

Advanced Vitreous State: The Physical Properties of Glass



Steve W. Martin

MSE Iowa State University

swmartin@iastate.edu



8/28/08 Lecture 1: Orientation

Students so far...

- Glass Class From Univ. Florida
- Gregory Grosso GGrosso@Transitions.com
- Matthew Strasberg mstrasberg@ufl.edu
- Karthik Gopalakrishnan gaka1umt@ufl.edu
- Robert Smith firefan@ufl.edu
- Allyson Barrett abarrett@dental.ufl.edu
- Prabhu Bellarmine pjbell@ufl.edu
- Matthew Cimoch mcimoch@ufl.edu

Students so far...

- The students from ISU are:
- Randilynn Christensen, rbchris@iastate.edu
- Christian Bischoff, Christian.m.bischoff@gmail.com
- Kristina Lord, krislord@iastate.edu

Students so far...

- From Alfred University
- Joshua M. Bartlett JMB9@alfred.edu
- Andrew B. Crawford ABC1@alfred.edu
- Kathryn Goetschius KLG1@alfred.edu
- Patrick K. Kreski: PKK1@alfred.edu

Students so far...

- From Clemson University
- YANG JING JINGY@clemson.edu
- CARLIE NATHAN A NCARLIE@clemson.edu
- CHEN PENGYU PENGYUC@clemson.edu
- MASSERA JONATHAN MASSERA@clemson.edu

Students so far...

- From Lehigh University
- Belwalkar, Amit A. aab306@lehigh.edu
- Saiyasombat, Chatree chs308@lehigh.edu
- Stockdale, Andrew W. aws3@lehigh.edu
- Stone, Adam R. ars208@lehigh.edu
- Wang, Shaojie shw206@lehigh.edu
- Zhao, Donghui doz206@lehigh.edu
- Jain, R c100@lehigh.edu

Students so far...

- From Penn State...

Students so far...

- From Missouri S &T....

Students so far...

- From Coe College...

Students so far...

- From the University of Michigan...

Students so far...

- From UC Davis....

Students so far...

- From University of Arizona...

Students so far...

- From....

Advanced Vitreous State – Introduction

■ The Details

- Meeting Times 1:00 – 2:15 EST

- Delivery Web Site...

 - <http://breeze.clemson.edu/vgc>

- Course Blackboard (with content) web site

- <https://bb.clemson.edu/webapps/portal/frameset.jsp>

- Additional course info and alternative access to important content through IMI site at...

 - <http://www.lehigh.edu/imi/PropertiesCourse.htm>

Advanced Vitreous State

- The syllabus:
- Syllabus
-
- Tuesday and Thursday
1:00 – 2:15 PM EST
- Beginning Aug. 28, 2008;
Last Class: Dec. 9
- Final exam: Dec. 11
Grades due: Dec. 15
- Textbook: Varshneya, 2nd edition - order directly from Professor Arun Varshneya

Advanced Vitreous State

■ Syllabus:

- Course Connection Practice Session Aug. 26
- 1st Class- Admin and Introduction to Content Aug. 28

- Volume Properties of glass: Steve Feller, Coe College Sept. 2, 4, 9

- Viscosity and Tg of Glass Dick Brow, University of Missouri S & T Sept. 11, 16, 18
- Thermal Properties of Glass John Kieffer, University of Michigan Sept. 23, 25, 30

- Mechanical Properties of Glass Jack Mecholsky, University of Florida Oct. 2, 9, 14

- MS&T No Class Oct. 6, 7, 8

Advanced Vitreous State

- Strengthening of Glass Oct. 16, 21
Arun Varshneya, Alfred University
- Passive Optical Properties of Glass Oct. 23, 28, 30
Pierre Lucas, University of Arizona
- Active Optical Properties of Glass Nov. 4, 6, 11
Denise Krol, University of CA at Davis
- Charge Polarization properties of Glass Nov. 13, 18, 20
Himanshu Jain, Lehigh University
- Thanksgiving week no classes Nov. 24-28
- Charge Conduction Properties of Glass: Dec. 2, 4, 9
Steve Martin, Iowa State Properties
- Course Summary and Wrap-up Dec. 11
- Grades in - last day Dec. 15

Advanced Vitreous State

- Questions...?

Advance Vitreous State

- HW
 - Each section
 - By the instructor
 - Graded by the instructor
 - Final grades assigned by “local” instructor

Fundamentals of the Glass Transition

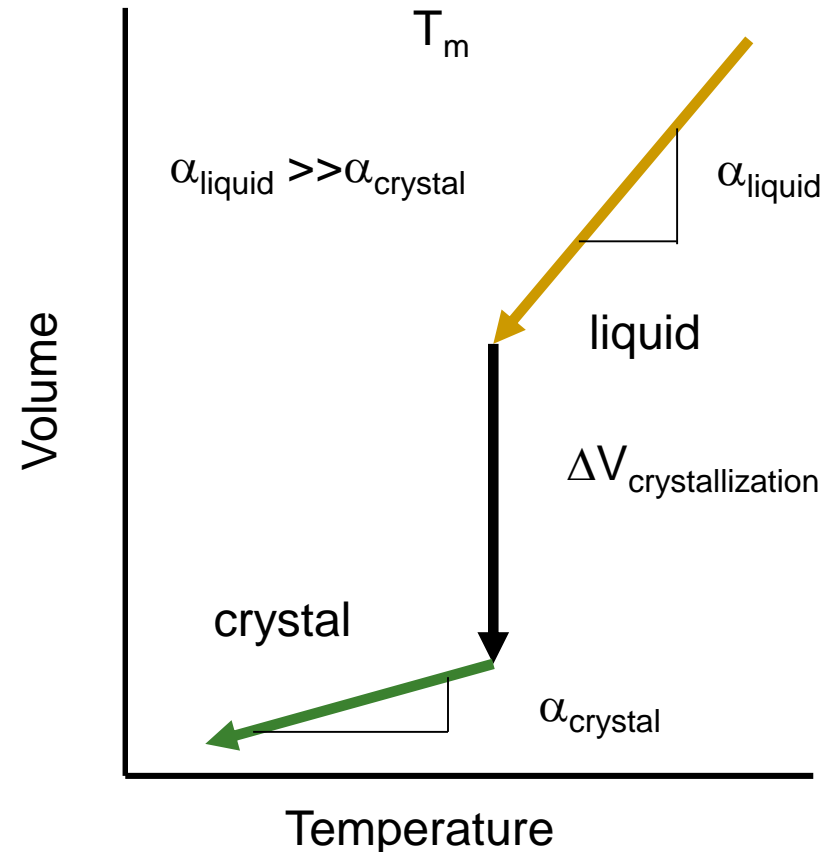
- The Glass Transition is a *Kinetic Transition*
 - Continuous changes in structure and properties
 - Structure and properties are continuous with temperature
 - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid
- Melting and Crystallization are *Thermodynamic Transitions*
 - Discontinuous changes in structure and properties and T_m
 - Structures are thermodynamically controlled and described by the Phase Diagram
 - T_{melting} and T_{liquidus} have fixed and specific values, 1710 °C for SiO_2 , for example

Glass Transition as a Kinetic Transition

- Let's construct a cooling curve for a liquid that will ultimately form a crystal
- Consider SiO_2 , $T_m = 1,710\text{ }^\circ\text{C}$
- Suppose we measure the volume of the liquid as it cools
- Sketch the temperature dependence of the volume from $2,000^\circ\text{C}$ to $25\text{ }^\circ\text{C}$ if one mole of SiO_2 (60 grams) is cooled at $10\text{ }^\circ\text{C}/\text{min}$.
 - 1st assume that thermodynamics controls the system, the liquid crystallizes where it should
 - 2nd assume kinetics controls the system, the liquid changes properties and structures only if it is given 'sufficient' time to change

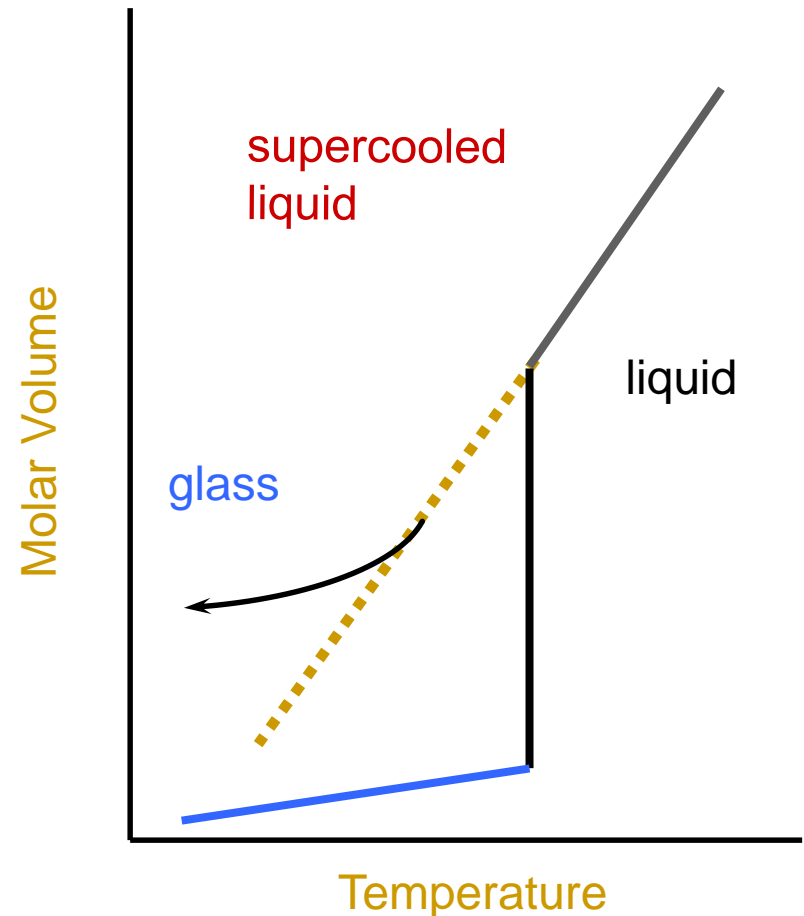
Crystallization is Controlled by Thermodynamics

- 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



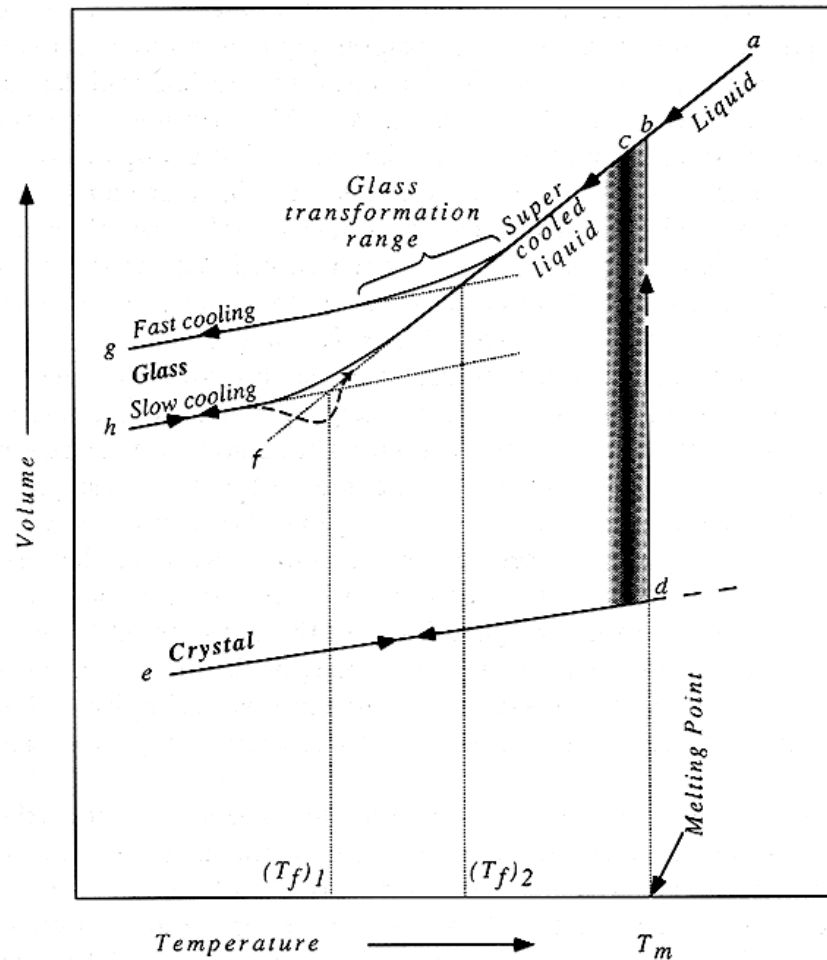
Glass Formation is Controlled by Kinetics

- 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

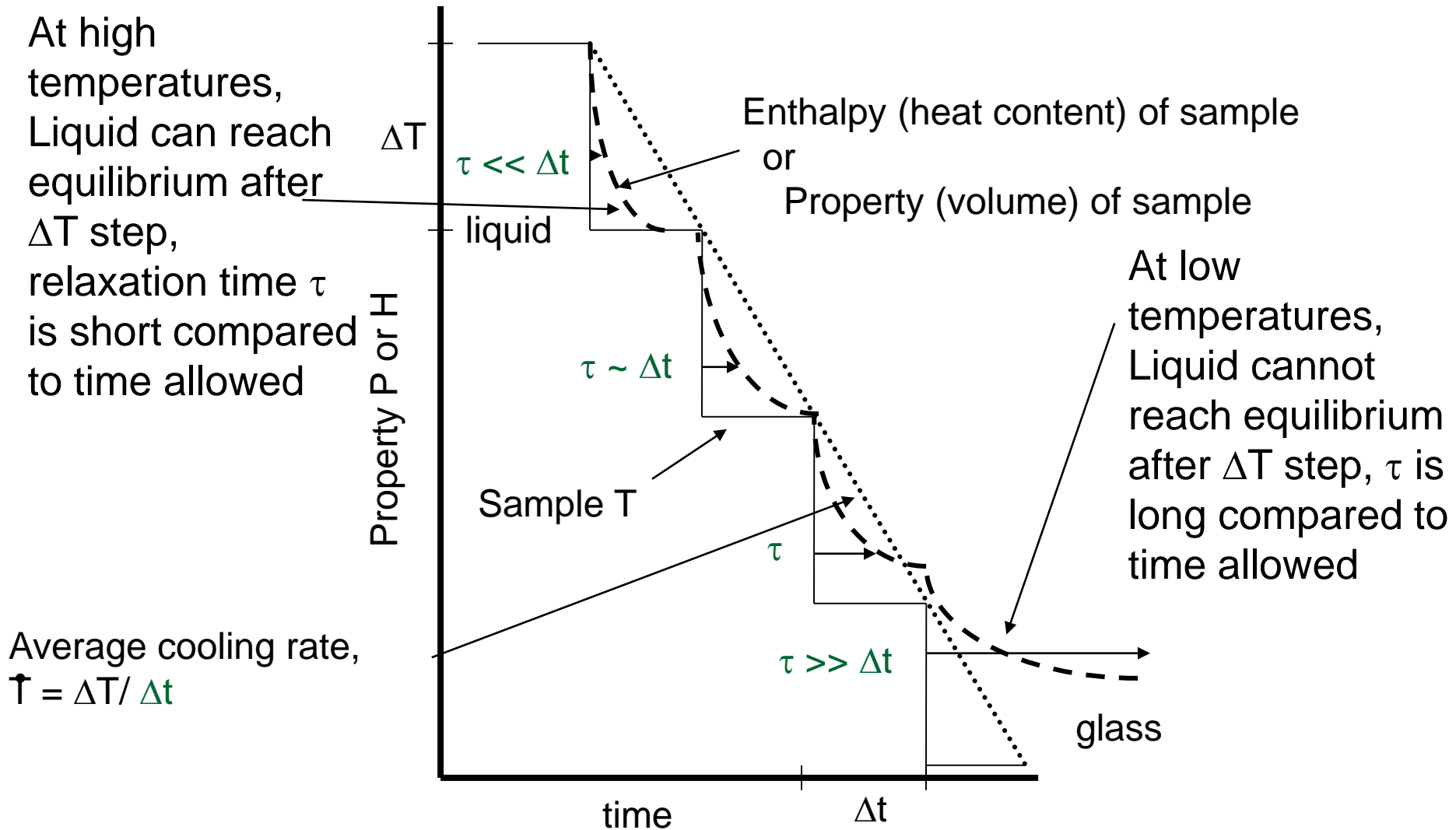


Lecture 1 ended here

The Glass Transition is a Kinetic Transition

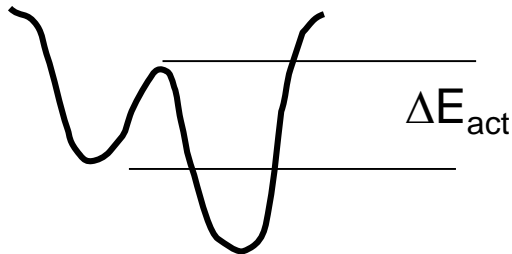


Time and Temperature Dependence of Properties



Temperature dependence of the internal time scale

- While the external time scale, Δt most often does not change,
- 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} and 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 $\Delta E_{act} > 0$

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

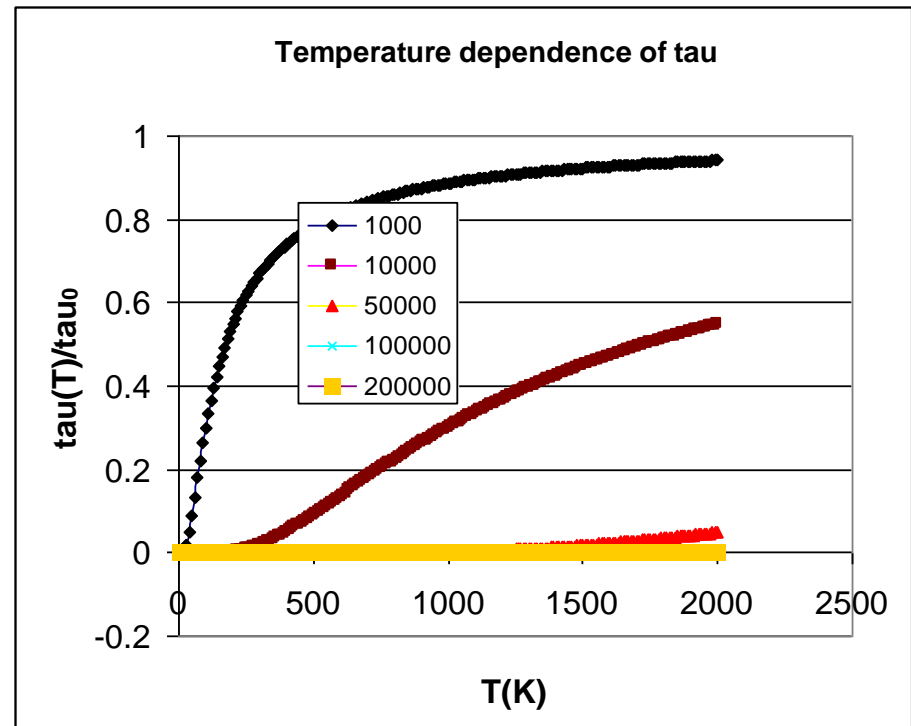
- $0 \leq 1$

- 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

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

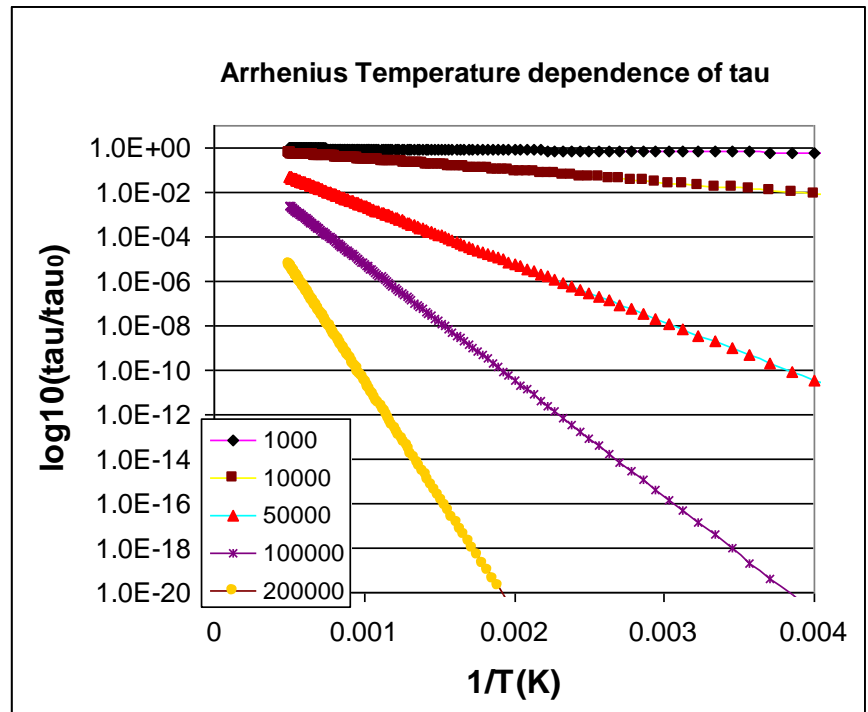


Temperature dependence of the internal relaxation time

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

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

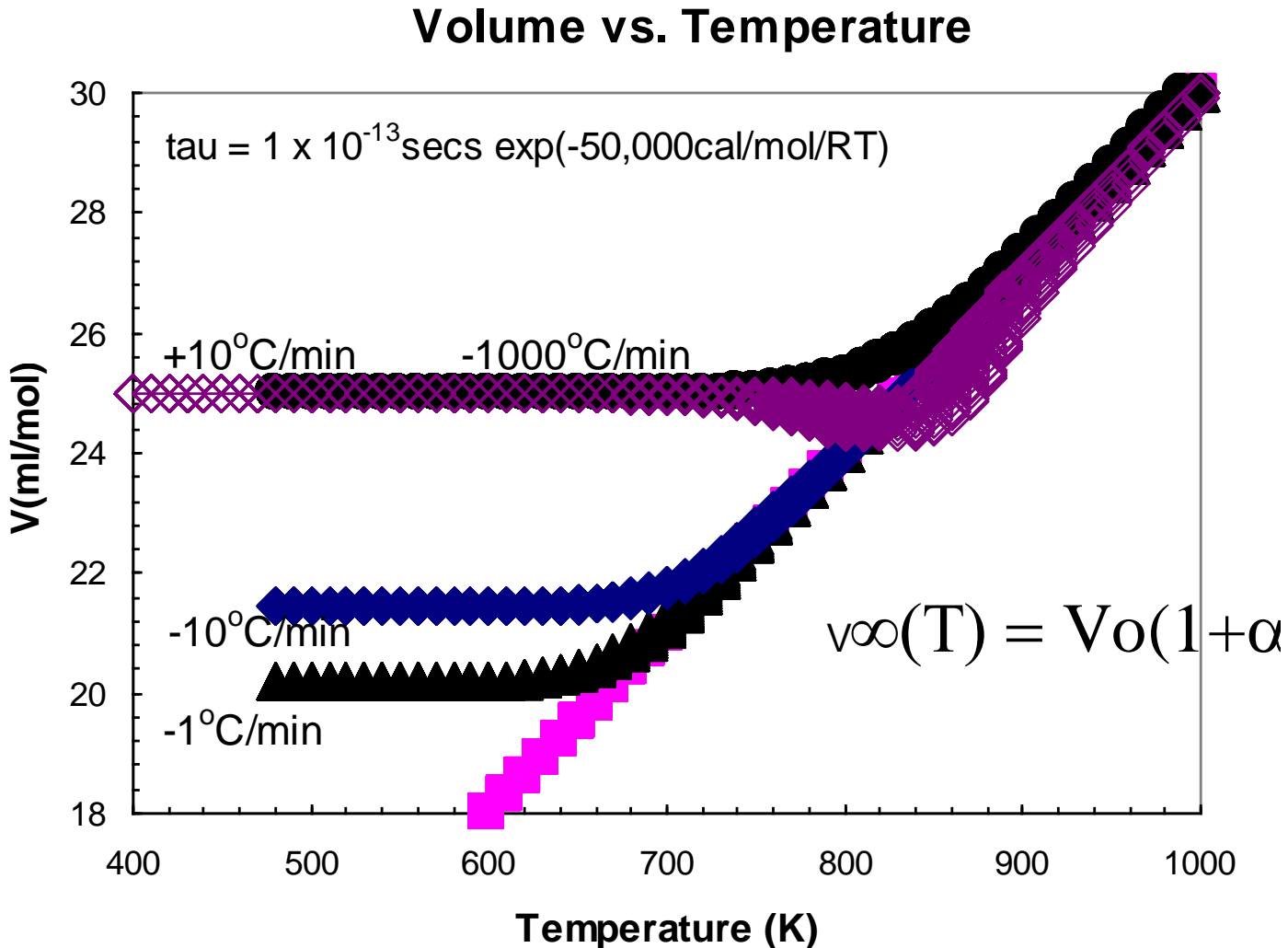
- $0 \leq 1$
- It is a thermal “probability” of motion
- High T, $kT \sim \Delta E_{act}$, high probability of motion
- Low T, $kT \ll \Delta E_{act}$ low probability of motion



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

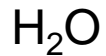
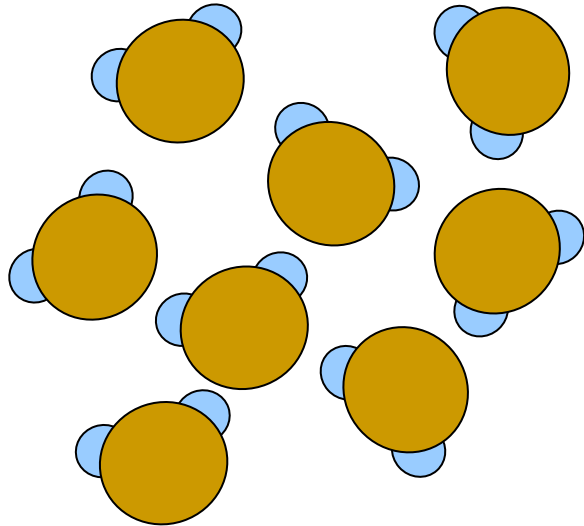
The Glass transition from Arrhenius T dependence of tau



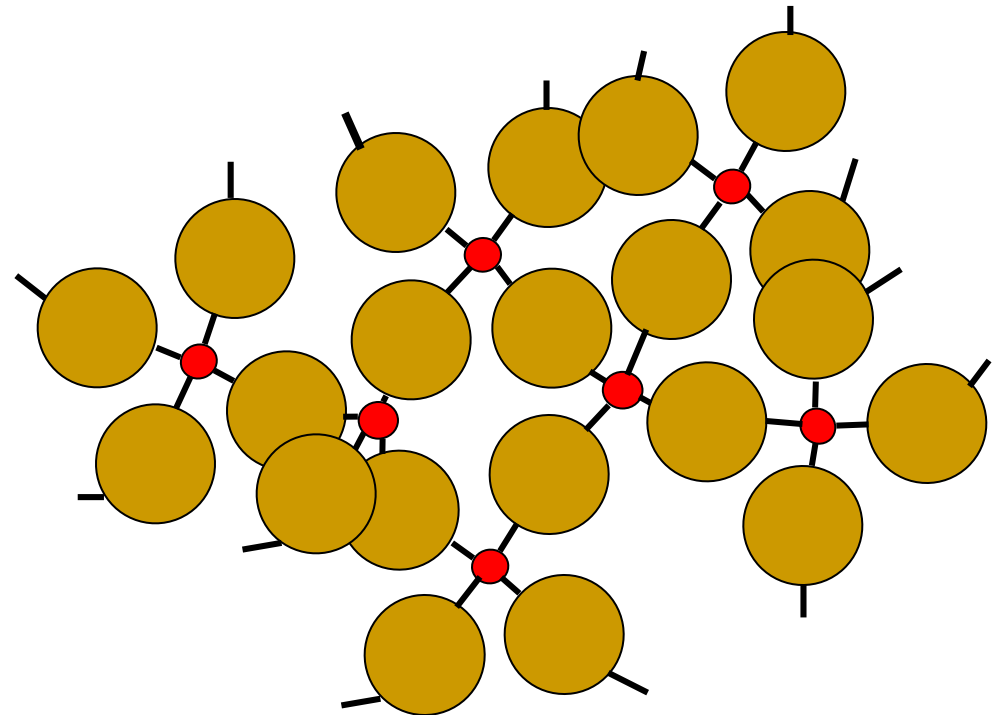
Examples of Poor and Good Glassformers

- Why is water, H_2O , found to be a very “weak” glass former
 - Requires cooling the liquid faster than $1,000,000\text{ }^\circ\text{C}/\text{min}$
 - 300 to 150K in 9 milliseconds!!
 - What is the atomic structure?
 - Talk to your neighbor and sketch the structure of 5 water molecules
- Why is silica, SiO_2 , found to be a very “strong” glass former
 - Can be cooled at $10^{-10}\text{ }^\circ\text{C}/\text{min}$ and still by-pass T_m without crystallizing
 - 2,000 $^\circ\text{C}$ to 1,000 $^\circ\text{C}$ in 20 million years!!
 - What is its atomic structure? Talk to your neighbor and sketch the structure of 5 SiO_2 molecular units

Structure of Water compared to Silica



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



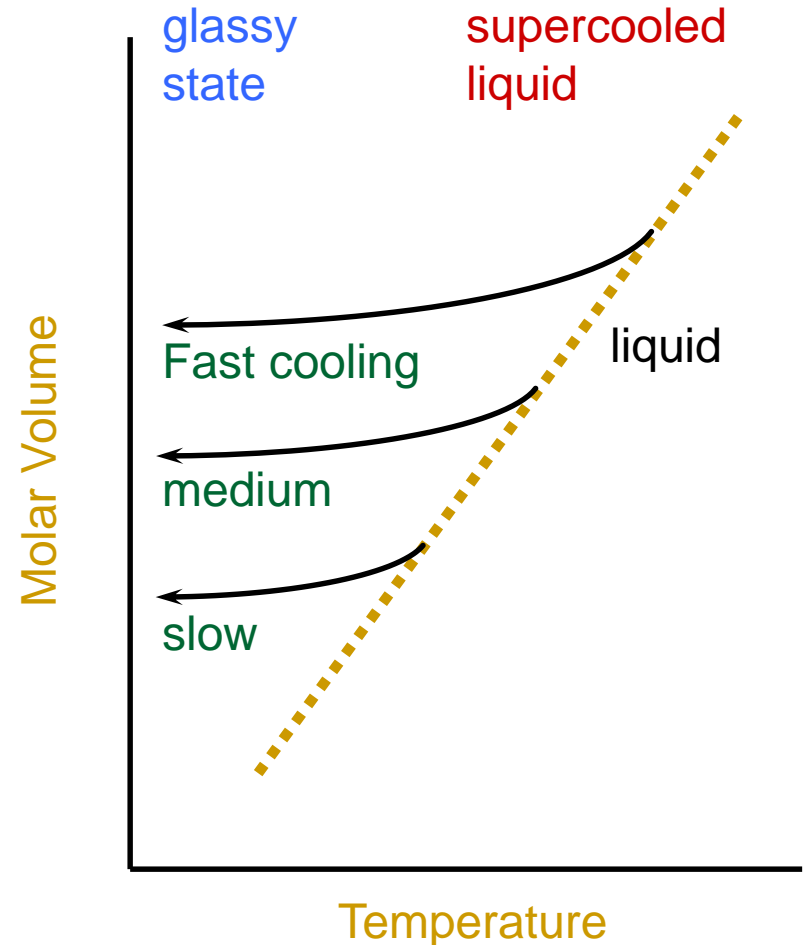
Each Si is tetrahedrally bonded to O, Si and O atoms cannot move unless other neighboring atoms also move

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
 - Slower cooling rates increase the time the liquid has to relax to the properties at the new temperature
 - Fast cooling freezes the structure of the liquid (glass) in at a higher temperature, therefore it has properties corresponding to these high temperatures
 - Slower cooling enables the structure to freeze in at a lower temperature and therefore the glass has properties corresponding to these lower temperatures

The Cooling Rate Affects the Properties of Glass

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

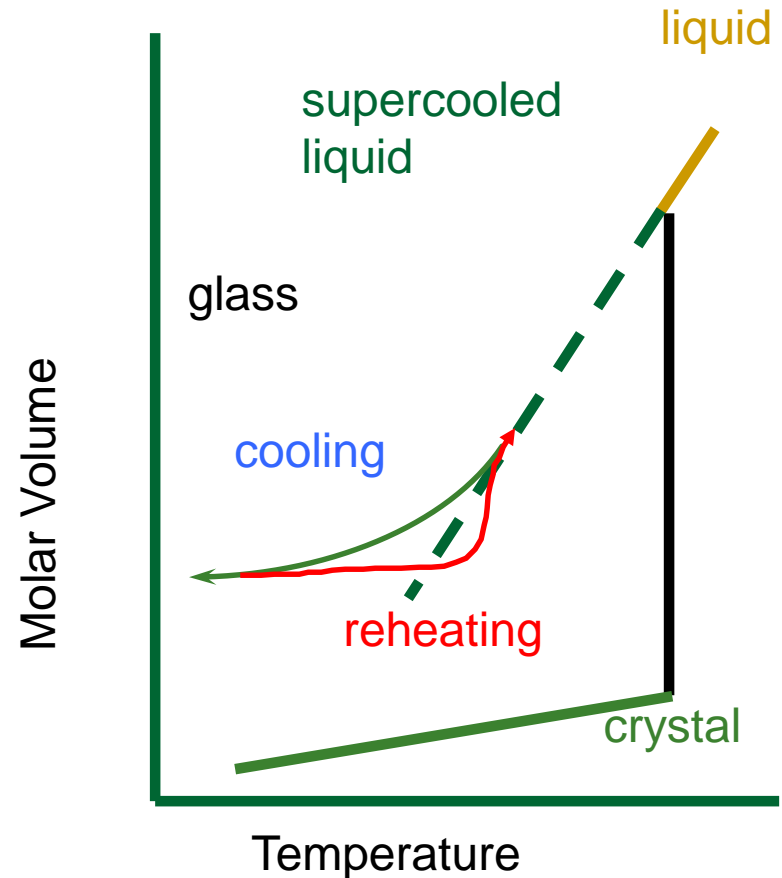


Glass Properties on Heating

- 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 $10^{\circ}\text{C}/\text{min}$ and then is reheated at $10^{\circ}\text{C}/\text{min}$.
- 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
- On reheating, the curve does not follow the same curve, as it would for a crystal
- T_g is higher on heating because of hysteresis
- The heating curve by-passes the cooling curve because the glass is frozen, it is “stuck” and does not want to change
- Soon above the T_g , however, the glass has the thermal energy necessary to become a liquid and the two curves rejoin



Glass Properties on Reheating

- Glasses arrested at progressively lower temperatures, the slower the cooling
- T_g decreases with decreasing cooling rate
- Slower cooling produces a lower T_g
- Faster cooling produces a higher T_g
- T_g is higher on heating because of hysteresis
- The heating curve by-passes the cooling curve because the glass is frozen, it is kinetically “stuck”
- Soon above the T_g , however, the glass has the necessary thermal energy to become a liquid and the two curves rejoin

