2010 Spring

“Amorphous Materials”

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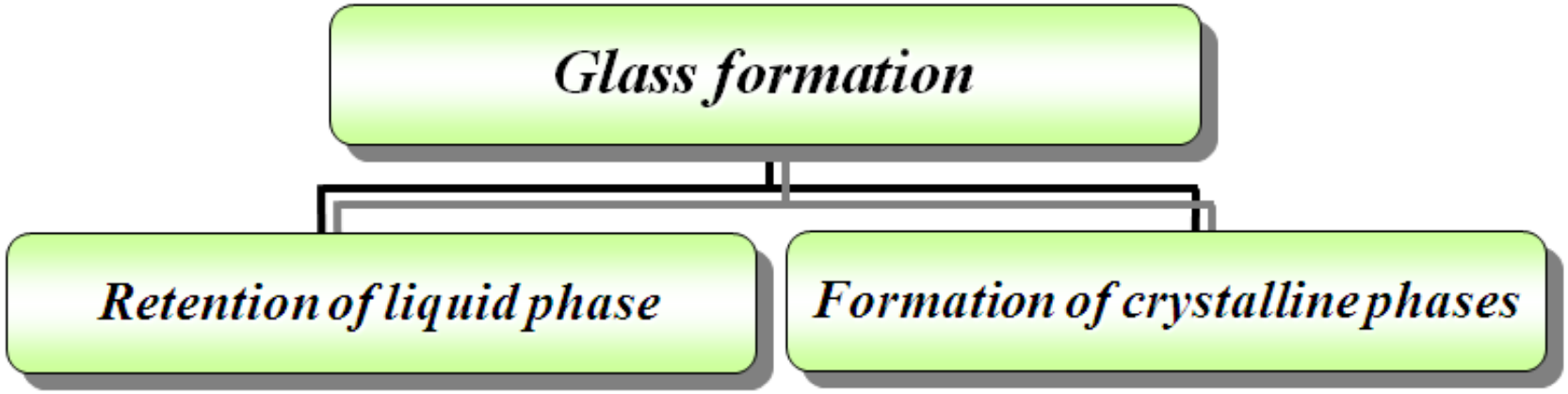


Glass Formation results when

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**

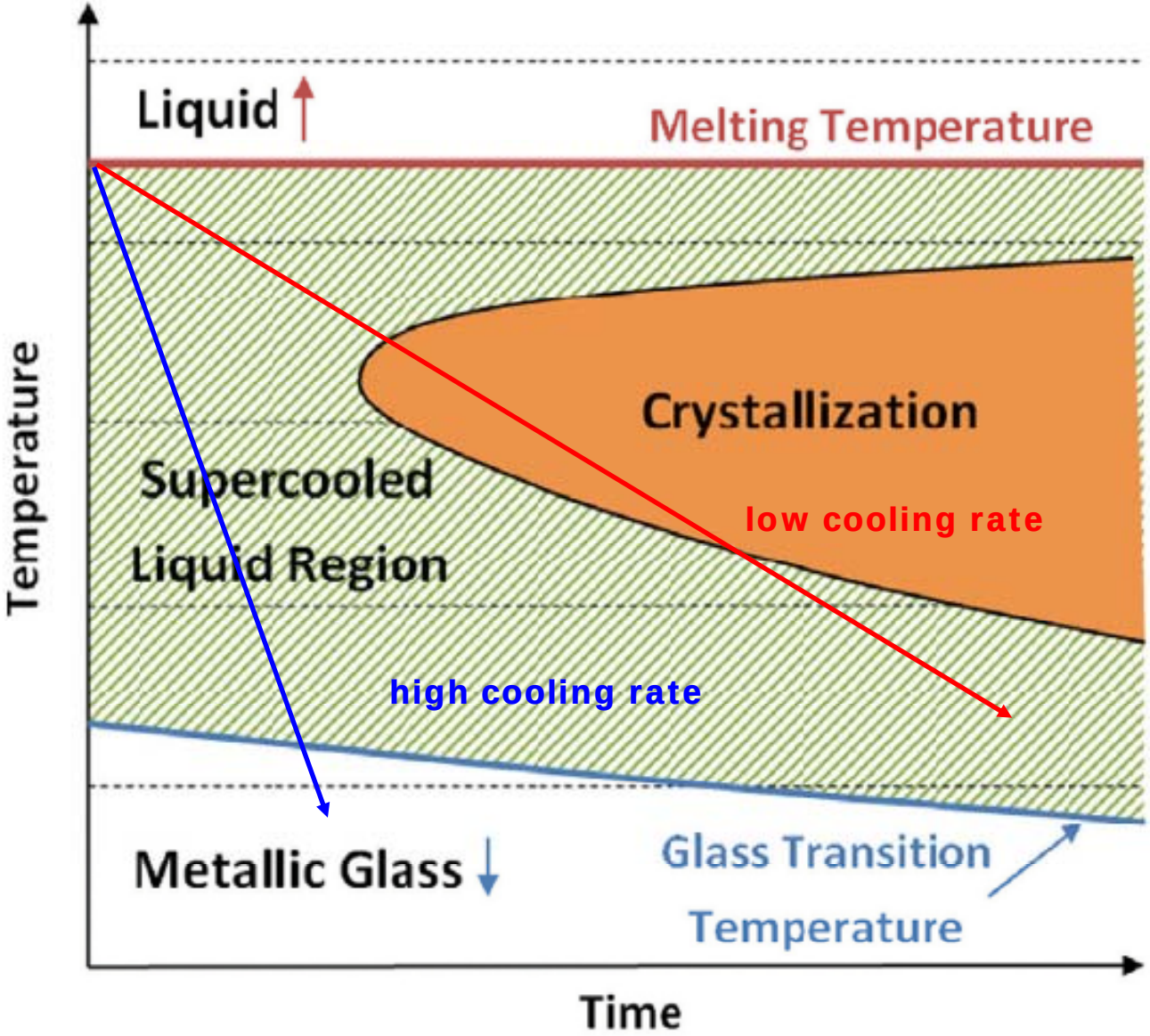
Kinetic Approach to Glass Formation

- **Kinetic approach to glass formation asserts:**
  - All liquids can be made into the glassy state
  - The question is how fast must the liquid be cooled?
  - Fast quenching, >> 100 K/sec, implies "marginal" glass forming ability
  - Slow cooling,<< 1 K/min **(0.017 K/s),** implies "strong" glass forming ability
  - The **critical cooling rate, R_c**, measures how fast a liquid must be cooled to avoid crystallization and render the liquid into the glassy state

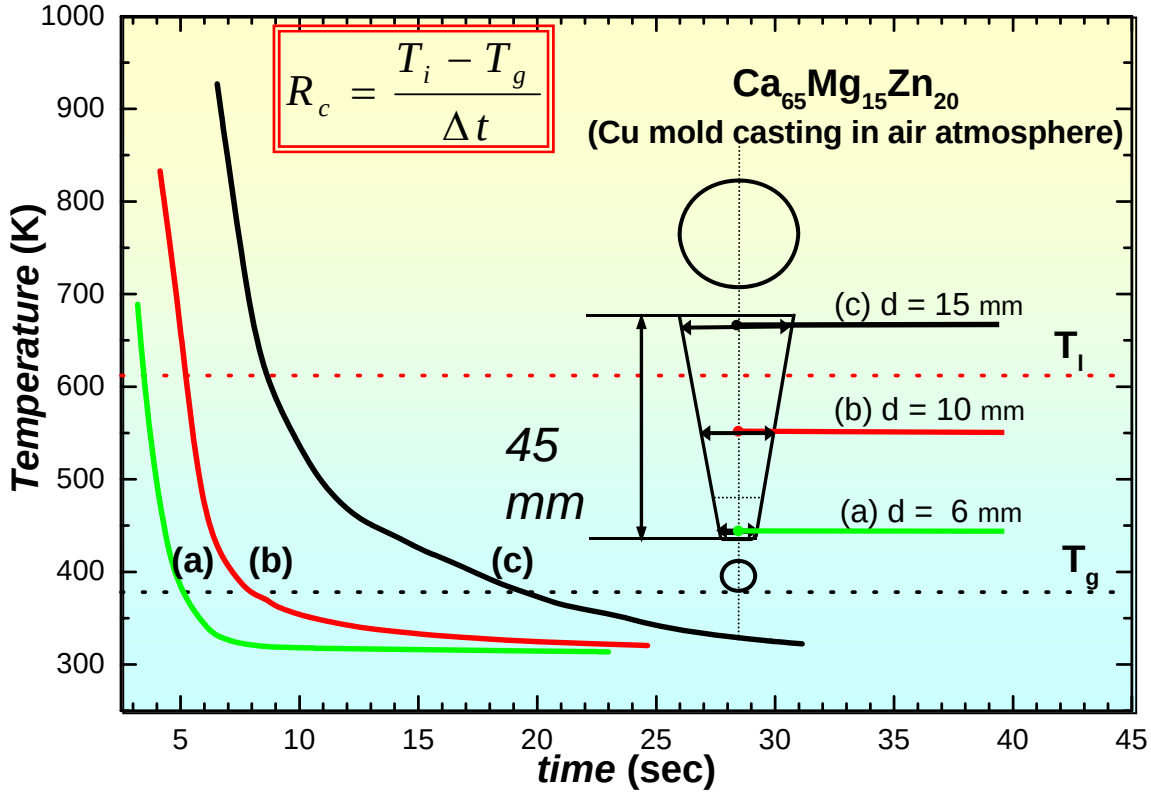
Calculating the Critical Cooling Rate

- The kinetic approach to glass formation then becomes:
  - What is the R_c value for a particular liquid?
    If R_c >> 100 K/sec, then the liquid is a poor glass former
    If R_c is << 1 K/min, the liquid is a good glass former
  - How can R_c be calculated?
  - What are the factors that control R_c?

Time Temperature Transformation diagram



Measurement of R_c in $Ca_{65}Mg_{15}Zn_{20}$ (D_{max}>15 mm)



top position : 20 K/s

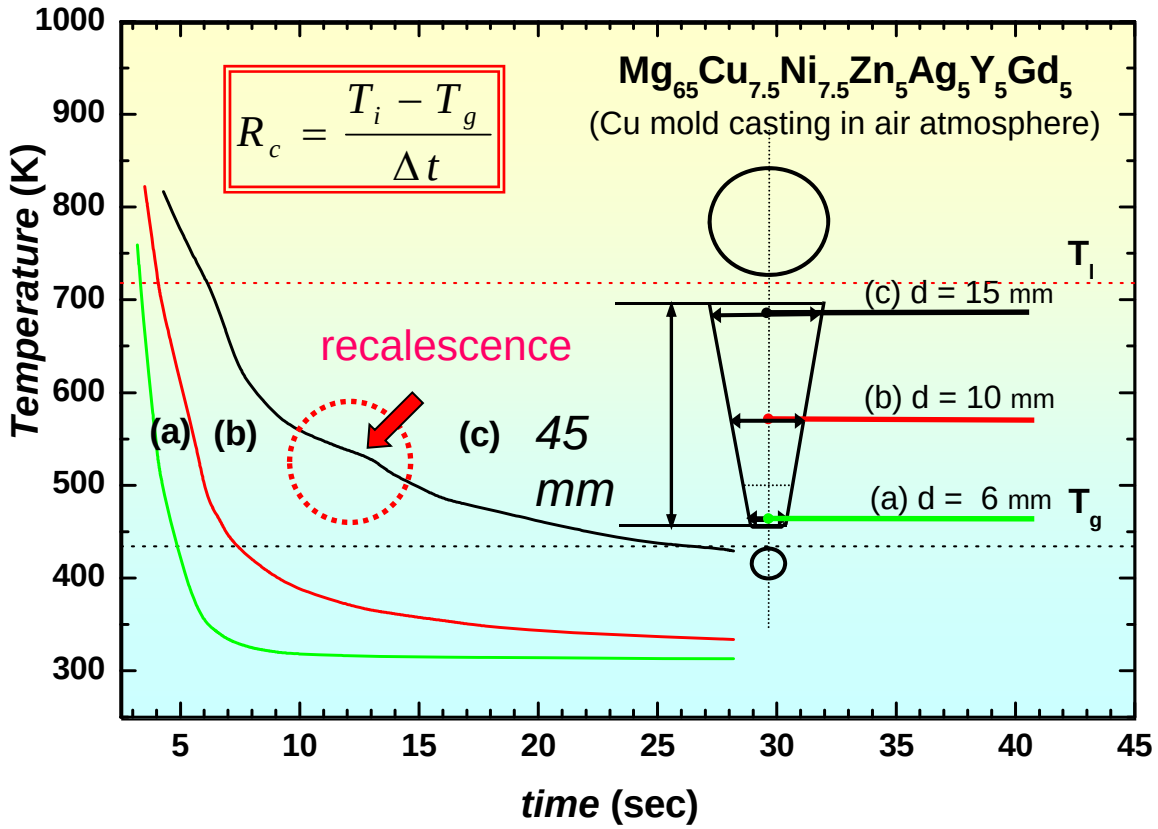
middle position : 93 K/s

bottom position : 149 K/s

*** Cooling curves measured at the center of the three transverse cross sections**

* J. Mater. Res. 19, 685 (2004)
* Mater. Sci. Forum 475-479, 3415 (2005)

Measurement of R_c in Mg BMG (D_{max}=14 mm)



top position : recalescence

middle position : 64K/s

bottom position : 137 K/s

*** Cooling curves measured at the center of the three transverse cross sections**

*** JAP 104, 023520 (2008)**

Bulk formation of a metallic glass: $Pd_{40}Ni_{40}P_{20}$

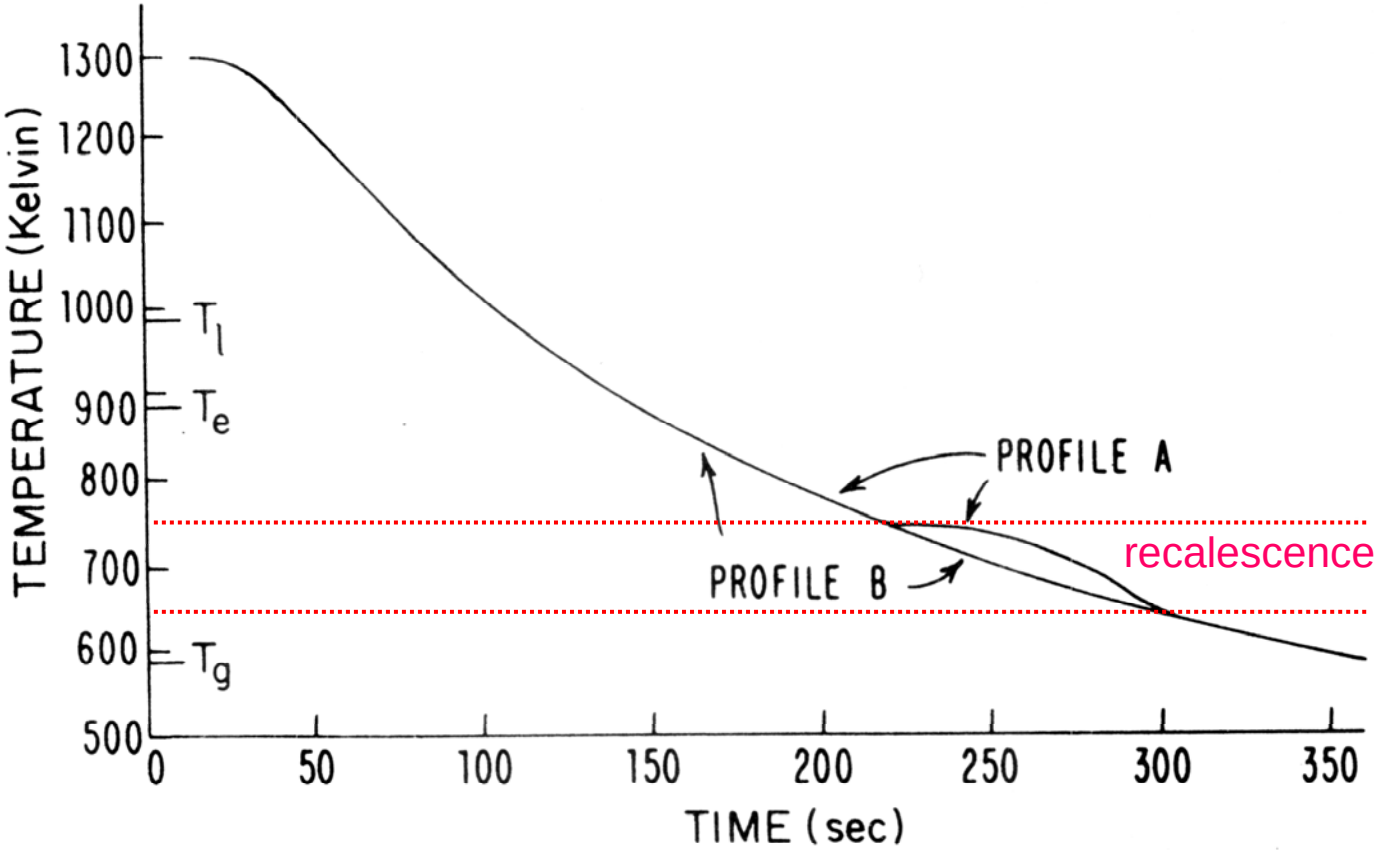


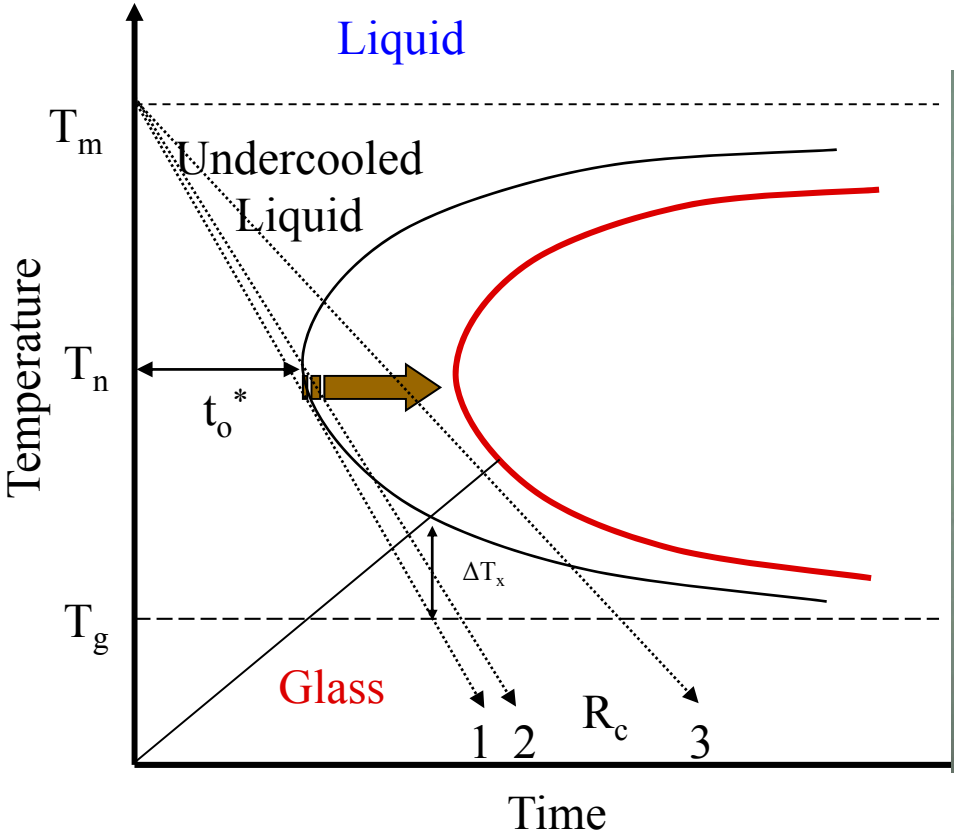
FIG. 2. Superposition of two cooling profiles: A—bulk crystallization which began at 740 K. B—formation of a glassy ingot.

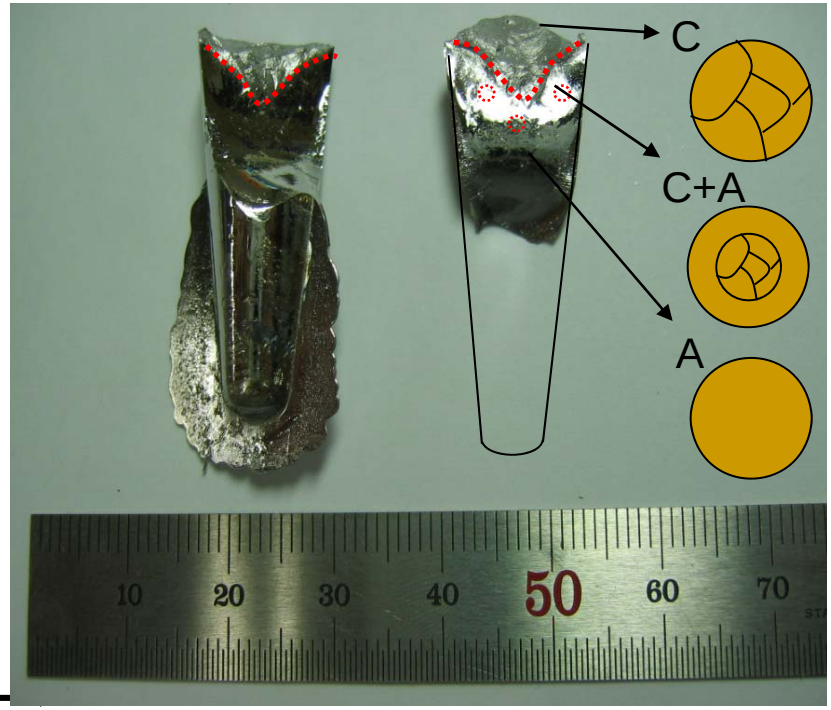
A.J. Drehman, A.L. Greer, D. Turnbull, Appl. Phys. Lett. 1982; 41: 716.

Time Temperature Transformation diagram

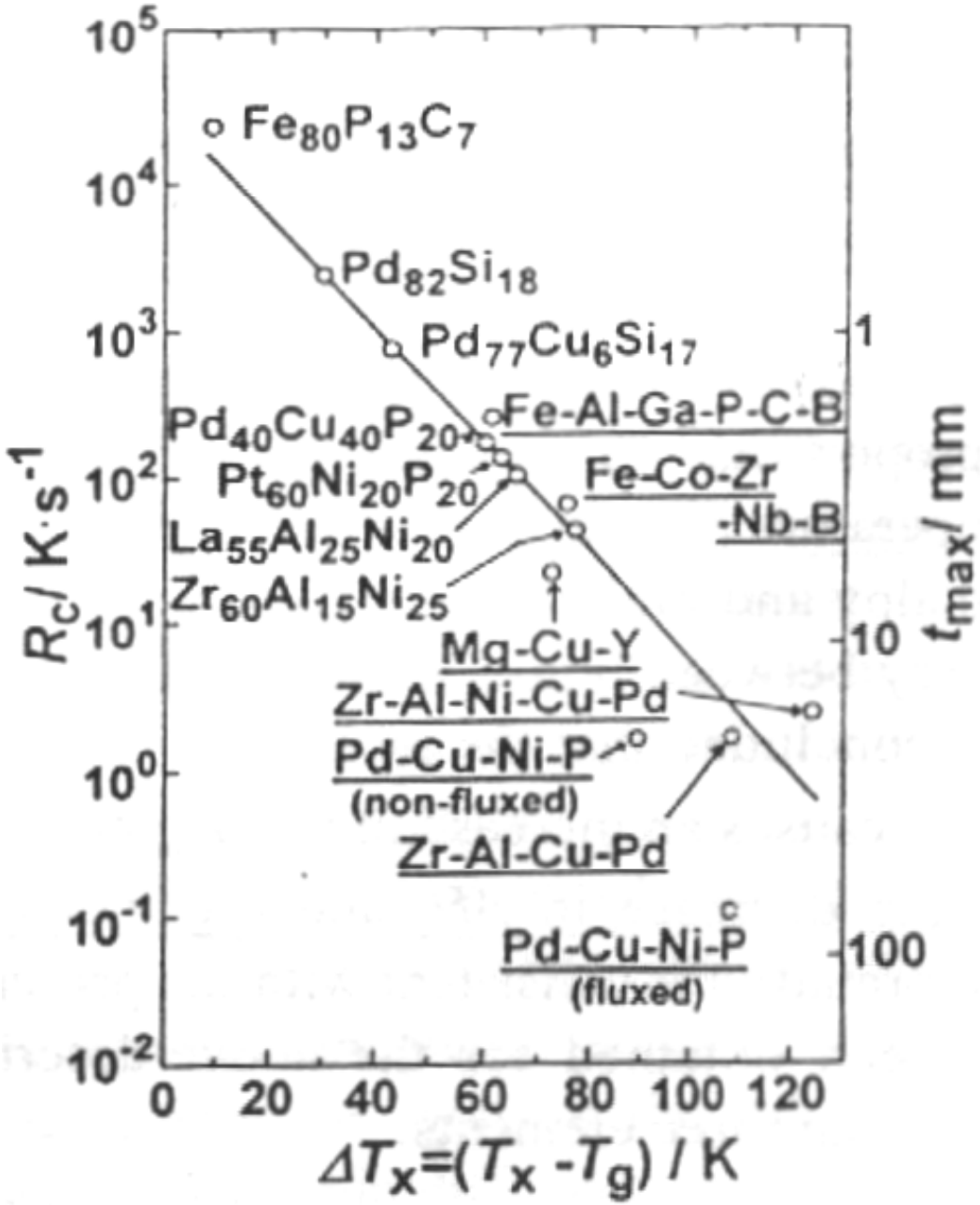
Critical cooling rate

$$R_c = \frac{T_m - T_n}{t_o^*}$$





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


$Fe_{80}P_{13}C_7$
$Pd_{82}Si_{18}$
$Pd_{77}Cu_6Si_{17}$
$Pd_{40}Cu_{40}P_{20}$
$Pt_{60}Ni_{20}P_{20}$
$La_{55}Al_{25}Ni_{20}$
$Zr_{60}Al_{15}Ni_{25}$
Fe-Al-Ga-P-C-B
Fe-Co-Zr
-Nb-B
Mg-Cu-Y
Zr-Al-Ni-Cu-Pd
Pd-Cu-Ni-P
(non-fluxed)
Zr-Al-Cu-Pd
Pd-Cu-Ni-P
(fluxed)
R_c / K·s^{-1}
t_{max} / mm
$\Delta T_x = (T_x - T_g)$ / K

Critical Cooling Rates for Various Liquids

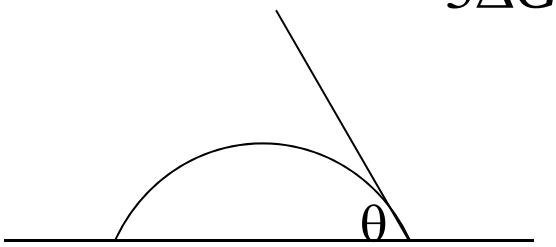
Table 3-5. Examples of Critical Cooling Rates (°C/s) for Glass Formation

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}

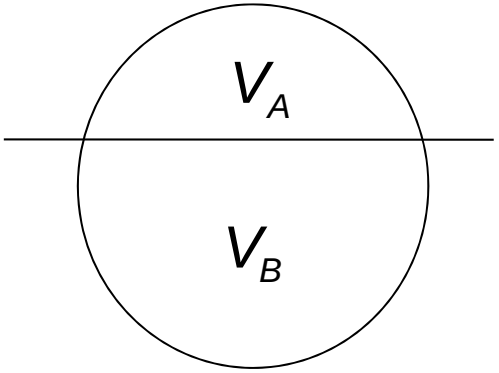
[a] After P. I. K. Onorato and D. R. Uhlmann, J. Non-Cryst. Sol., 22(2), 367–378 (1976).

Barrier of Heterogeneous Nucleation

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



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



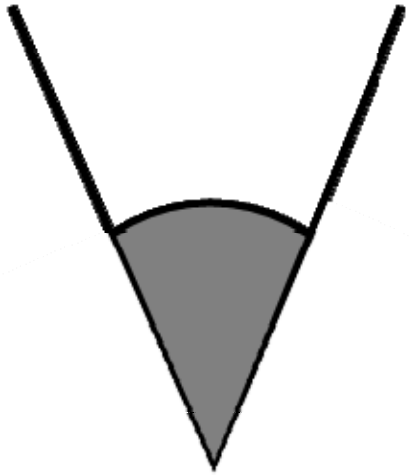
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

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

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

Nucleation Barrier at the crevice

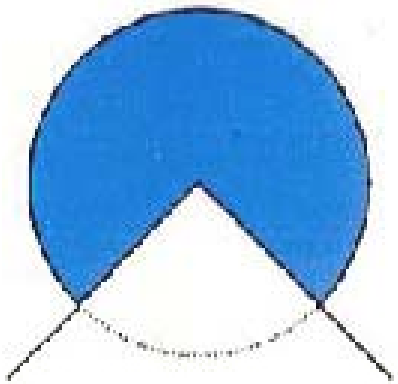
What would be the shape of nucleus and the nucleation barrier for the following conditions?



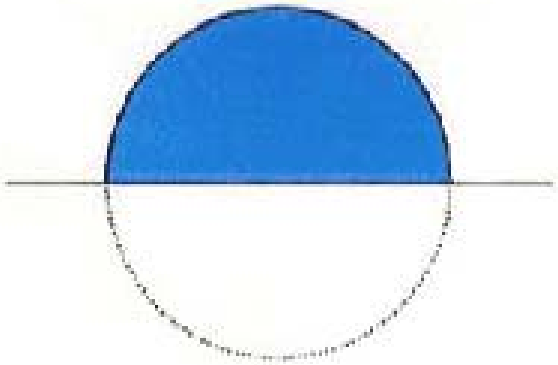
contact angle = 90

groove angle = 60

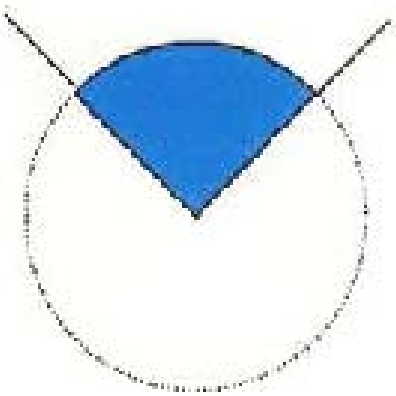
$$\frac{1}{6}\Delta G^*_{\text{homo}}$$



$$\frac{3}{4}\Delta G^*_{\text{homo}}$$

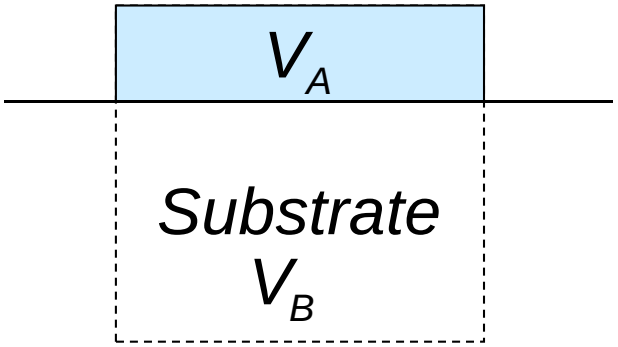


$$\frac{1}{2}\Delta G^*_{\text{homo}}$$

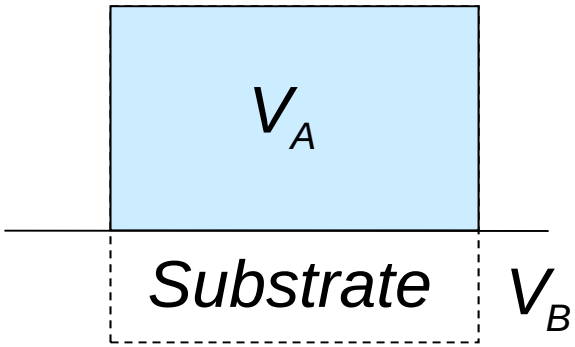


$$\frac{1}{4}\Delta G^*_{\text{homo}}$$

How do we treat the non-spherical shape?



Good Wetting



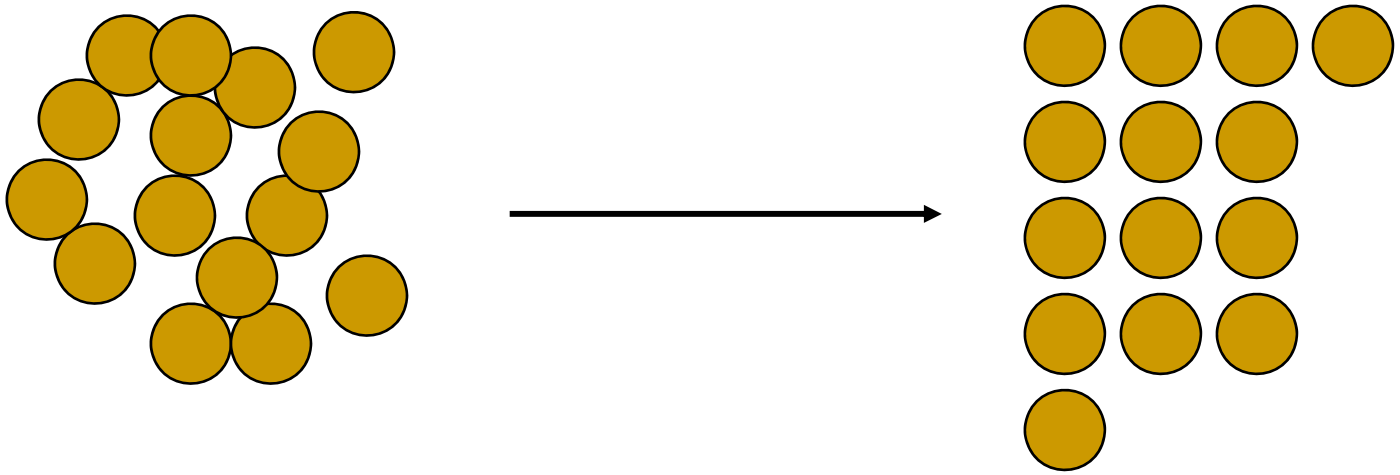
Bad Wetting

$$\Delta G^*_{sub} = \Delta G^*_{homo} \left(\frac{V_A}{V_A + V_B} \right)$$

Effect of good and bad wetting on substrate

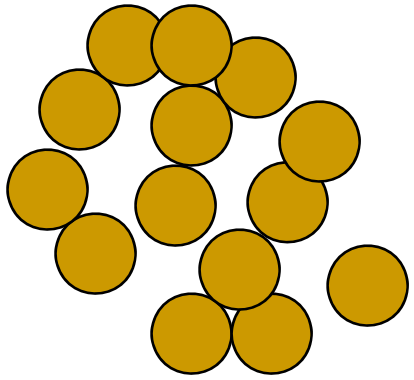
Nucleation and Growth Rates Control R_c

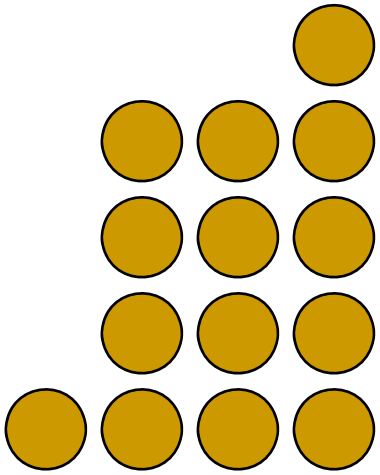
- Nucleation, the first step…
- First process is for microscopic clusters (nuclei) of atoms or ions to form
  - Nuclei possess the beginnings of the structure of the crystal
  - Only limited diffusion is necessary
  - Thermodynamic driving force for crystallization must be present



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

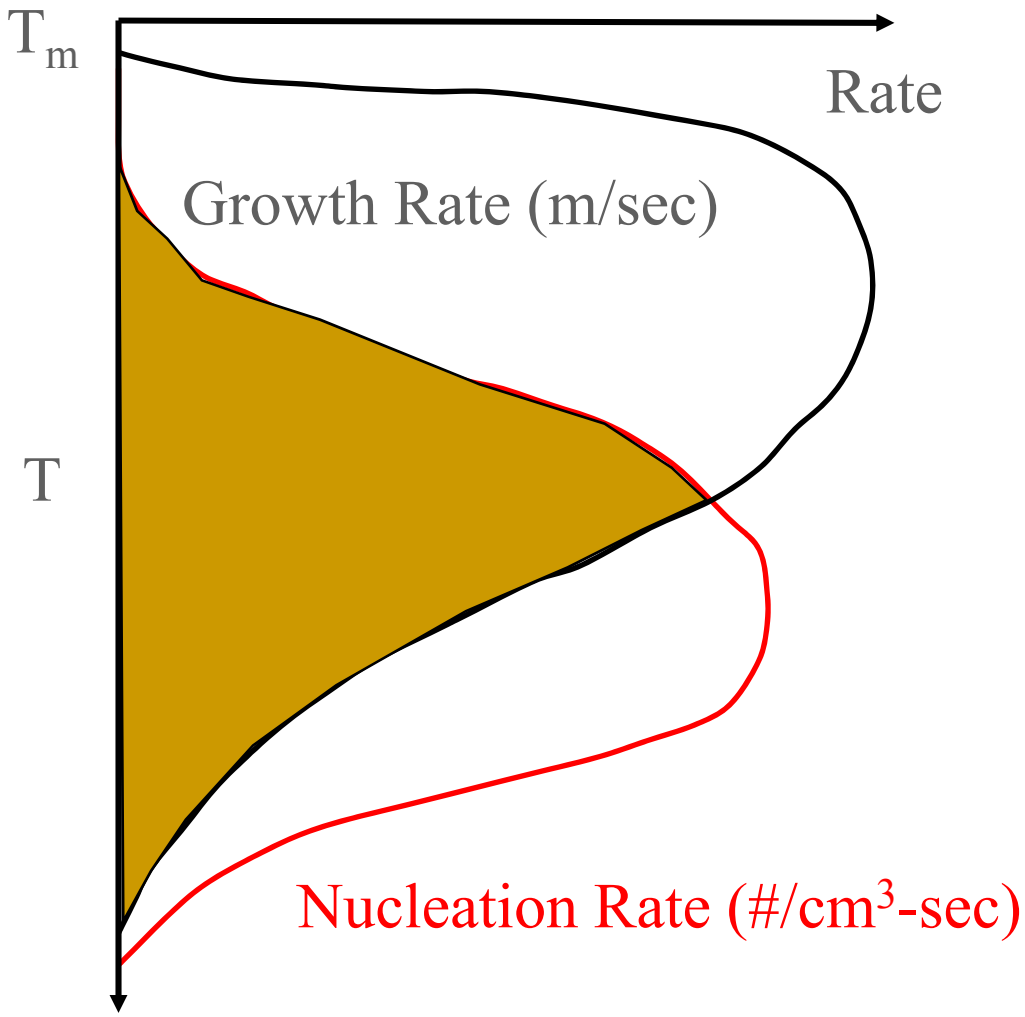




Nucleation and Growth Control R_c

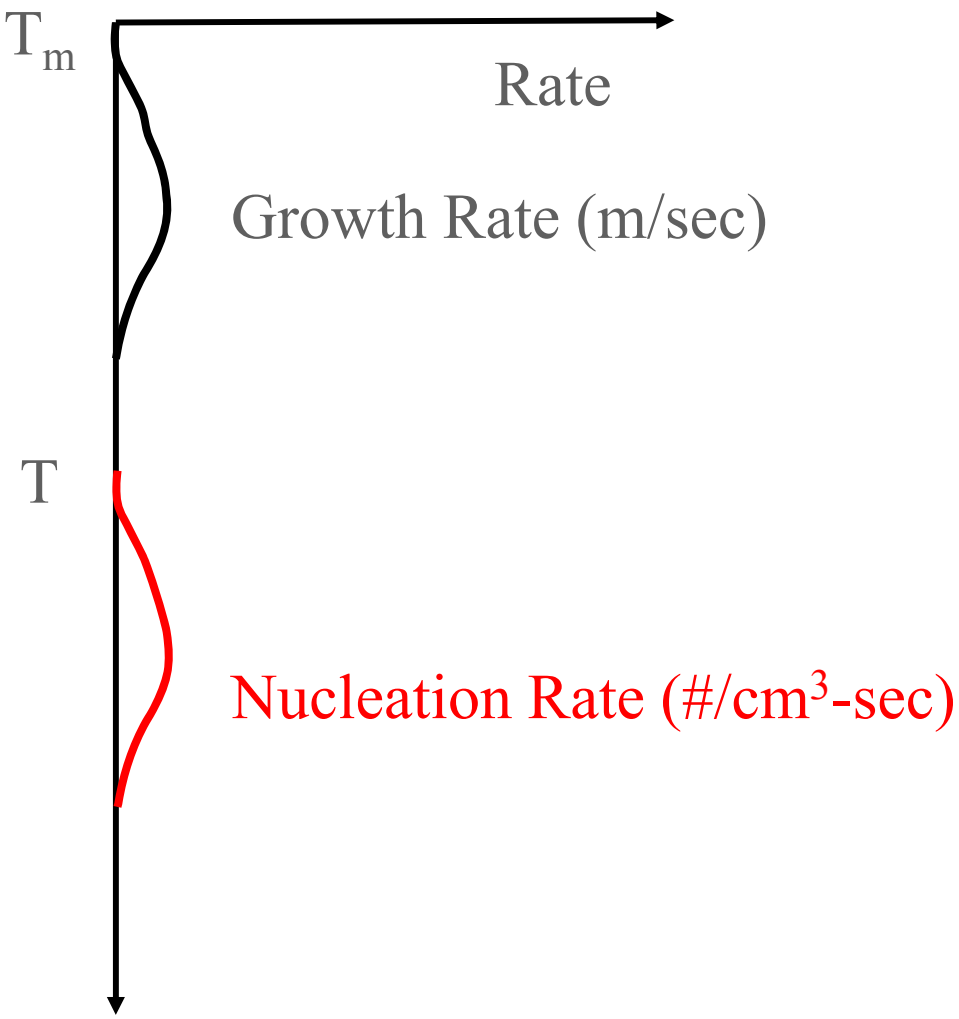
- Poor glass formers:
  - Liquids which quickly form large numbers of nuclei close to T_m
  - That grow very quickly
- Good glass formers
  - Liquids that are sluggish to form nuclei even far below T_m
  - That grow very slowly

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

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

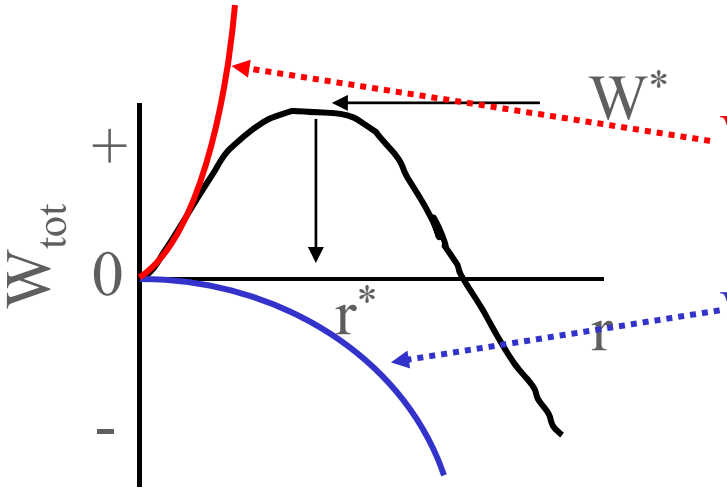
Nucleation Rate Theory

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

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 ~ 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

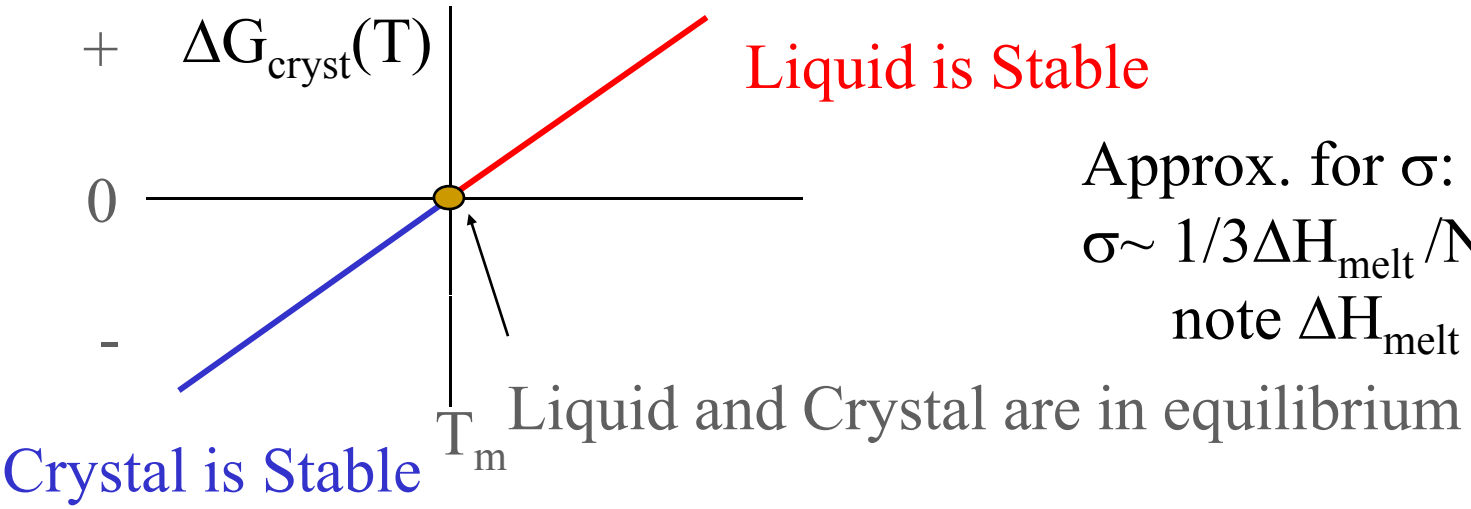
$\Delta G_{cryst}(T)$, the Gibb's Free-Energy of Cryst. per unit volume, V_m

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

- 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)

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



Approx. for σ:

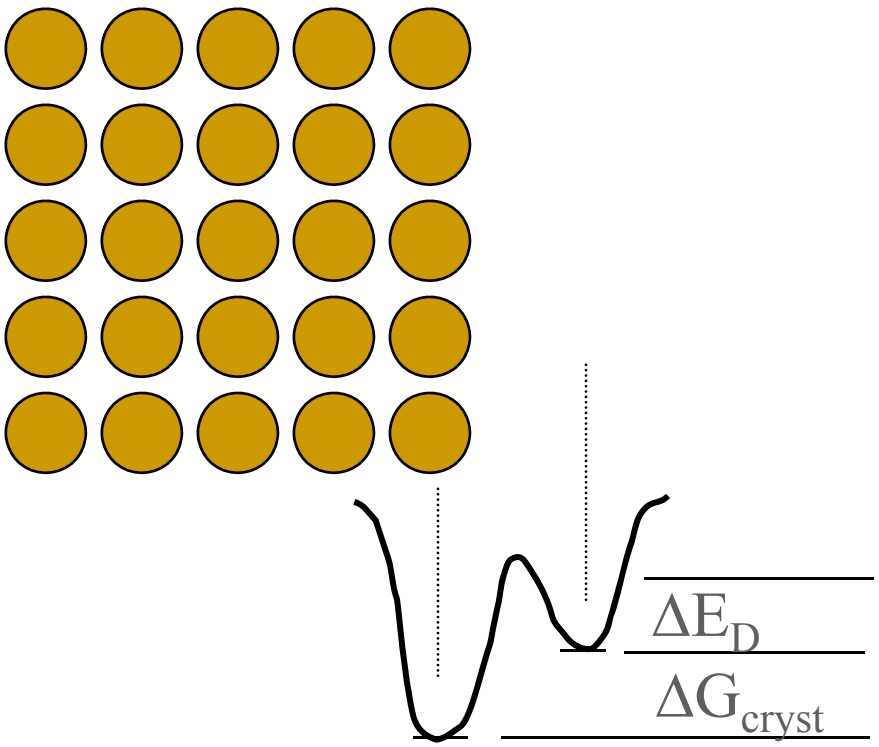
$\sigma \sim 1/3\Delta H_{melt}/N^{1/3}V_m^{2/3}$

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

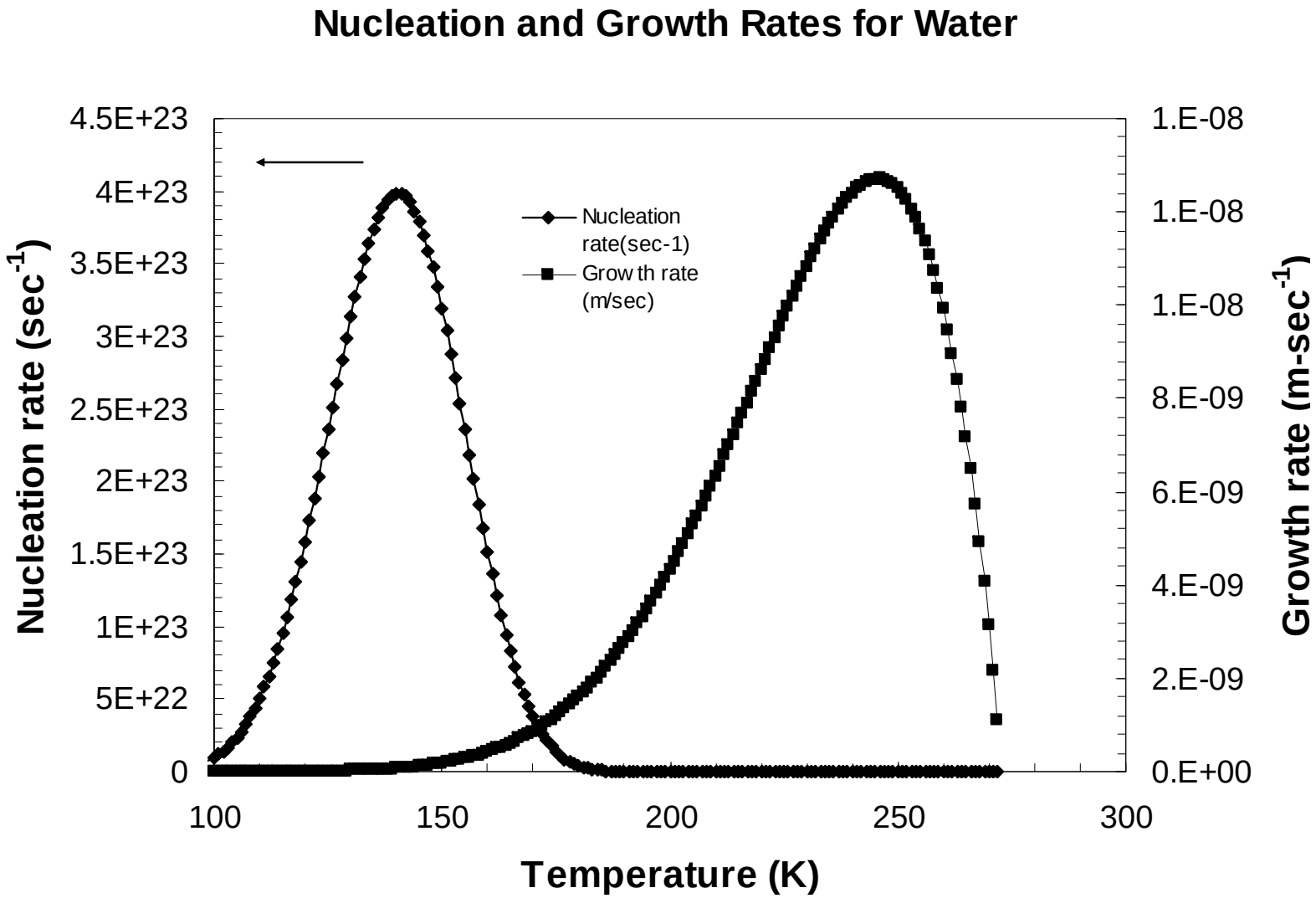
$$D(T) = a^2 \nu \exp\left[\frac{-\Delta E_D}{RT}\right] = \left(\frac{fRT}{3N\pi a\,\eta(T)}\right)$$

Stokes-Einstein relation between D and η

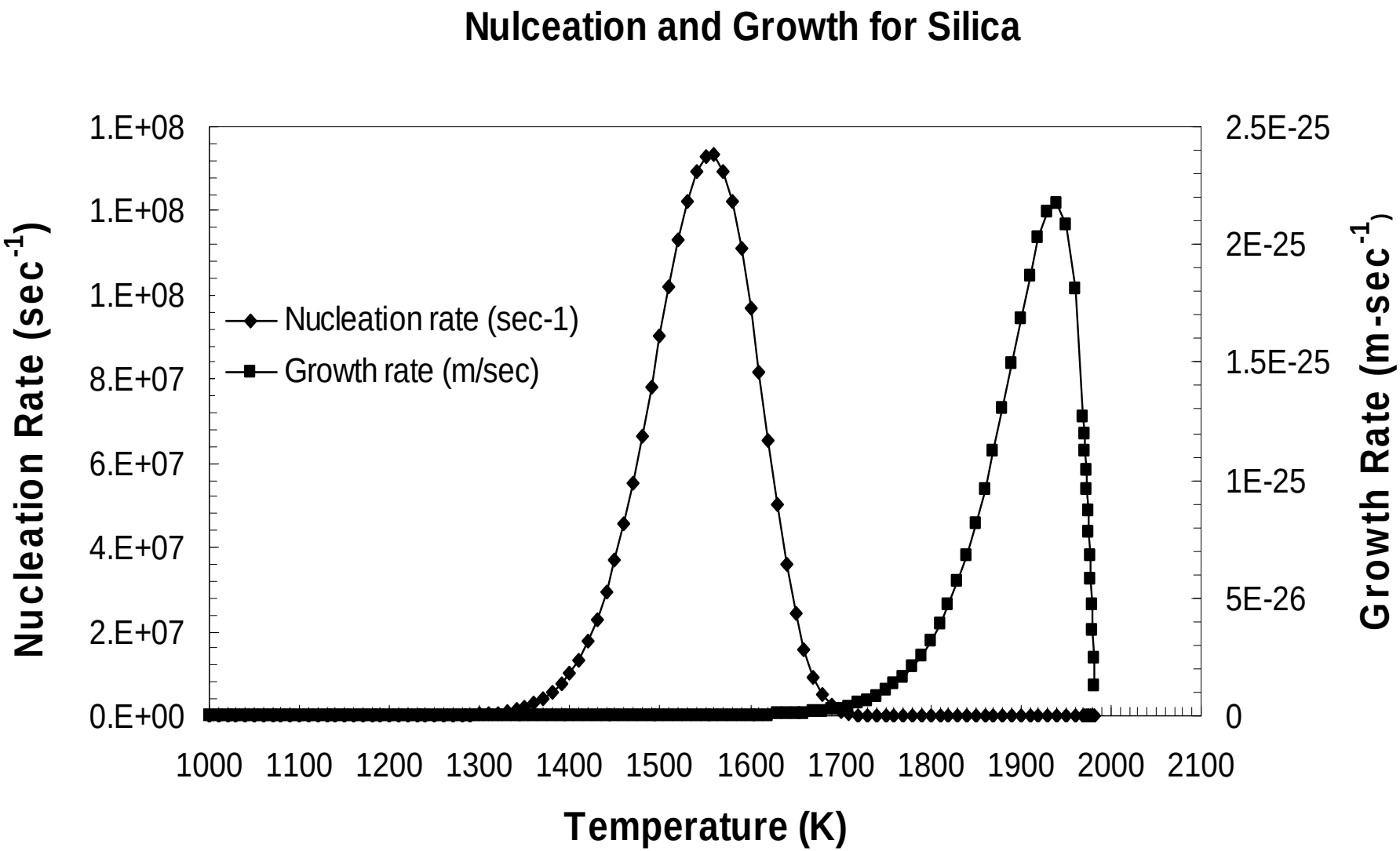
Hence:

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

Nucleation and Growth Rates



Nucleation and Growth Rates



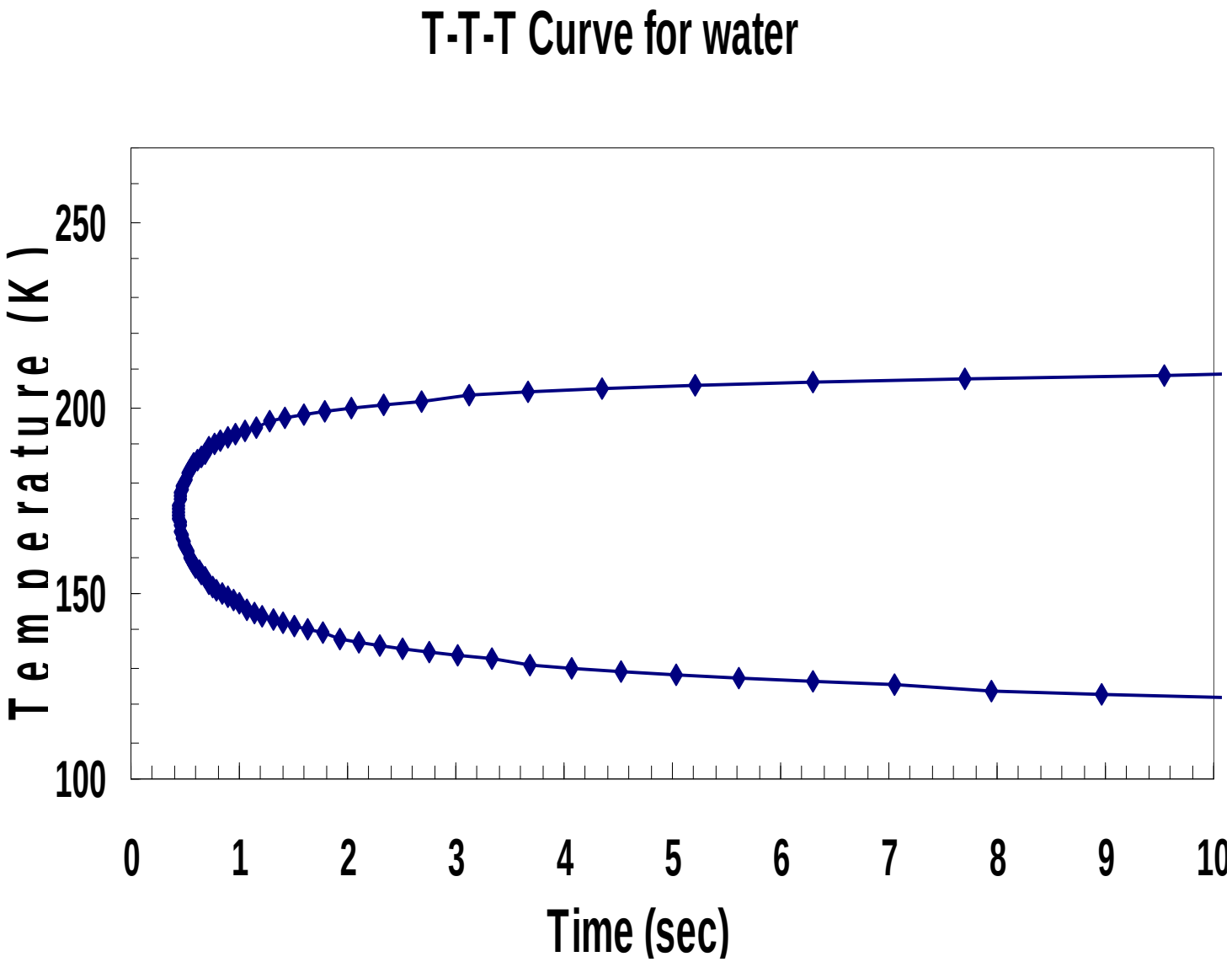
Time–Temperature–Transformation Curves (TTT)

- 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?

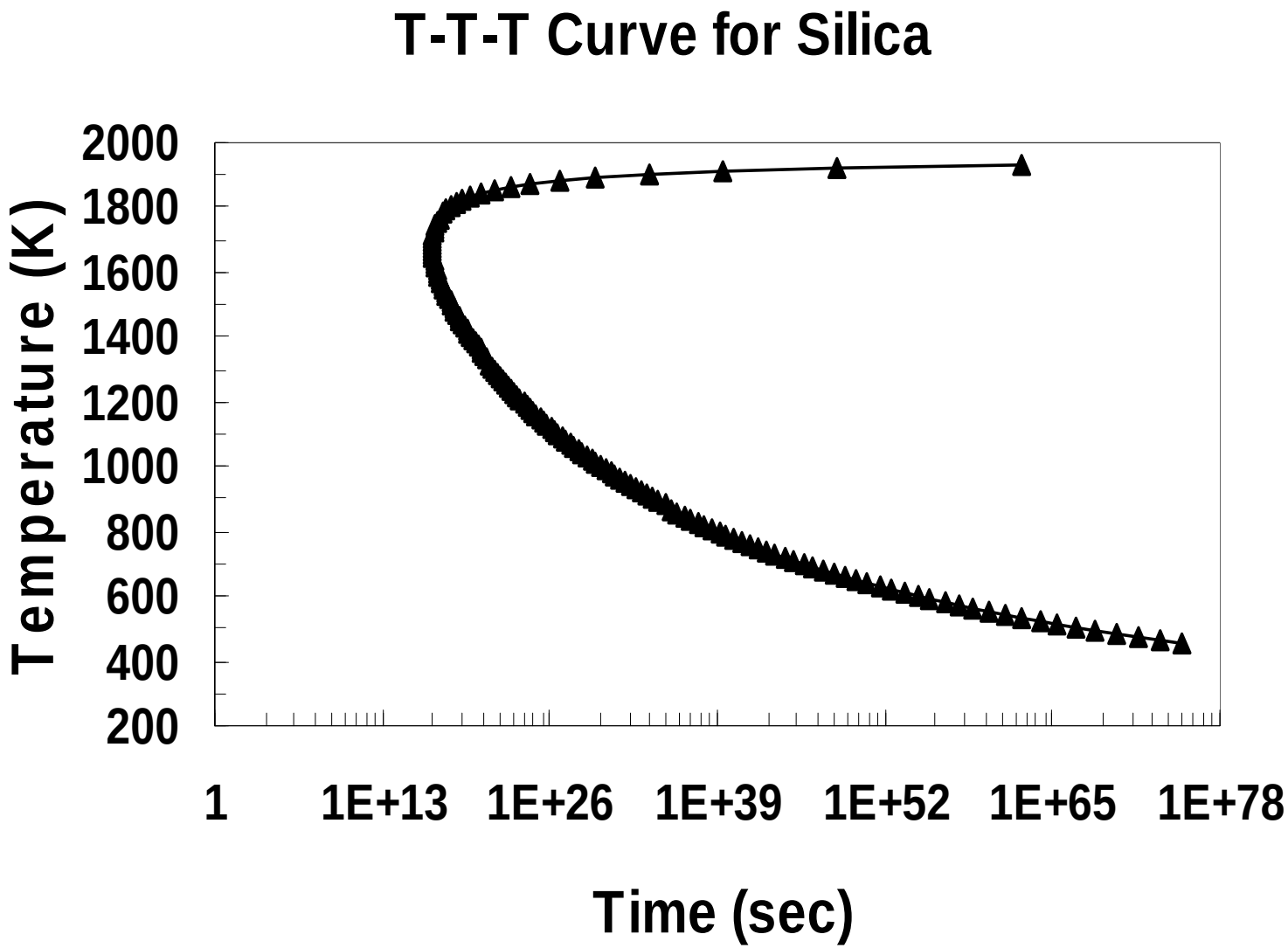
- $X(t,T) \sim \pi I(T) \mu(T)^3 t^4/3$

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

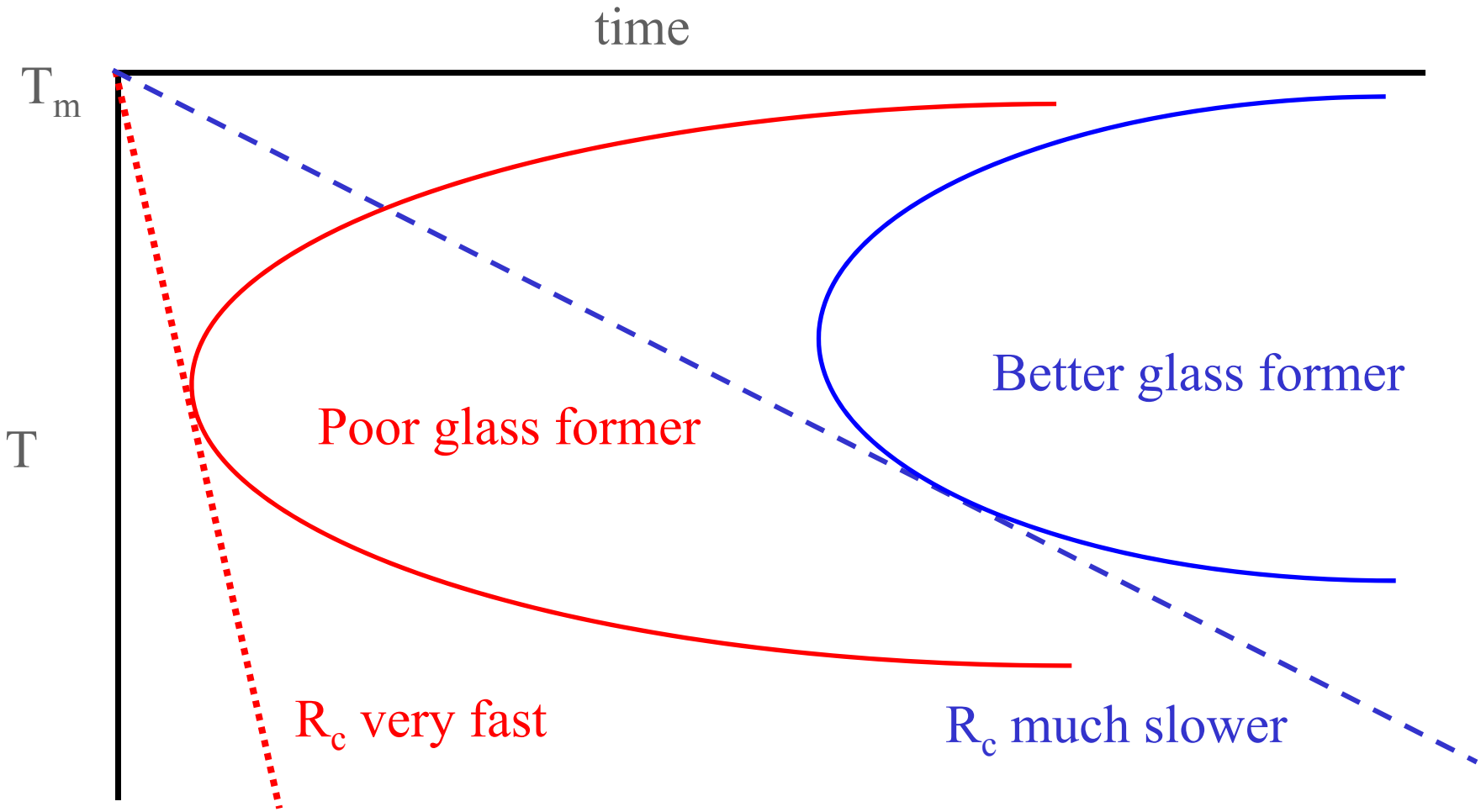
Time Transformation Curves for Water



Time Transformation Curves for Silica



TTT curves and the critical cooling rate, R_c



Summary

Glass formation results when the internal structural timescale of the liquid **becomes** or is **forced to become** significantly longer than the external time scale of the surroundings near the melting or liquidus temperature of the liquid

- Create high viscosity of the liquid (= dense packed structure) near the melting point of the liquid that frustrates crystallization
  - Network bonding favorable for high viscosity
  - Configurational complexity that frustrates crystallization pathways
  - Suppress the melting point through compositional complexity to slow crystallization process
- Surpass crystallization processes by limiting available to system for them to occur
  - Exceed critical cooling rate in region near and below the fusion point of the liquid