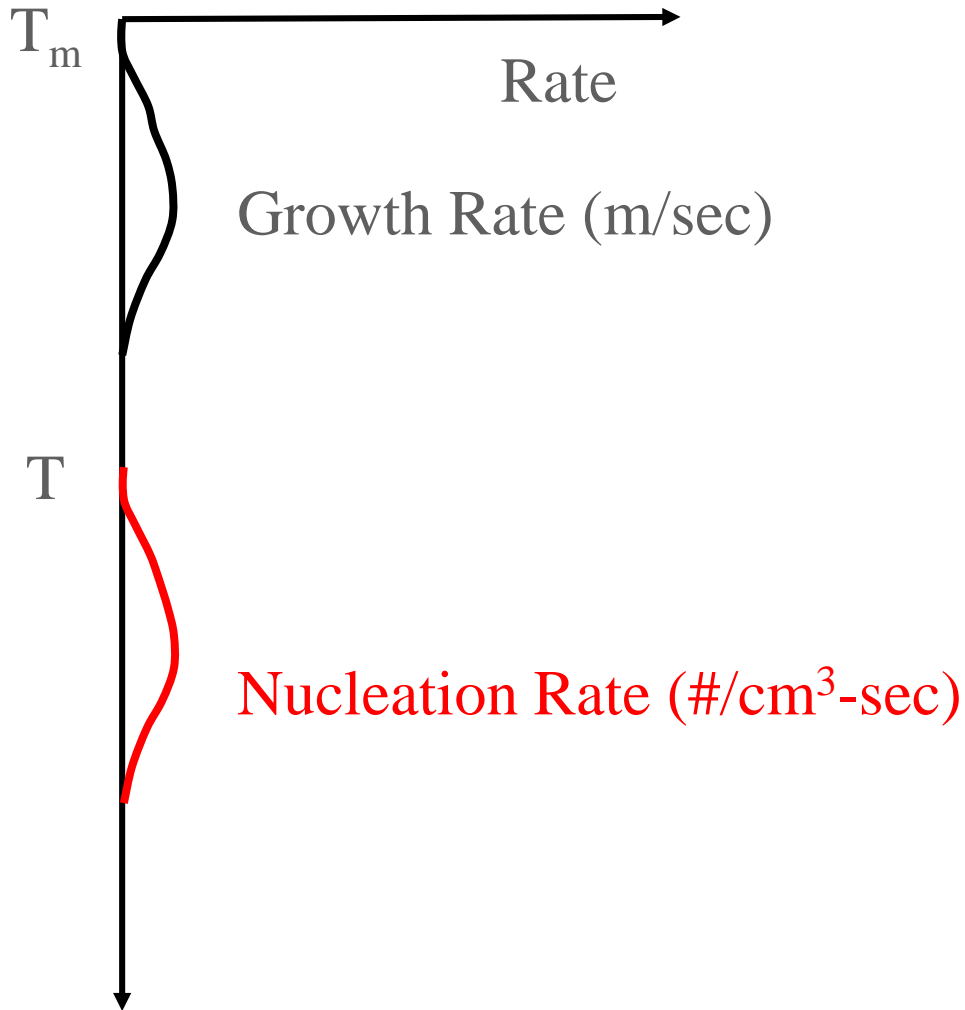
- **No overlap of growth and nucleation rates**

- 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

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

Number density   **Fastest motion**   **Thermodynamic probability**   **Diffusion probability**

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

= ρ N/Atomic, molecular, formula weight

ν = vibration frequency $\sim 10^{13}$ sec^{-1}
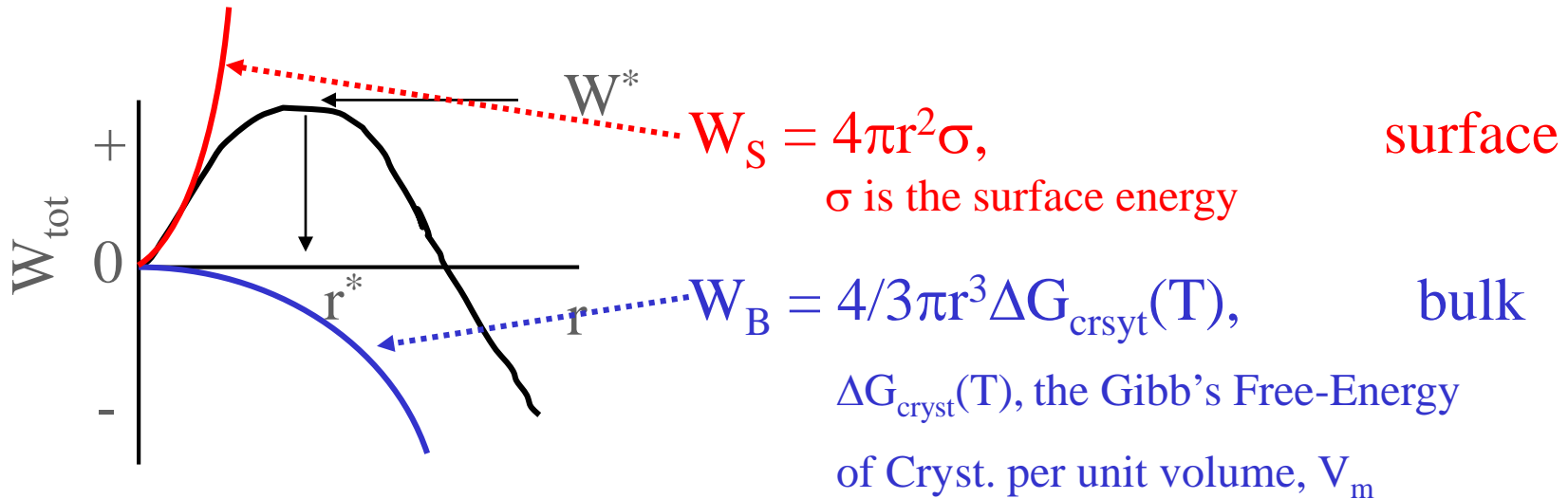
N = Avogadro's number

= 6.023×10^{23} atoms/mole

W^* = thermodynamic energy barrier to form nuclei

ΔE_D = diffusion energy barrier to form nuclei
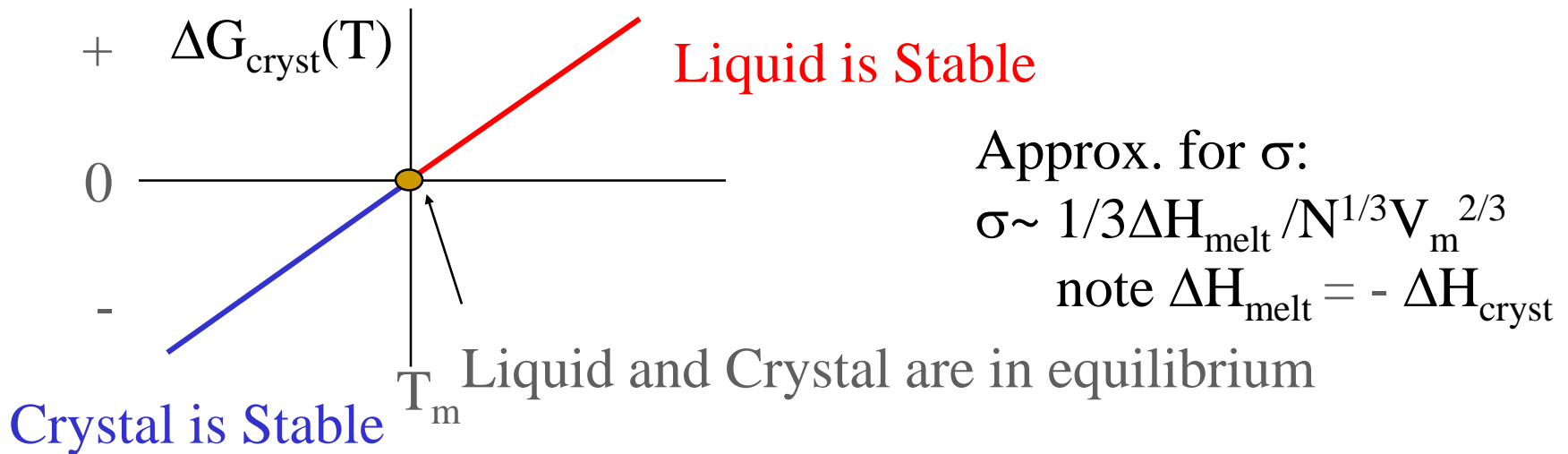
$\sim$ viscosity activation energy

Nucleation Rate – Thermodynamic barrier W*

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^*, $(\partial W(r)/\partial r)_{r=r^*} = 0$

- $r^* = -2\sigma/\Delta G_{cryst}(T)$

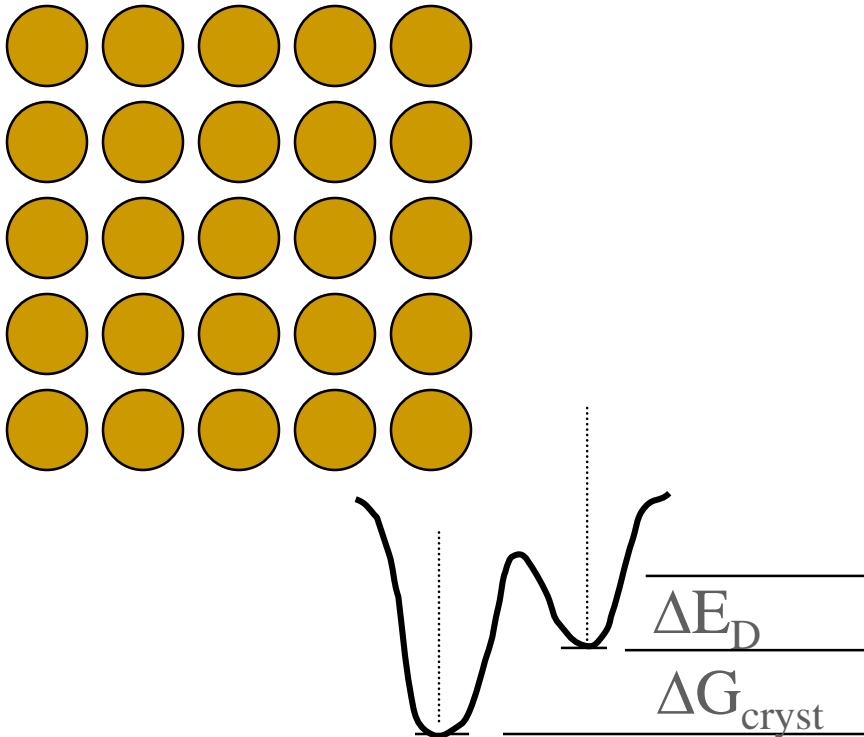- $W(r^*) \equiv W^* = 16\pi \sigma^3/3(\Delta G_{cryst}(T))^2$

Nucleation Rate I(T)

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

- $\Delta G_{cryst}(T) = \Delta H_{cryst}(T_m)(1 - T/T_m)/V_m \equiv \Delta H_{cryst}(T_m)(\Delta T_m/T_m)$

$+$ $\Delta G_{cryst}(T)$

Liquid is Stable

0

Approx. for σ:
$\sigma \sim 1/3\Delta H_{melt}/N^{1/3}V_m^{2/3}$
note $\Delta H_{melt} = -\Delta H_{cryst}$

$-$

T_m Liquid and Crystal are in equilibrium

Crystal is Stable

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

Growth Rates - $\mu(T)$

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

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

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

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

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

Growth Rates - μ(T)

Diffusion coefficient, D

$$D(T) = a^2 \nu \exp\left[\frac{-\Delta E_D}{RT}\right] = \left(\frac{fRT}{3N\pi a \eta(T)}\right)$$
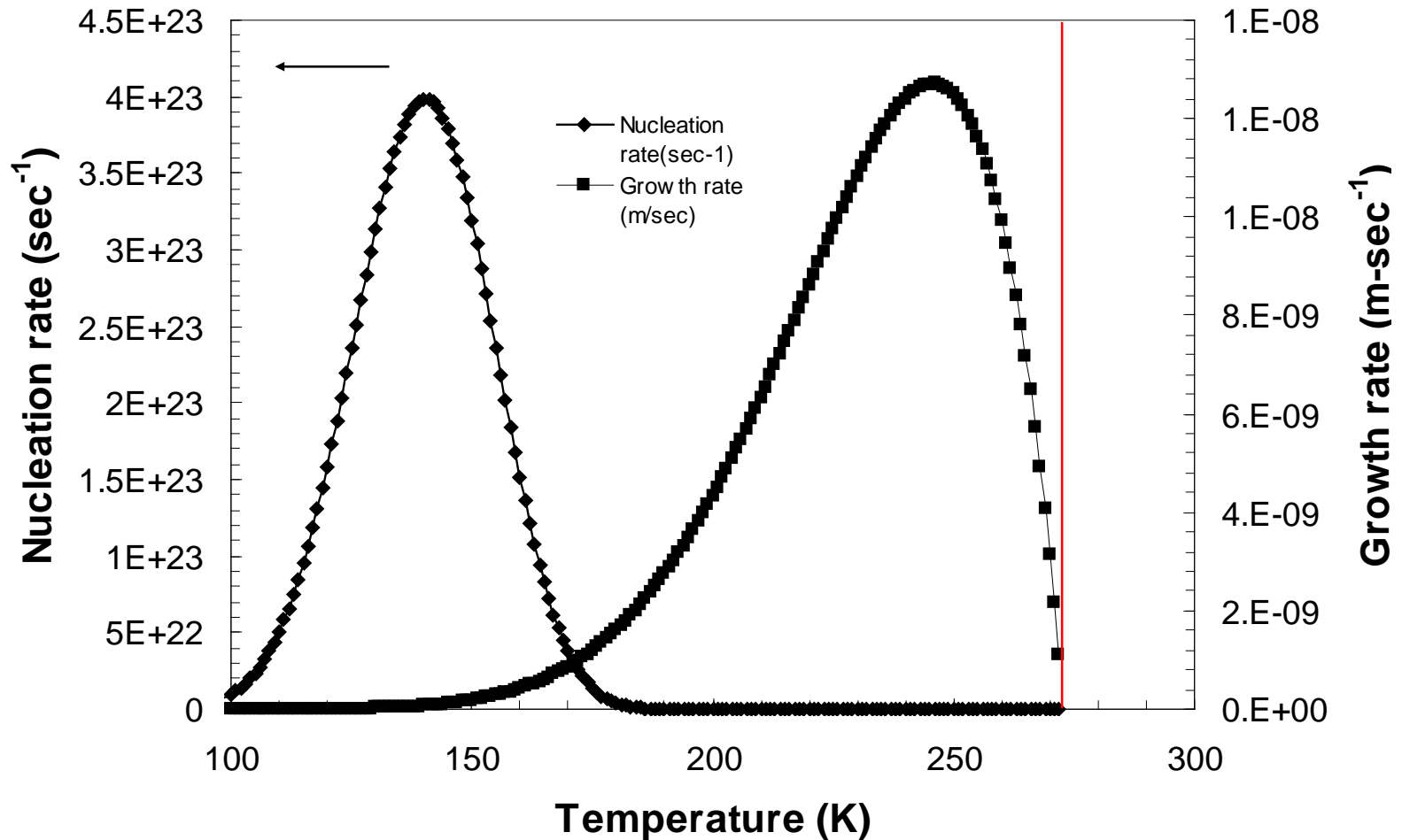
Stokes-Einstein relation between D and η $\quad D = \dfrac{k_B T}{6\pi \eta r}$

Hence:

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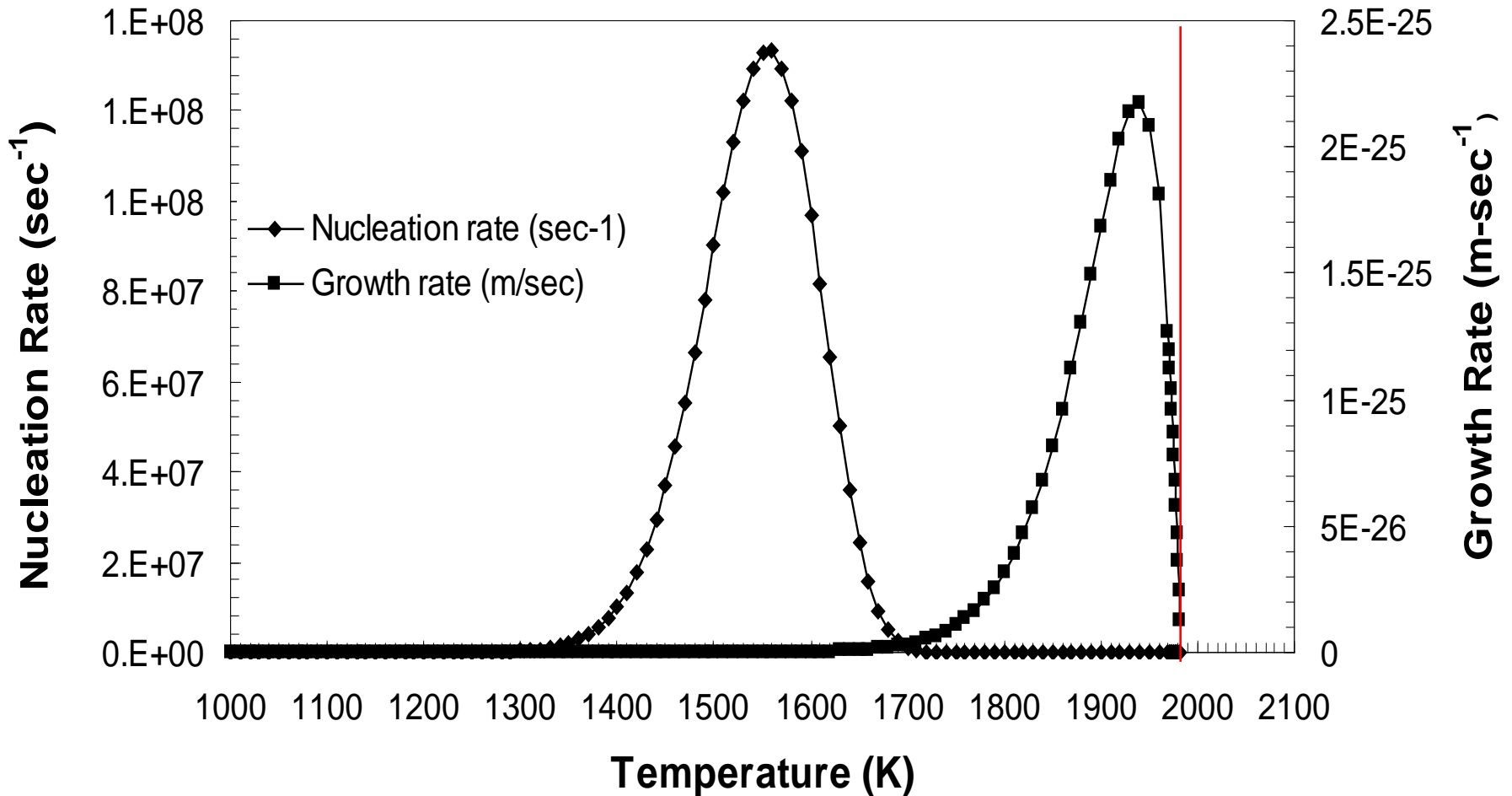
Nucleation and Growth Rates

Nucleation and Growth Rates for Water

Nucleation and Growth Rates

Nulceation and Growth for Silica

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?

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

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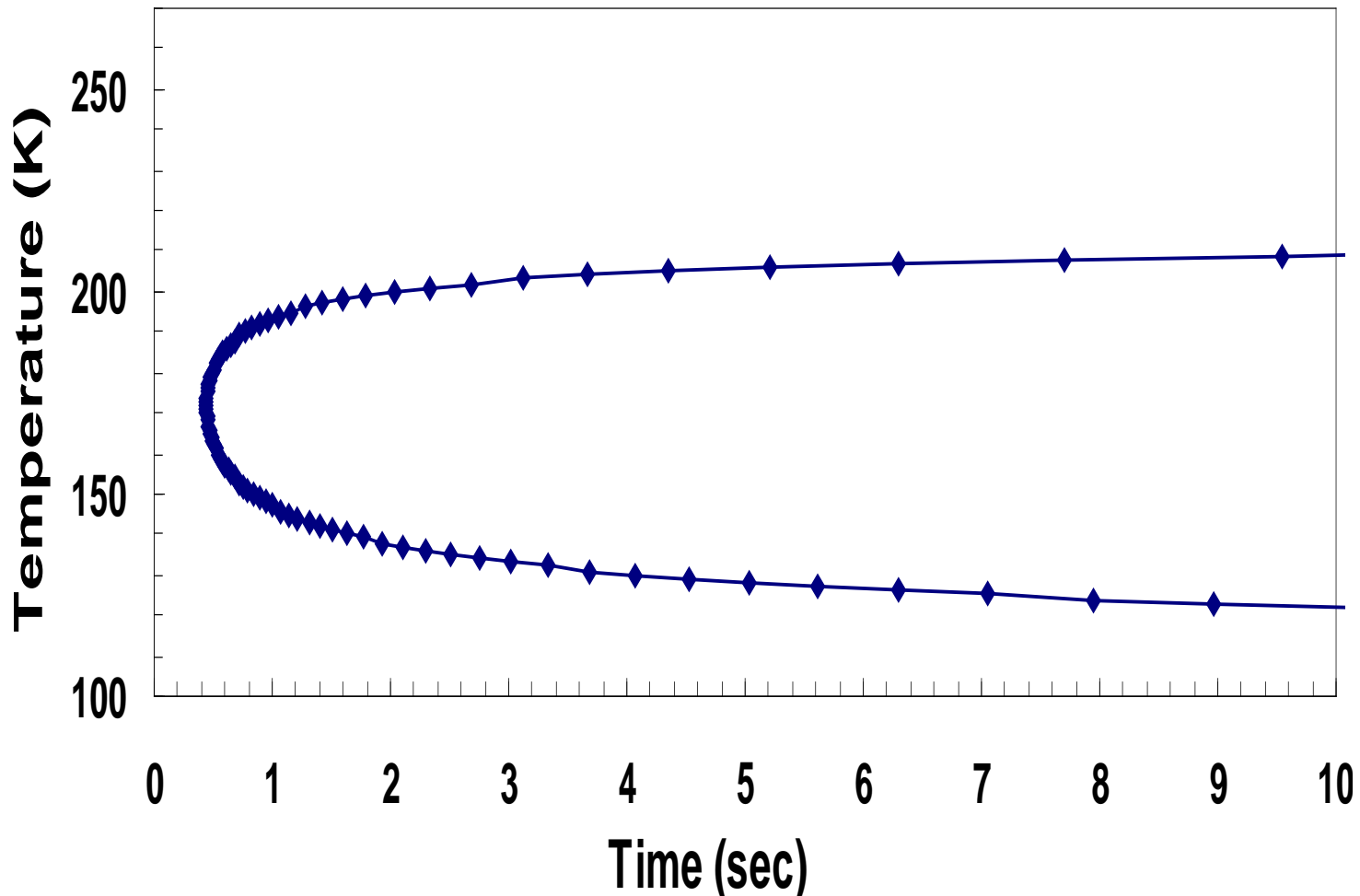
Nucleation rates

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

Growth rates

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

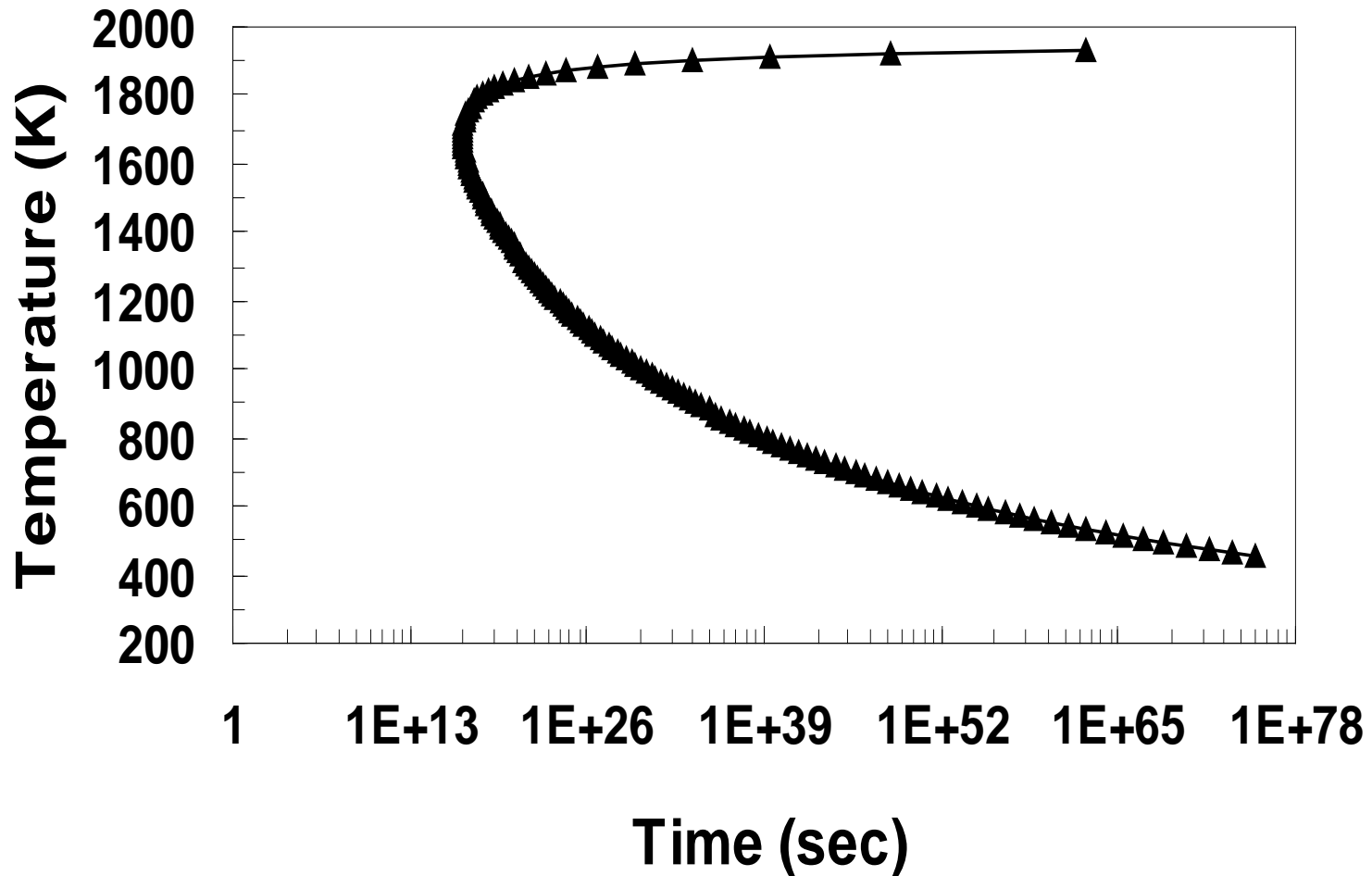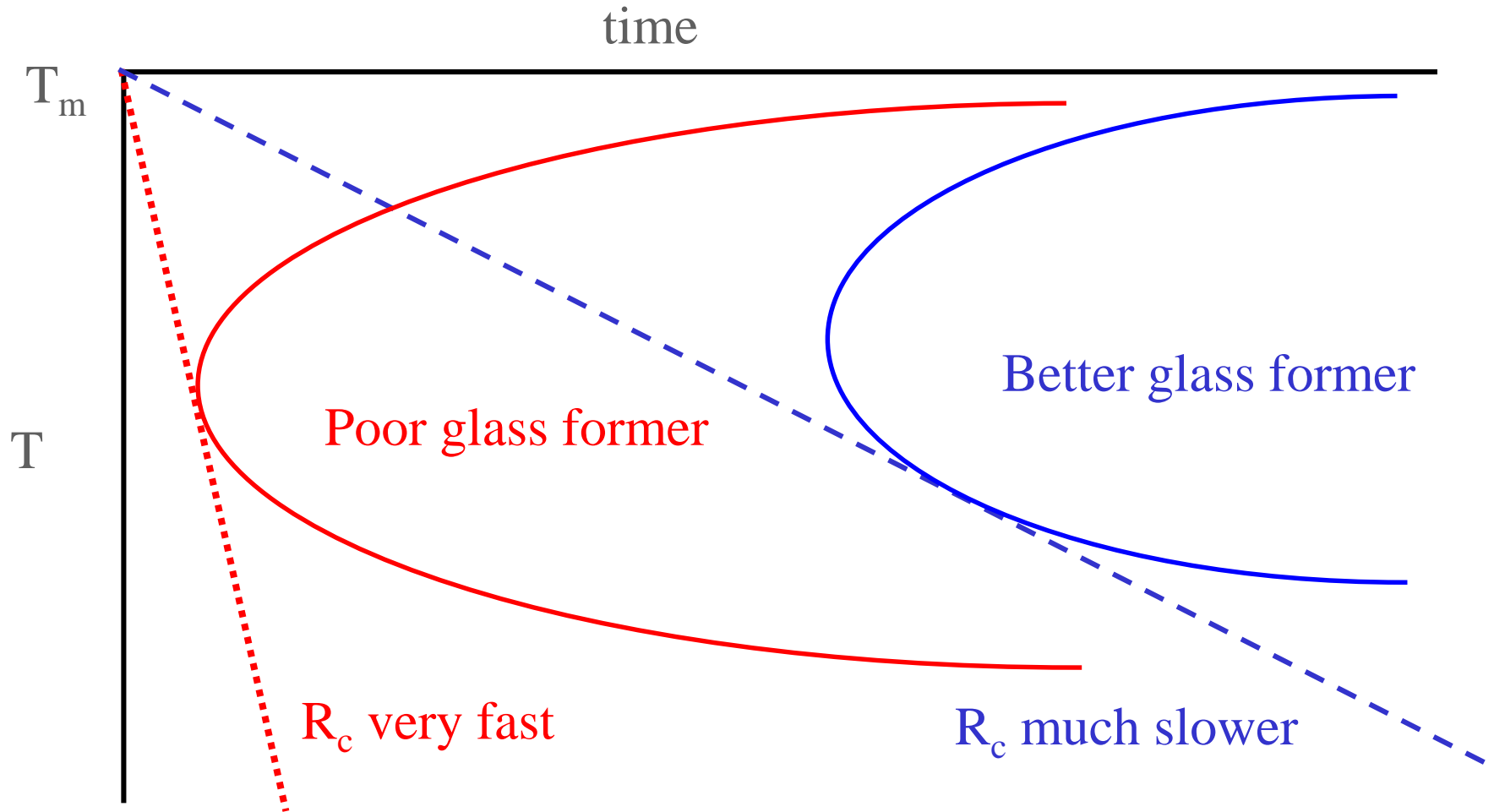# Time Transformation Curves for Water

T-T-T Curve for water

Time Transformation Curves for Silica

T-T-T Curve for Silica
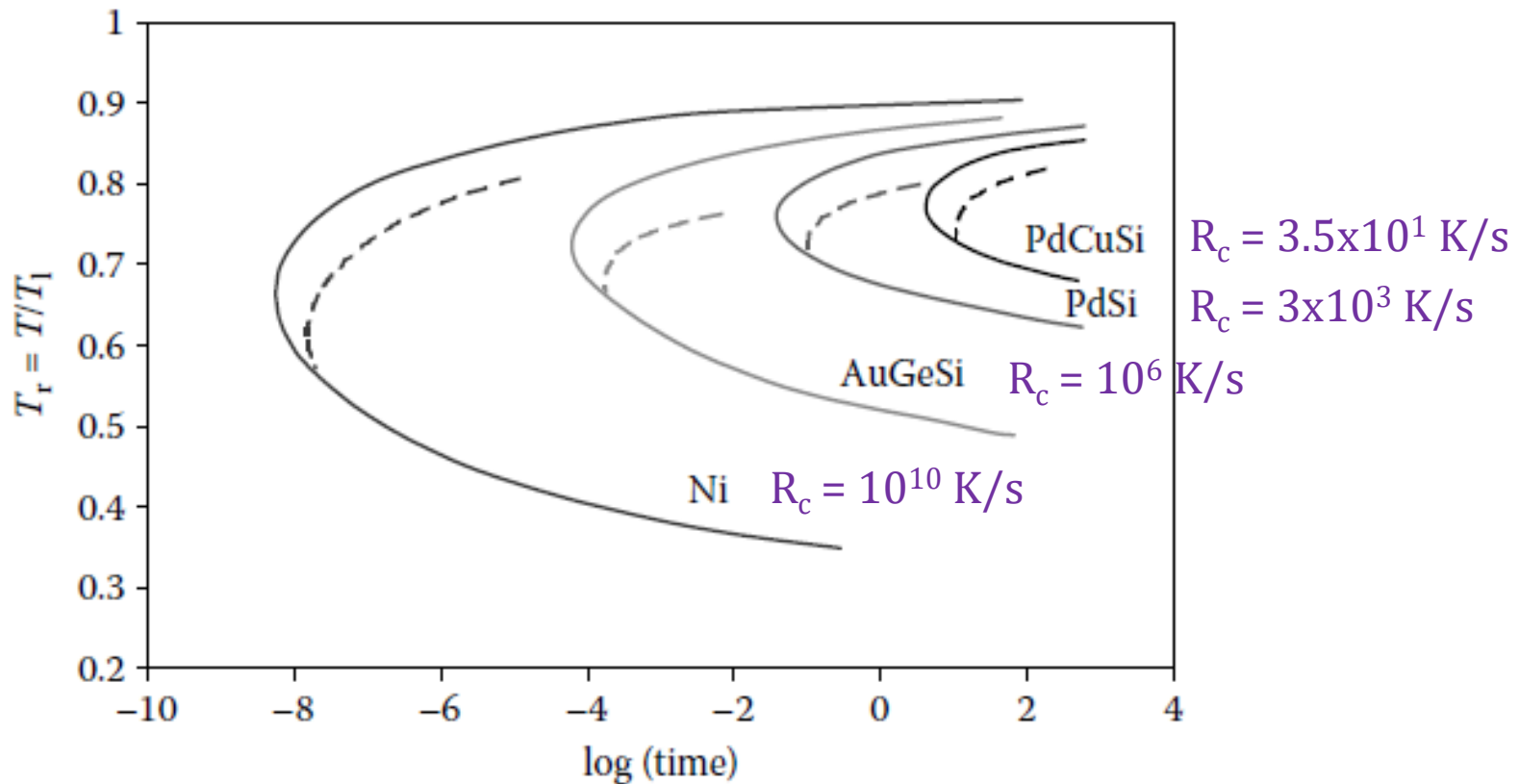
TTT curves and the critical cooling rate, R_c

time

T_m

T

Poor glass former

Better glass former

R_c very fast

R_c much slower

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

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