

Lecture 13: The Fictive and Glass Transition Temperatures

March 2, 2010

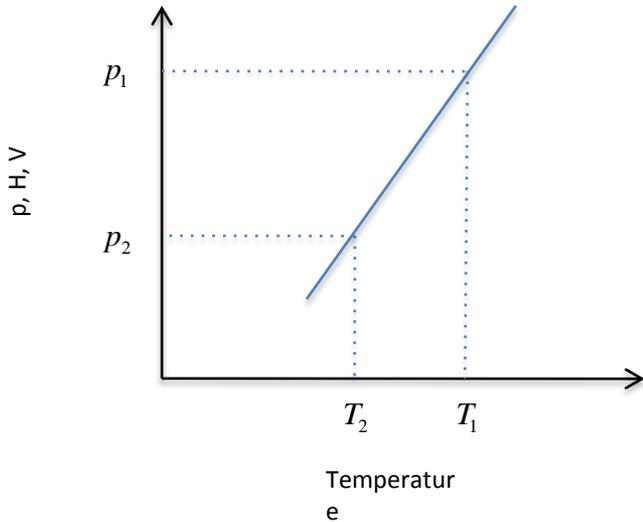
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Consider some property, p , of a liquid. p may be the enthalpy, volume etc... of the liquid.

What happens to the p of the liquid, if it is cooled quickly enough that it doesn't crystallize yet slowly enough that it does not become a glass ?



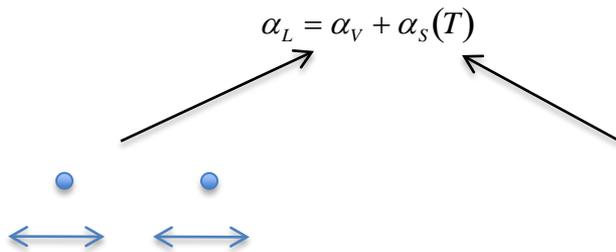
How does p vary as the temperature is varied from T_1 to T_2 ?

$$p(T_2) = p(T_1) + \alpha_L \Delta T$$

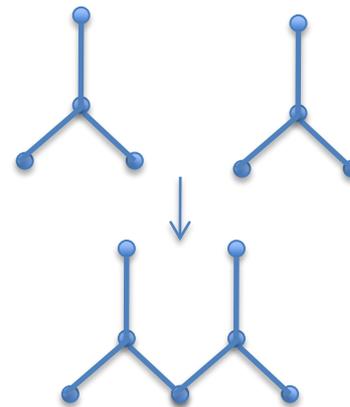
Clearly α_L is the slope of the p vs T graph

$$\alpha_L = \frac{\Delta p}{\Delta T}$$

α_L is made up of two contributions: $\alpha_{\text{vibration}}$ and $\alpha_{\text{structural relaxation}}$.

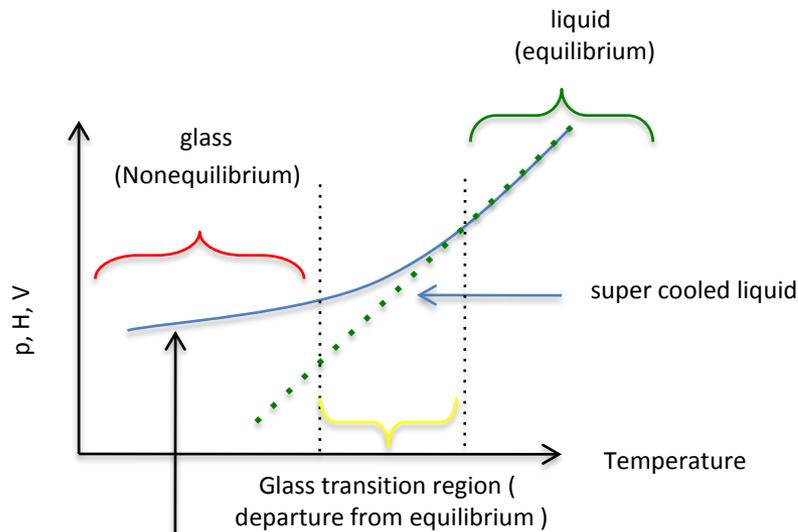


Two atoms vibrating in an atomic potential such as the Morse potential.



α_s is temperature dependent. Structural relaxation is less likely as the temperature is lowered and the viscosity increases.

What happens to the p of the liquid, if the liquid is cooled fast enough so that it doesn't crystallize and yet fast enough that it no longer cools along the super cooled liquid line ?



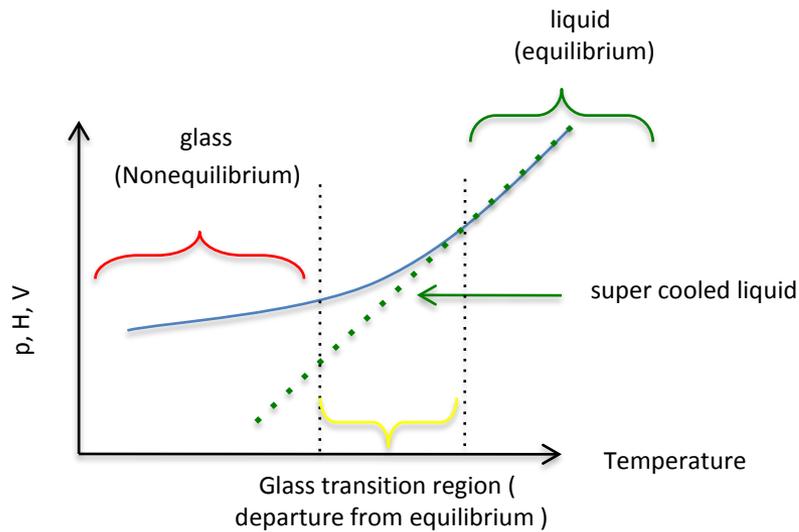
$$\alpha_g = \frac{\Delta p}{\Delta T} = \alpha_v < \alpha_L$$

The main contribution to α_g is the vibrational contribution which is identical to that of the liquid.

Why is the slope of p vs T in the liquid region larger than the p vs T slope in the glass region ?

Since the viscosity in the glass region is large, little structural relaxation can occur.

What happens in each of the separate regions ?



In the **liquid** region, relaxation processes are almost instantaneous compared to the observation time.

$$\tau_{relaxation}^{liquid} \ll t_{observation}$$

In the **glass** region, relaxation processes are so slow that they are not observed during the observation time.

$$\tau_{relaxation}^{glass} \gg t_{observation}$$

In the **glass transition** region, relaxation times are comparable to the observation time.

$$\tau_{relaxation}^{glass-transition} \approx t_{observation}$$

There is another way to describe these three regions i.e. the Deborah Number.

The definition of the Deborah number is

$$D \equiv \frac{t_{\text{int}}}{t_{\text{ext}}} = \frac{\tau_{\text{relax}}}{t_{\text{obs}}}$$

The name “Deborah” number comes from the Bible. It is named in honor of the prophetess Deborah, who sings “...the mountains flowed before the Lord...” (Judges 5:5).

The properties we experience are those that we measure on our own time scale i.e. $t_{\text{ext}}=t_{\text{obs}}$.

In the liquid region, $\tau_{\text{relax}} \ll t_{\text{obs}}$. Therefore, $D < 1$. A system is ergodic.

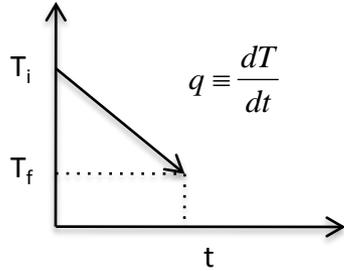
In the glass region, $\tau_{\text{relax}} \gg t_{\text{obs}}$. Therefore, $D > 1$. A system is nonergodic.

In the glass transition region, $\tau_{\text{relax}} \sim t_{\text{obs}}$. Therefore, $D \sim 1$. Hence, the glass transition constitutes a **breakdown of ergodicity**.

NOTE: The same experiment may be ergodic for one observer and nonergodic for a different observer.

e.g. For God, $D \llllll 1$

What is the effect of different linear cooling rates ? i.e.



Note the slope of the p vs. T graph in the glass region is constant.

$$\alpha_g = \alpha_v = \text{constant}$$

p, H, V

q_3 faster than q_2

q_2 faster than q_1

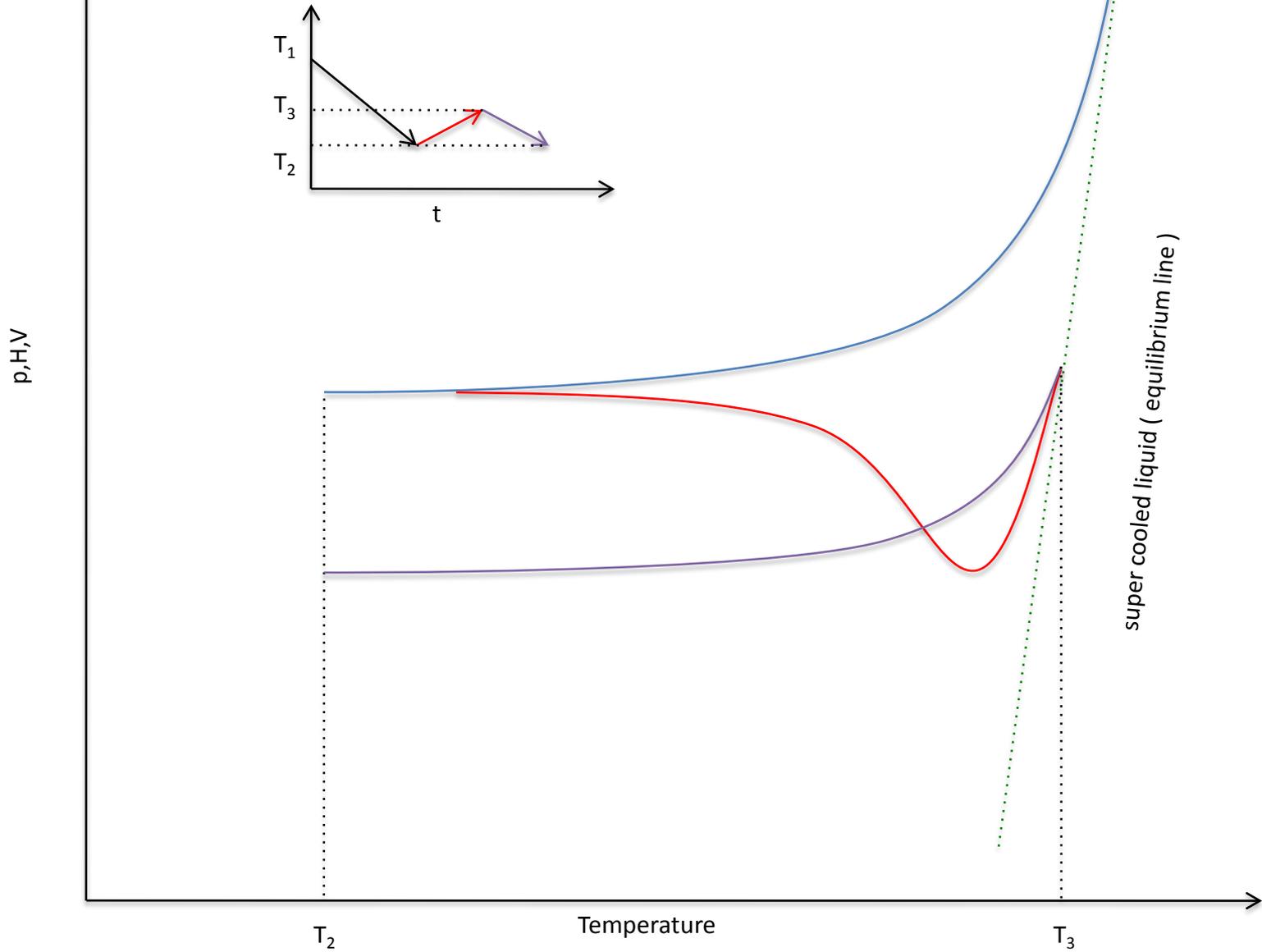
q_1

$$q_1 < q_2 < q_3$$

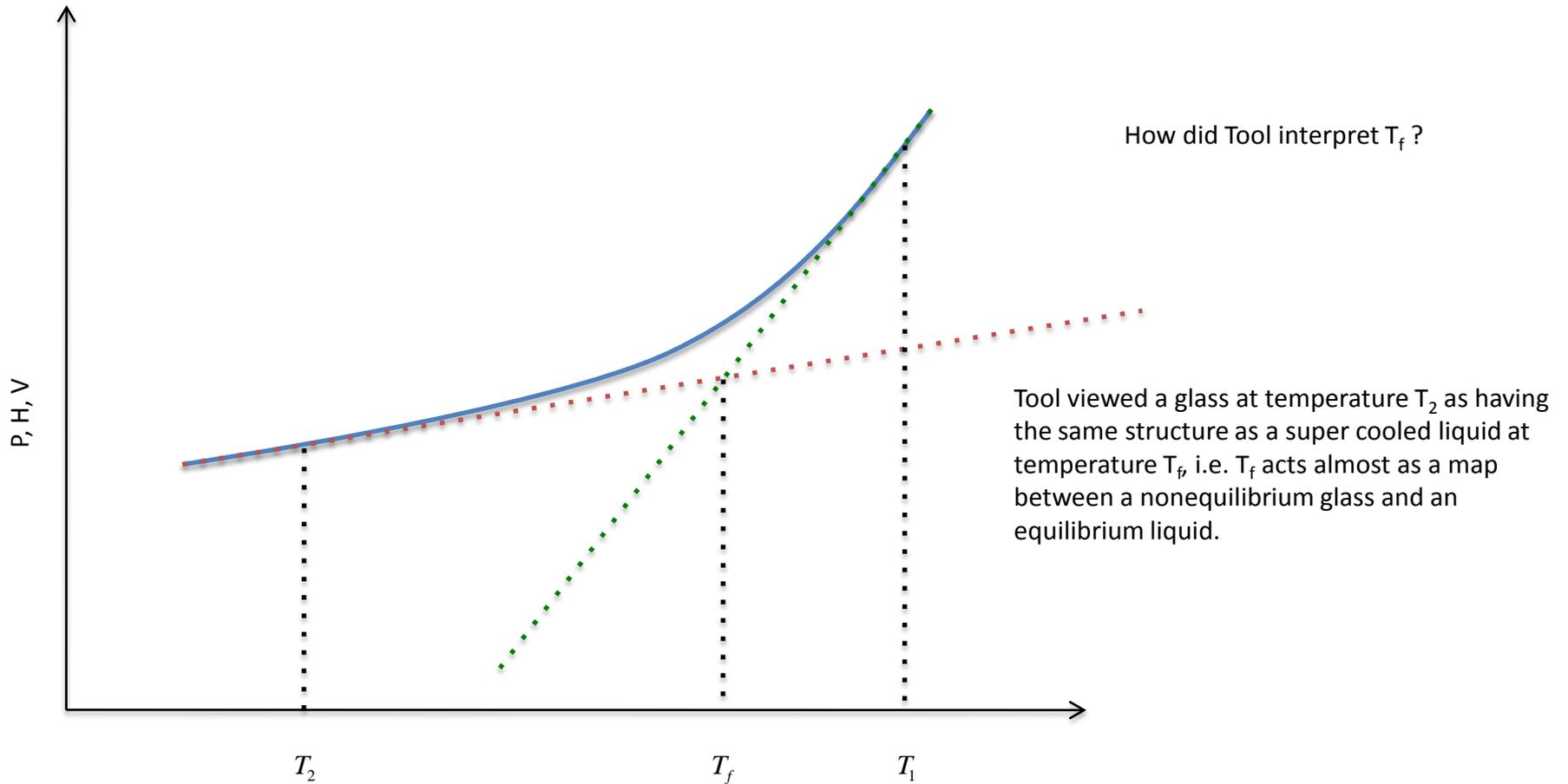
super cooled liquid (equilibrium line)

Temperature

What happens if we reheat and recool after a linear cooling ?



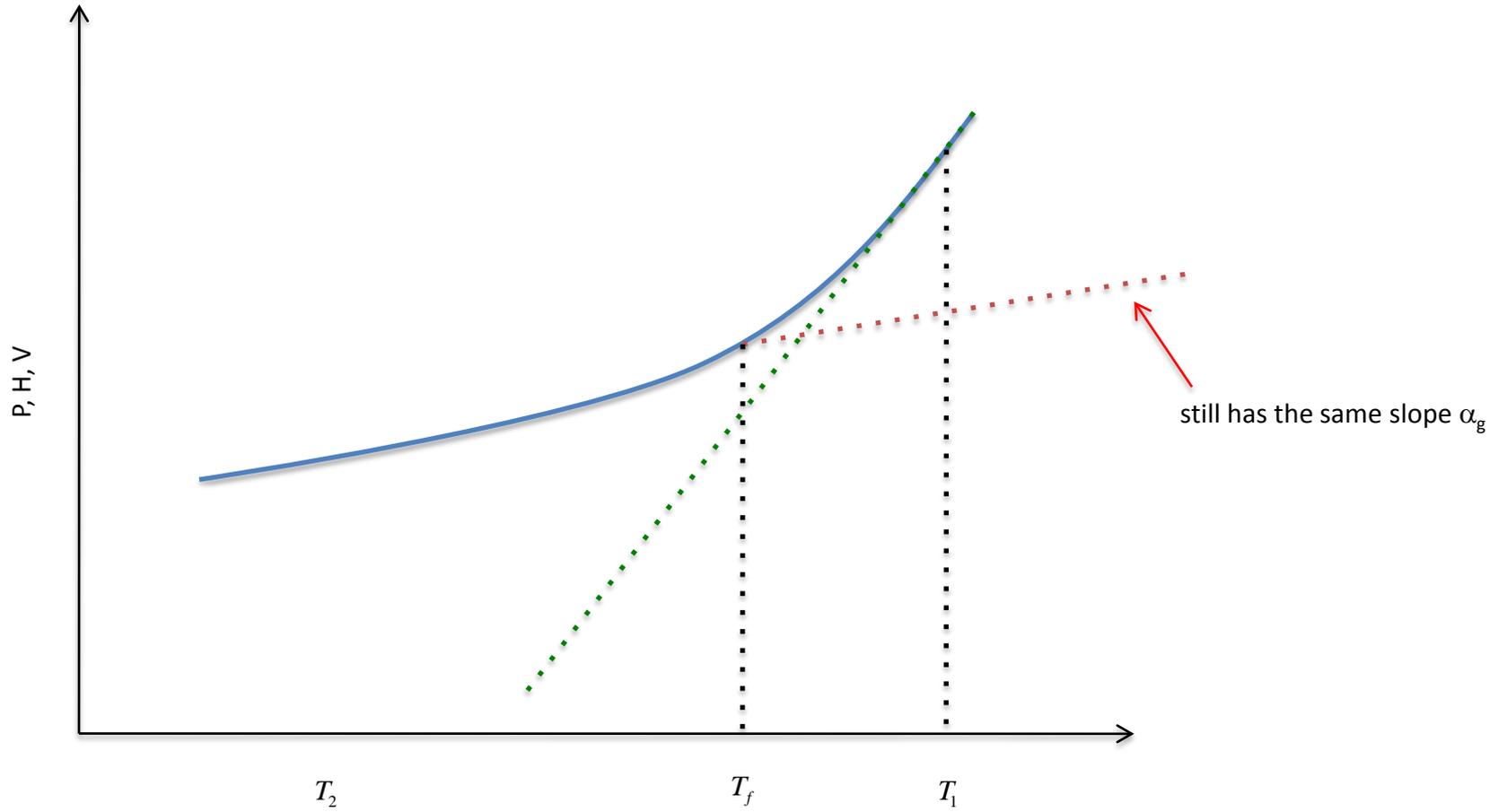
What is the Fictive temperature and how do you define it ?



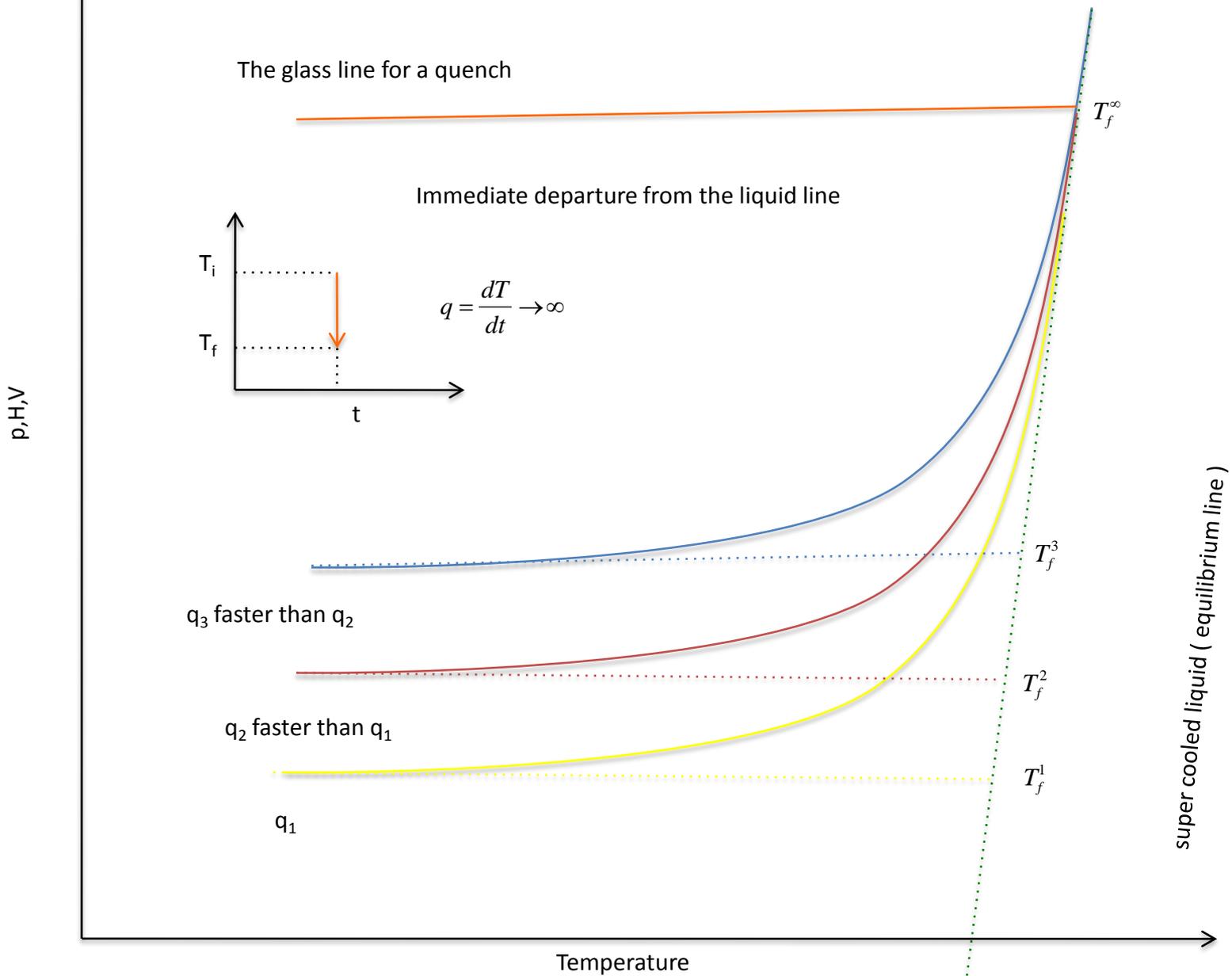
T_f is an artificial temperature used to describe the glassy state.

Later, we will investigate the classic experiments of Ritland who directly tested this assertion of Tool's.

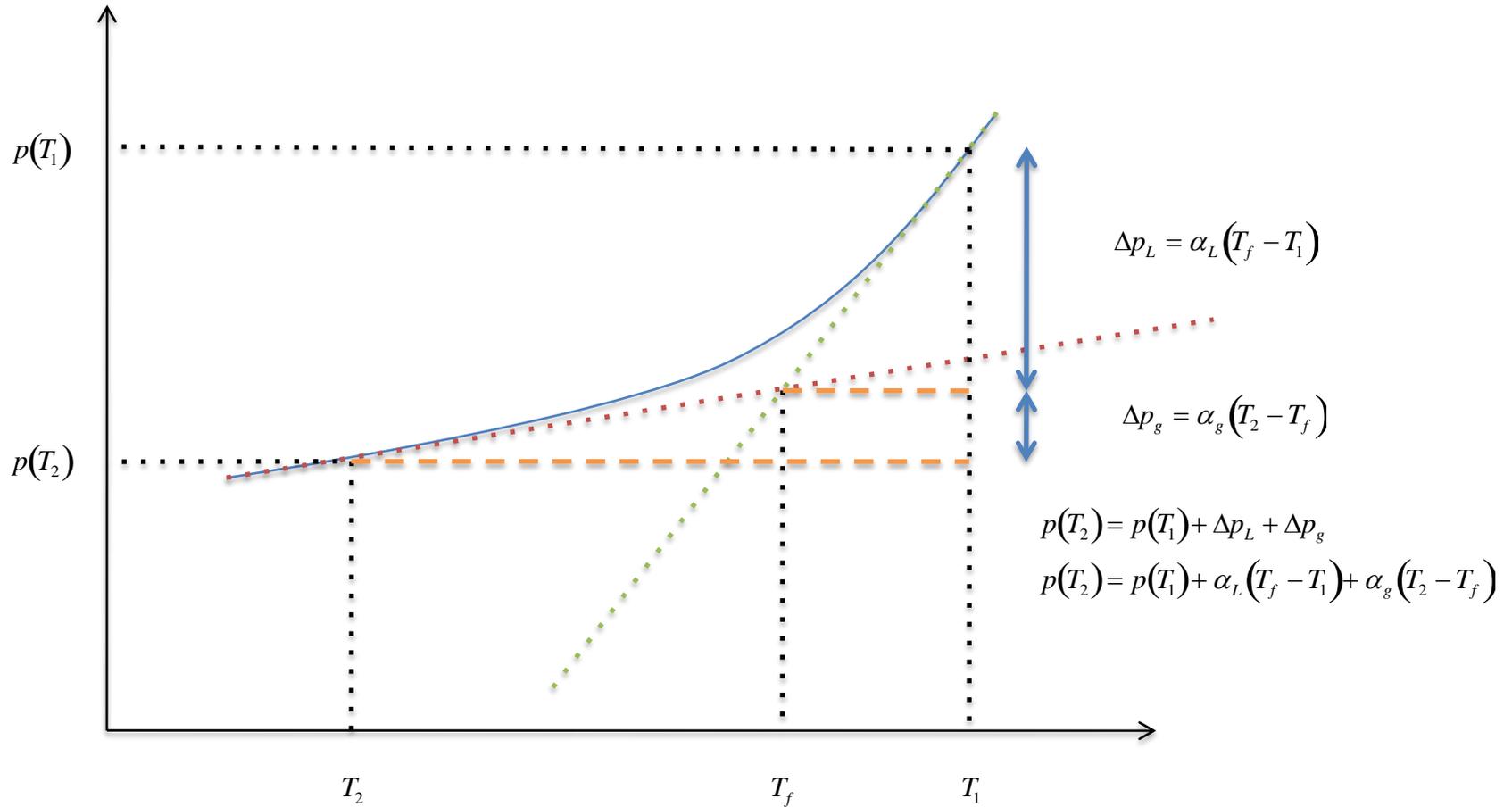
How do you define T_f , if you are in the glass transition region and not the glass region ?



What effect does the cooling rate have on the Fictive temperature ?



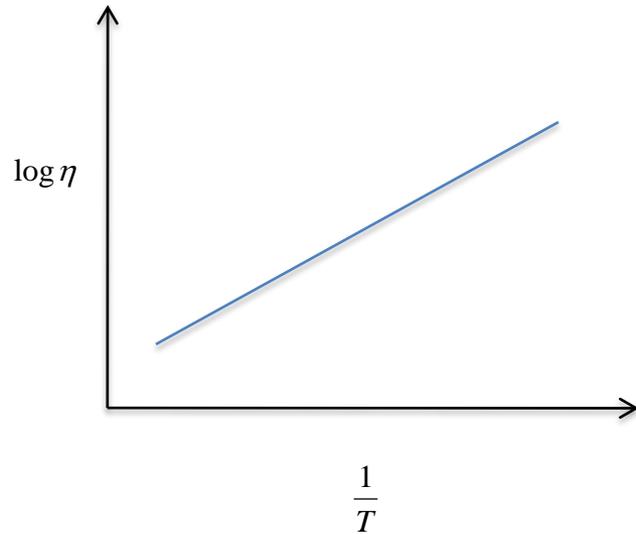
How can we make use of the Fictive temperature ?



In the next lecture, we'll use this expression when deriving Tool's equations.

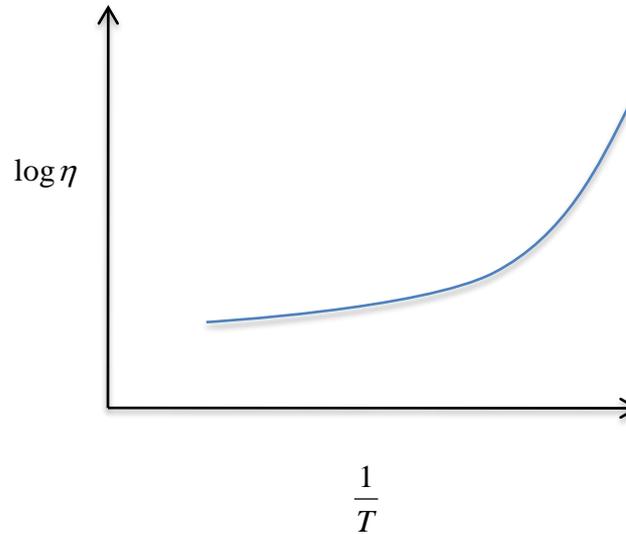
How can we formally define the glass transition temperature ?

First let's measure the viscosity of a **liquid** as a function of temperature and make the plot shown below. One of two types of graphs will result.



A Strong **Liquid** (Arrhenius Behavior)

$$\eta = \eta_0 e^{\frac{\Delta H}{RT}}$$



A Fragile **Liquid** (Non Arrhenius Behavior)

Almost all glasses are fragile.

The words strong and fragile have nothing to do with mechanical strength

Are there any empirical fits to the $\log \eta$ vs $1/T$ graph for fragile liquids ?

1. One of the more commonly used fits is VFT. It is named after Vogel, Fulcher, and Tamman.

$$\log \eta_{VFT} = \log \eta_o + \frac{A}{T - T_o} \quad \text{where } \eta_o, A, \text{ and } T_o \text{ are constants.}$$

or

$$\eta = \eta_o e^{-\frac{A}{T - T_o}} \quad \text{Often in the literature, VFT will be written in terms of the relaxation time } \tau. \text{ Recall } \eta = G\tau.$$

2. Another commonly used and extremely useful expression is Adams-Gibbs. In the Adams-Gibbs model, the liquid is viewed as a collection of smaller units that can be rearranged, i.e. can undergo relaxation. In the literature, these smaller units are called CRR's or cooperatively rearranging regions. The relaxation time or η is then given by

$$\tau_{AG} = \tau_o e^{-\frac{\Delta H}{S_c T}}$$

where S_c is the configuration entropy of the smallest unit of the liquid that can undergo relaxation and ΔH is the activation barrier that must be overcome by these smallest unit in order to relax. Note that the size of these units which can rearrange varies with temperature. Therefore, both S_c and ΔH must also vary with temperature. As the temperature lowers, the size of these rearranging units decrease and so must S_c since $S_c = k_B \ln W$ where W is the number of ways the unit can be rearranged.

How does Angell define the glass transition temperature T_g ?

Angell defines the glass transition temperature to occur when the $\log \eta = 12$.

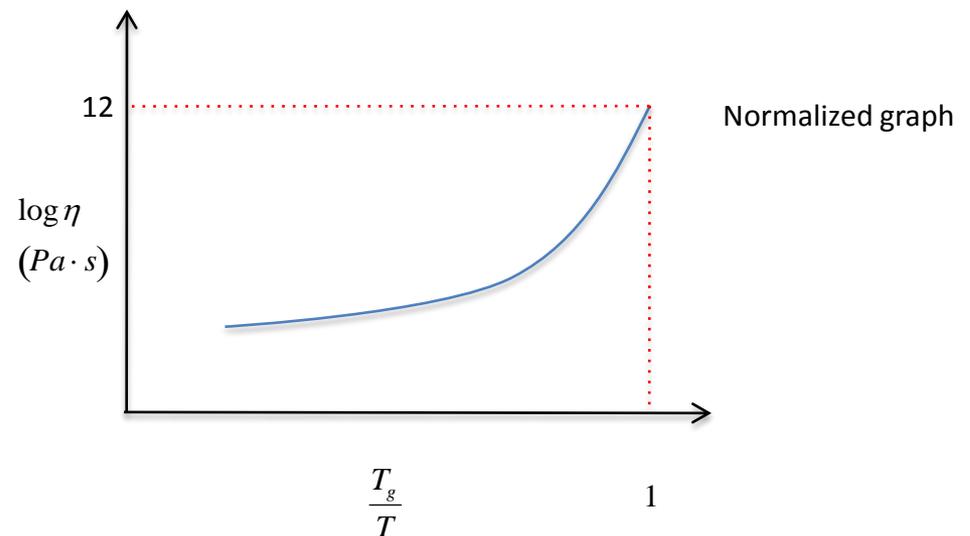
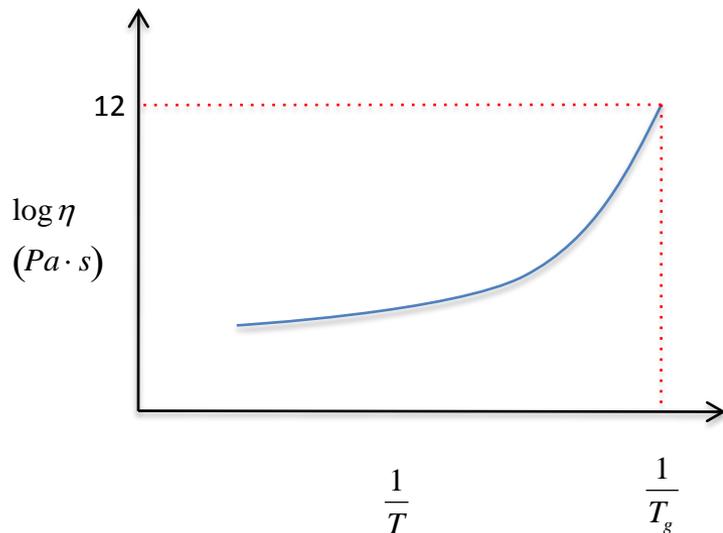
This corresponds to the relaxation time equaling the observation time

i.e. $\tau_{relax} \sim t_{obs}$. Angell uses an observation time of 100s.

The glass transition temperature, T_g , is real physical property of the **liquid**.

(Unlike T_f which is artificially used to describe the glassy state.)

Using this definition, Angell is able to normalize the $\log \eta$ vs. $1/T$ graphs as shown below.



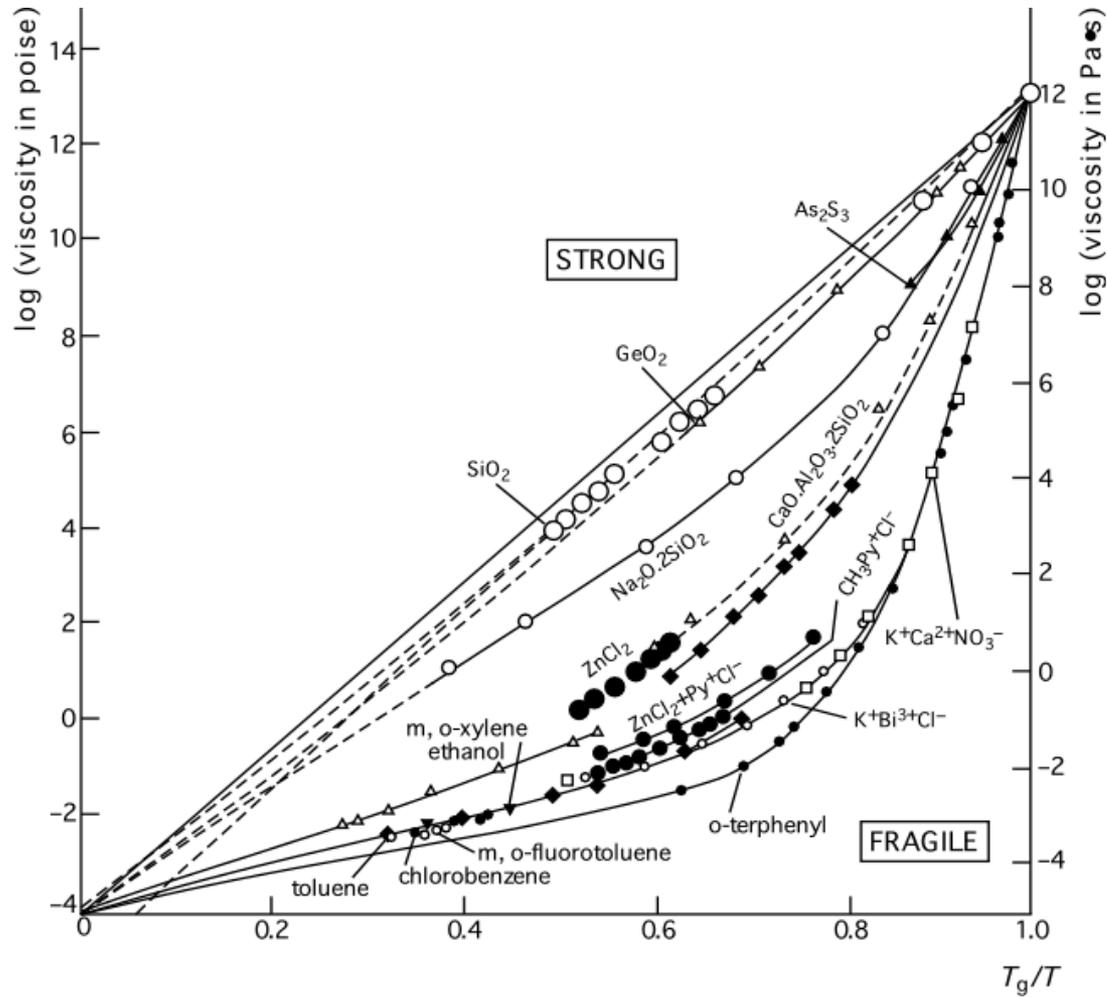
The viscosity and relaxation time are connected by Maxwell's equation (Look back at lectures 1)

$$\eta = \tau_{relax} G_{\infty}$$

where G_{∞} is the infinite frequency shear modulus. It is approximately 10 GPa.

We can now look at multiple sets of data at once i.e. the “Angell Plot”.

Ref: A.K. Varshneya, *Fundamentals of Inorganic Glasses.*



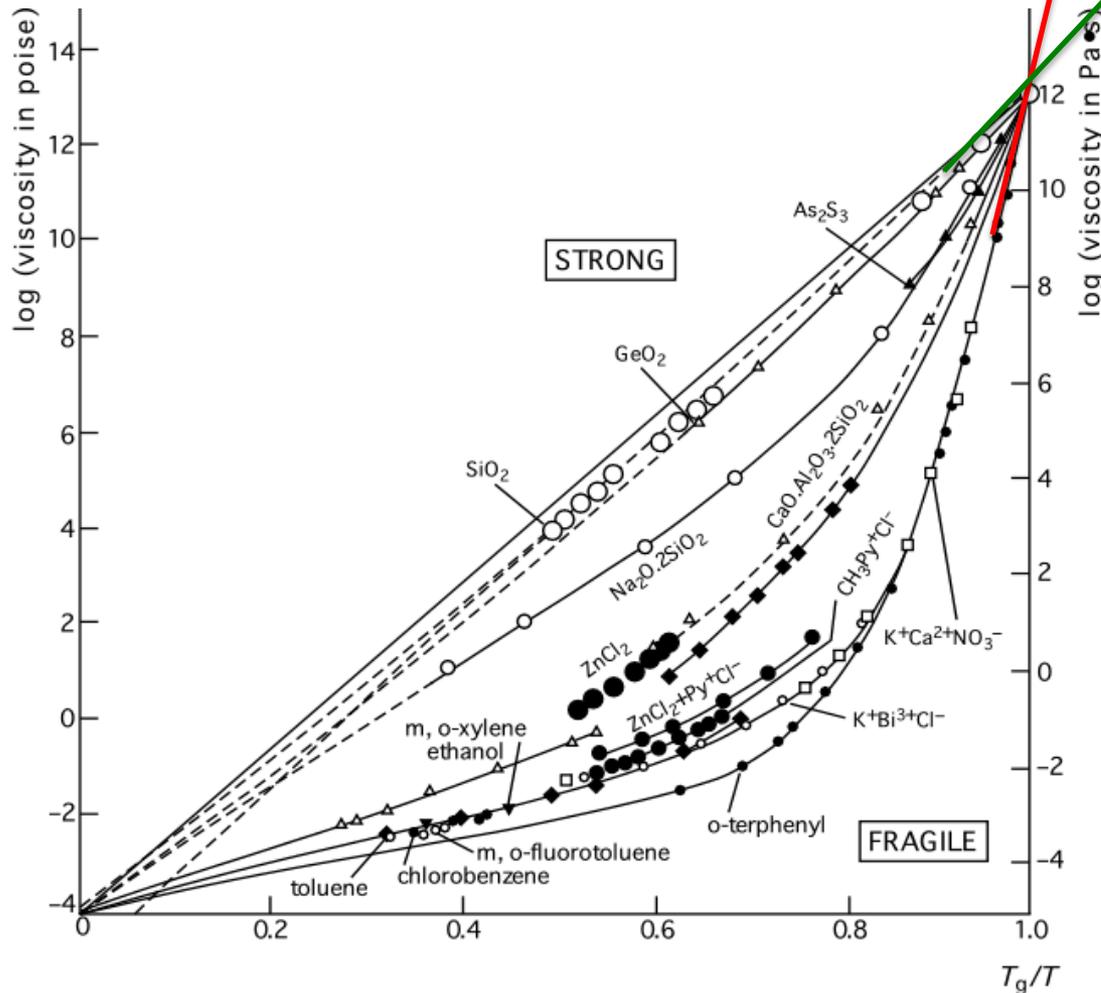
Note that all the lines are extrapolated to $\log \eta = -4$ at $T = 0$.

We can now define a new term called the fragility.

Definition of Fragility:
$$m \equiv \left. \frac{d \log \eta}{d(T_g/T)} \right|_{T=T_g}$$

It is the slope. It is a measure of how "fragile" a liquid is.

Ref: A.K. Varshneya, *Fundamentals of Inorganic Glasses*.

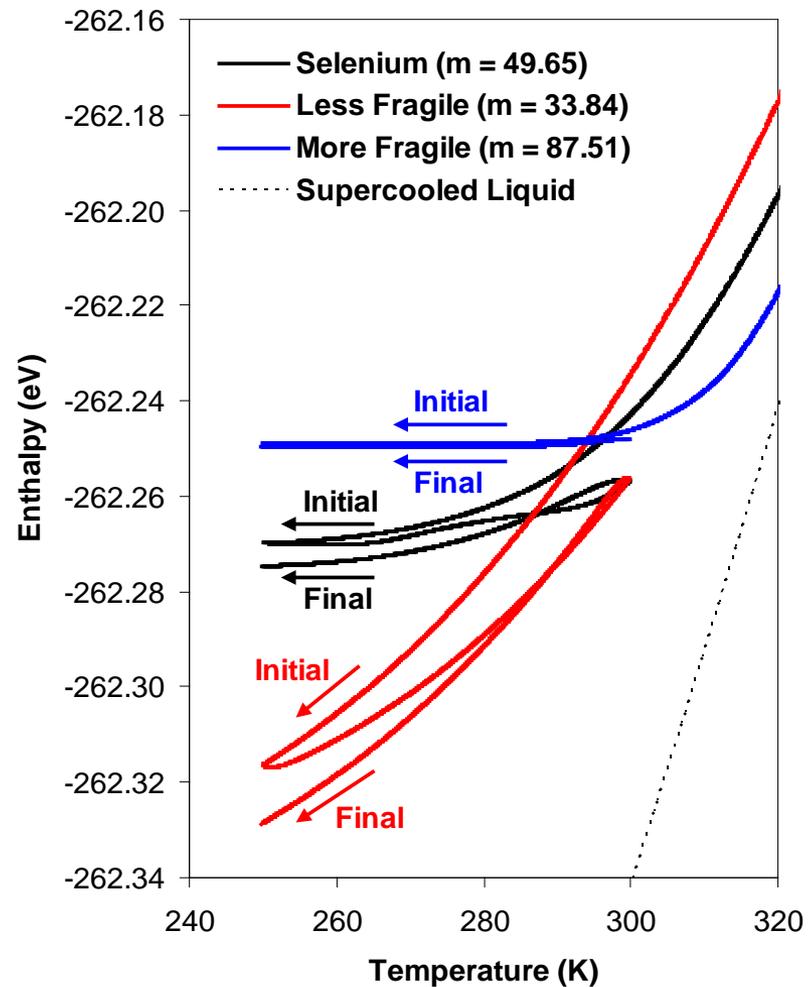
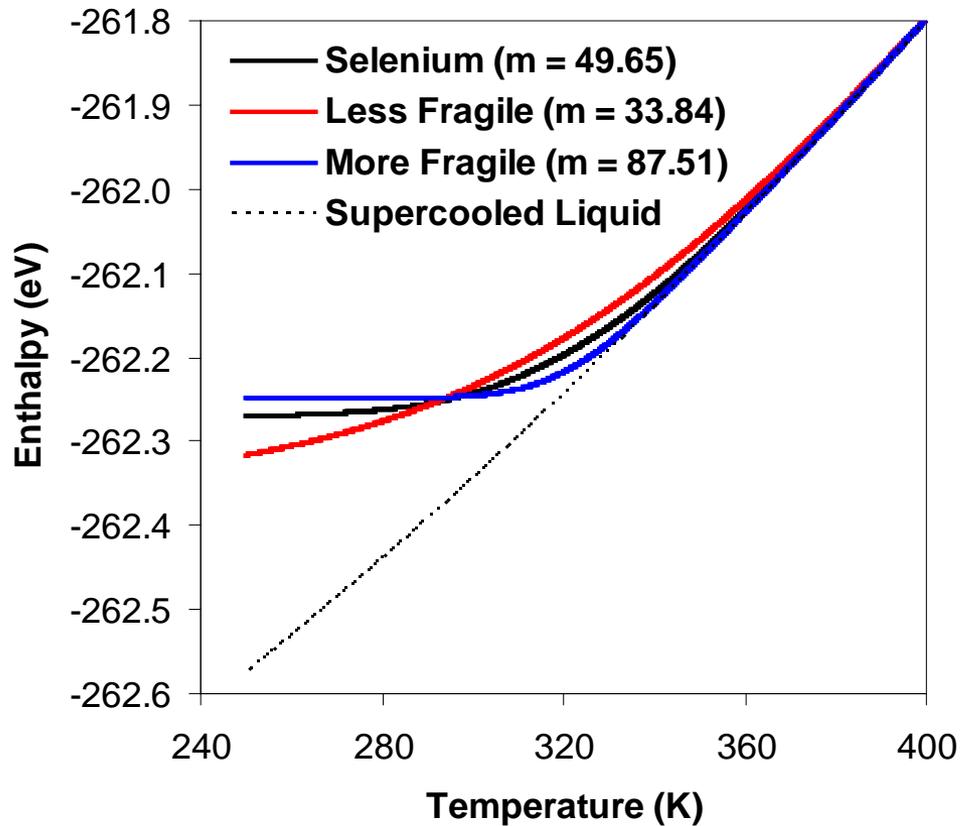


There is a minimum to fragility. The minimum of fragility is the slope of the strong line !

Question:

What are the causes and consequences of fragility?

Consequences of Fragility on the Sharpness of the Glass Transition and the Relaxation of a glass upon reheating and cooling.



Ref: C.A. Angell, *Chem. Rev.*, **102**, 2627 (2002)

Consequences of Fragility on the Sharpness of the Glass Transition and Relaxation

- Increasing fragility increases the sharpness of the glass transition.
- This relation has been noted previously by Angell for measured heat capacity data.
- As the fragility of a liquid increases, the amount of relaxation decreases.
- The reason for this will have to wait until Dr. Gupta's enthalpy lectures. (Stay Tuned)
- If you can wait, read the Mauro and Loucks paper

J.C. Mauro and R.J. Loucks *PRE* **78**, 021502 (2008)

Is it valid to view the a glass at temperature T as having the same structure as a liquid at temperature T_f ? i.e. Is T_f the temperature at which the structure of a glass is frozen ?

The answer is no! This was first shown by Ritland in 1956 and later by Napolitano and Spinner.

What did Ritland do ?

What properties would depend on structure ? Index of refraction, electrical resistivity, etc ...

Obtain two glass samples prepared by different thermal paths, i.e. a linear cooled sample and a sample held and equilibrated at some higher temperature.

Adjust the cooling rate until the glass has the same index of refraction as the equilibrated sample. The same index of refraction implies the same structure, and hence the same fictive temperature assuming that Tool's idea is correct.

Compare the electrical resistivities of these samples. In principle, if they have the same structure that should have the same electrical resistivity.

They do not. This raises questions as to whether Tool's idea of T_f being the temperature of the glass at which its structure is "frozen in" is correct.

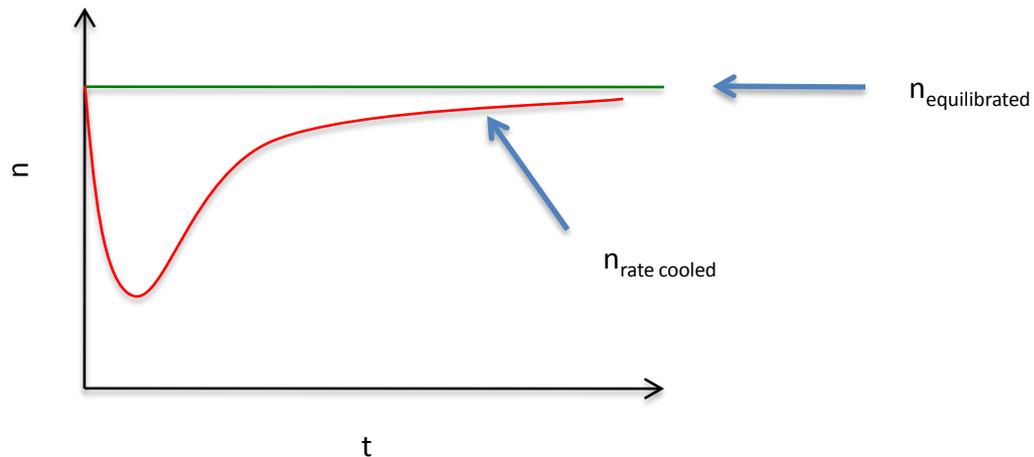
Ritland did another classic glass experiment. The crossover experiment.

Ritland prepared two samples: 1) Equilibrate a sample at 530° C. This means that the T_f of this sample is 530°C.

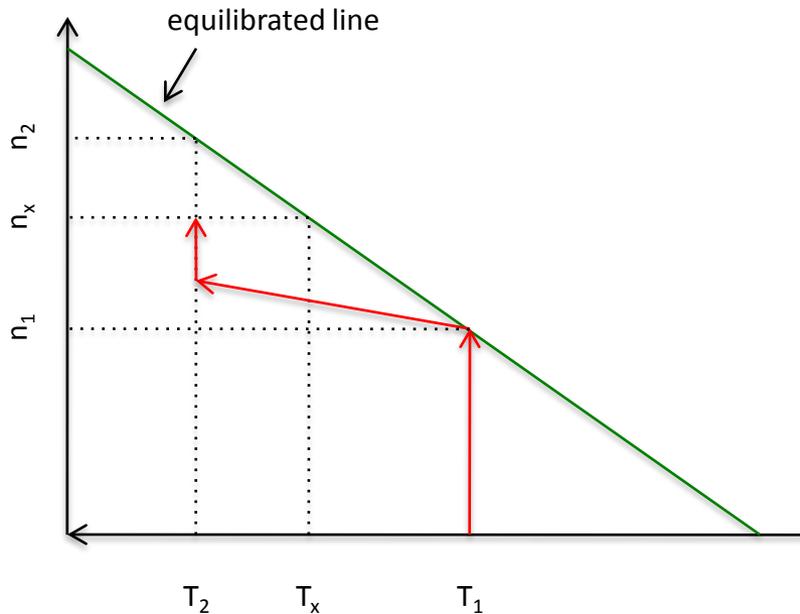
2) Rate cooled a sample in such a way that the sample had the same index of refraction as the equilibrated sample.

Again, if Tool's original concept of the T_f representing the temperature at which the structure of the liquid is "frozen" into the glass is correct, then the two samples should have the same T_f 's. The same index of refractions should correspond to the same structure and according to Tool the same T_f . The only difference between the two samples are their thermal histories.

Ritland then took the rate cooled sample and placed it in a 530°C furnace. He measured the index of refraction of the rate cooled sample at various times. In principle, the index of refraction of the rate cooled sample should not change since it is being held. This is what he observed.



Napolitano and Spinner performed a similar experiment. They measured the index of refraction for a glass equilibrated at various temperatures



A glass sample is held at T_1 until it is equilibrated. The index of the sample is now n_1 .

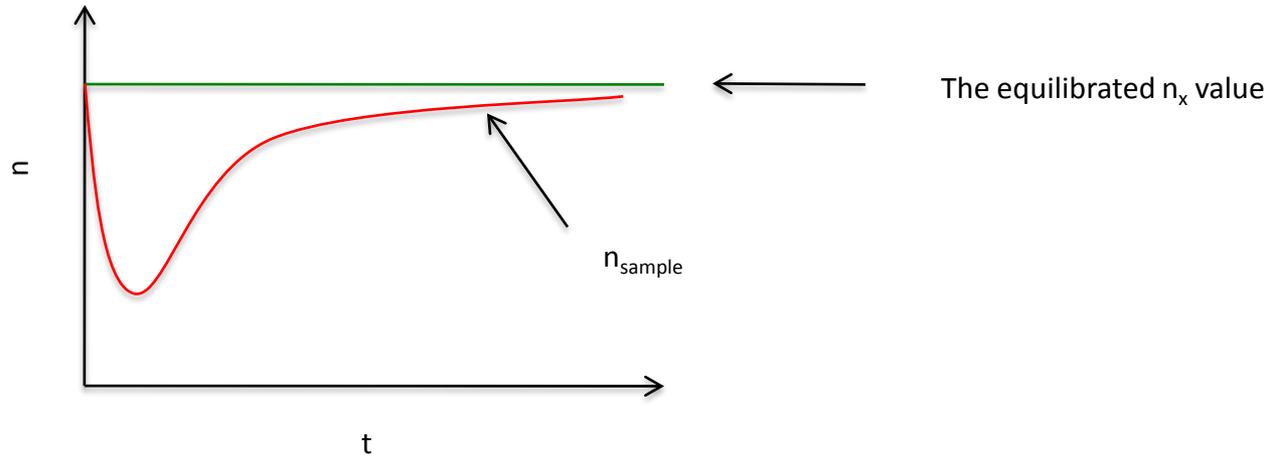
Once the sample is equilibrated at T_1 it is removed and placed in a furnace at temperature T_2 . This is followed by an instantaneous change in the index of refraction.

At temperature T_2 , the sample relaxes toward the new equilibrium value of n_2 . When the sample reaches the value of n_x which corresponds to an equilibrium sample temperature of T_x it is removed and placed in a furnace held at temperature T_x . The index of refraction is then measured as a function of time.

Since the sample has the same index of refraction as the equilibrated sample, it should have the same structure and T_f . In principle, nothing should happen to the sample if it is held in at furnace at temperature T_x .

They observed similar results as Ritland !

Their results are very similar to Ritland's.



All of these experiments show that one T_f is not sufficient to describe the glassy state. If you wish to use a Fictive temperature, you need more than one !

In the next lecture, we will discuss in detail Napolitano's and Macedo's very clever solution.

In the literature, there are three main ways that the Fictive Temperature is defined.

Structure. The fictive temperature is where the structure freezes. The fictive temperature distribution serves as a map from equilibrium to nonequilibrium phase space distributions:

Property values. May have practical value, but many caveats. Different properties would have different fictive temperatures. No connection to microscopic physics.

Relaxation processes. Here a new fictive temperature is defined as each relaxation mode freezes. Does not try to map equilibrium to nonequilibrium states.

Of all of these definitions, the structure definition is the easiest to test.

The most general and most generous definition of the fictive temperature is to assume that there are an infinite number of fictive temperatures given by

$$p_i[T(t)] = \int_0^{\infty} h[T_f, T(t)] p_i^{eq}(T_f) dT_f \quad \text{where} \quad \int_0^{\infty} h[T_f, T(t)] dT_f = 1$$

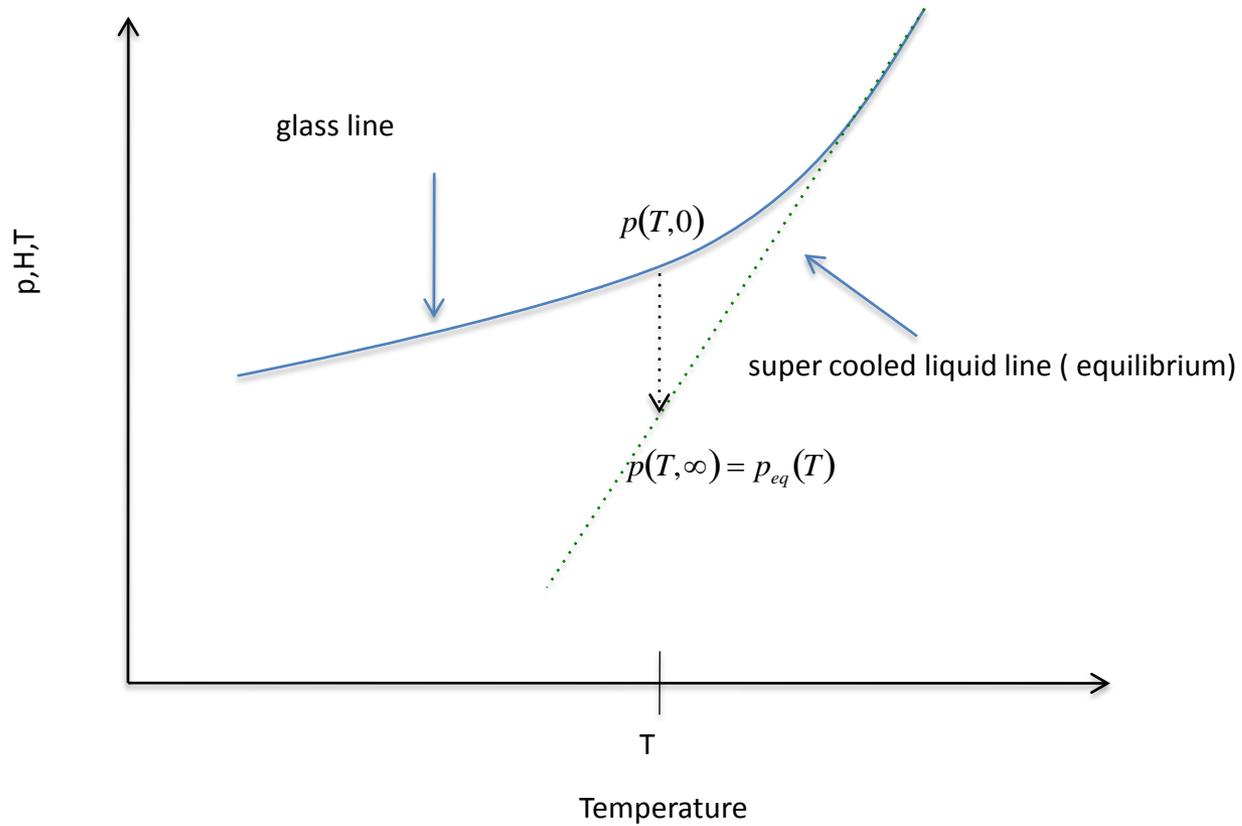
The h function is the distribution of Fictive temperatures.

What will we talk about tomorrow ?

What does relaxation mean ?

or

How does p “relax” toward the super cooled liquid line ?



Don't forget the quiz after Thursday lecture !!!!!!!!!!!