

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

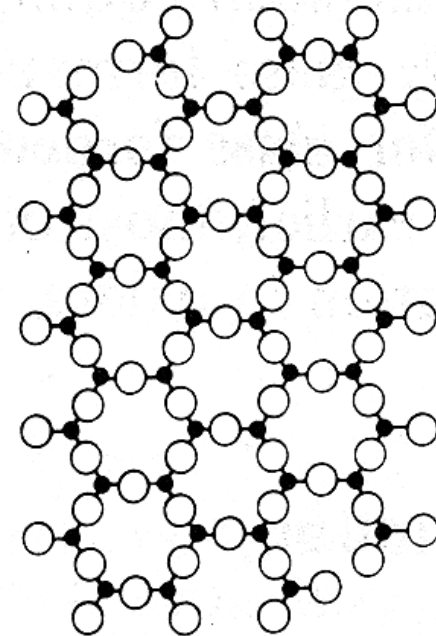
- *Understand and be able to apply the relationships between atomic level structure and ease at which a system will form glass*
- *Understand and be able to apply Zacharaisen's Rules for glass formation*
- *Be able to apply understanding of the three different types of additives, modifiers, intermediates, 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

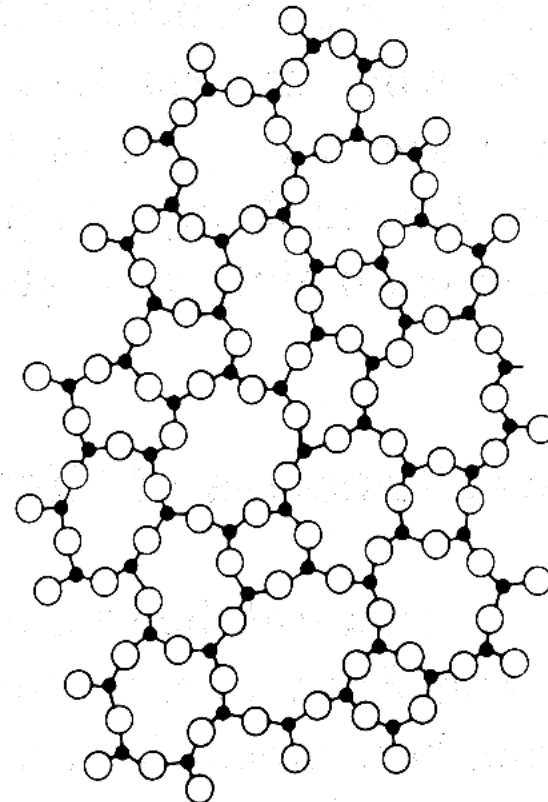
- Crystalline materials exhibit a periodic array of atoms and/or ions
- Each atom/ion in the material has a specific location that is periodic in the crystalline structure
- Each location can be exactly specified once the crystalline structure is defined
- Defects in the structure occur when the position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



(a)

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



(b)

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?

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 , $\text{Na}_2\text{O} + \text{CaO} + \text{SiO}_2$
 - 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*
 - $-(\text{CH}_2)_n-$
 - 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*
 - $\text{Ca}(\text{NO}_3)_2 + \text{KNO}_3$

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

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*

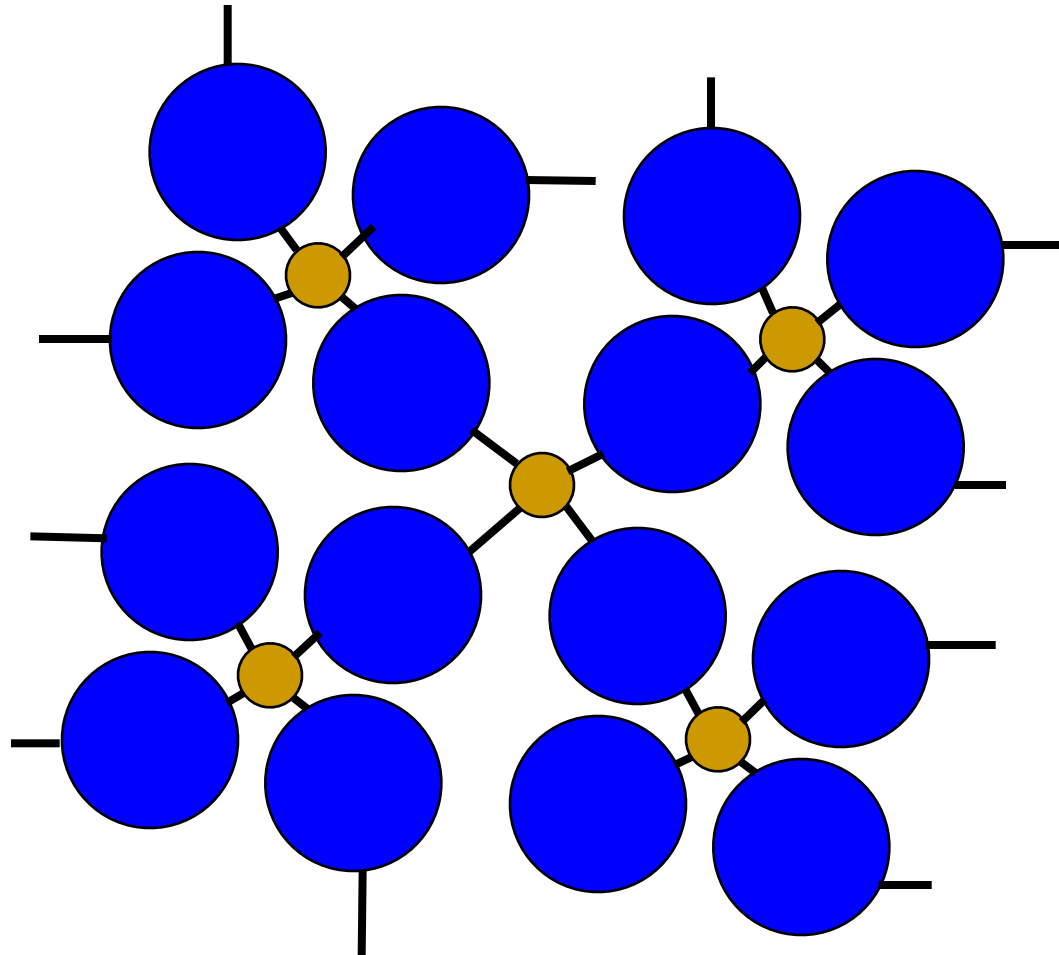
Zacharaisen's Rules for Glass Formation

- Apply these rules to the following:
 - $\text{SiO}_{4/2}$
 - B_2O_3 or $\text{BO}_{3/2}$

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

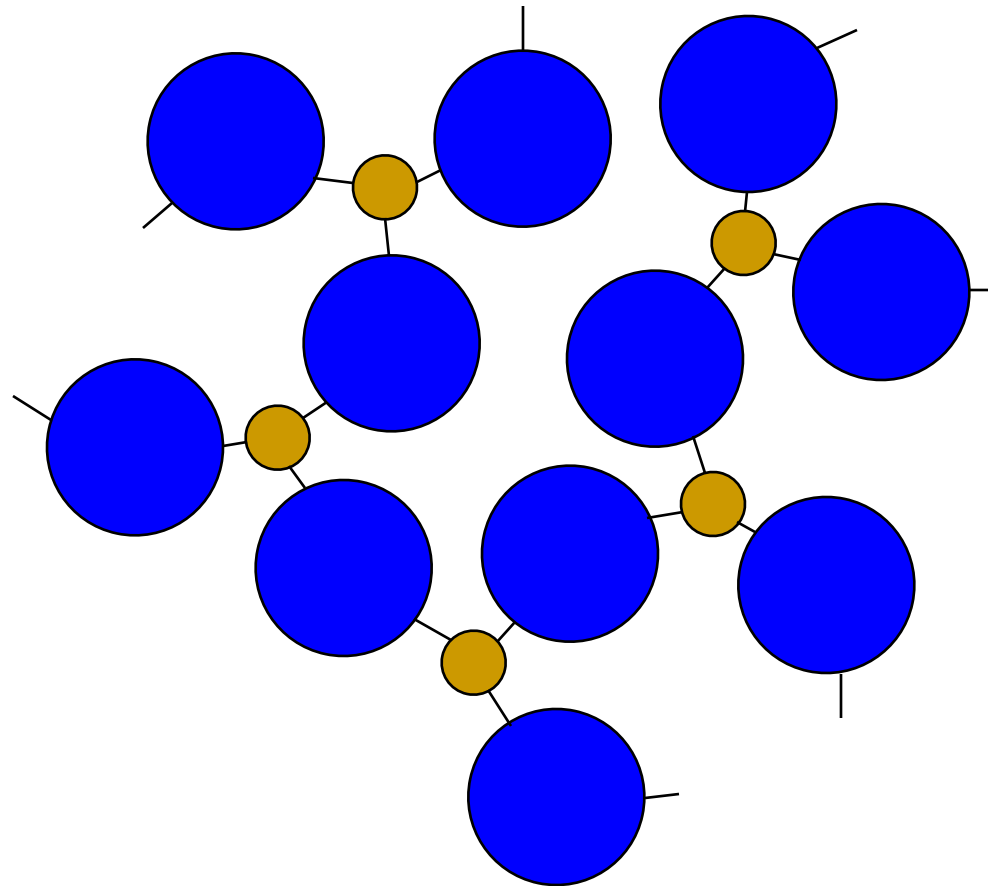
Zacharaisen's Rules for Glass Formation

■ $\text{SiO}_{4/2}$



Zacharaisen's Rules for Glass Formation

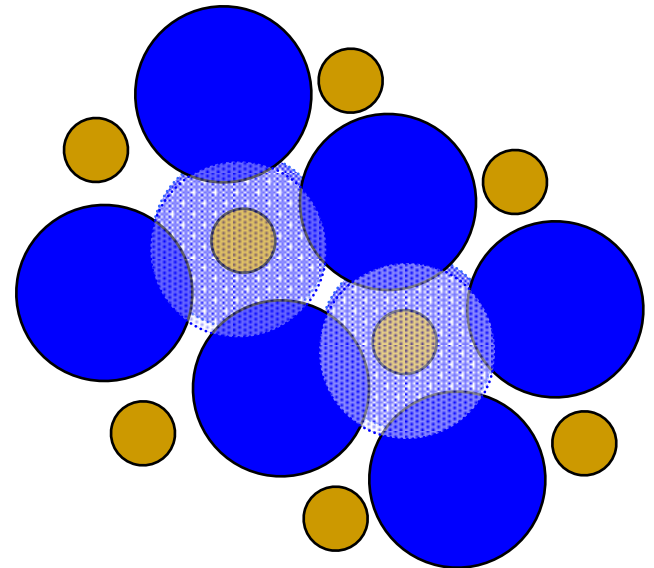
- B_2O_3 or $BO_{3/2}$



Zacharaisen's Rules for Modifiers

Ca_1O_1 (CaO) Closed-packed cubic

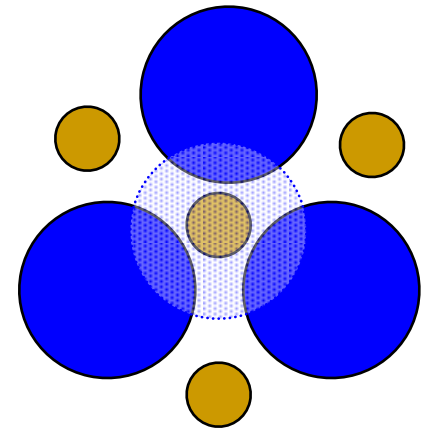
- Ca occupying all octahedral sites
- Octahedral sites = Ca = O



Zacharaisen's Rules for Modifiers – M_2O

Na_2O_1 (Na_2O) Closed-packed cubic

- Na occupying tetrahedral sites
- Tetrahedral sites = $2 \times O = Na$



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 form 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

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

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 (kcal)	Coordination number ^b	Single-bond strength (kcal)
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

Intermediates (Oxides) – assist in glass formation

	M in MO _x	Valence	Dissociation energy E_d per MO _x (kcal)	Coordination number ^b	Single-bond strength (kcal)
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

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

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

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

Dietzel's Field Strength Model

Table 3-3. Field Strengths of Various Ions^a

Element	Valence <i>Z</i>	Ionic radius (for <i>CN</i> =6) <i>r</i> in Å	Most frequent coordination number <i>CN</i>	Ionic distance for oxides <i>a</i> 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	Network modifier $Z/a^2 \approx 0.1 \dots 0.4$
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	
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	

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	} Intermediate $Z/a^2 \approx 0.5 \dots 1$
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	
Fe	3	0.67	6	1.99	0.76	
			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	

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	} Network former $Z/a^2 \approx 1.5 \dots 2.0$
Ge	4	0.44	4	1.66	1.45	
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].

Glass forming compositions

- How would you classify the following compositions? Glassforming or not?
- $0.15\text{Na}_2\text{O} + 0.35\text{Al}_2\text{O}_3 + 0.50\text{SiO}_2$
- $0.35\text{Na}_2\text{O} + 0.15\text{CaO} + 0.25\text{Al}_2\text{O}_3 + 0.25\text{SiO}_2$

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
 - $\text{SiO}_{4/2}$ easily supercools due to the high connectivity of the liquid through strong $-\text{O}-\text{Si}-\text{O}-$ 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, $\gg 100^\circ\text{C}/\text{sec}$, implies “marginal” glass forming ability
 - Slow cooling, $\ll 1^\circ\text{C}/\text{min}$, 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

Critical Cooling Rates for Various Liquids

Table 3-5. Examples of Critical Cooling Rates ($^{\circ}\text{C/s}$) 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
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ 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}

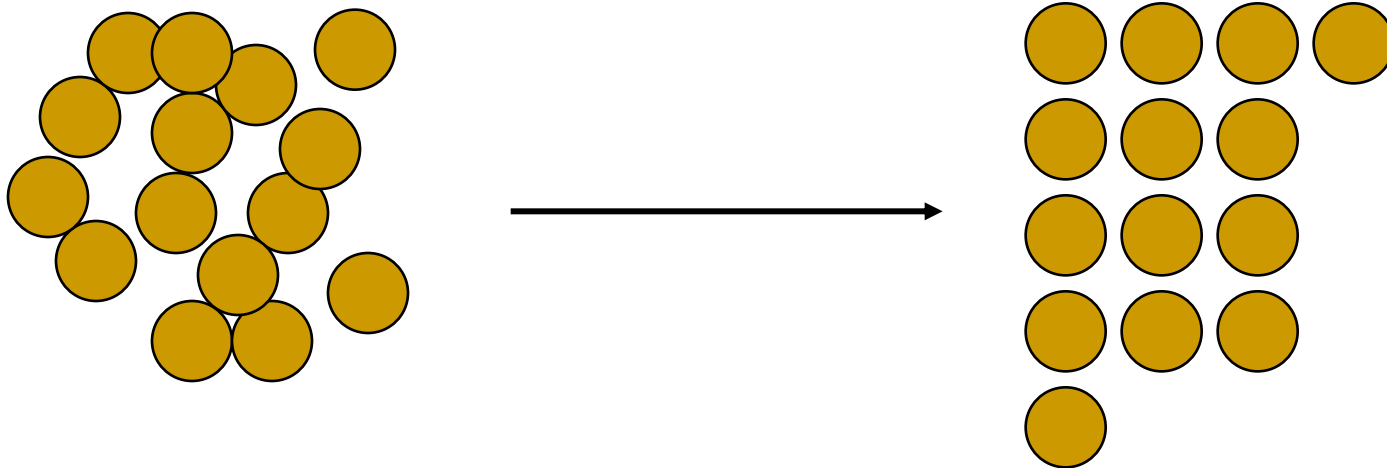
^a After P. I. K. Onorato and D. R. Uhlmann, *J. Non-Cryst. Sol.*, 22(2), 367–378 (1976).

Calculating the Critical Cooling Rate

- The kinetic approach to glass formation then becomes:
 - What is the R_c value for a particular liquid?
 - If $R_c \gg 100^\circ\text{C}/\text{sec}$, then the liquid is a poor glass former
 - If R_c is $\ll 1^\circ\text{C}/\text{min}$, then the liquid is a good glass former
 - How can R_c be calculated?
 - What are the factors that control R_c ?

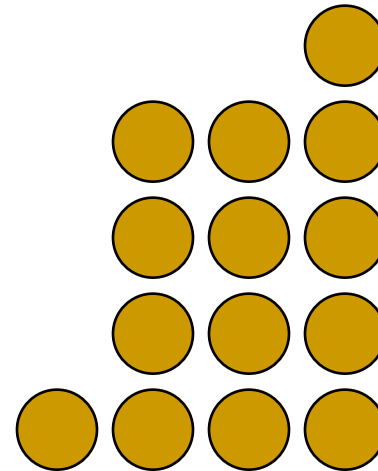
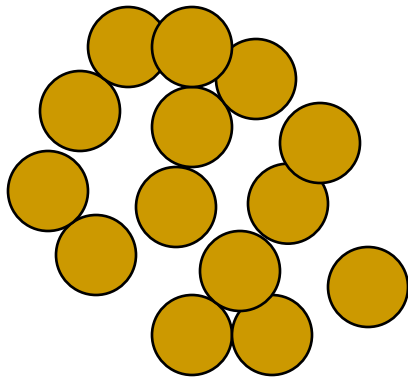
Nucleation and Growth Rates Control R_c

- 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

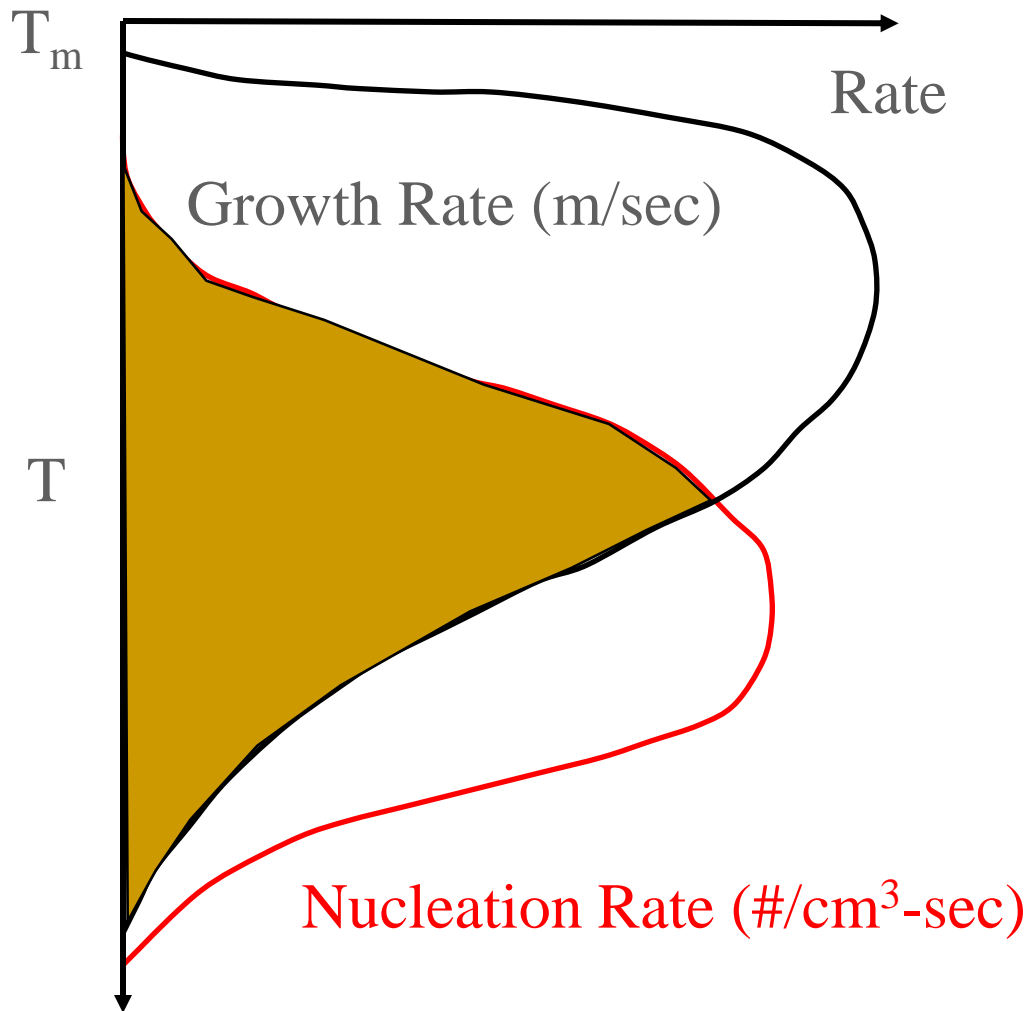
- Growth processes then enlarge existing nuclei
- Smallest nuclei often redissolve
- Larger nuclei can get larger
- Thermodynamics favors the formation of larger nuclei



Nucleation and Growth Control R_c

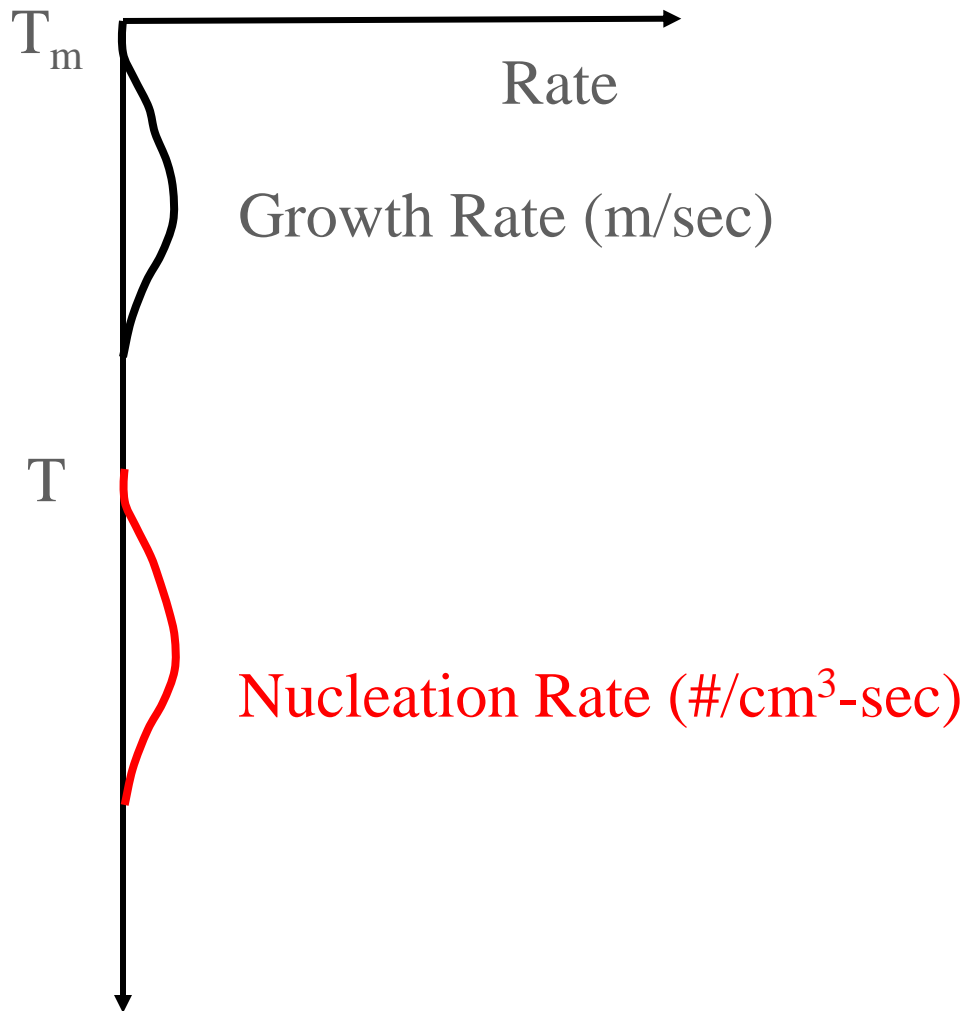
- Poor glass formers:
 - Liquids which quickly form large numbers of nuclei close to T_m
 - That grow very quickly
- Good glass formers
 - Liquids that are sluggish to form nuclei even far below T_m
 - That grow very slowly

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 \times
fastest motion possible \times
thermodynamic probability of
formation \times
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

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

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

N = Avogadro's number

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

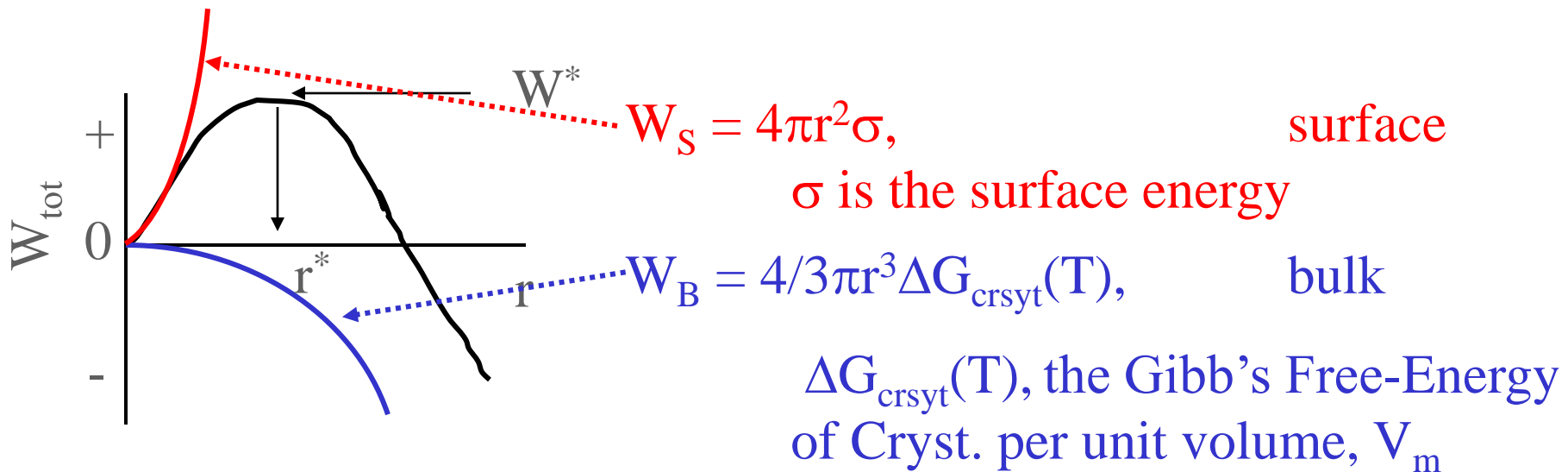
W^* = thermodynamic energy barrier to form nuclei

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

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

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

Nucleation Rate – Thermodynamic barrier W^*

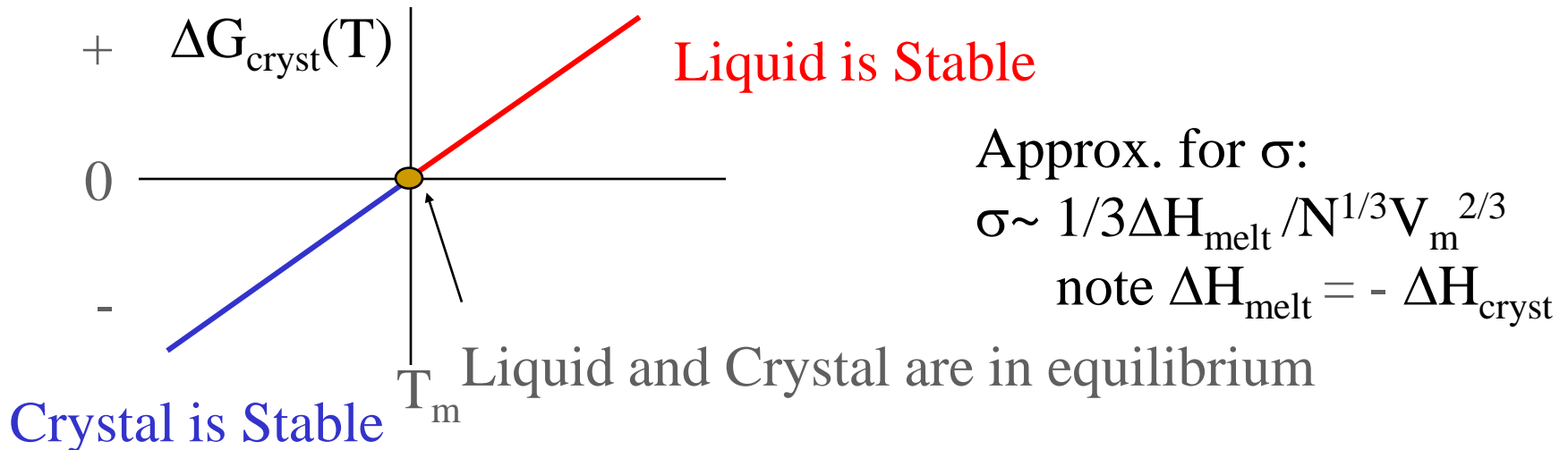


$$W_{\text{tot}} = W_S + W_B$$

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

Nucleation Rate $I(T)$

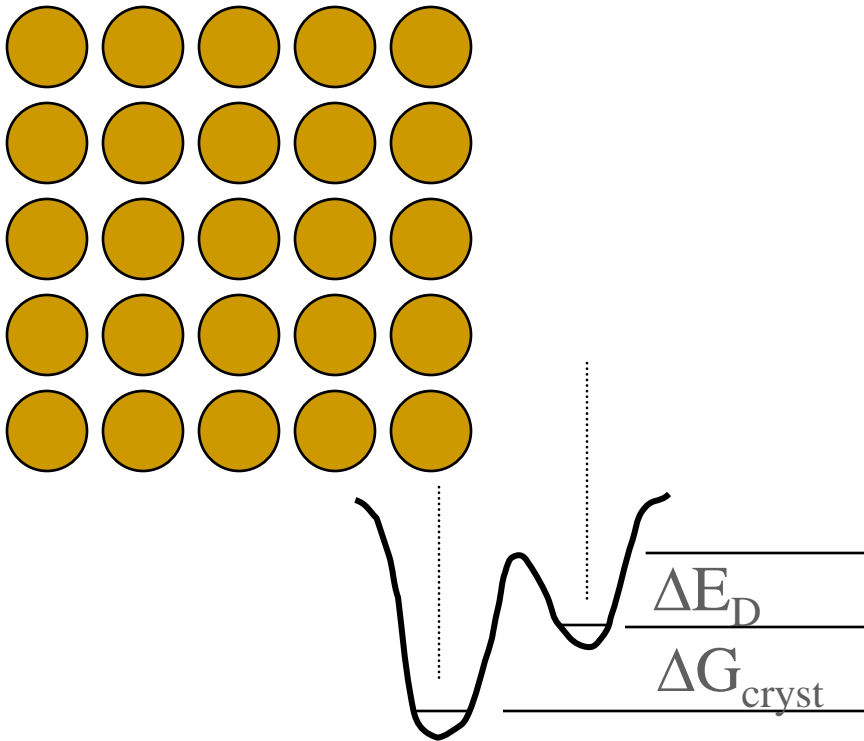
- $I = n \nu \exp(-N \frac{16 \pi \sigma^3}{3(\Delta G_{cryst}(T))^2} / RT) \exp(-\Delta E_D / RT)$
- $\Delta G_{cryst}(T) = \Delta H_{cryst}(T_m)(1 - T/T_m) / V_m \equiv \Delta H_{cryst}(T_m)(\Delta T_m / T_m)$



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

Growth Rates $\mu(T)$

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



$$v_{l \rightarrow c} = v \exp(-\Delta E_D / RT)$$

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

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

$$v \exp(-\Delta E_D / RT) -$$

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

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

Growth Rates - $\mu(T)$

Diffusion coefficient, D

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

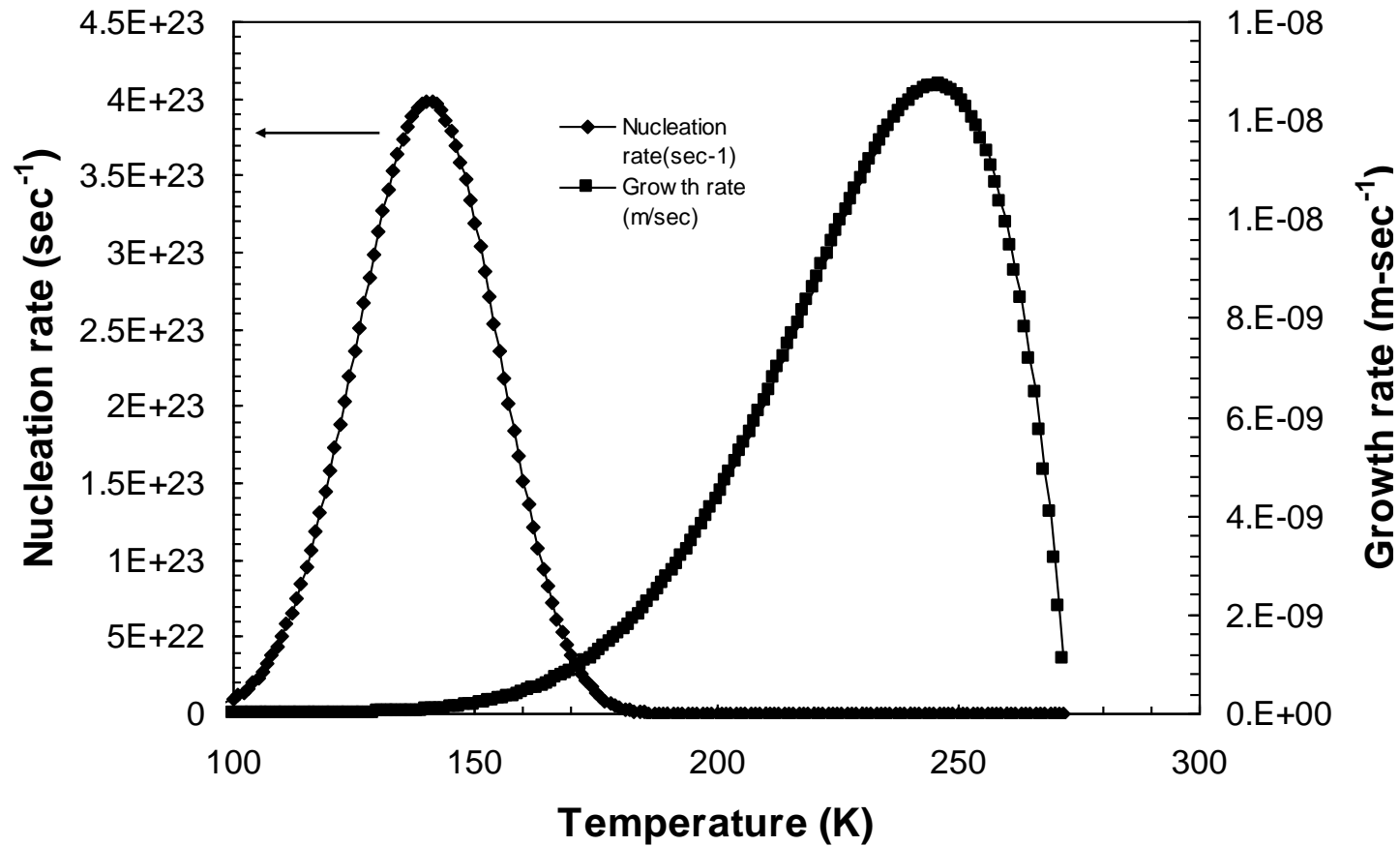
Stokes-Einstein relation between D and η

Hence:

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

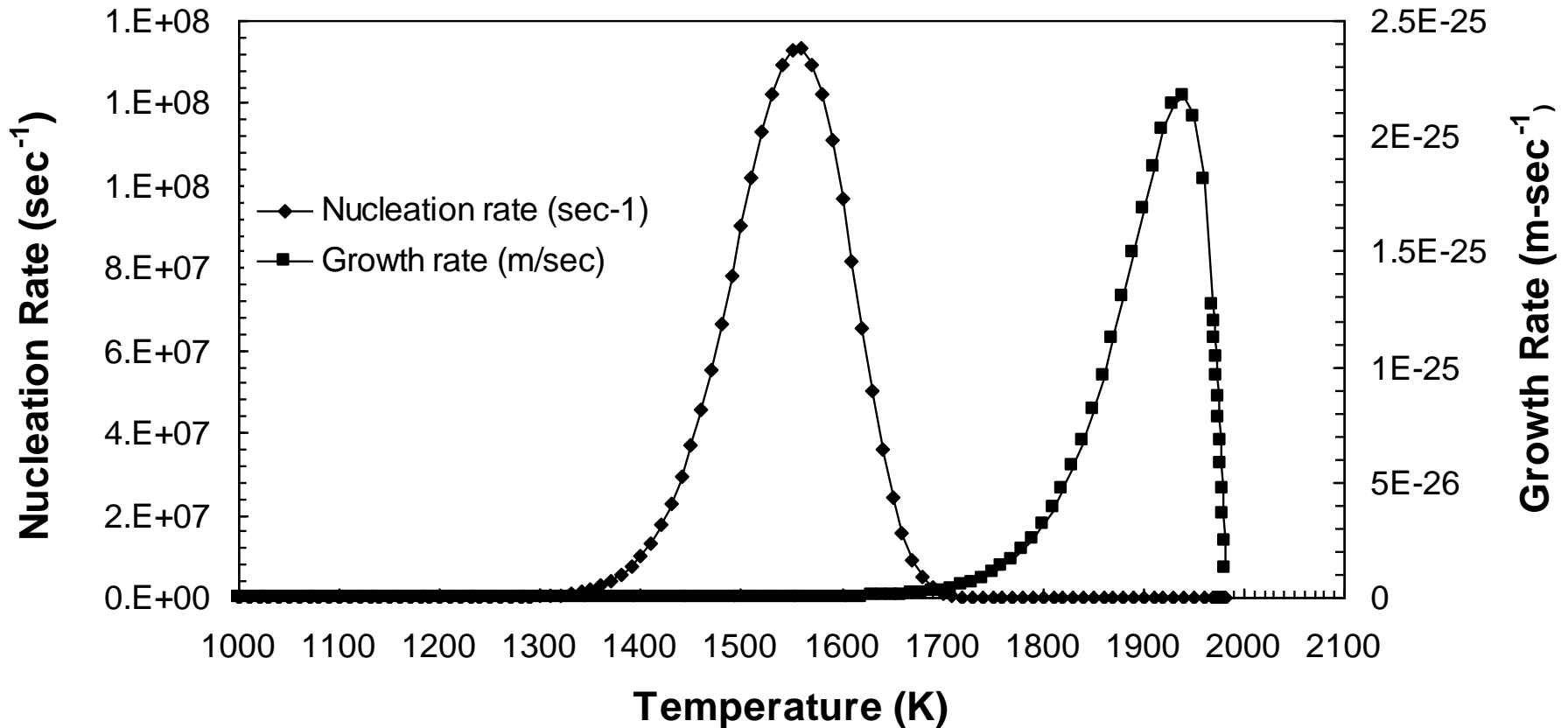
Nucleation and Growth Rates

Nucleation and Growth Rates for Water



Nucleation and Growth Rates

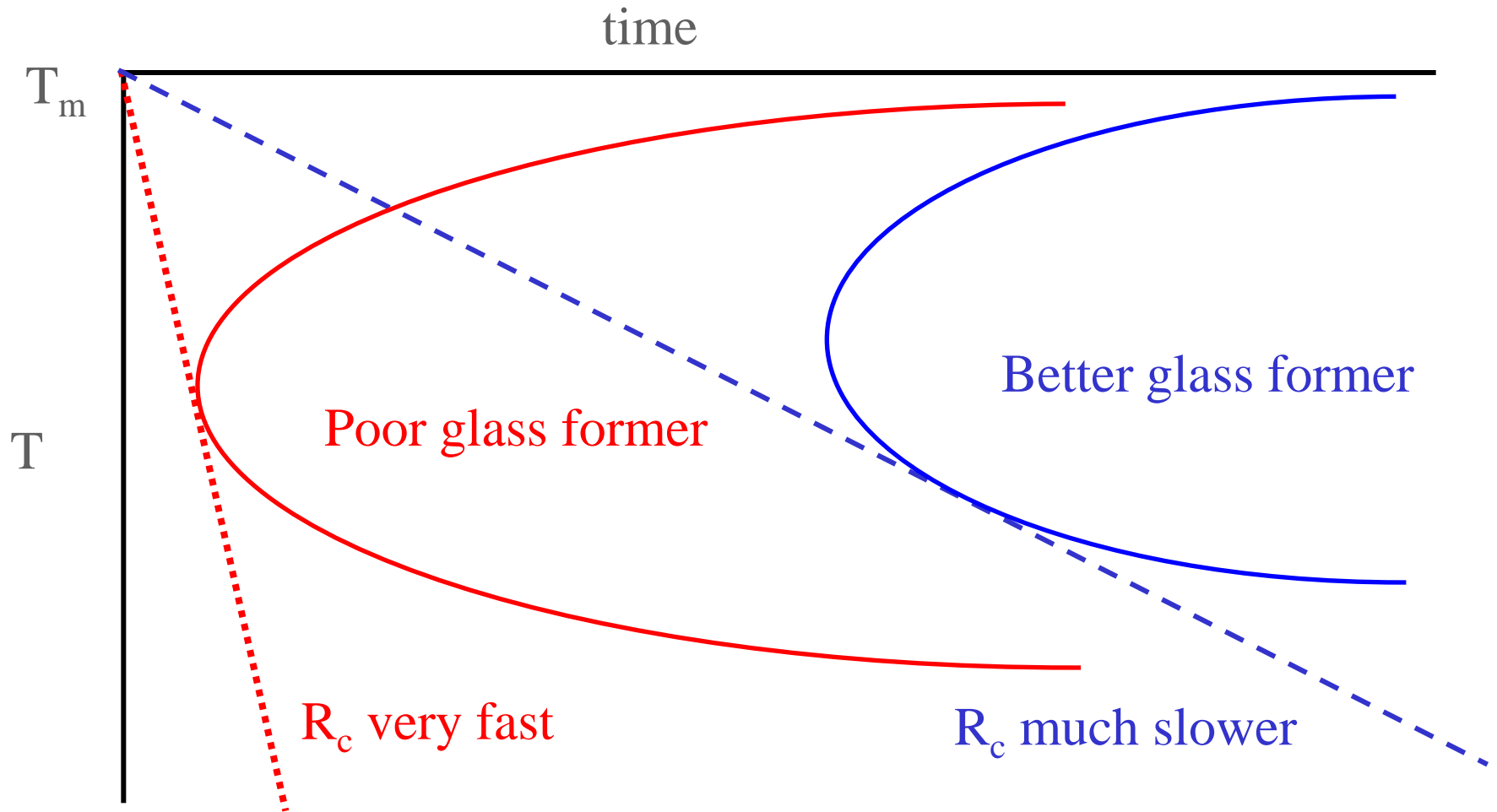
Nucleation and Growth for Silica



Time – Temperature – Transformation Curves (TTT)

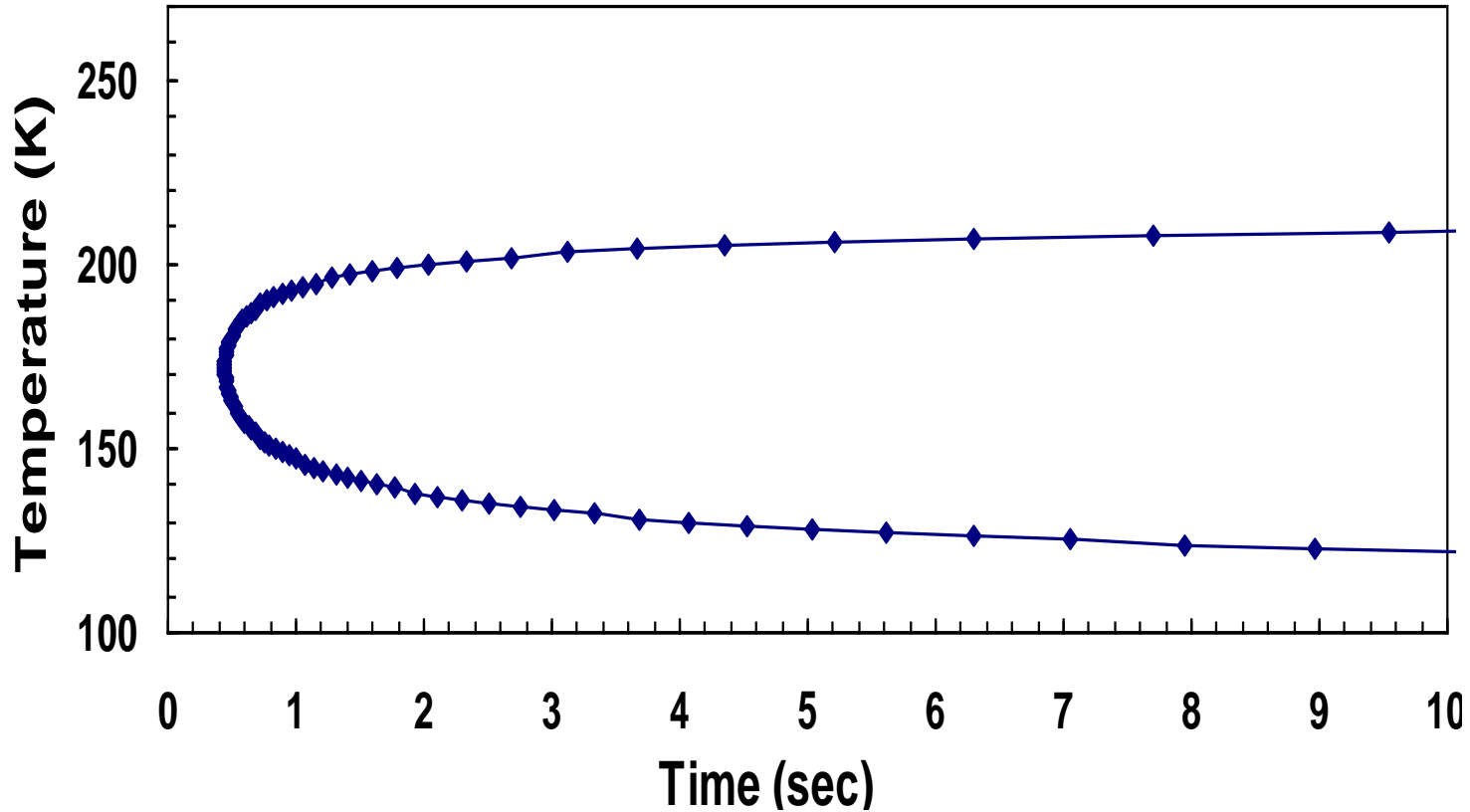
- How much time does it take at any one temperature for a given fraction of the liquid to transform (nucleate and grow) into a crystal?
- $X(t, T) \sim \pi I(T) \mu(T)^3 t^4 / 3$
- where X is the fractional volume of crystals formed, typically taken to be 10^{-6} , a barely observable crystal volume

TTT curves and the critical cooling rate, R_c



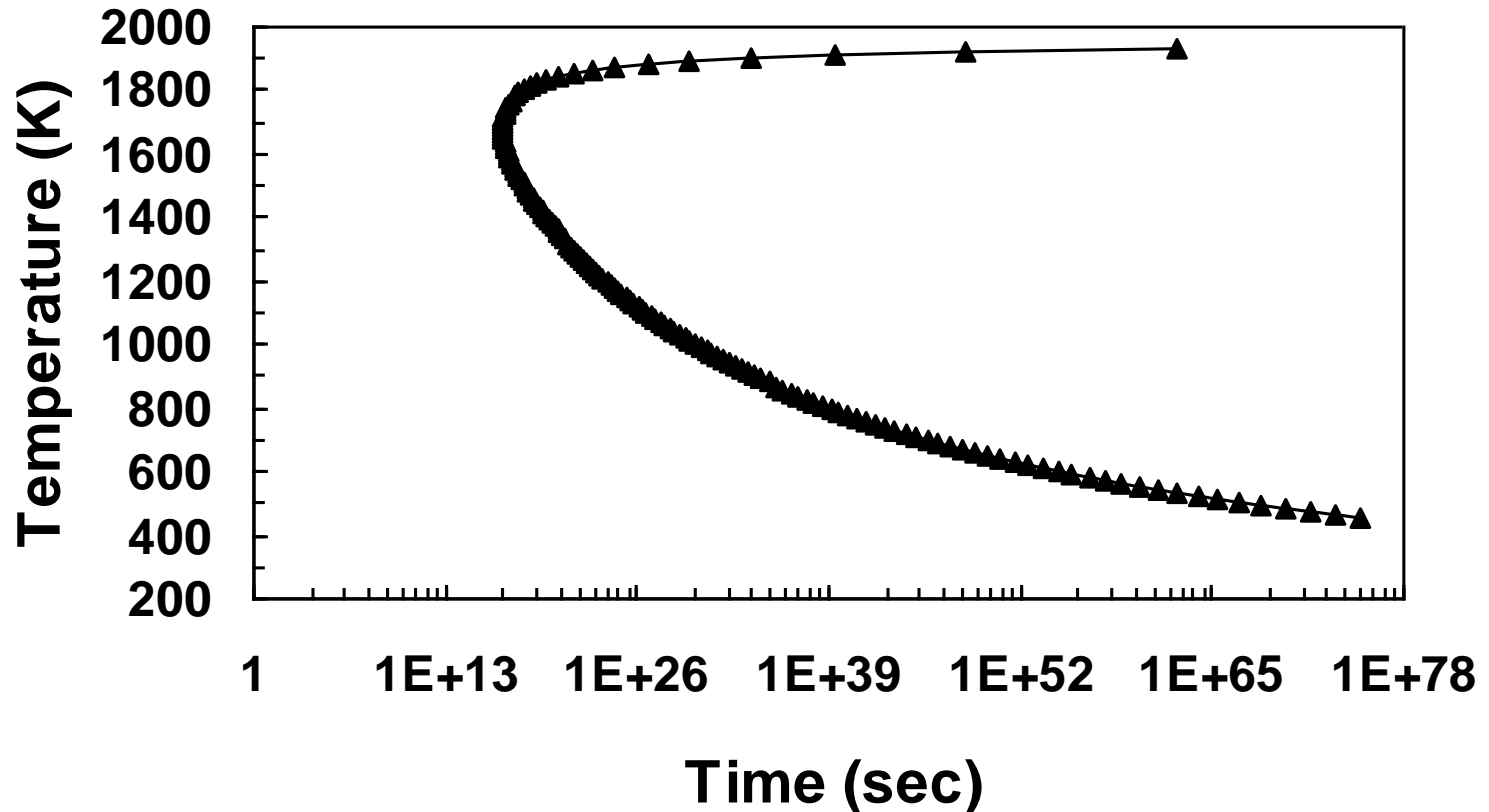
Time Transformation Curves for Water

T-T-T Curve for water



Time Transformation Curves for Silica

T-T-T Curve for Silica



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