Advanced Vitreous State: The Structure of Glass

Section 1: Lecture 1 - Fundamentals of the Glass Transition:

The Glass Transition is a Kinetic Transition with Thermodynamic Signatures

- *Examine the differences between a kinetic and thermodynamic transition*
- *Develop the affect of the "internal" and "external" timescales and how each can lead to glass formation*
- *Investigate the affect of cooling rate on the volume of glass*
- *Recognize the origin of the hysteresis affect in the glass transition*
- *Distinguish the "Thermodynamic Signatures" of the glass transition*
- *The Enthalpy and heat capacity functions in the glass transition region*
- *The Entropy function in the glass transition region*

Fundamentals of the Glass Transition

- The Glass Transition is a *Kinetic Transition*
  - Continuous changes in structure and properties
    - Between the liquid and solid (glassy) states
    - As the liquid is (typically) cooled
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid
  - There is no "Thermodynamic driving force" for the glass transition
  - The glass transition occurs simply because of a dramatically diverging difference between timescales ***internal*** and ***external*** to the cooling liquid

Fundamentals of the Glass Transition

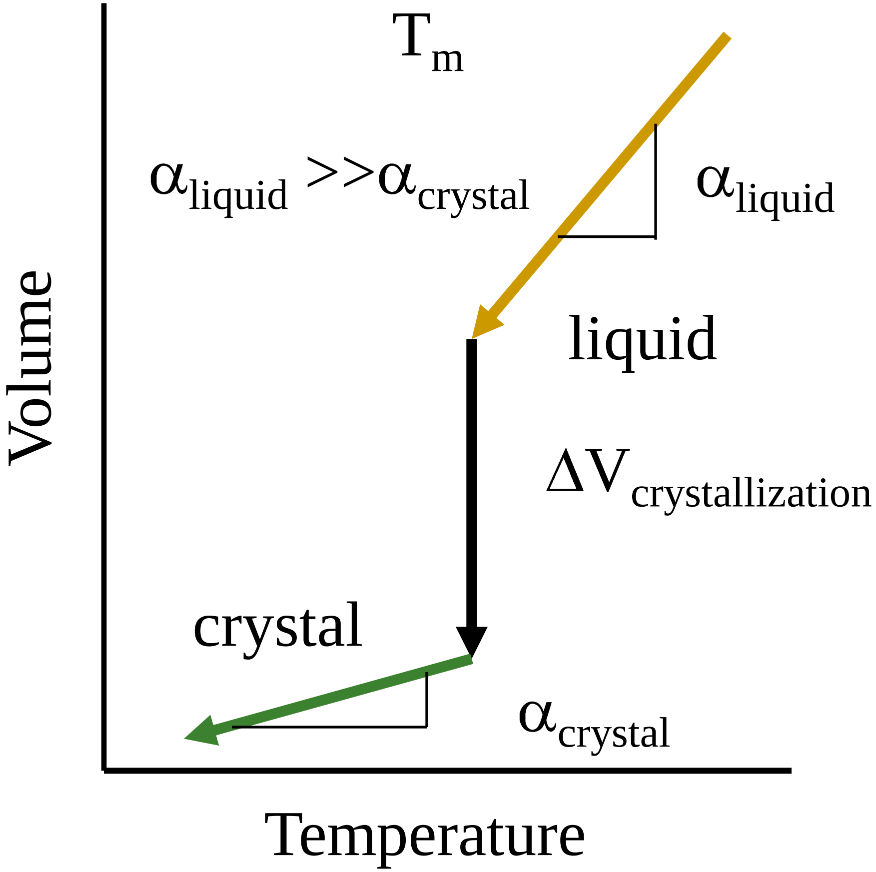
- Melting and Crystallization are:
  - *Thermodynamic Transitions*
  - Discontinuous changes in structure and properties at Tm
  - Structures are thermodynamically controlled by the chemical potentials of the phases
  - Away from the temperature where the two chemical potentials are different
  - There exists a Thermodynamic driving force to convert one phase into the Thermodynamically preferred phase
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values
    - 273.15 ^{o}C for water for example
    - Under given Thermodynamic conditions

Glass Transition is a Kinetic Transition

- Let's construct a cooling curve for a liquid that will ultimately form a crystal
- Consider NaCl, T_m = 812 ^{o}C
- Suppose we measure the volume of NaCl as it cools
- Sketch the temperature dependence of the volume from 1000 ^{o}C to 600 ^{o}C if one mole of NaCl (58 grams) is cooled at 10 ^{o}C/min.
  - 1st assume that thermodynamics controls the system, the liquid crystallizes where it should

Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The Crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α

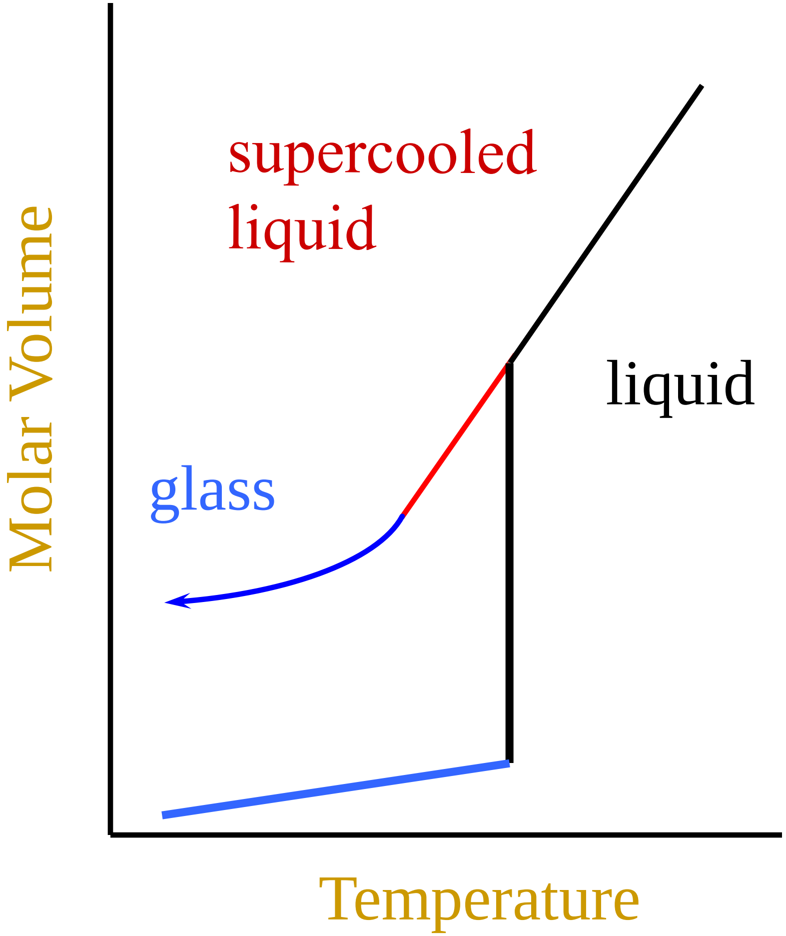


Glass Transition as a Kinetic Transition

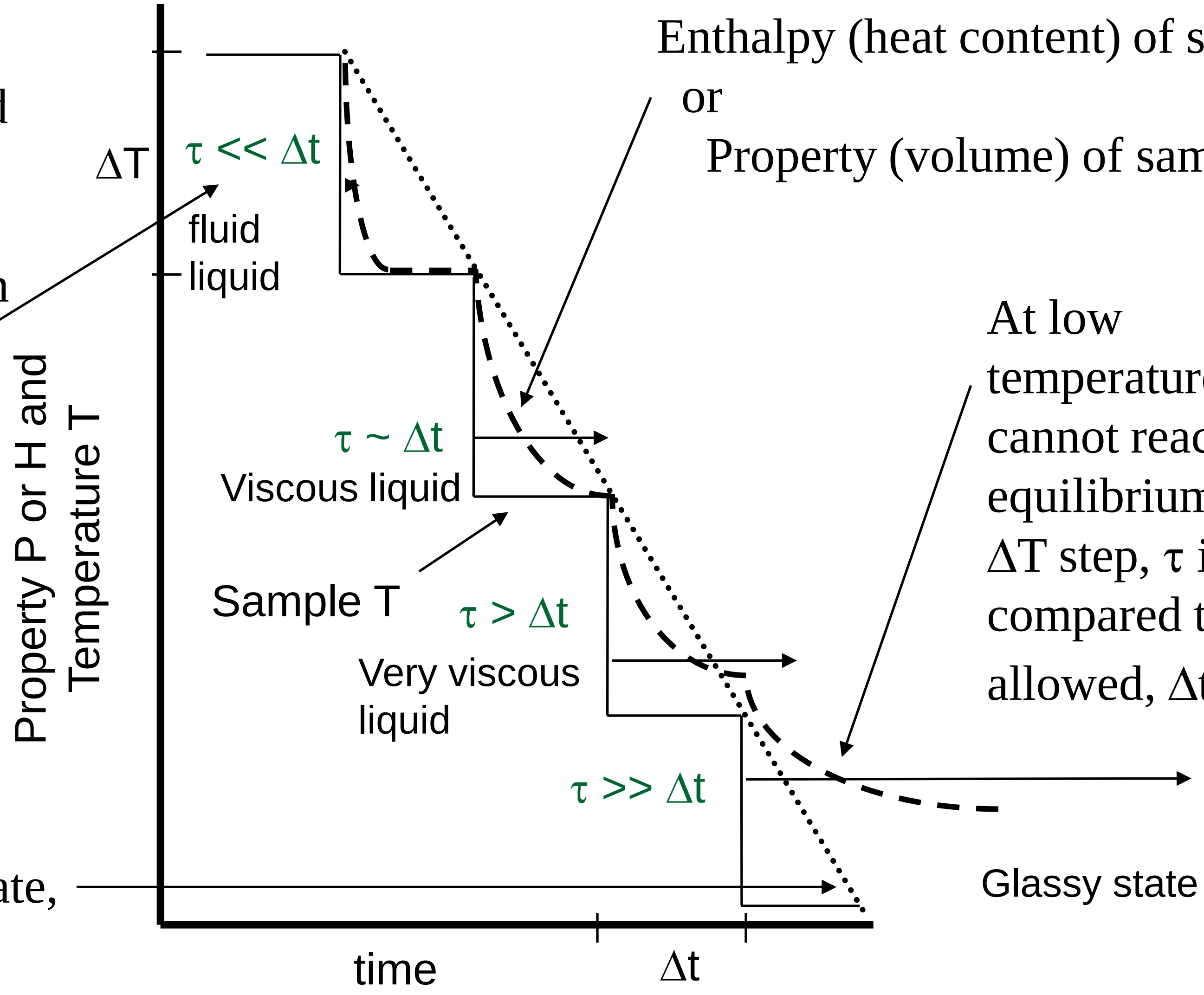
- Now assume kinetics controls the system, the liquid changes properties and structures only if it is given ‘sufficient” time to change

Glass Formation is Controlled by Kinetics

- Glass forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a high viscosity that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - "Internal" time scale controlled by the viscosity (bonding) of the liquid
  - "External" timescale controlled by the cooling rate of the liquid



Time and Temperature Dependence of Properties



At high temperatures, fluid liquid can reach equilibrium after ΔT step, relaxation time τ is short compared to time step, Δt

Enthalpy (heat content) of sample
or
Property (volume) of sample

At low temperatures, liquid cannot reach equilibrium after ΔT step, τ is long compared to time allowed, Δt

Average cooling rate,

$$\dot{T} = \Delta T / \Delta t$$

Glass Transition is a Kinetic Transition

- Glass formation is a kinetic transition, therefore, it depends upon the kinetics of the process
  - The internal timescale, τ, for the process is controlled by the atomic or ionic bonding between atoms or ions
    - Strong and numerous bonding increases, τ
    - Weak and limited bonding decreases, τ
    - Viscosity $\propto$ relaxation time, $\eta = G\tau$

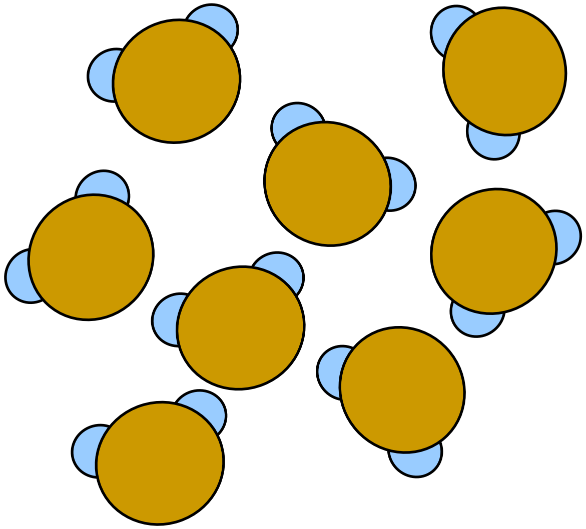
Glass Transition is a Kinetic Transition

- The external timescale, Δt, is controlled by the experiment or process, i.e., how fast is the liquid cooled
  - Is it purposefully quenched very fast? Δt is short
    - milli to micro seconds
  - Is it allowed to cool naturally under prevailing conditions?
    - seconds to minutes
  - Or is it “insulated” and allowed to cool very slowly, Δt is long
    - Hours, days, weeks

Examples of Poor Glass Formers

- Why is water, H_2O, found to be a very “weak” glass former
  - Requires cooling the liquid faster than 1,000,000 ^{o}C/min
  - 300 to 150K in 9 milliseconds
  - What is the atomic structure?
  - Talk to your neighbor and sketch the structure of 5 to 10 water molecules
  - And discuss why you think water cannot be easily quenched to the glassy state without crystallization

Chemical Structure of Water



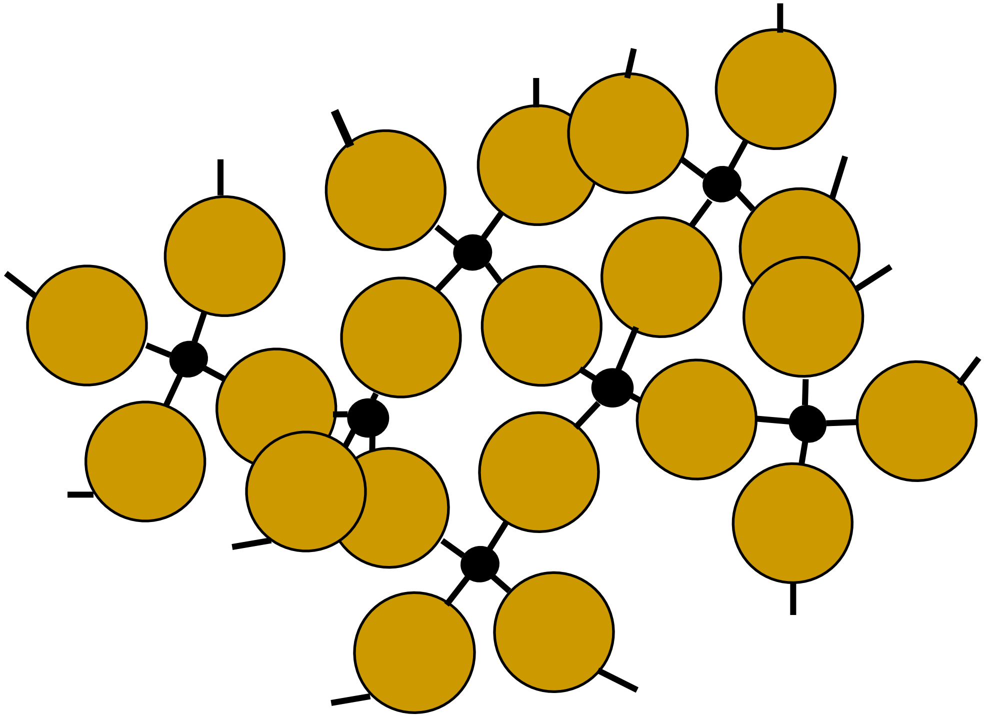
H_2O

No bonding between molecules and molecules can easily flow by each other

Examples of “Good” Glass Formers

- Why is silica, SiO_2, found to be a very “strong” glass former
  - Can be cooled at 10^{-10}C/min and still by-pass Tm without crystallizing
  - 2,000 ^{o}C to 1,000 ^{o}C in 20 million years!!
  - What is its atomic structure? Talk to your neighbor and sketch the structure of 5 to 10 SiO_2 molecular units

Chemical Structure of Silica

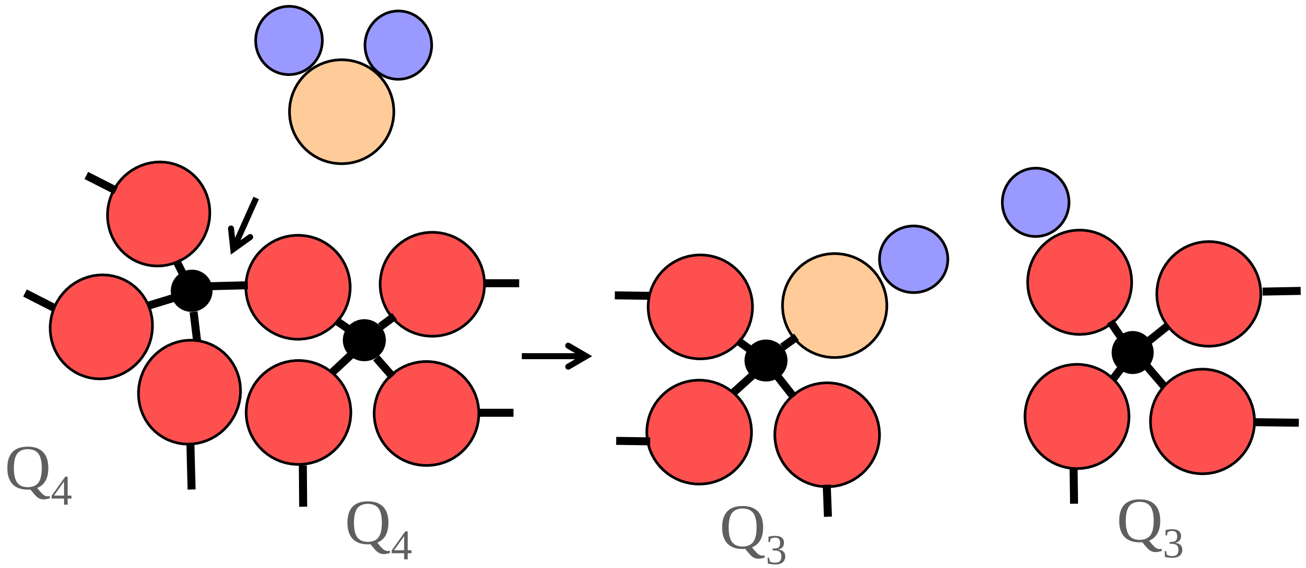


$SiO_{4/2}$

Each Si is tetrahedrally bonded to O, each O is bonded to two Si. Si and O atoms cannot move unless other neighboring atoms also move

Conversion between good and poor glass formers

- Network forming structures, bridging oxygens, can be converted into network breaking structures, non-bridging oxygens, through added oxygen anions that "depolymerize" the chemical network of SiO_2
- Q_2 structures (2 bridging oxygens) are the limit for reasonable glass formation



Cooling Rate Affects Properties of Glass

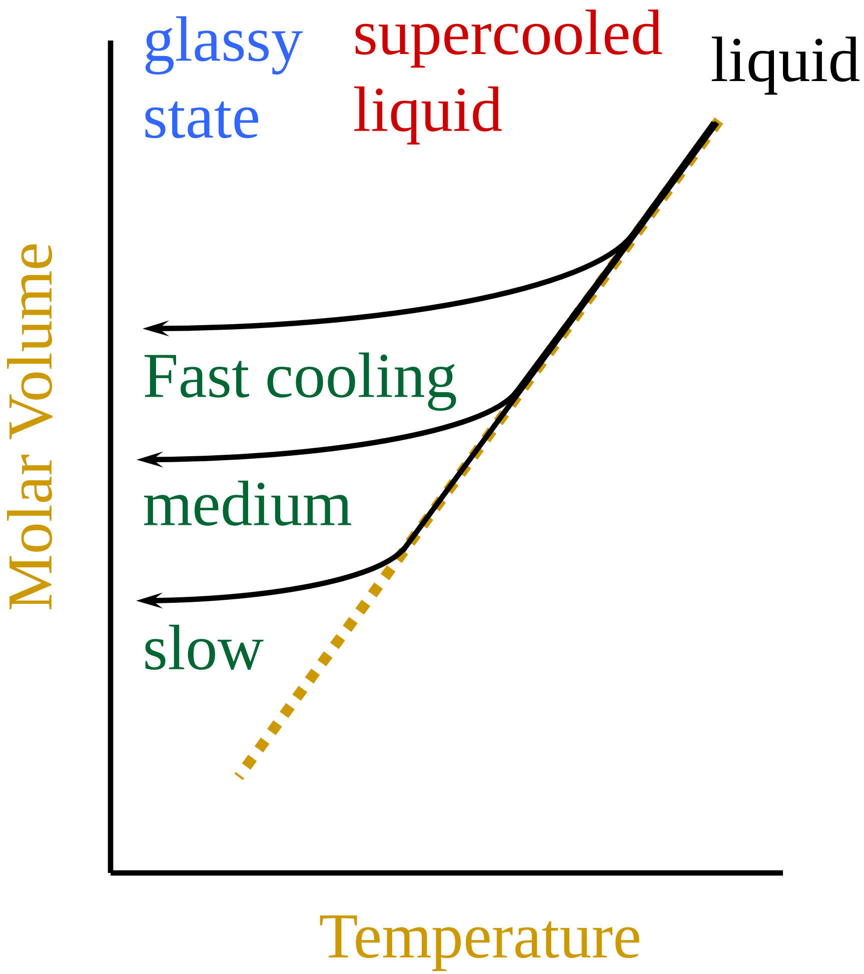
- Cooling rate, the external time scale, affects the properties of glass
  - Faster cooling rates decrease the time the liquid has to “relax” - the time to readjust to the temperature change - to the properties at the new (lower) temperature
  - Fast cooling freezes the structure of the liquid (glass) in at a higher temperature, therefore it has properties corresponding to these high temperatures

Cooling Rate Affects Properties of Glass

- Cooling rate, the external time scale, affects the properties of glass
  - Slower cooling rates increase the time the liquid has to relax to the properties at the new temperature
  - Slower cooling enables the structure to freeze in at a lower temperature and therefore the glass has properties corresponding to these lower temperatures
  - Sufficiently slow cooling of course will eventually enable the liquid to explore and find the crystalline phase space of that composition

The Cooling Rate Affects the Properties of Glass

- Faster cooling freezes in the glass higher temperatures
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slow enough that the liquid can relax to properties at lower temperatures, glass is eventually formed at a lower temperature

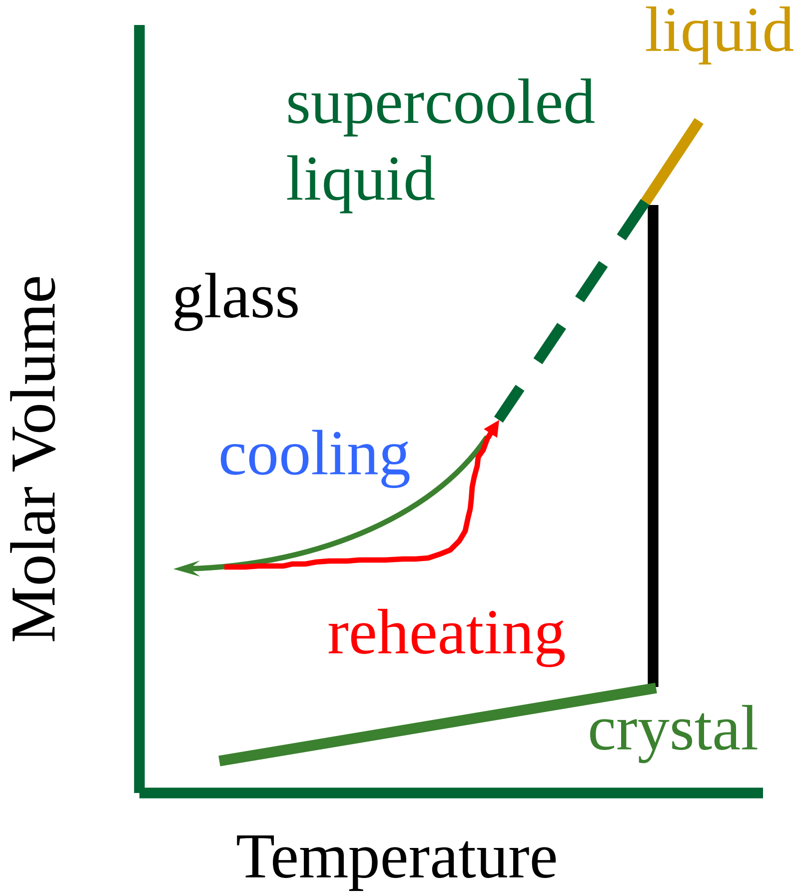


Glass Properties on Heating

- If a glass is reheated, how do the properties change?
- Sketch a temperature plot for a glass that has been cooled at a average rate of 10ºC/min and then is reheated at 10ºC/min.
- How does the volume change upon reheating?
- Does it follow the same curve as the cooling curve?
- Does it follow a different path?

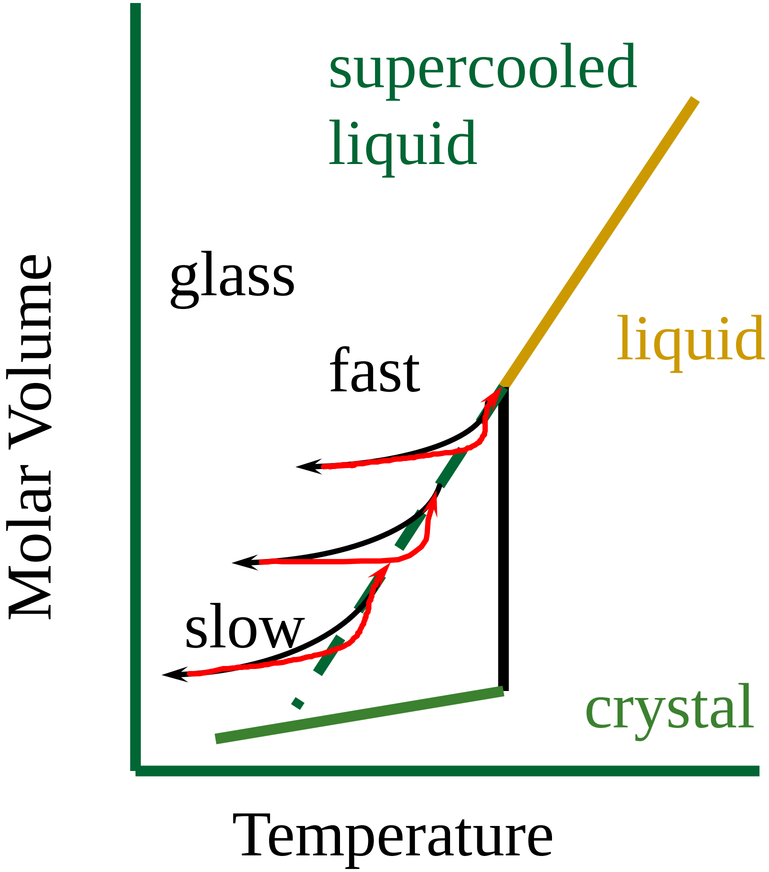
Glass Properties on Heating

- Liquid is “arrested” in the glassy solid state on cooling
- The heating curve by-passes the cooling curve because heating the glass is different than cooling the liquid
- Tg is higher on heating because of hysteresis
- Soon above the Tg, however, the glass has the thermal energy necessary to rejoin the liquid state



Glass Properties on Reheating

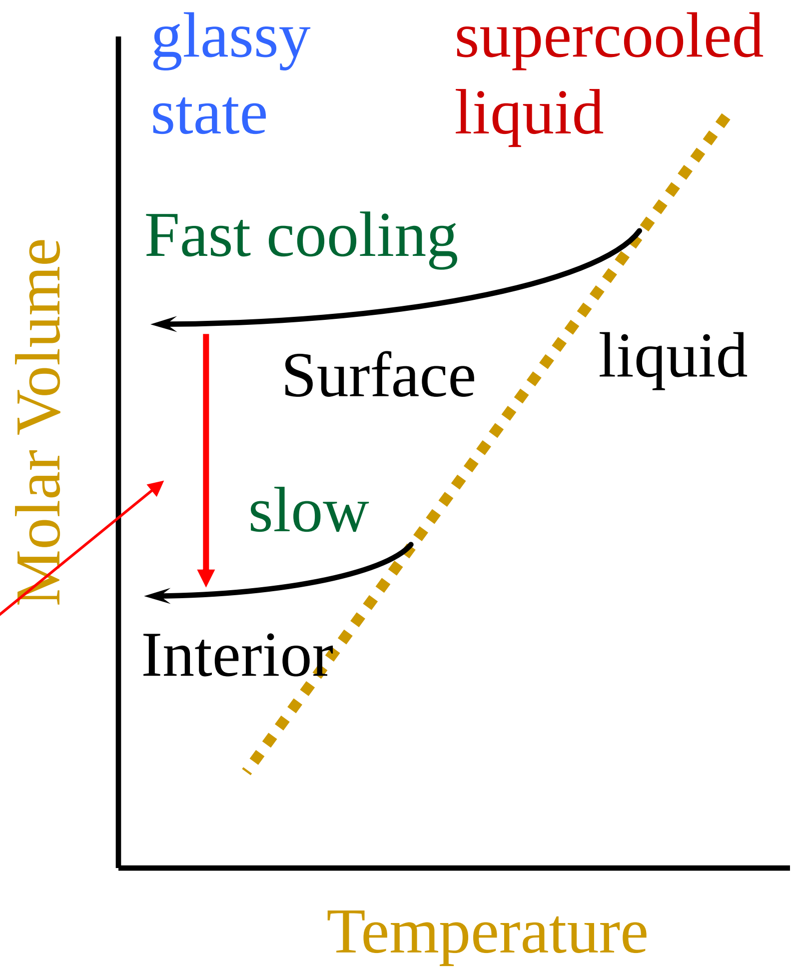
- Glasses arrested at progressively lower temperatures, the slower the cooling
- Tg decreases with decreasing cooling rate
- Slower cooling produces a lower Tg
- Faster cooling produces a higher Tg
- Tg is higher on heating because of hysteresis
- Soon above the Tg, however, the glass has the necessary thermal energy to become a liquid and the two curves rejoin



Tempered Glass

- The inside of a hot glass sheet will cool slower than the outside
- Use the volume – temperature diagrams just presented to describe how glass is thermally tempered

- *Compressional forces are created by interior liquid continuing to shrink while exterior surface is “frozen”*



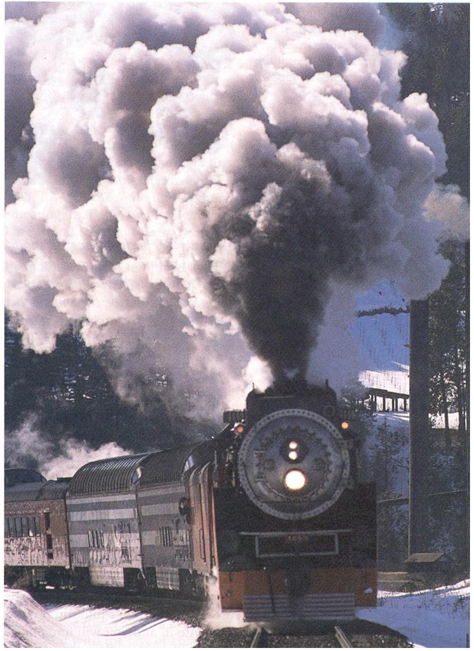
Thermodynamics of the Glass Transition

- So far we've looked at the kinetics of the glass transition
- Describing the transition as a falling out of equilibrium with cooling
- Viscosity relaxation time governs rate at which the liquid can respond to changes in its environment
    - Faster cooling forces liquid to "fall" out of equilibrium faster
    - Slower cooling allows liquid to "stay" in equilibrium longer
- Two time scales were introduced
    - The *internal time scale* of the glass forming liquid, τ_{int}
        - Governed primiarily by the temperature dependence of the structure of the liquid
    - The *external time scale* of the observer, τ_{ext}
        - Governed primarily by the cooling rate imposed on the liquid

Thermodynamics of the Glass Transition

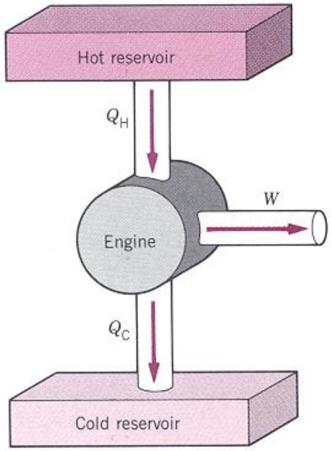
- *Be able to use the enthalpy changes in the glass transition region to calculate the heat differences between the liquid and glassy state*
- *Be able to use the entropy changes in the glass transition region to calculate the Kauzmann temperature for a liquid*
- *Be familiar with the Gibb's Free-Energy changes in the transition region to*
- *Be able to calculate thermodynamic quantities for supercooled liquids and glasses given heat capacity data*

The Enthalpy Function, H(T)



- The change in energy in a system performing (undergoing) a process is equal to the amount of heat consumed by the system minus the amount of work done by the system
  - $\Delta E = q - w$ = heat flow into the system minus work done by the system
  - Heat flow q = the Enthalpy change for the process at constant Pressure
  - $q = \Delta H = H_2 - H_1$

    = Enthalpy of state 2(final state) – Enthalpy of state 1(initial state)

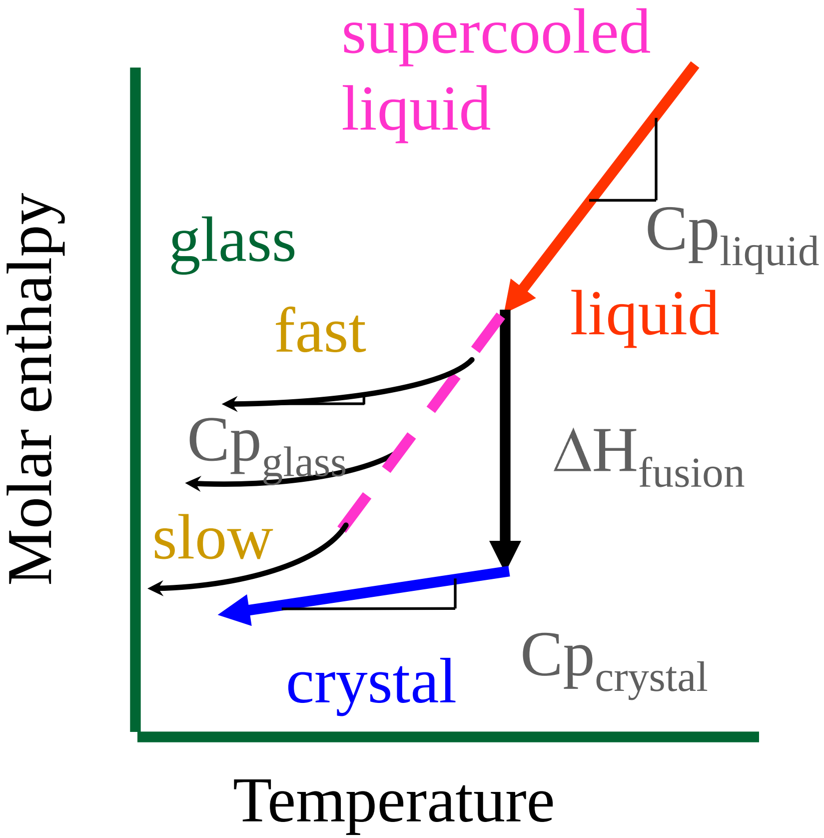


Enthalpy function for glass forming liquids

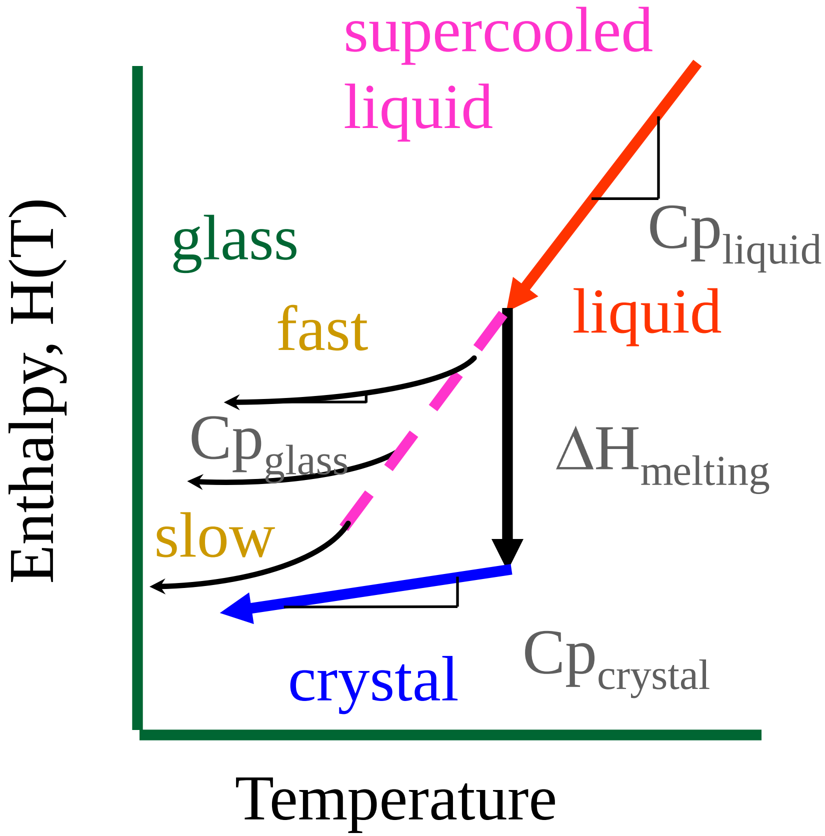
- Now consider the temperature dependence of the Enthalpy for a liquid cooled from above its melting point to room temperature along two cooling paths:
  - First assume thermodynamic equilibrium holds and the liquid readily crystallizes at its melting (freezing) point to form the equilibrium crystalline phase and then continues to cool to room temperature
  - Second, assume kinetics holds and the liquid by-passes the equilibrium crystallization and super-cools to the glassy state.

Enthalpy Changes in the Glass Transition Region

- H(T) decreases continuously with cooling
- Slope of the H(T) curve is the heat capacity which changes from liquid-like to solid-like values in the transition region
- Change in heat capacity at the glass transition ΔCp(Tg) measures the differences between the liquid and solid (glassy) Cp values
- Sub-Tg annealing and relaxation can occur if liquid is given sufficient time to relax to lower enthalpy state



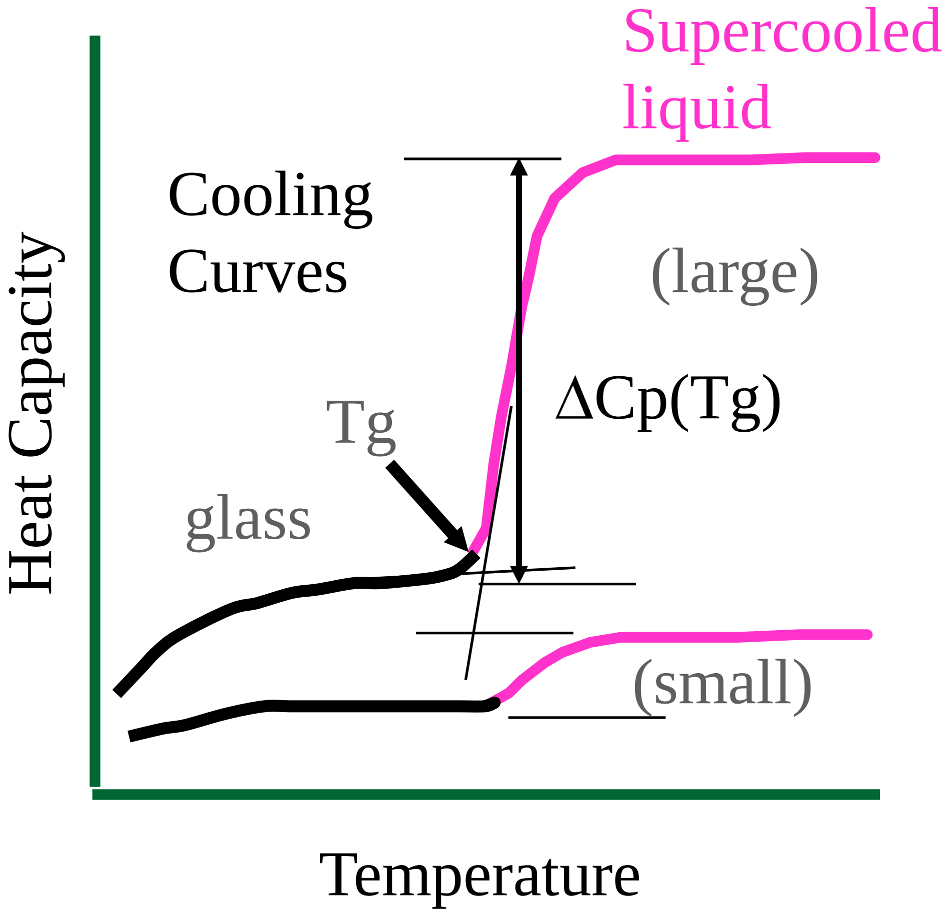
Heat Capacity Changes in the glass transition range



- Knowing that Cp(T) is the temperature derivative of the Enthalpy function
  - Turn to your neighbor and sketch what you expect for the temperature dependence of Cp on cooling a glass forming liquid

Heat Capacity changes at Tg ΔCp(Tg) on cooling

- The change in slope in enthalpy at Tg is a measure of the difference between heat capacity of the liquid and the glass
- Heat capacity of glasses arises mostly from vibrational contributions
  - rotational and translational degrees of freedom have been “frozen” out
- Heat capacities of liquids arise from all three contributions
  - rotational, translational, and vibrational



Heat Capacity changes at Tg $\Delta Cp(Tg)$

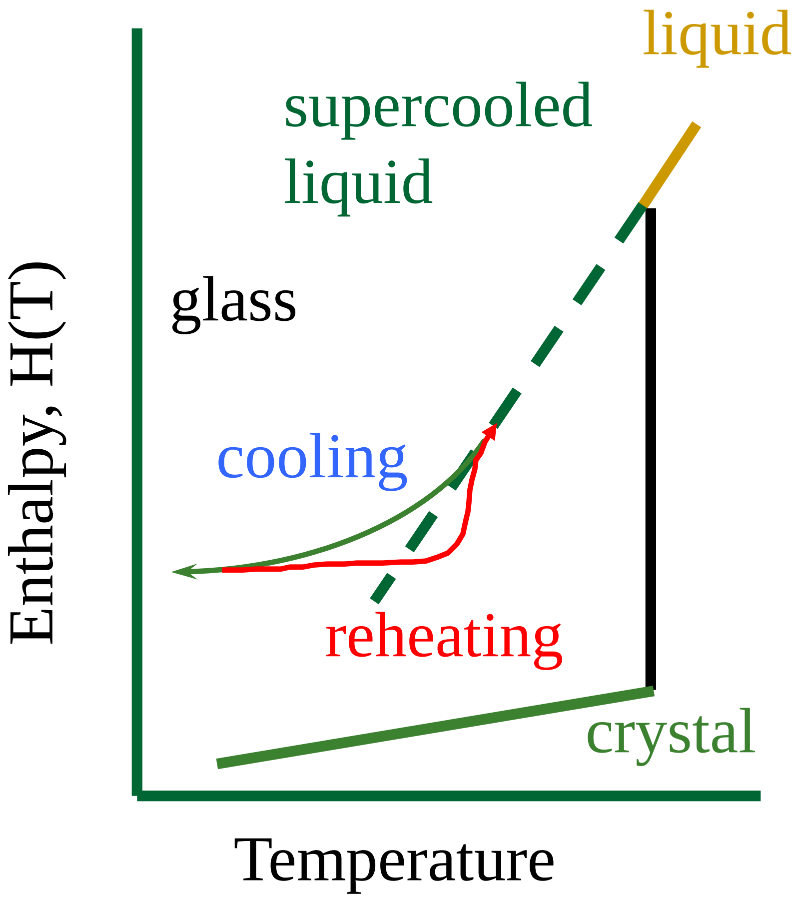
- Glass transition occurs when:
  - Thermal energy, heat, being input into the glass has filled all the available thermal degrees of freedom, vibrations, in the glass
  - The vibrational states are essentially filled and at maximum amplitude
  - Additional heat supplied to the glass must be accommodated by other degrees of freedom
  - Rotational and translational degrees of freedom now become available and as such, Cp_{liquid} is typically > Cp_{glass}

Heat Capacity Changes at Tg ΔCp(Tg)

- Covalently bonded liquids exhibit “strong” rigidly held structures (SiO_2, for example)
  - Generally exhibit higher glass transition temperatures and smaller ΔCp(Tg) values
- Molecular or ionic salt liquids exhibit “fragile”, weakly held structures (sucrose, for example)
  - Generally exhibit lower glass transition temperatures and larger ΔCp(Tg) values
- Behaviors can be interchanged by chemically changing the liquid
  - Depolymerizing covalent liquids through non-bridging oxygens

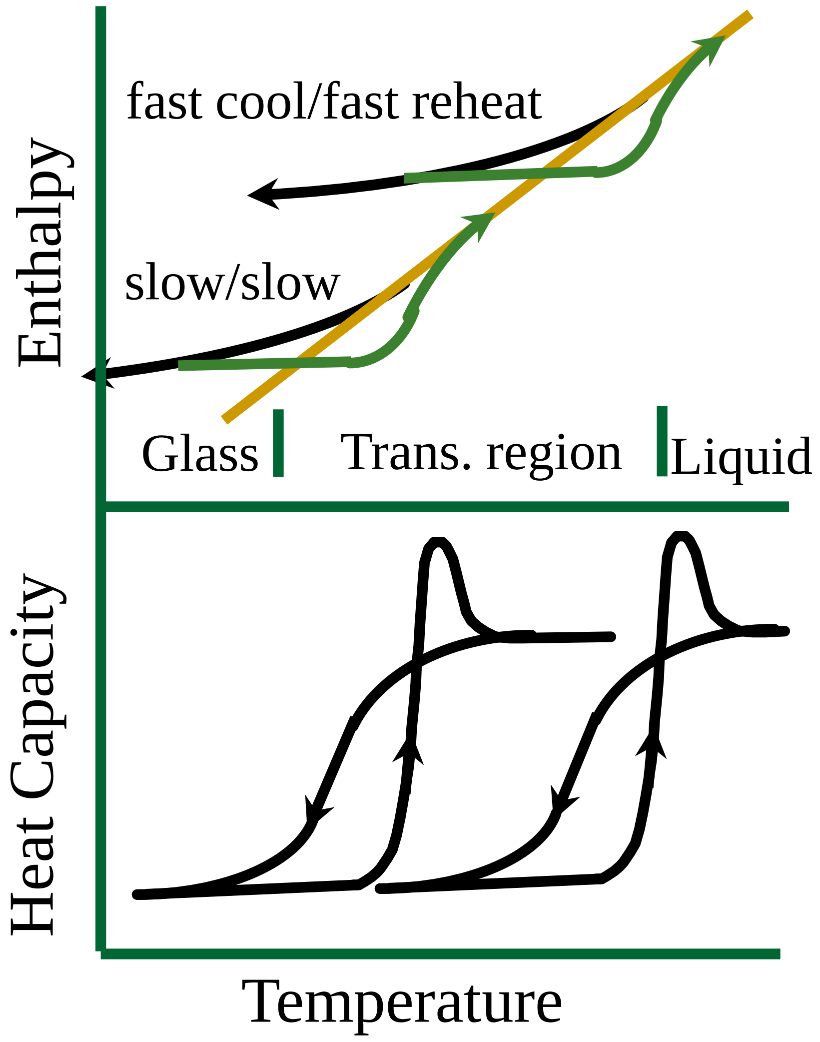
Heat capacity changes at Tg on heating

- Now consider reheating a glass that has been formed from the liquid state
    - Sketch the expected Cp curve for the Enthalpy curve to the right



The Glass Transition

- The extent of the hysteresis loop also causes the “overshot” in the glass transition
- The heat capacity overshoot is the most common example of this
- On reheating the cooled glass, the reheat curve “overshoots” the cooling curve and as such creates a peak, also termed “overshoot”, in the heat capacity curve.
- The overshoot in the heat capacity curve is a direct manifestation of the activation energy in the glass transition - activated process



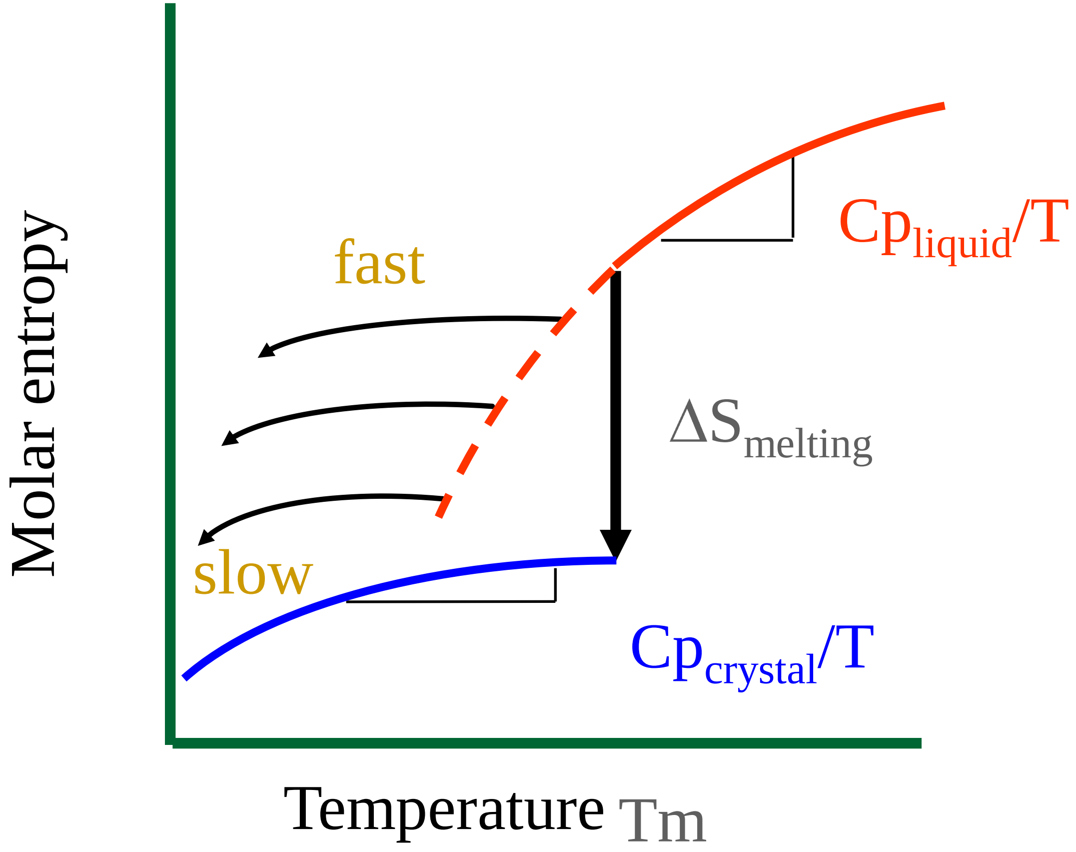
Temperature dependence of the Entropy, S(T)

- Entropy measures the disorder in the system
  - It is always positive, and always increases with temperature
  - Hot things are always more disordered than cool things
    - Entropy can go to zero at 0 K

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} \left(\frac{\partial S(T)}{\partial T} \right)_P dT = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

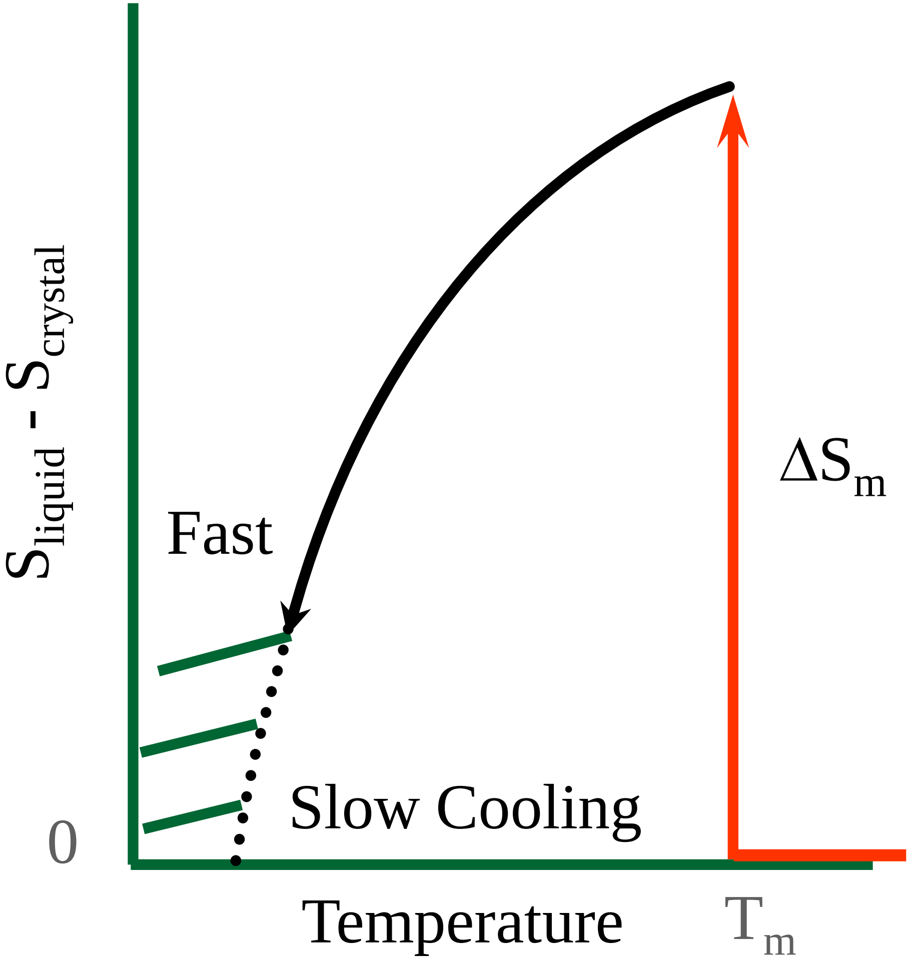
- If the Cp(T) of solid TiO_2 is 17.97 + 0.28 x 10^{-3}T - 4.35 x $10^{-5}/T^2$ cal/mole-K, the ΔH_{melt} is 16 kcal/mole, and the Cp(T) for the liquid is 21.4 cal/mole-K plot the S(T) and calculate the change in entropy when 10 lbs. TiO_2 is cooled from 2500 K to room temperature?

Temperature Dependence of the Entropy S(T)



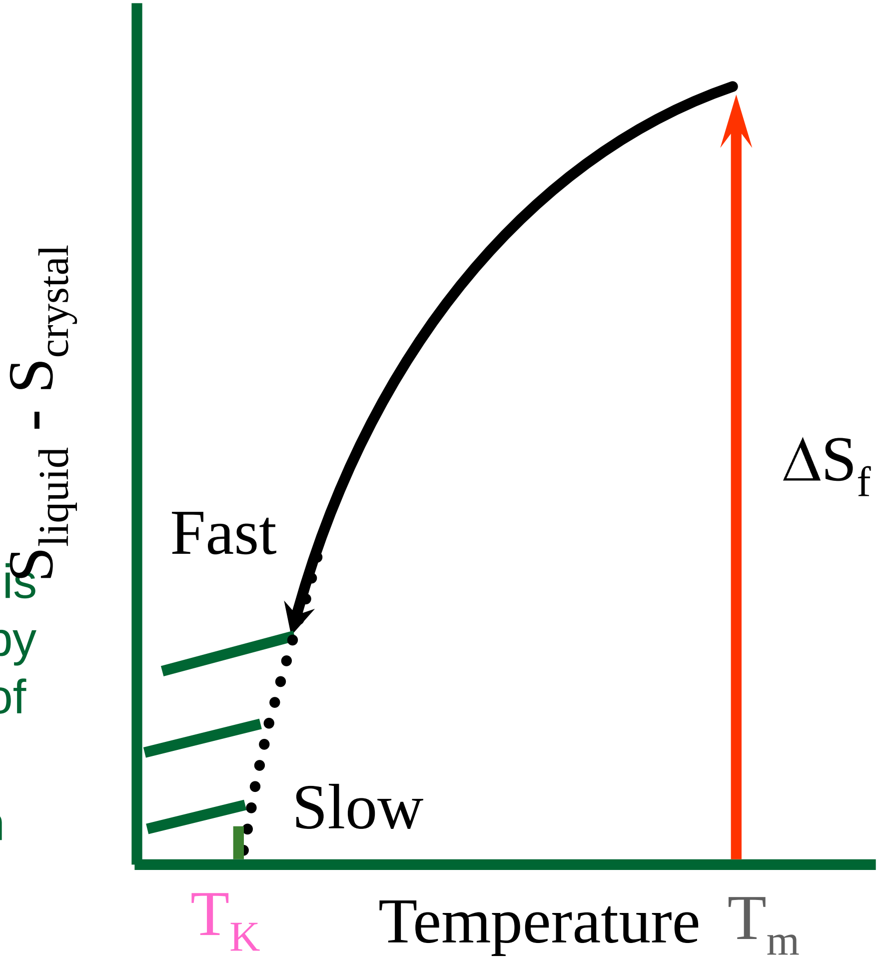
Entropy Changes at Tg

- Entropy is intimately linked to liquid state behavior
  - Highly disordered liquid being reversibly ordered at the freezing point to the the crystalline phases
  - Corresponding reversible change in entropy, ΔH(Tf)/Tf
- Glass forming liquids exhibit continuously changing entropy that shows no discontinuities
  - Entropy decreases with temperatures
  - At Tg, continuously changes from liquid-like values to solid like values



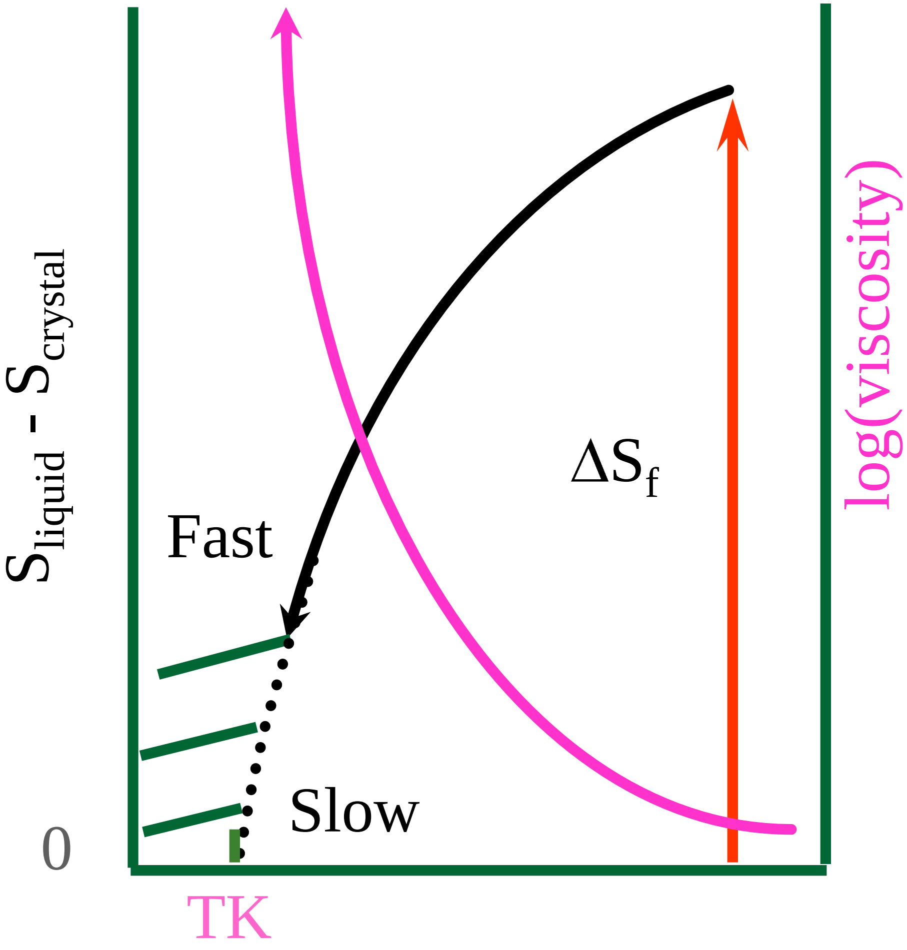
The “Kauzmann” Paradox

- If entropy curve continued along meta-stable equilibrium liquid line
    - At some temperature below Tg, the entropy of the liquids would appear to decrease below that of the crystal
    - How could a liquid, with its inherent structural disorder, have an entropy lower than that of the corresponding crystal
    - The Kauzmann temperature, T_K, is the temperature where the entropy of the liquid would intersect that of the equilibrium crystal
    - Glass at this temperature is often called an “*ideal glass*”



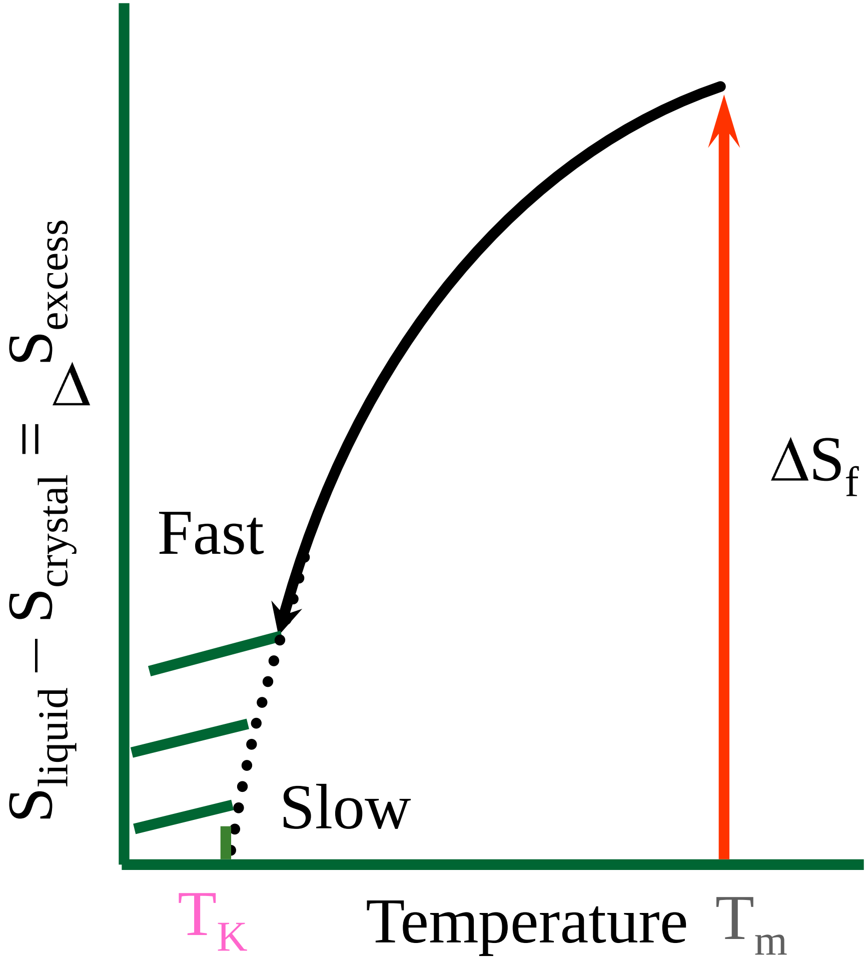
Kauzmann Paradox

- Simultaneous to rapidly decreasing entropy
  - Viscosity is increasing
  - Structural relaxation time is rapidly increasing
  - Time required for the liquid to continue to follow the equilibrium line becomes dramatically longer
- Liquid falls out of equilibrium at a temperature above the Kauzmann temperature because the time required for it to remain in equilibrium simply becomes much longer than the experimental time scale



Excess Entropy ΔS_{excess} of the Supercooled Liquid

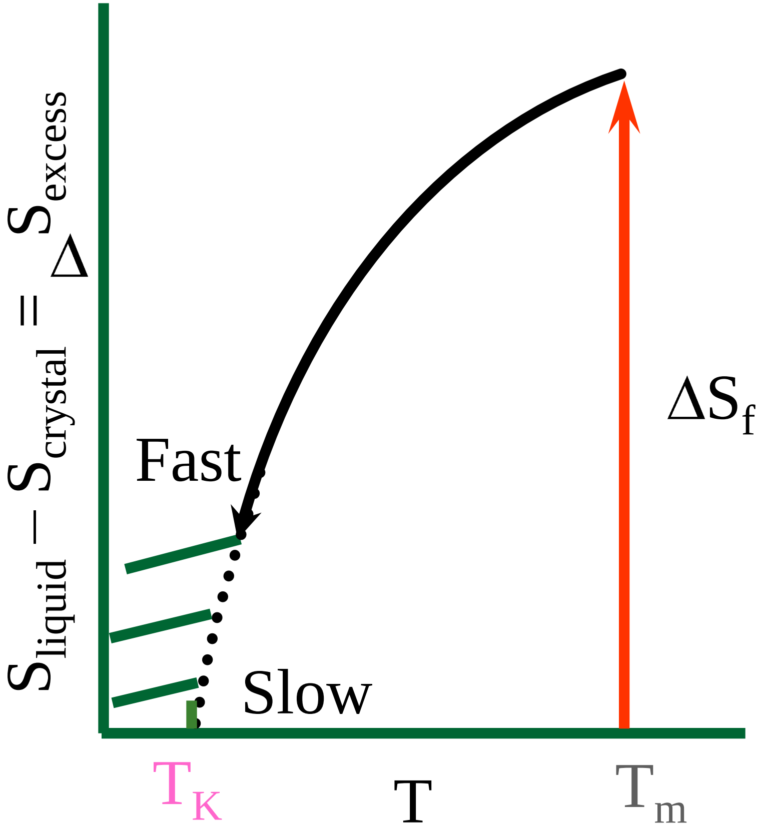
- The important quantity is the extra entropy the liquid has above that of the crystal at the same supercooled temperature
  - Equilibrium liquids above the melting point have no excess entropy
  - Supercooled liquids have excess entropy because they have not “lost” the entropy of melting given to the liquid on melting
  - A supercooled liquid, at maximum has the entropy of melting to lose below Tm
  - At T_K the liquid has lost all of this entropy



Excess Entropy ΔS_{excess} of the Supercooled Liquid

$$\Delta S_{excess}(T) = \Delta S_{melting} + \int_{T_m}^{T} \frac{\left(Cp_{liquid}(T) - Cp_{crystal}(T)\right)}{T} dT$$

- At just above the melting point, $\Delta S_{excess}(\geq T_m) = 0$
- At just below the melting point, $\Delta S_{excess}(\leq T_m) = \Delta S_m$
- As T decreases below T_m ΔS_{excess} decreases due to the loss of entropy through cooling.
- At the Kauzmann temperature, all of the entropy gained by the liquid by not crystallizing has been lost through cooling



Summary

- Glass formation occurs because of a mismatch between:
  - Internal time scale of the cooling liquid
  - External time scale imposed by the surroundings
- If τ_{int} becomes >> than τ_{ext}, then glass formation will result
  - $\tau_{crystallization}$ must be greater than both of these
  - Glass formation becomes dependent on both conditions
  - Chemical bonding of the liquid governs τ_{int}
- Reheating a glass is a different process than cooling a liquid
  - Hysteresis produces divergent cooling and heating curves
- Enthalpy function is similar to the volume function
  - Hysteresis produces overshoot in Cp on heating
- Entropy function measures disorder in the liquid and glassy states
  - Kauzmann paradox occurs for the “ideal glass state where Excess entropy of the liquid vanishes below that of the apparent crystalline phase

Next time

- Section 1: Lecture 2: Conditions for Glass Formatiom
  - Structural approach to glass formation
    - How can τ_{internal} be increased for glass formation result?
  - Kinetic approach to glass formation
    - How far must τ_{external} be decreased for glass formation to result?