Advanced Vitreous State: The Structure of Glass

Section 1: Lecture 2 – Fundamentals of Glass Formation: Structural and Kinetic Approaches

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

Optimizing $\tau_{internal}$ for glass formation – Structural approach to glass formation
- *Understand and be able to apply the relationships between atomic level structure and ease at which a system will form glass*
- *Understand and be able to apply Zacharaisen's Rules for glass formation*
- *Be able to apply understanding of the three different types of additives, modifiers, intermediates, and glass formers, to multi-component systems to predict whether a particular composition will be glass forming or not.*

Estimating $\tau_{external}$ for glass formation – Kinetic approach to glass formation
- *Understand and be able to use nucleation and growth theory*
- *Understand and be able to use TTT curves*
- *Understand and be able to calculate critical cooling rates*

Structural Approach to Glass Formation

- Crystalline materials exhibit a periodic array of atoms and/or ions
- Each atom/ion in the material has a specific location that is periodic in the crystalline structure
- Each location can be exactly specified once the crystalline structure is defined
- Defects in the structure occur when the position and atom/ion type do not agree with that prescribed by the crystal structure

A_2O_3 (B_2O_3)

(a)

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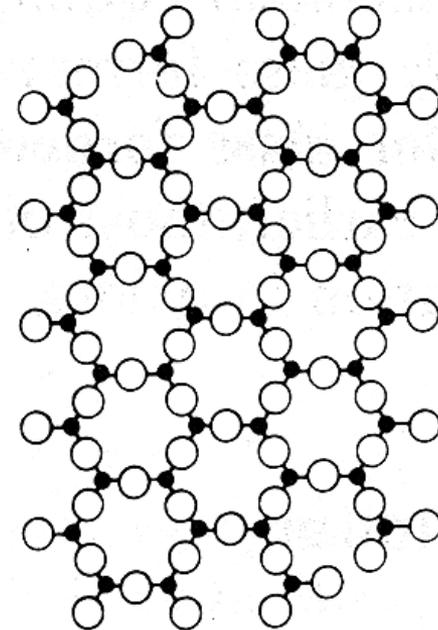
Structural Approach to Glass Formation

- Amorphous materials lack this long range order
- There is no prescription for which atoms/ions are located at which locations
- However, the energetics of bond formation are very strong
- Atoms will align themselves chemically to:
  - Balance charge in ionic materials
  - Minimize bond energies by filling appropriate bonding orbitals
- Hence, local structure is disordered, but there are still many similarities to the crystalline phase
  - Coordination numbers are ~ same
  - Bond lengths are ~ same
  - Bond Angles are ~ same

A_2O_3 (B_2O_3)

(b)

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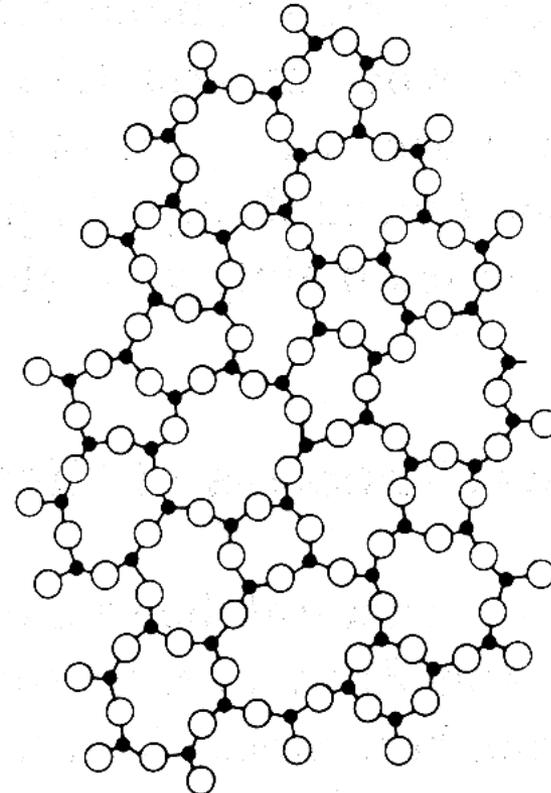
Structural Approach to Glass Formation

- 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

  - Structural Approach to Glass Formation
    - What internal structures promote glass formation?
    - How can structures be developed that increase the viscosity and frustrate crystallization processes?

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Structural Approach to Glass Formation

- Using structure to promote glass formation
  - Develop atomic bonding structures in the system that produce large viscosity near the melting point
    - *Silicate liquids and glasses*
      - *SiO_2 , Na_2O + CaO + SiO_2*
  - Develop large molecular structures that due to their size prevent and/or frustrate the organization into the crystalline structure
    - *Polymeric liquids with large polymer chains*
      - *$-(CH_2)_n-$*
    - Develop complex local and variable structures in the liquid that on cooling have a large number of possible structural motifs to follow and as a result no one structure is favored over another
      - *Molten salt liquids with a number of components*
      - *$Ca(NO_3)_2$ + KNO_3*

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Zacharaisen's Rules for Glass Formation

- Glass formation requires long range continuous bonding in the liquid to produce:
    - High viscosity
    - 3 - Dimensional bonding
    - Strong individual bond strength
    - "Open" structure that is not efficiently packed
    - Corners of polyhedra are shared to increase "connectivity"
    - Bonds for bridges between corner sharing polyhedra

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Zacharaisen's Rules for Glass Formation

- Oxygen atoms are linked (bonded) to no more than two atoms

- Oxygen coordination around glass forming cations is small, 3, 4

- Cation polyhedra share corners and not edges or faces

- At least three corners are shared

William H. Zachariasen, Journal of the American Chemical Society
54 (1932) 3841-3851

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Zacharaisen's Rules for Glass Formation

- Apply these rules to the following:
  - $SiO_{4/2}$
  - B_2O_3 or $BO_{3/2}$

- Apply these rules to the following:
  - CaO
  - Na_2O

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Zacharaisen's Rules for Glass Formation

- $SiO_{4/2}$

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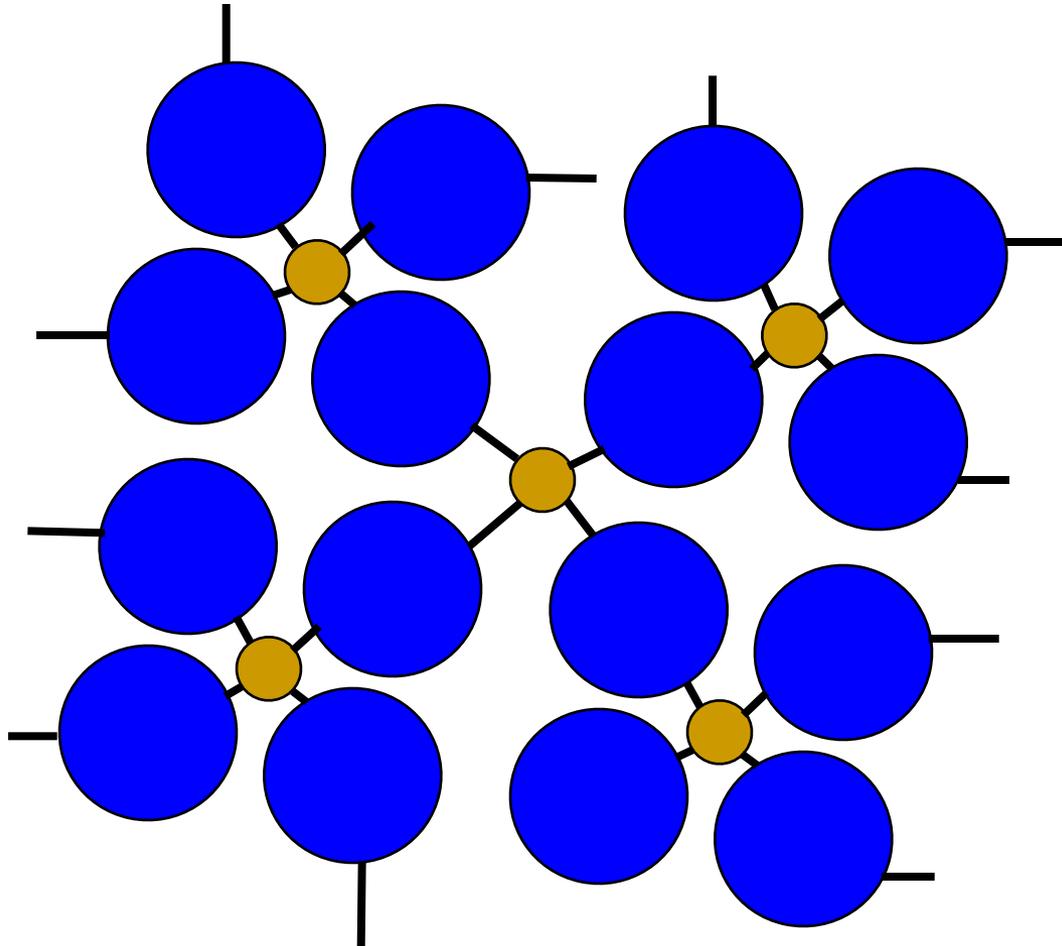
Zacharaisen's Rules for Glass Formation

- B_2O_3 or $BO_{3/2}$

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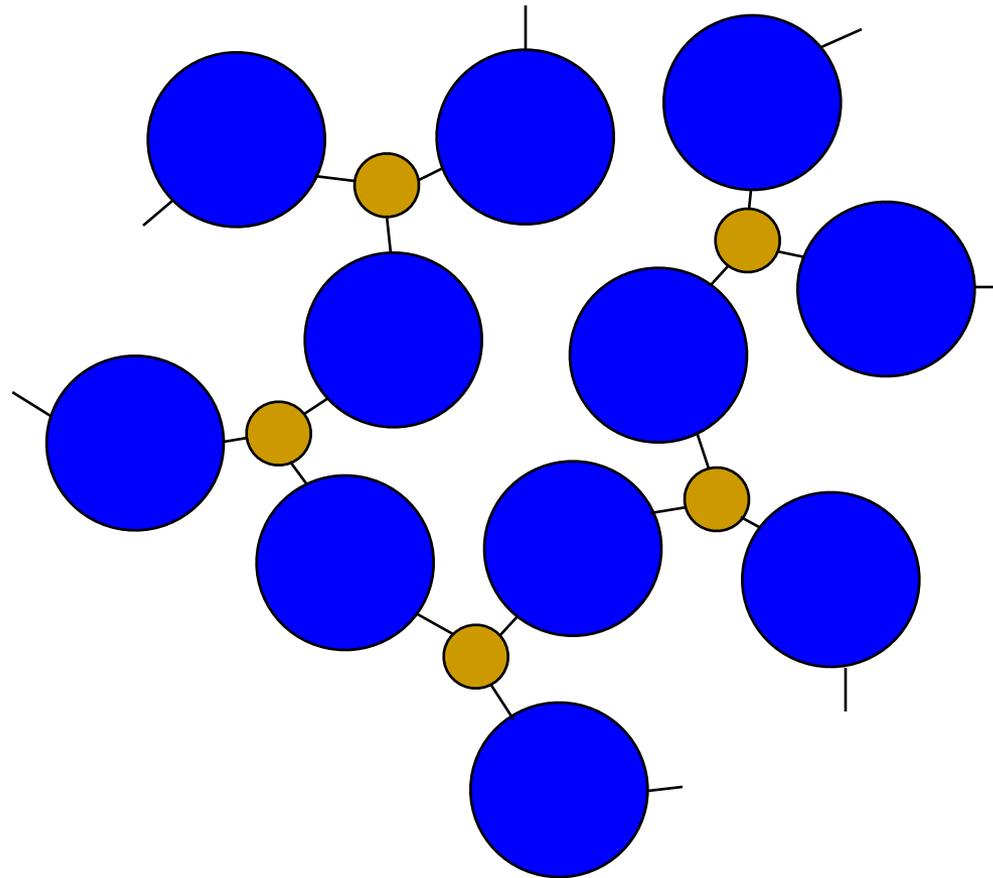
Zacharaisen's Rules for Modifiers

Ca_1O_1 (CaO) Closed-packed cubic
- Ca occupying all octahedral sites
- Octahedral sites = Ca = O

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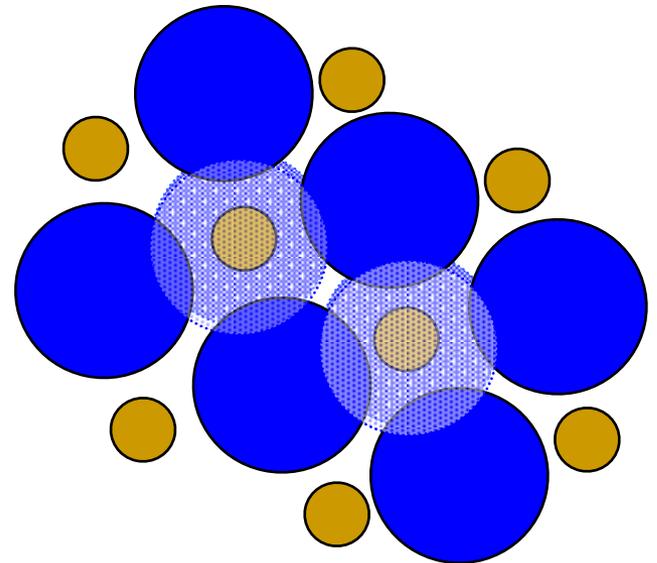
Zacharaisen's Rules for Modifiers – M_2O

Na_2O_1 (Na_2O) Closed-packed cubic
- Na occupying tetrahedral sites
- Tetrahedral sites = 2 x O = Na

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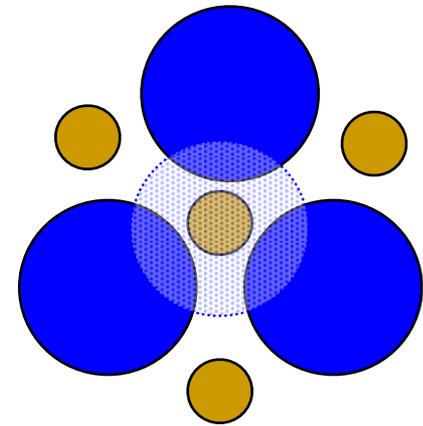
Sun's Bond Strength Model

- Glass formation is brought about by both:
    - Connectivity of bridge bonds
    - Strong Bonds between atoms (ions)
- Sun classified oxide according to their bond strengths
    - Glass formers form strong bonds to oxygen – rigid network, high   viscosity
    - Modifiers from weak bonds to oxygen – Disrupt, modify, network
    - Intermediates form intermediate bonds to oxygen – can't form glasses on their own, but aid with other oxides to form glasses

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Sun's Bond Strength Model

- **Glass formers**

  Greater than 80 kcal/mole bond strength with oxygen

  - B_2O_3, SiO_2, Geo_2, P_2O_5, Al_2O_5….

- **Intermediates**

  Between 60 to 80 kcal/mol bond strength with oxygen

  - TiO_2, ZnO, PbO….

- **Modifiers**

  Less than 60 kcal/mole bond strength with oxygen

  - Li_2O, Na_2O, K_2O, MgO, CaO….

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Glass Formers (Oxides) – form glasses on their own

Table 3-2. Single Bond Strengths for Oxides[a]

	M in MO_x	Valence	Dissociation energy $E_{d'}$ per MO_x (kcals)	Coordination number[b]	Single-bond strength (kcals)
Glass formers	B	3	356	3	119
	Si	4	424	4	106
	Ge	4	431	4	108
	Al	3	402–317	4	101–79
	B	3	356	4	89
	P	5	442	4	111–88
	V	5	449	4	112–90
	As	5	349	4	87–70
	Sb	5	339	4	85–68
	Zr	4	485	6	81

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Intermediates (Oxides) – assist in glass formation

	M in MO_x	Valence	Dissociation energy $E_{d'}$ per MO_x (kcals)	Coordination number[b]	Single-bond strength (kcals)
Intermediates	Ti	4	435	6	73
	Zn	2	144	2	72
	Pb	2	145	2	73
	Al	3	317–402	6	53–67
	Th	4	516	8	64
	Be	2	250	4	63
	Zr	4	485	8	61
	Cd	2	119	2	60

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Modifiers (Oxides) – degrade glass formation

Modifiers					
	Sc	3	362	6	60
	La	3	406	7	58
	Y	3	399	8	50
	Sn	4	278	6	46
	Ga	3	267	6	45
	In	3	259	6	43
	Th	4	516	12	43
	Pb	4	232	6	39
	Mg	2	222	6	37
	Li	1	144	4	36
	Pb	2	145	4	36
	Zn	2	144	4	36
	Ba	2	260	8	33
	Ca	2	257	8	32
	Sr	2	256	8	32
	Cd	2	119	4	30
	Na	1	120	6	20
	Cd	2	119	6	20
	K	1	115	9	13
	Rb	1	115	10	12
	Hg	2	68	6	11
	Cs	1	114	12	10

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Classifying Oxides

- How would each of the following be classified?
  - SiO_2, B_2O_3, P_2O_5
  - TiO_2, PbO
  - Na_2O, CaO, ZnO

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Dietzel's Field Strength Criteria

- Sun classifies Al as both a glass former and an intermediate
    - Al_2O_3 does not form glass at normal quenching rates
    - More factors are important than just bond strength
        - Small cations with high charge – glass formers
        - Large cations with small charge – modifiers
        - Medium sized cations with medium charge - intermediates

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Dietzel's Field Strength Model

Table 3-3. Field Strengths of Various Ions[a]

Element	Valence Z	Ionic radius (for CN =6) r in Å	Most frequent coordination number CN	Ionic distance for oxides a in Å	Field strength at distance of O^2 ions Z/a^2	Function in glass structure
K	1	1.33	8	2.77	0.13	
Na	1	0.98	6	2.30	0.19	
Li	1	0.78	6	2.10	0.23	
Ba	2	1.43	8	2.86	0.24	Network modifier $Z/a^2 \approx 0.1 \ldots 0.4$
Pb	2	1.32	8	2.74	0.27	
Sr	2	1.27	8	2.69	0.28	
Ca	2	1.06	8	2.48	0.33	
Mn	2	0.91	6	2.23	0.40	
Fe	2	0.83	6	2.15	0.43	

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Intermediates – assist in glass formation

Element	Valence Z	Ionic radius (for CN =6) r in Å	Most frequent coordination number CN	Ionic distance for oxides a in Å	Field strength at distance of O^2 ions Z/a^2	Function in glass structure
Mn	2	0.83	4	2.03	0.49	
Mg	2	0.78	6	2.10	0.45	
			4	1.96	0.53	
Zr	4	0.87	8	2.28	0.77	
Be	2	0.34	4	1.53	0.86	Intermediate
Fe	3	0.67	6	1.99	0.76	$Z/a^2 \approx 0.5 \ldots 1$
			4	1.88	0.85	
Al	3	0.57	6	1.89	0.84	
			4	1.77	0.96	
Ti	4	0.64	6	1.96	1.04	

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Glass forming oxides – form glass on their own

Element	Valence Z	Ionic radius (for $CN = 6$) r in Å	Most frequent coordination number CN	Ionic distance for oxides a in Å	Field strength at distance of O^2 ions Z/a^2	Function in glass structure
B	3	0.20	4	1.50	1.34	
Ge	4	0.44	4	1.66	1.45	Network former $Z/a^2 \approx 1.5 \ldots 2.0$
Si	4	0.39	4	1.60	1.57	
P	5	0.34	4	1.55	2.1	
B	3	0.20	3	1.36	1.63	

[a] After Dietzel [11].

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Glass forming compositions

- How would you classify the following compositions? Glassforming or not?
- $0.15Na_2O + 0.35Al_2O_3 + 0.50SiO_2$
- $0.35Na_2O + 0.15CaO + 0.25Al_2O_3 + 0.25SiO_2$

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Advanced Vitreous State: The Structure of Glass

Section 1: Lecture 2 – Fundamentals of Glass Formation: Structural and Kinetic Approaches

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

Kinetic Theory of Glass Formation

- *Understand and be able to use nucleation and growth theory*

- *Understand and be able to use TTT curves*

- *Understand and be able to calculate critical cooling rates*

Kinetic Approach to Glass Formation

- Glass formation requires the by-passing of the crystallization events at T_m
  - Structural approach is to create high viscosity to frustrate nucleation and growth processes
  - $SiO_{4/2}$ easily supercools due to the high connectivity of the liquid through strong –O-Si-O- bonding
- 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°C/sec, implies "marginal" glass forming ability
  - Slow cooling,<< 1°C/min, 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

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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).

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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°C/sec, then the liquid is a poor glass former
    - If R_c is << 1°C/min, the the liquid is a good glass former
    - How can R_c be calculated?
    - What are the factors that control R_c?

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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

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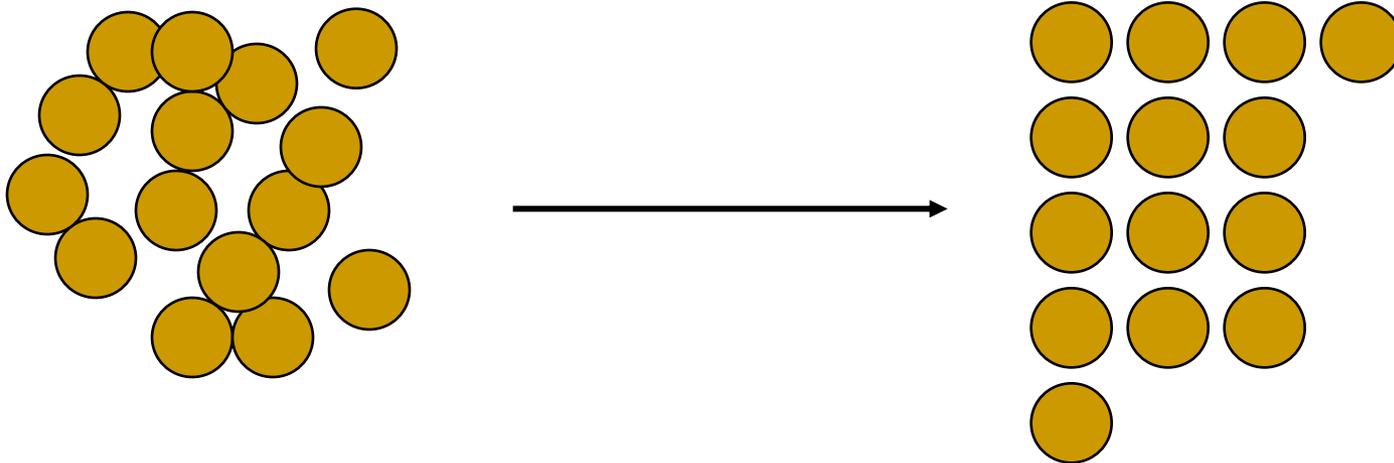
Growth of crystals from nuclei

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

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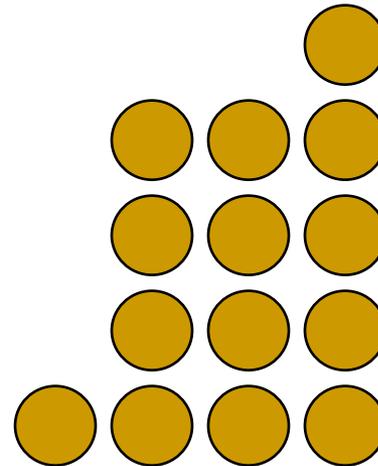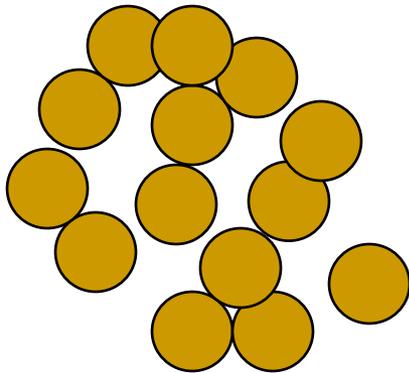
Nucleation and Growth Control R_c

- **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

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Nucleation and Growth Rates – Poor Glass Formers

T_m

T

Rate

Growth Rate (m/sec)

Nucleation Rate (#/cm³-sec)
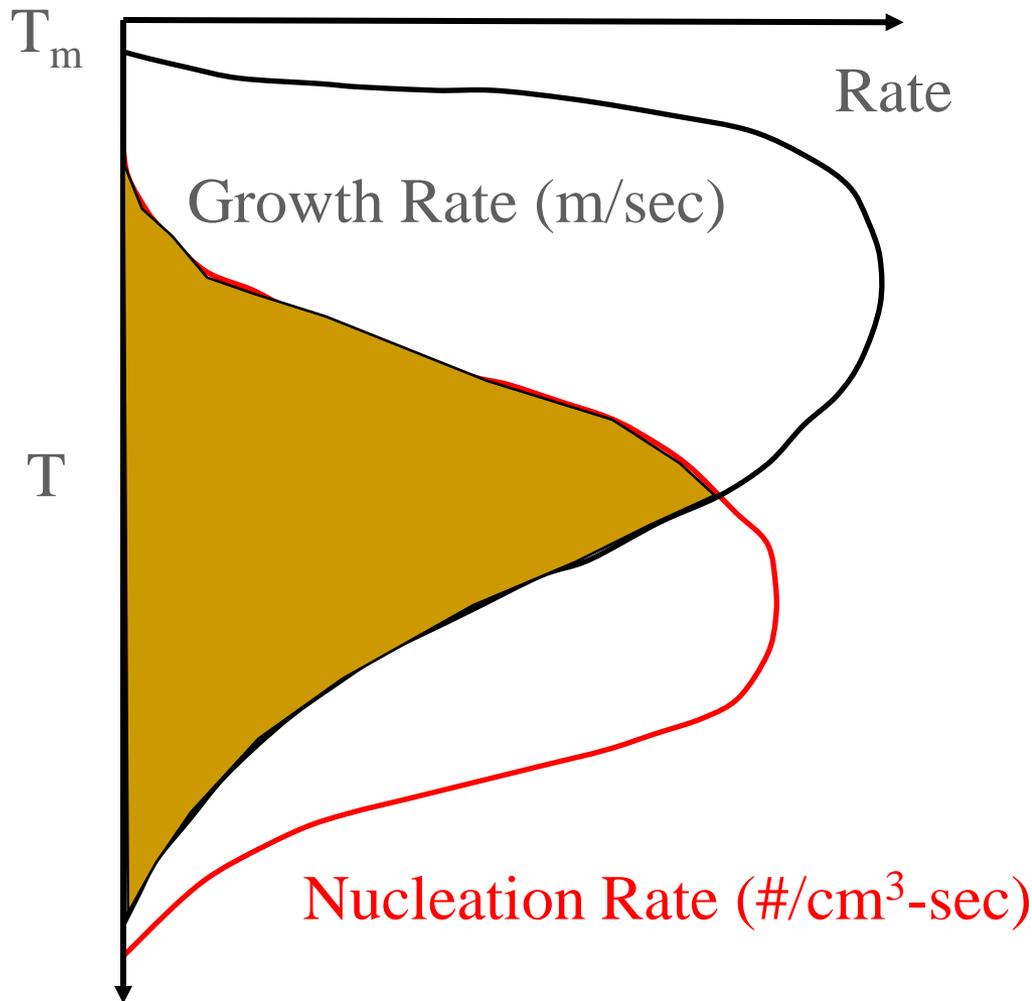
- Strong overlap of growth and nucleation rates
- Nucleation rate is high
- Growth rate is high
- Both are high at the same temperature

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Nucleation and Growth Rates – Good Glass Formers

Rate

T_m

Growth Rate (m/sec)

T

Nucleation Rate (#/cm^3-sec)
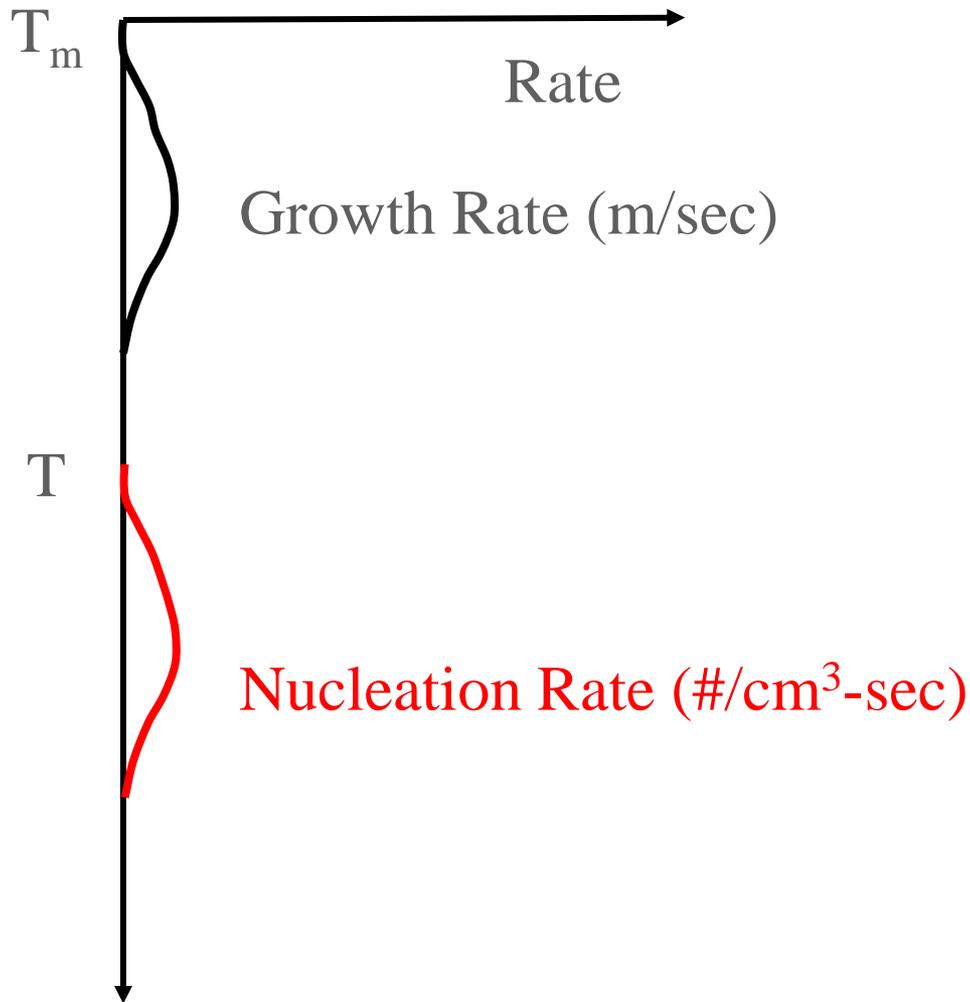
- No overlap of growth and nucleation rates
- Nucleation rate is small
- Growth rate is small
- At any one temperature one of the two is zero

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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

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Nucleation Rate Theory

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

Number density   Fastest motion   Thermodynamic probability   Diffusion probability

$$n = \text{number density of atoms, molecules, or formula units per unit volume}$$

$$= \rho \, N/\text{Atomic, molecular, formula weight}$$

$$\nu = \text{vibration frequency} \sim 10^{13} \text{ sec}^{-1}$$

$$N = \text{Avogadro's number}$$

$$= 6.023 \times 10^{23} \text{ atoms/mole}$$

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

$$\Delta E_D = \text{diffusion energy barrier to form nuclei}$$

$$\sim \text{viscosity activation energy}$$

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A word about the $f(x,T) = \exp(-x/T)$ function

- This function is bounded between 0 and 1
- As x >> 0, f >> 1
- As x >> ∞, f >> 0
- As T >> 0, f >> 0
- As T >> ∞, f >> 1
- Sketch a series of curves for T dependence on linear f and log f
- Linear T and 1/T

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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

$\Delta G_{crsyt}(T)$, the Gibb's Free-Energy of Cryst. per unit volume, V_m
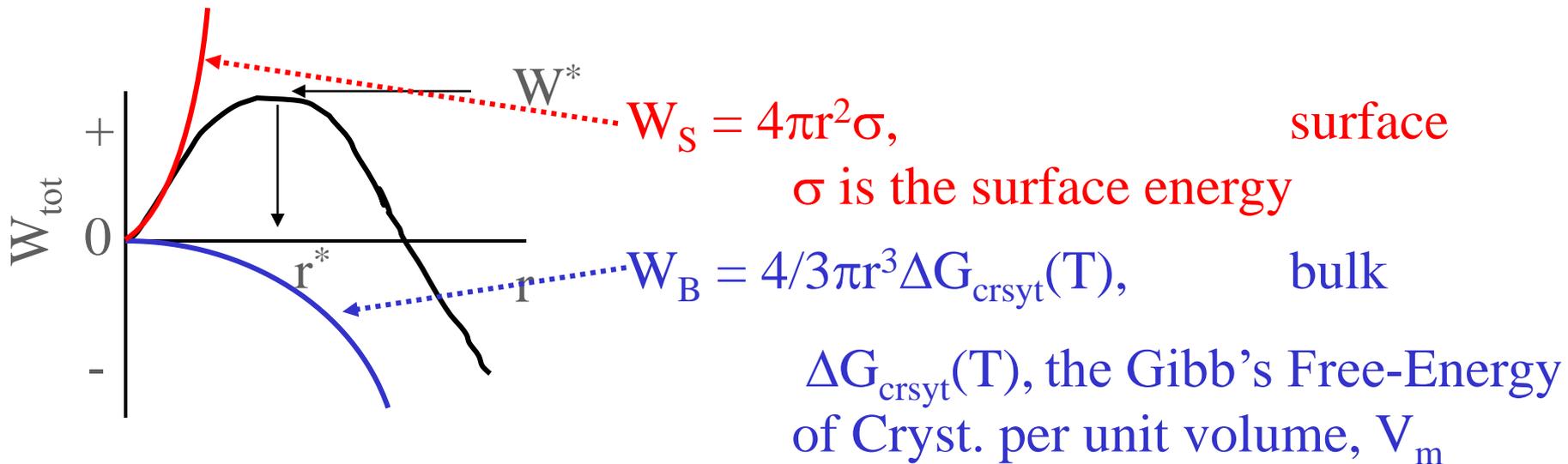
$W_{tot} = W_S + W_B$

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

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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

$-$

Crystal is Stable T_m Liquid and Crystal are in equilibrium

Approx. for σ:

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

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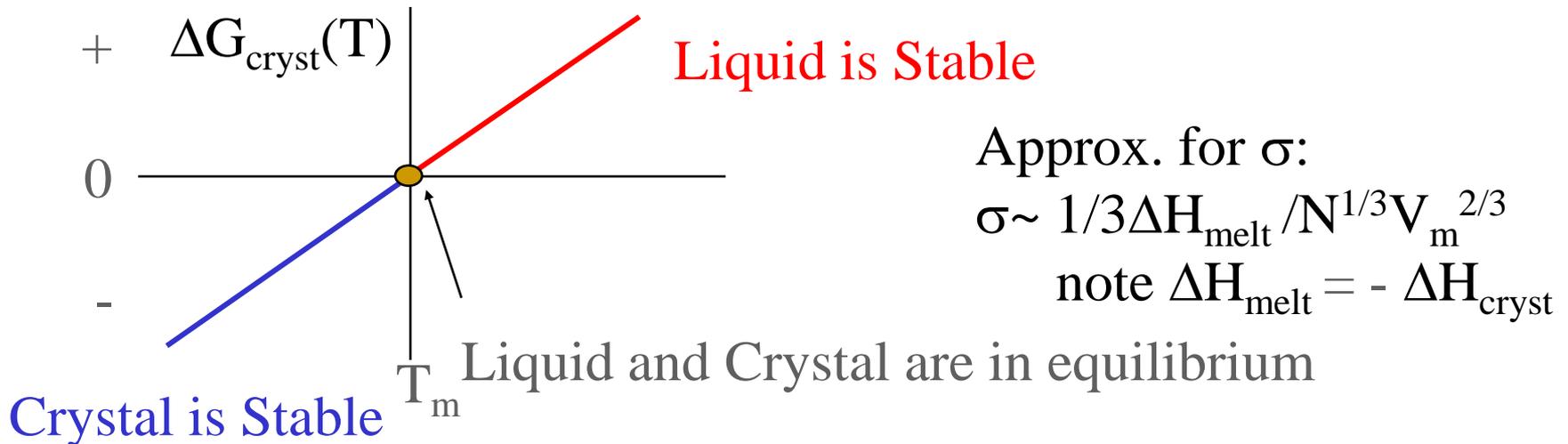
$$I = n\nu\exp\left\{\left(\frac{16\pi\Delta H_{cryst}}{81\,RT}\right)\left(\frac{T_m}{\Delta T}\right)^2\right\}\exp\left\{\frac{-\Delta E_D}{RT}\right\}$$

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Growth Rates $\mu(T)$

- Crystal growth requires
  - Diffusion to the nuclei surface
  - Crystallization onto the exposed crystal lattice
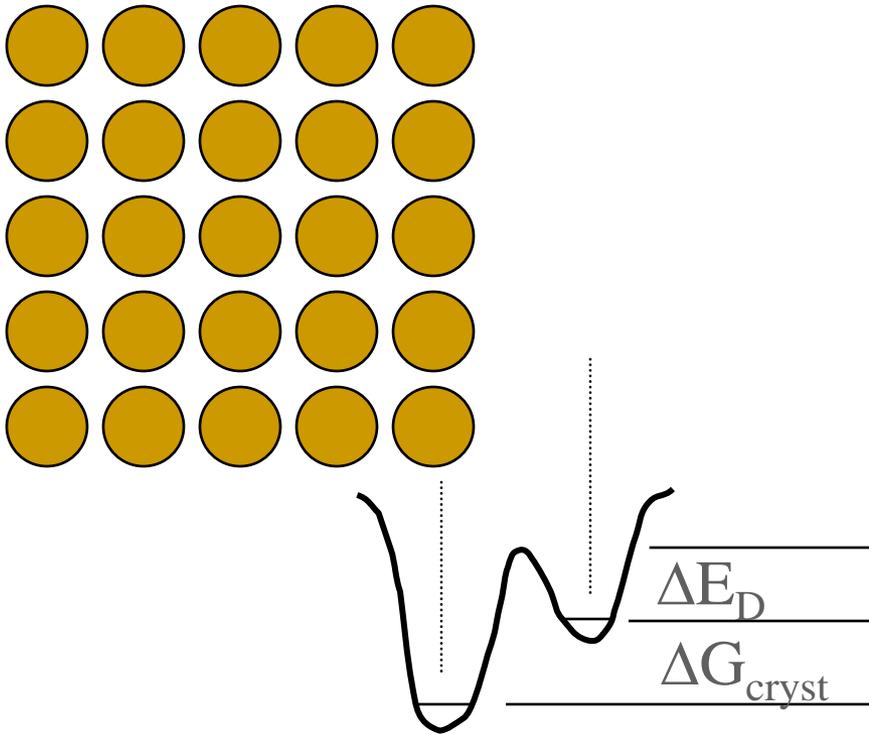
$$\nu_{l \to c} = \nu \exp(-\Delta E_D / RT)$$

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

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

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

ΔE_D

ΔG_{cryst}

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

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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:

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

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Nucleation and Growth Rates

Nucleation and Growth Rates for Water

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Nucleation and Growth Rates

Nulceation and Growth for Silica

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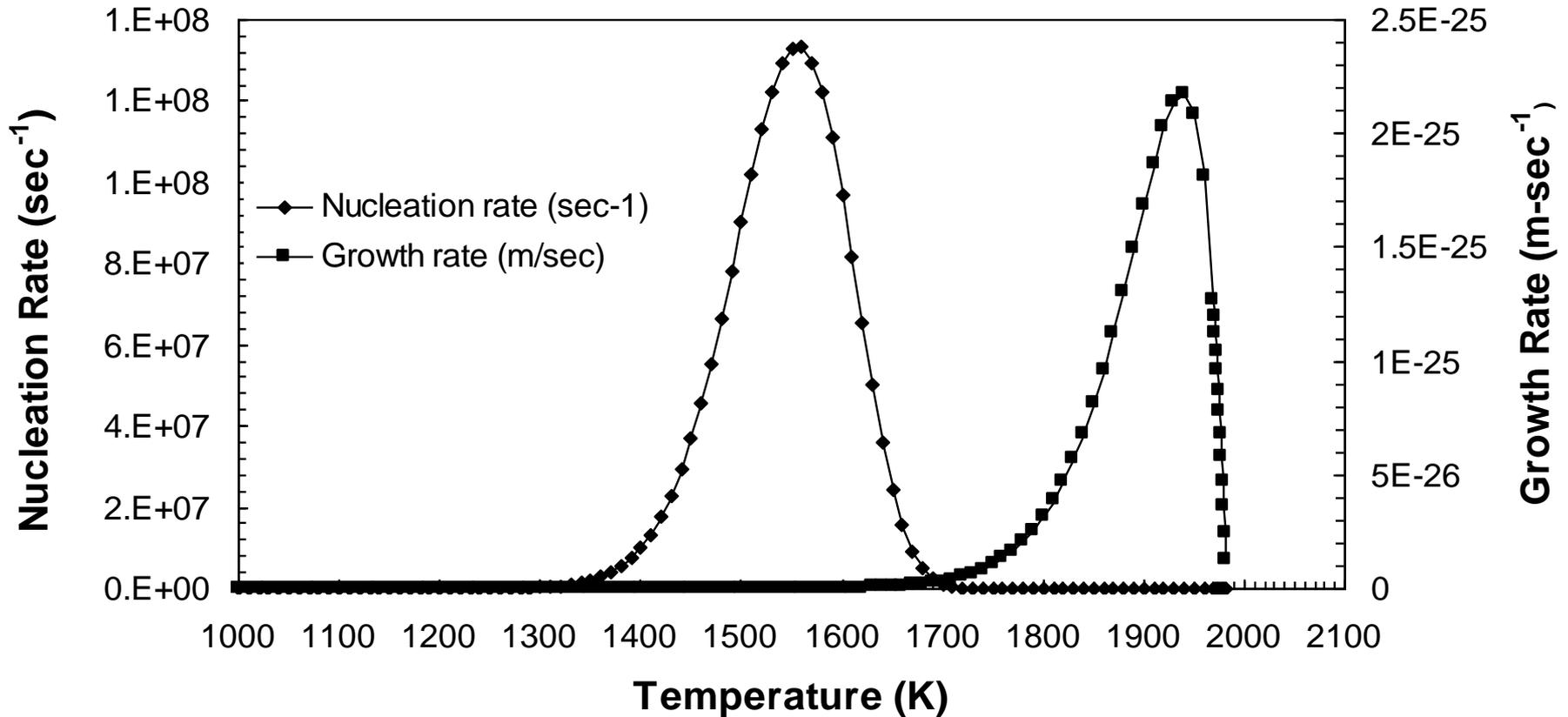
# Time – Temperature – Transformation Curves (TTT)

- 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

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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

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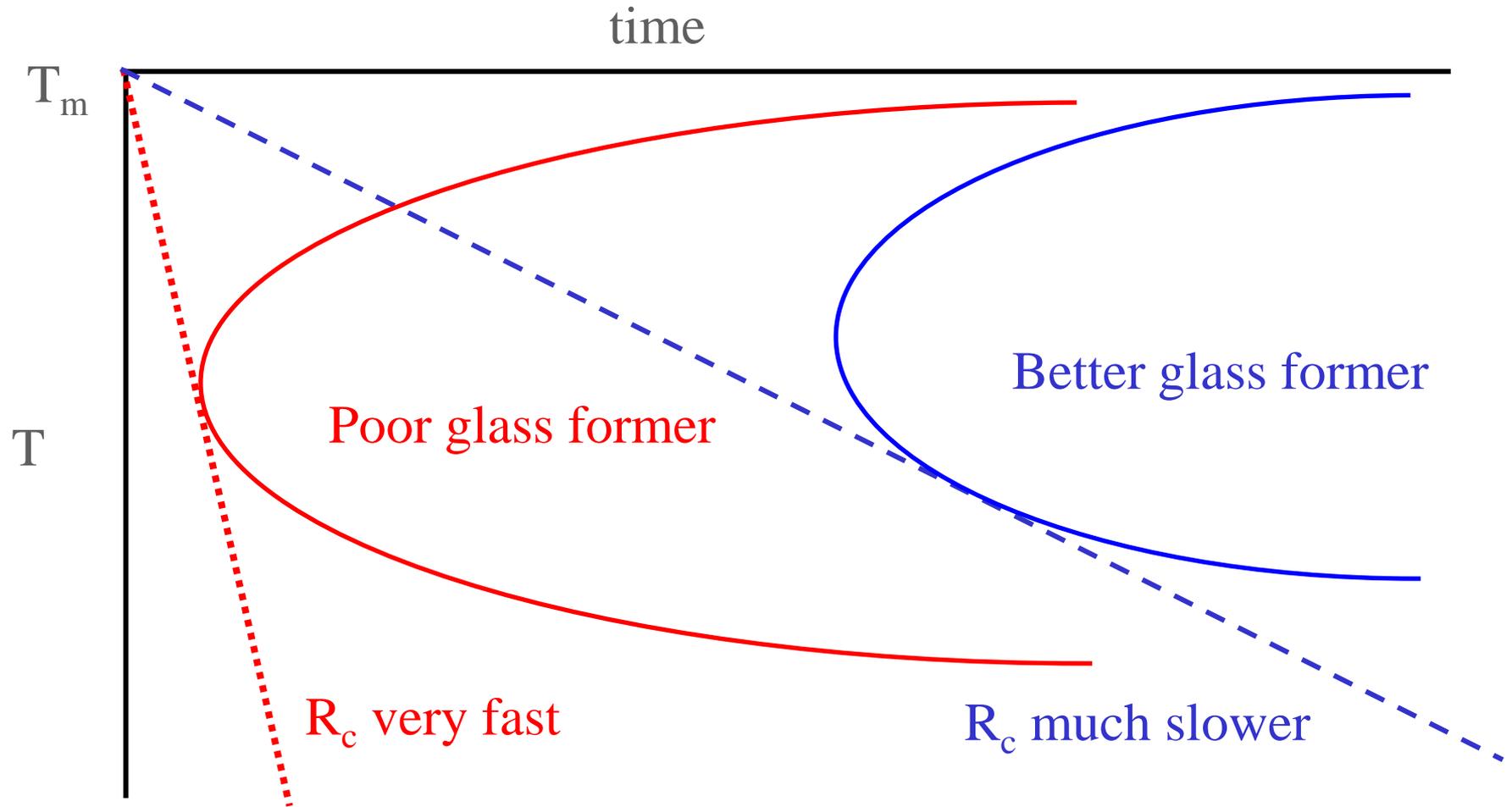
Time Transformation Curves for Water

T-T-T Curve for water

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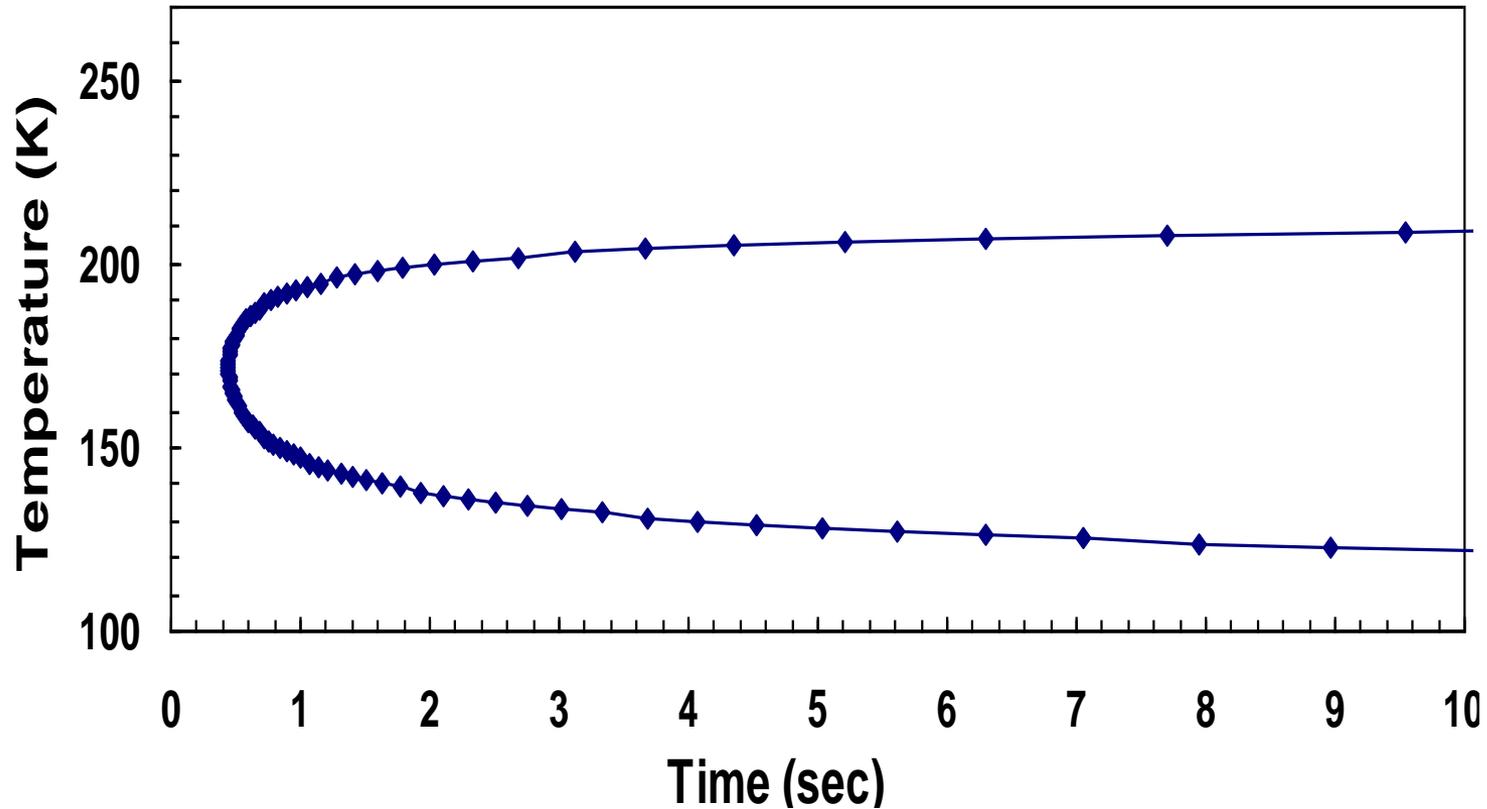
Time Transformation Curves for Silica

T-T-T Curve for Silica

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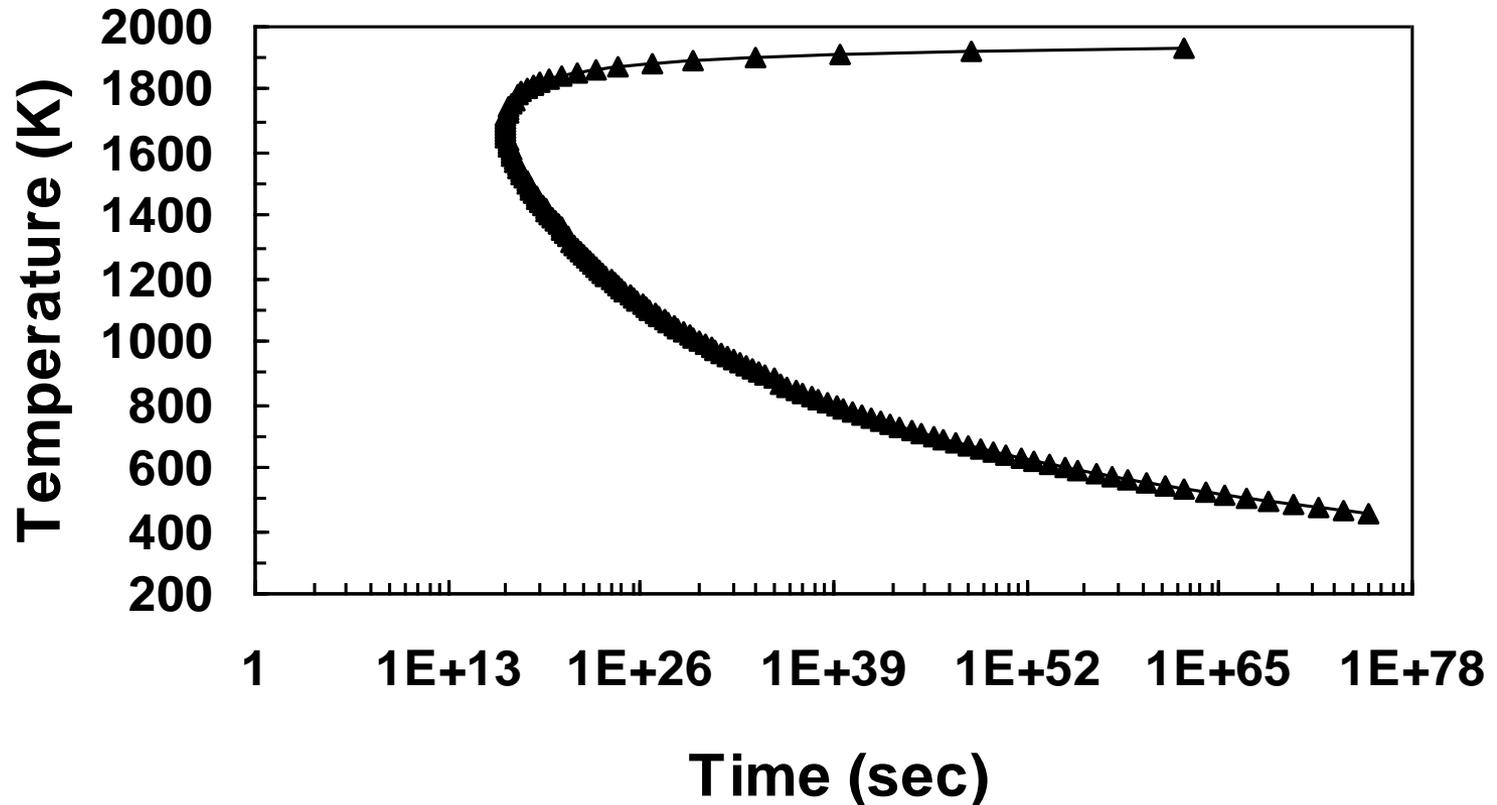
Summary

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 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

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