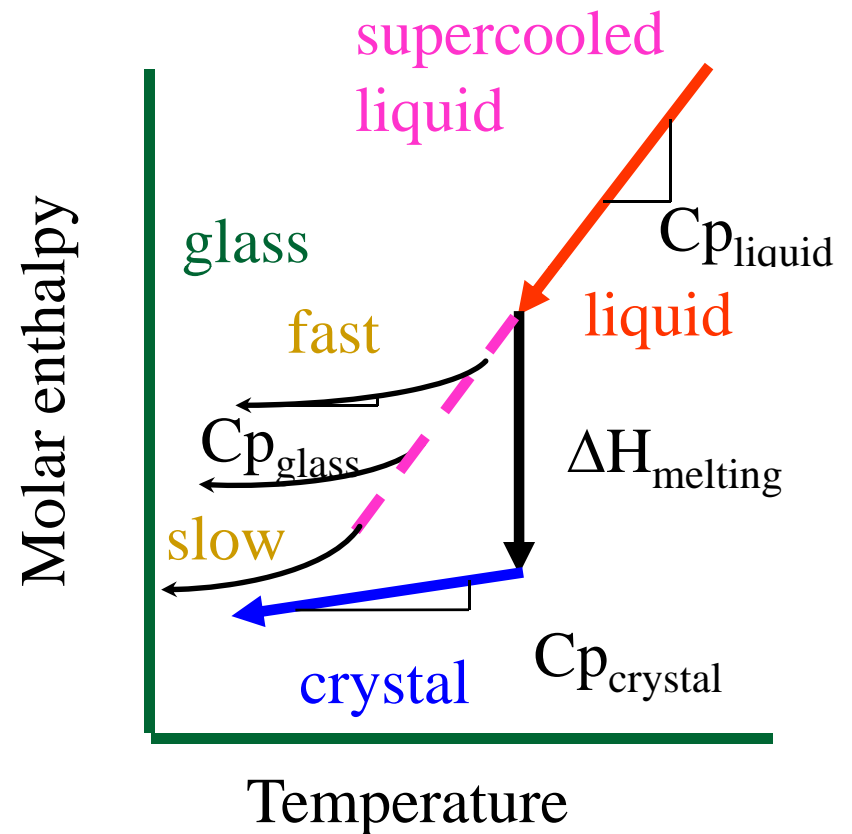

Relaxation in Glass

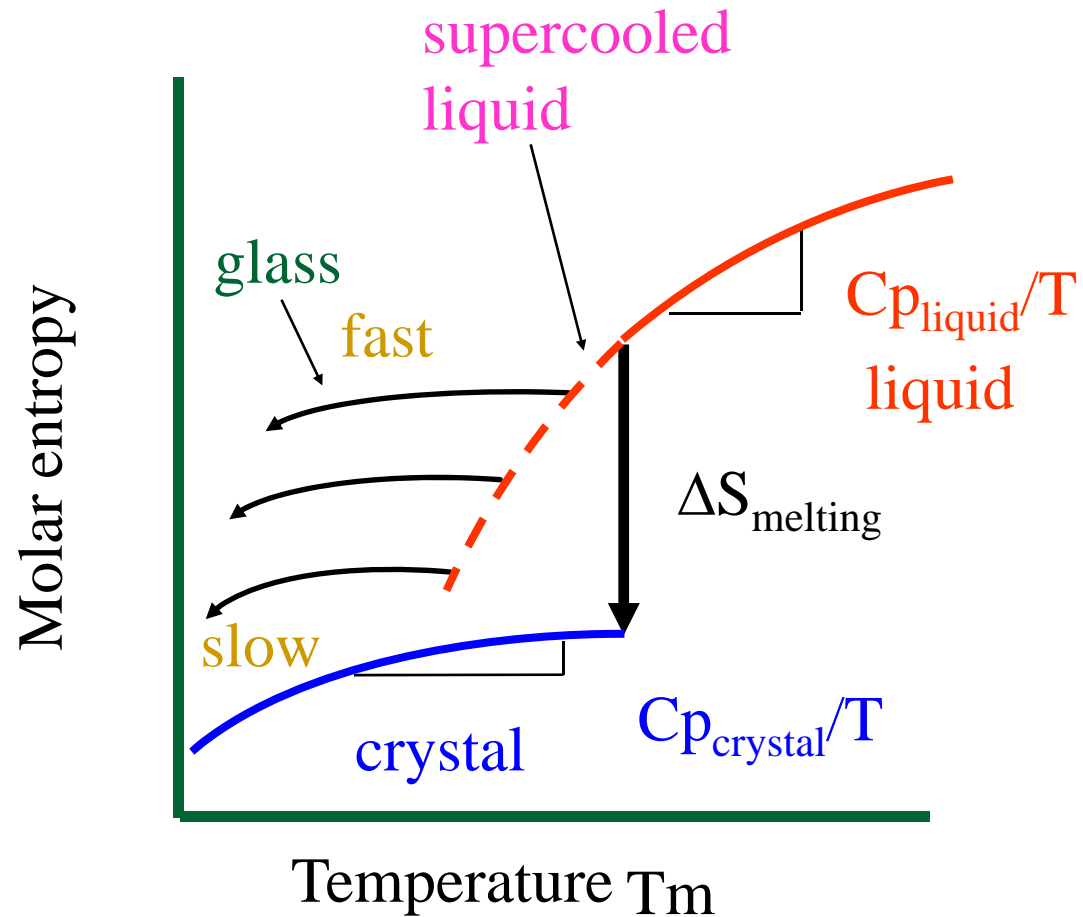
Lecture 12: The Glass Transition as a Kinetic Transition

Enthalpy Changes in the Glass Transition Range

- $H(T)$ 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 $\Delta C_p(T_g)$ measures the differences between the liquid and solid (glassy) C_p values
- Sub- T_g annealing and relaxation can occur if liquid is given sufficient time to relax to lower enthalpy state

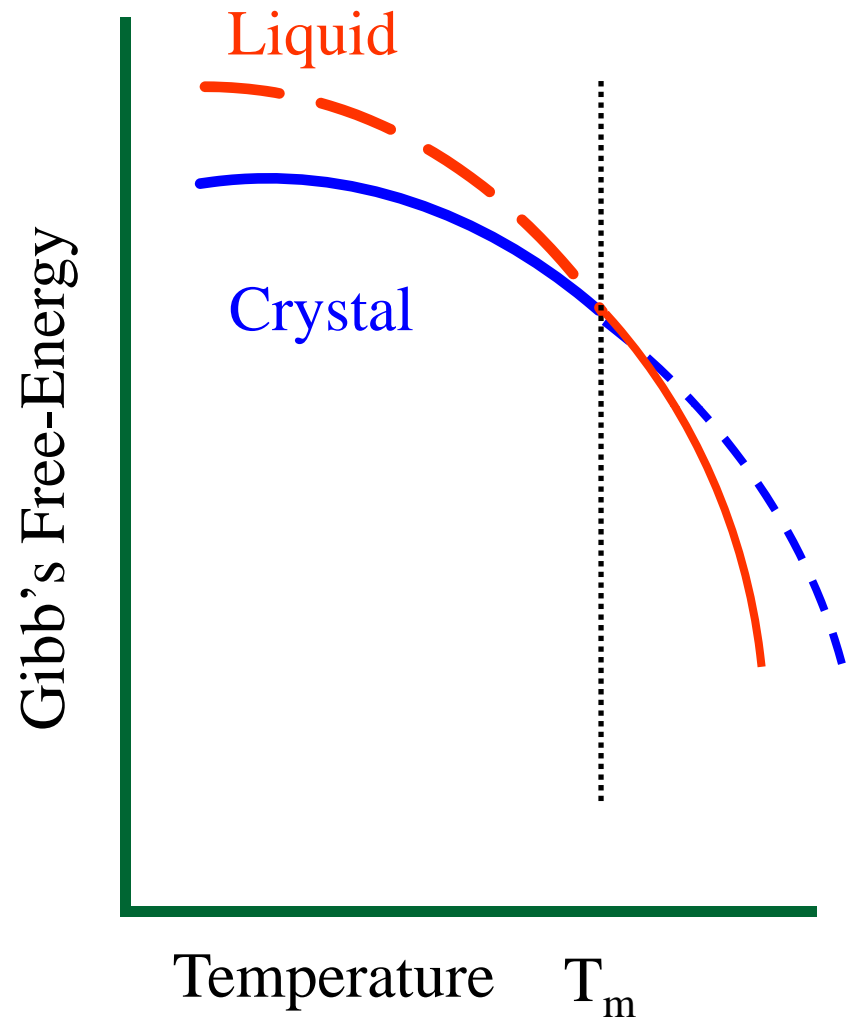


Entropy Changes in the Glass Transition Range



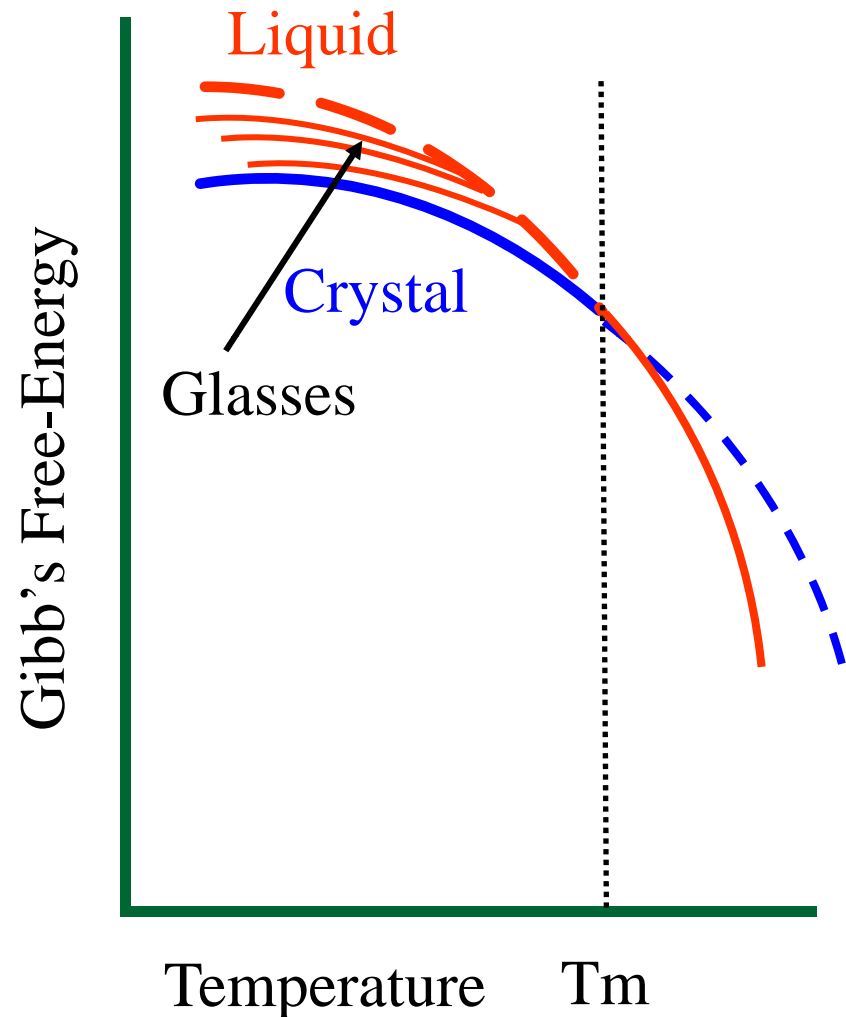
Gibb's Free-Energy Changes in the Glass Transition Range

- $G = H - TS$
- Gibbs' Free-Energy change at T_m is continuous, there is no "Latent Free-Energy Change" as is the case for the enthalpy and entropy
- At the melting point
 - $G_{\text{liquid}} = G_{\text{crystal}}$
- Below the melting point
 - $G_{\text{liquid}} > G_{\text{crystal}}$ and
 - $\Delta G_{\text{crystallization}} < 0$
- Above the melting point
 - $G_{\text{liquid}} > G_{\text{crystal}}$
 - $\Delta G_{\text{melting}} < 0$
- At any point $\left(\frac{\partial G(T)}{\partial T} \right)_P = -S(T)$



Gibb's Free-Energy Changes in the Glass Transition Range

- Glasses then “fall off” the liquid line at progressively lower temperatures the slower the cooling rate
- Gibbs' Free-Energy of the glass behaves more like the crystal than the liquid
- Glass transition range is the range of T where the Gibb's Free-Energy changes from “liquid-like” values to “solid-like” values



Fundamentals of the Glass Transition

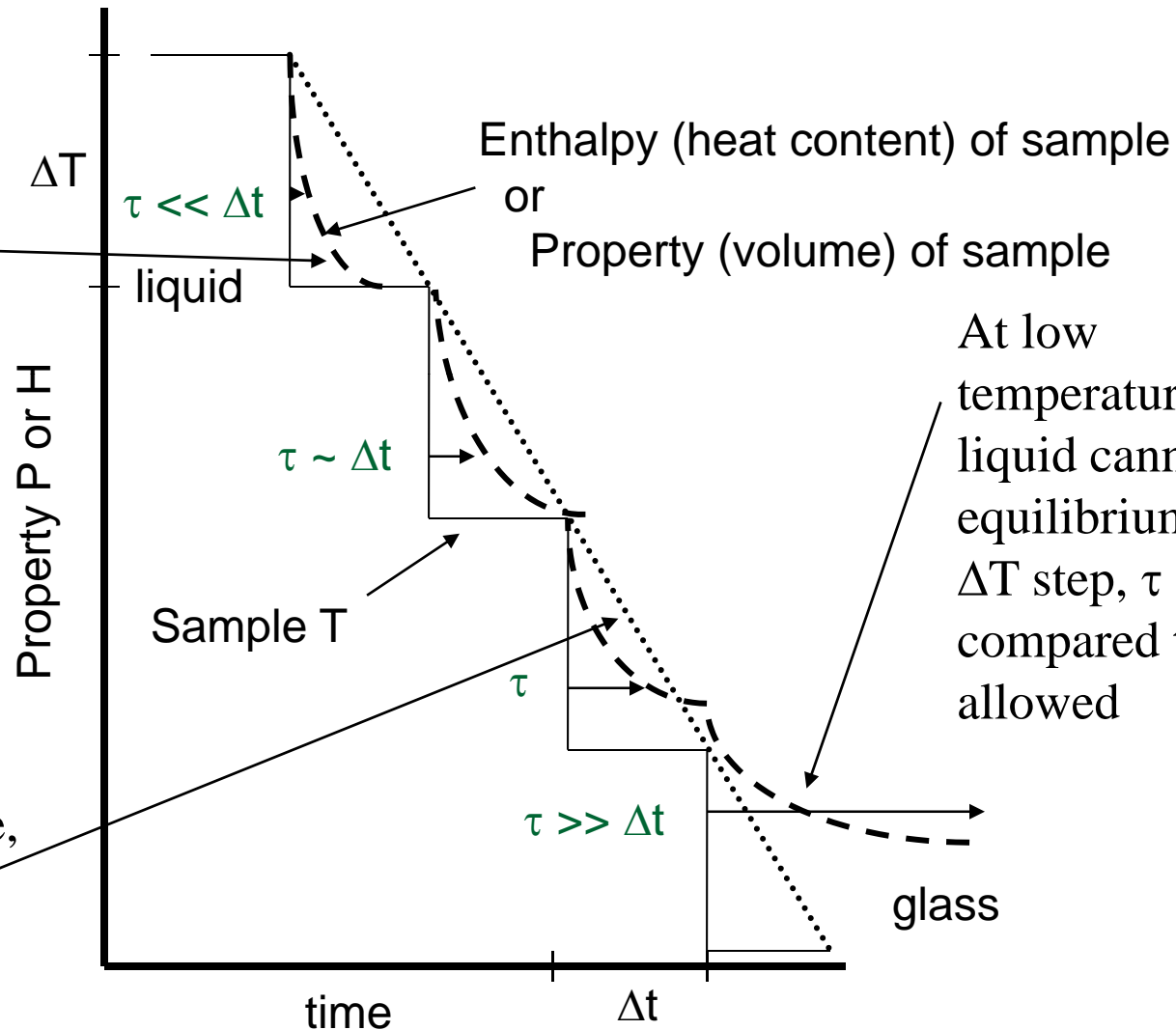
- The Glass Transition is a *Kinetic Transition*
 - Continuous changes in structure and properties
 - Structure and properties are continuous with temperature
 - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

Time and Temperature Dependence of Properties

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

Average cooling rate,

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



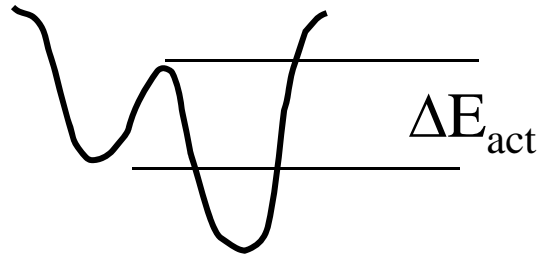
At low temperatures, the liquid cannot reach equilibrium after ΔT step, τ is long compared to time allowed

Temperature dependence of the internal time scale

- While the external time scale, Δt most often does not change,

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

- The internal timescale can be strongly temperature dependent,



- Rearrangement of the liquid requires breaking of bonds between atoms (ions)
- This requires thermal energy
- The relative magnitude of the energy barrier to motion, ΔE_{act} to the available thermal energy, kT determines the probability of “getting over” the energy barrier

$$\tau(T) = \tau_o \exp\left[\frac{\Delta E_{act}}{kT}\right]$$

- Arrhenius temperature dependence of the “relaxation time”

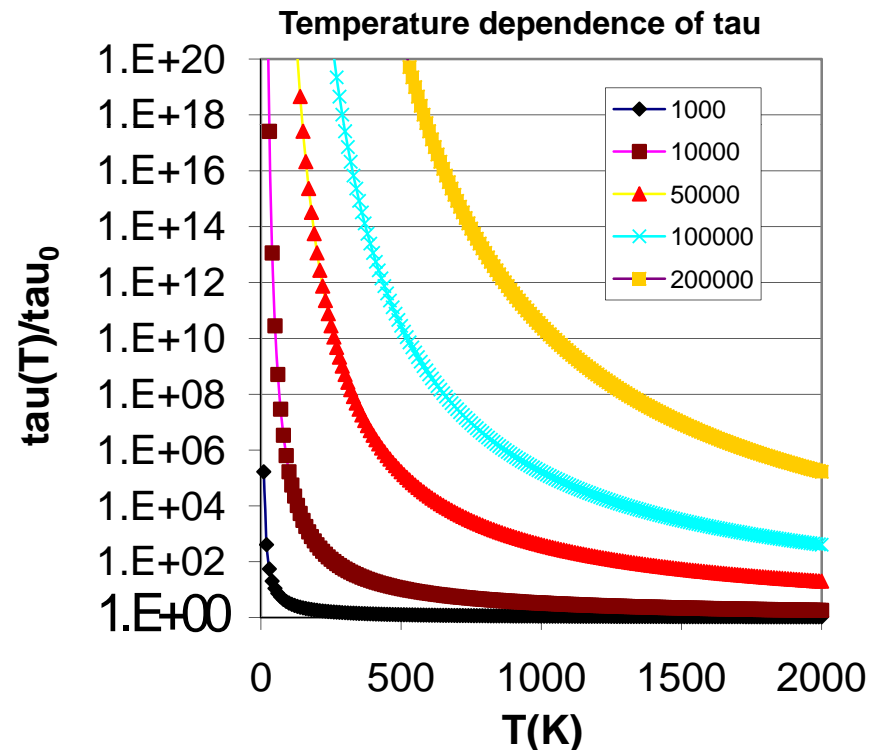
Temperature dependence of the internal relaxation time

- For $\Delta E_{act} > 0$

$$\tau(T) / \tau_0 = \exp\left[\frac{\Delta E_{act}}{kT}\right]$$

- $0 \leq 1$
- It is a thermal “probability” of motion
- High T, $kT \sim \Delta E_{act}$, high probability of motion
- Low T, $kT \ll \Delta E_{act}$ low probability of motion

$$\frac{\tau(T)}{\tau_0} = \exp\left[\frac{\Delta E_{act}}{kT}\right]$$



Temperature dependence of the internal relaxation time

- For $\Delta E_{act} > 0$

$$\log_{10} \left(\frac{\tau(T)}{\tau_o} \right) = \frac{\Delta E_{act}}{2.303kT}$$

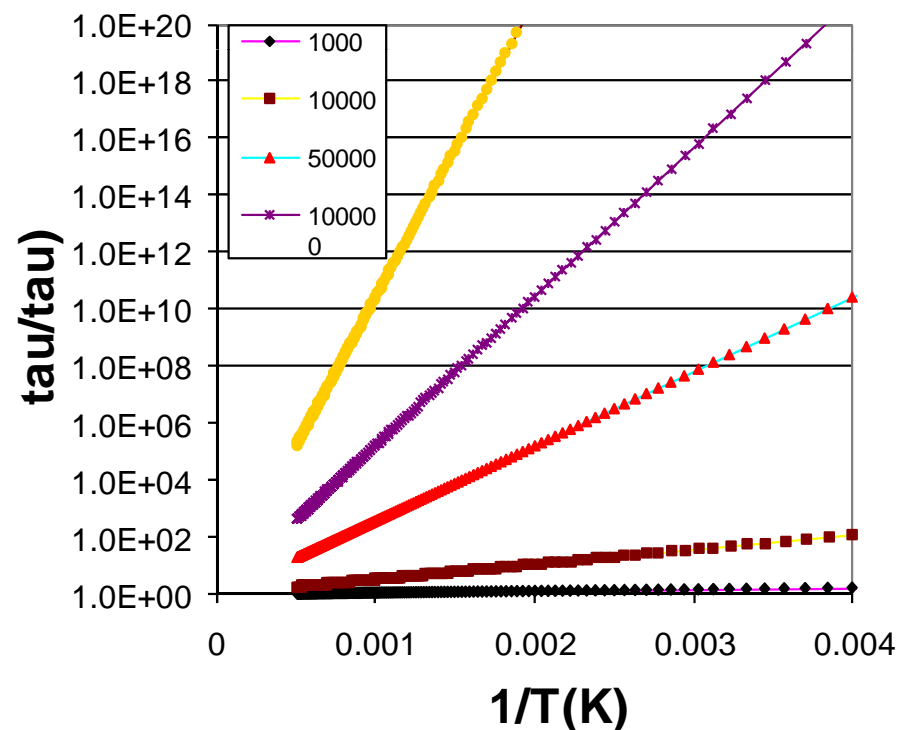
- $0 \leq 1$

- It is a thermal “probability” of motion

- High T, $kT \sim \Delta E_{act}$, high probability of motion

- Low T, $kT \ll \Delta E_{act}$ low probability of motion

Arrhenius Temperature dependence of tau



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 the viscosity
 - Weak and limited bonding decreases the viscosity
 - Viscosity \propto relaxation time, $\eta = G\tau$
 - 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
 - Is it just allowed to cool naturally under prevailing conditions?
 - Or is it “insulated” and allowed to cool very slowly, Δt is long

Glass Transition is a Kinetic Transition

- Assume that the “relaxation” following a temperature jump is also “exponential”

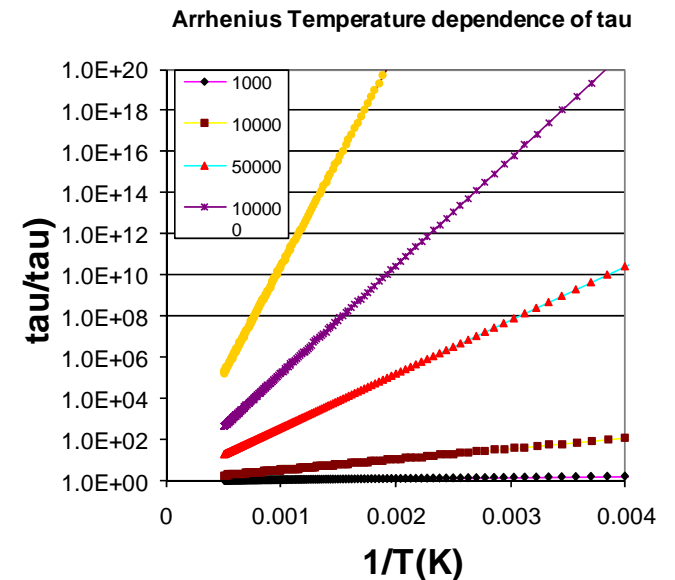
$$\varphi(t) = \exp\left(\frac{-t}{\tau(T)}\right)$$

- Note that ~ 5 relaxation time are required for nearly complete relaxation

$$\exp\left(\frac{-5\tau}{\tau}\right) = \exp(-5) = 0.007 \sim 0.01 \sim 1\%$$

- Note that 99% of change has occurred
- Now consider

$$\Delta E_{\text{act}} \sim 50,000 \text{ J/mol}, \tau_0 \sim 10^{-13} \text{ sec}$$



Glass Transition is a Kinetic Transition

- Now consider an example:
- Consider starting at a temperature, T_0 above T_m where the viscosity is low and the relaxation time τ is short compared to an experimental time step Δt following a temperature step ΔT :

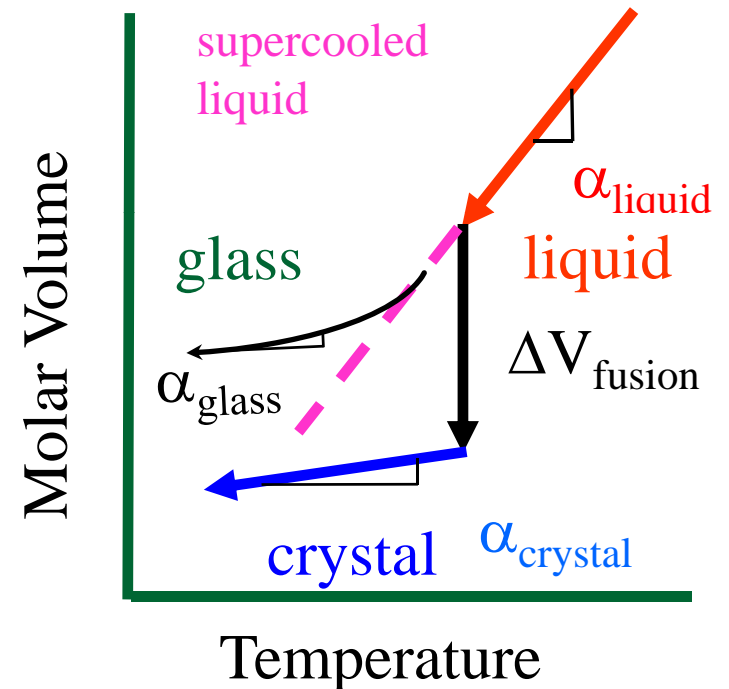
$$V(T_0, t_0) \equiv V_0$$

$$V(T, t_0 + \Delta t) = V_0 + V_0 \Delta T \alpha(T) = V_0 (1 + \Delta T \alpha(T))$$

- Now, for the second step suppose the relaxation time τ is still short compared to an experimental time step Δt following a temperature step ΔT :

$$V(T, t_0 + 2\Delta t) = V_0 (1 + \Delta T \alpha(T)) (1 + \Delta T \alpha(T))$$

$$\dots V(T, t_0 + n\Delta t) = V_0 (1 + \Delta T \alpha(T))^n$$



Glass Transition is a Kinetic Transition

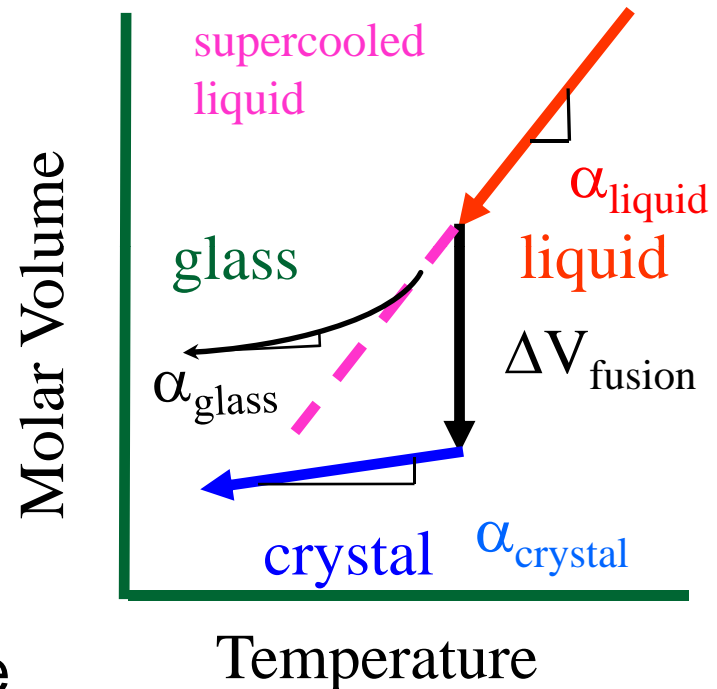
- Now consider the case where the extent of relaxation depends upon the time it takes for relaxation to occur:

$$\varphi(t) = \exp\left(\frac{-t}{\tau(T)}\right)$$

- The amount of relaxation:

$$1 - \varphi(t) = 1 - \exp\left(\frac{-t}{\tau(T)}\right)$$

- $\tau \rightarrow 0 \rightarrow 1 - \varphi(-t/0) = 1$ complete change
- $\tau \rightarrow \infty \rightarrow 1 - \varphi(-t/\infty) = 0$, no change



Glass Transition is a Kinetic Transition

- Relaxation, therefore depends upon the τ and Δt relationship:

$$V(T_0, 0) \equiv V_0$$

$$V(T_1, \Delta t_1) = \underbrace{V_0}_{\text{The original volume}} + \underbrace{V_0 \Delta T_1 \alpha(T_1)}_{\text{The instantaneous volume change due to } \Delta T_1 \text{ change to } T_1} \left(1 - \exp\left(\frac{-\Delta t_1}{\tau(T_1)}\right) \right) = V_0 \left(1 + \Delta T_1 \alpha(T_1) \left(1 - \exp\left(\frac{-\Delta t_1}{\tau(T_1)}\right) \right) \right)$$

The original volume

The instantaneous volume change
due to ΔT_1 change to T_1

The extent of relaxation after Δt_1 time step at T_1 with relaxation time $\tau(T_1)$

Temperature and Time Dependent Volume

- After two time steps...

$$V(T_0, t_0) \equiv V_0$$

$$V(T_1, 0 + \Delta t) = V_0 \left(1 + \Delta T_1 \alpha(T_1) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_1)}\right) \right) \right)$$

$$V(T_1, \Delta t) = V_0 \left(1 + \Delta T \alpha(T_1) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_1)}\right) \right) \right)$$

$$V(T_2, 2\Delta t) = V(T_1, \Delta t) + V(T_1, \Delta t) \Delta T_2 \alpha(T_2) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_2)}\right) \right)$$

$$V(T_2, 2\Delta t) = V_0 \left(1 + \Delta T \alpha(T_1) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_1)}\right) \right) \right) +$$

$$V_0 \left(1 + \Delta T \alpha(T_1) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_1)}\right) \right) \right) \Delta T_2 \alpha(T_2) \left(1 - \exp\left(\frac{-\Delta t}{\tau(T_2)}\right) \right)$$

Exercises.....

- $\Delta t = 1$ second
- $\tau_0 = 10^{-13}$ seconds
- $\Delta E_{act} = 5,000$ cal/mole
- $\tau(300K)$?
-
- Fully relaxed
- $\tau(80K)$?
-
- not relaxed
- $\tau(60K)$?
-
- For $\Delta E_{act} = 50,000$ cal/mole
- $\tau(300K)$?
-
- Not relaxed
- For $\Delta E_{act} = 50,000$ cal/mole
- $\tau(1000K)$?
-
- Relaxed

$$\tau(T) = \tau_0 \exp\left[\frac{\Delta E_{act}}{RT}\right]$$

$$R = 1.987 \text{ cal / mole} - K$$

Exercises.....

- Now consider the “elastic” volume change
- Take $V_0 \sim 35$ ml/mol
- Take $\alpha_{\text{liquid}} \sim 400$ ppm/K
- Take $\Delta T = 1$ K
- Start at 1200 K
- What is V at 1170K?
-
- What is τ at 1170K?
-
- What is V at 800K?
-
- What is τ at 800K?
-
- What is $\sim T_g$?
-

$$V(T, t_0 + n\Delta t) = V_0(1 + \Delta T \alpha(T))^n$$

Exercises...

- Now add relaxation component...
- Take $V_0 \sim 35$ ml/mol
- Take $\alpha_{\text{liquid}} \sim 400$ ppm/K
- Take $\Delta T = 1$ K
- Take $\Delta t = 1$ second
- Start at 1200 K
- What is V at 1199K, 1 second?
-
- What is τ at 1198K, 2 seconds?
-

- What about at 1170K?
- What about 1100K?

$$\varphi(t) = \exp\left(\frac{-t}{\tau(T)}\right)$$

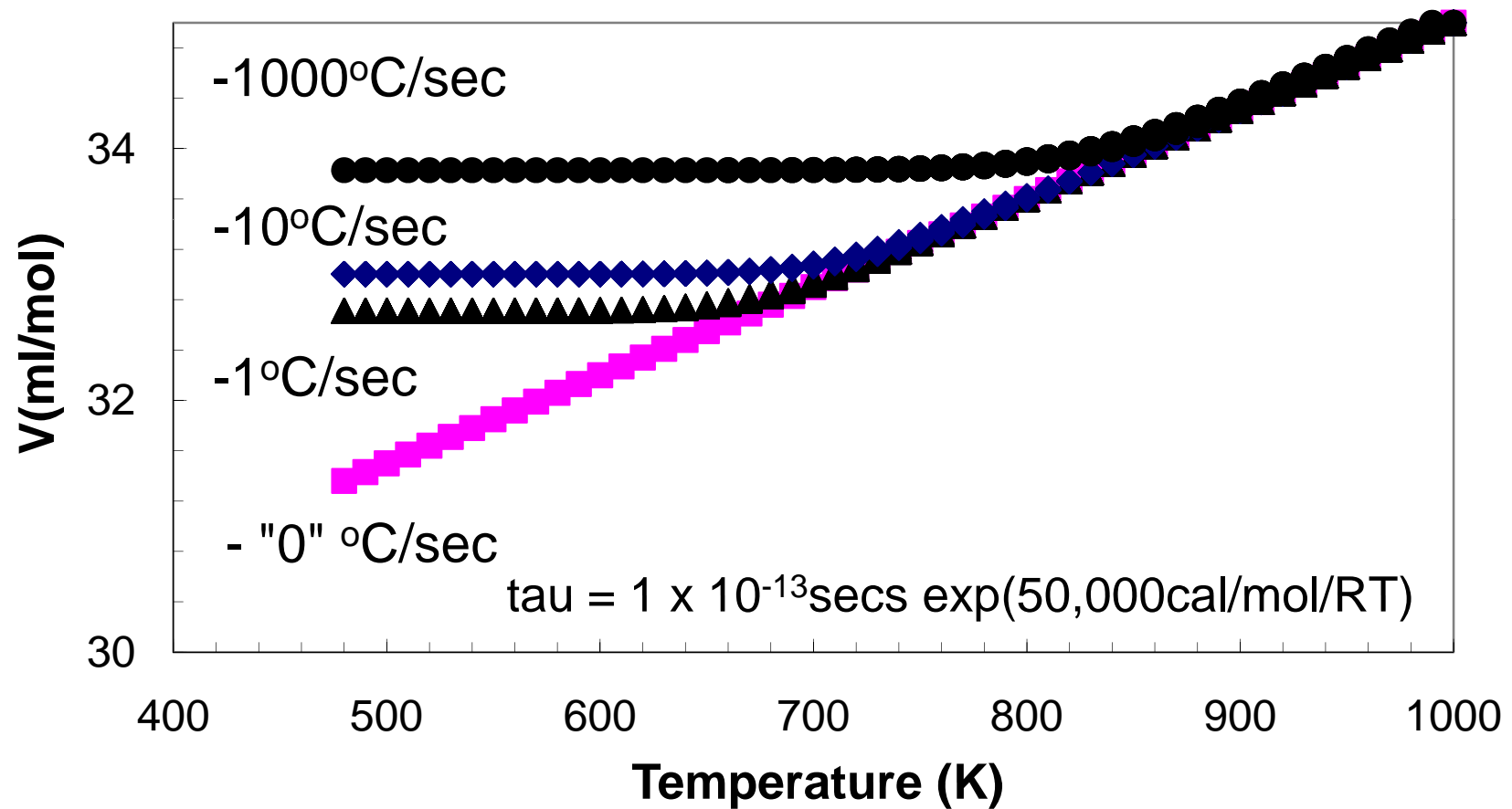
$$\tau(T) = \tau_o \exp\left[\frac{\Delta E_{act}}{RT}\right]$$

$$R = 1.987 \text{ cal / mole} - K$$

$$V(T_1, \Delta t_1) = V_0(1 + \Delta T_1 \alpha(T_1)) \left(1 - \exp\left(\frac{-\Delta t_1}{\tau(T_1)}\right)\right)$$

The Glass Transition from Arrhenius T dependence of tau and exponential relaxation

Volume vs. Temperature



Homework...

- Reconstruct Glass Transition cooling behavior using -10 C/second cooling rate, Arrhenius temperature dependence of relaxation time and exponential relaxation function.
- Extra Credit...
- Reconstruct faster (1000 C/sec) and slower cool (1 C/sec) cooling rates
- Extra Extra Credit...
- Construct reheating curve for -10 C/second cooling curve at a reheat rate of + 10C/second
- Extra Extra Extra Credit, Construct reheating curve for -1 and -1000 C/second cooling curves at a reheat rate of + 10C/second