Lecture 14:Relaxation and the Tool-Narayanaswamy-Moynihan Equation

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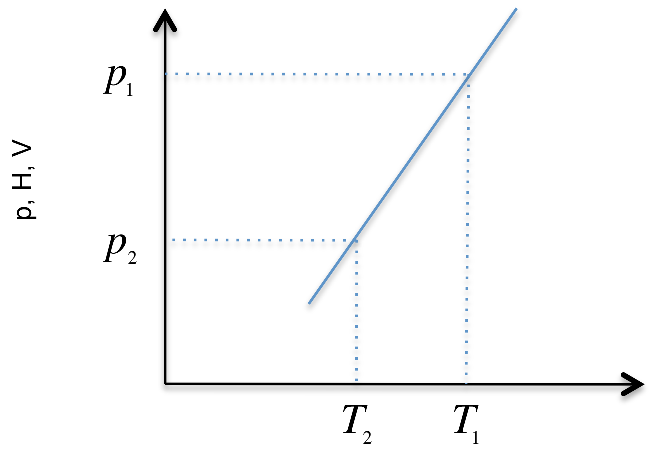
First a very quick brief review



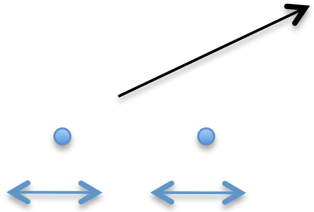
$$p(T_2) = p(T_1) + \alpha_L \Delta T$$

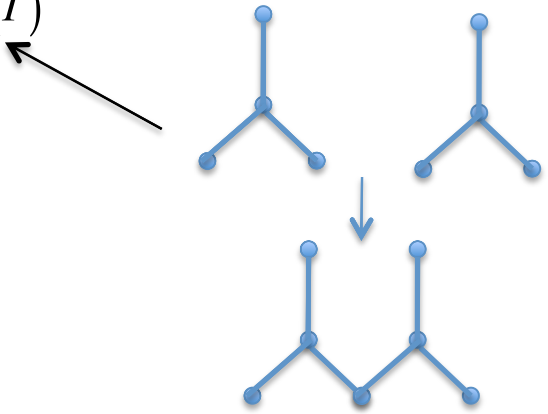
α_L is the slope of the p vs T graph

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

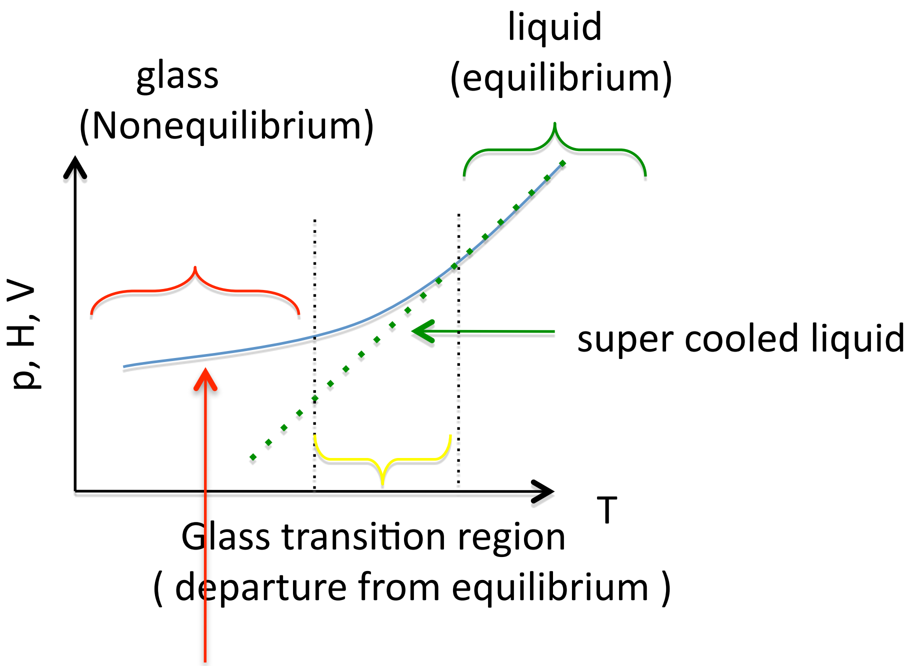
α_L is made up of two contributions: $\alpha_{\text{vibration}}$ and $\alpha_{\text{structural relaxation}}$.

$$\alpha_L = \alpha_V + \alpha_S(T)$$





What happens when a liquid is cooled ?



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

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

$$\tau^{liquid}_{relaxation} << t_{observation}$$

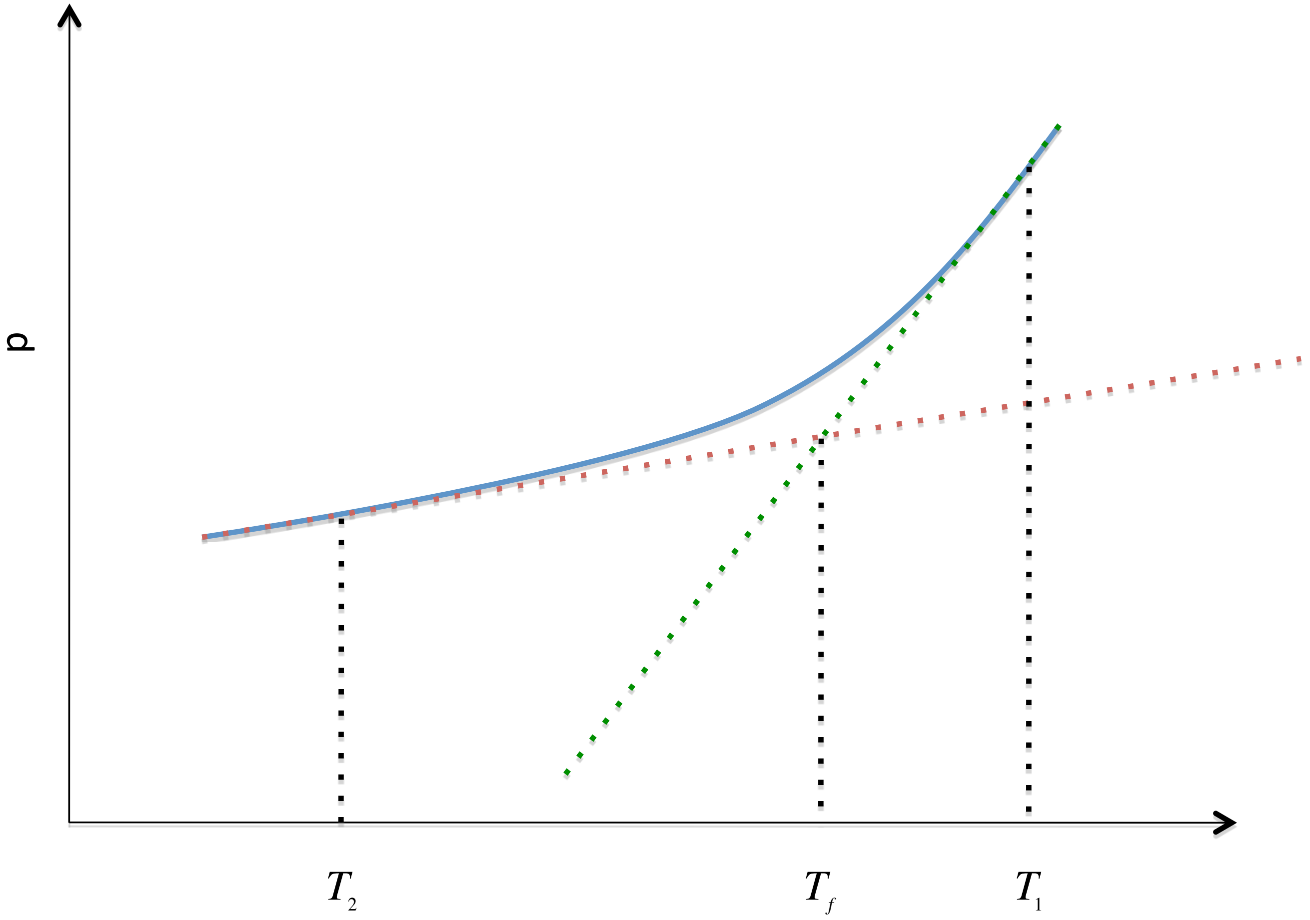
In the **glass** region, relaxation processes are so slow that they are not observed during the observation time.

$$\tau^{glass}_{relaxation} >> t_{observation}$$

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

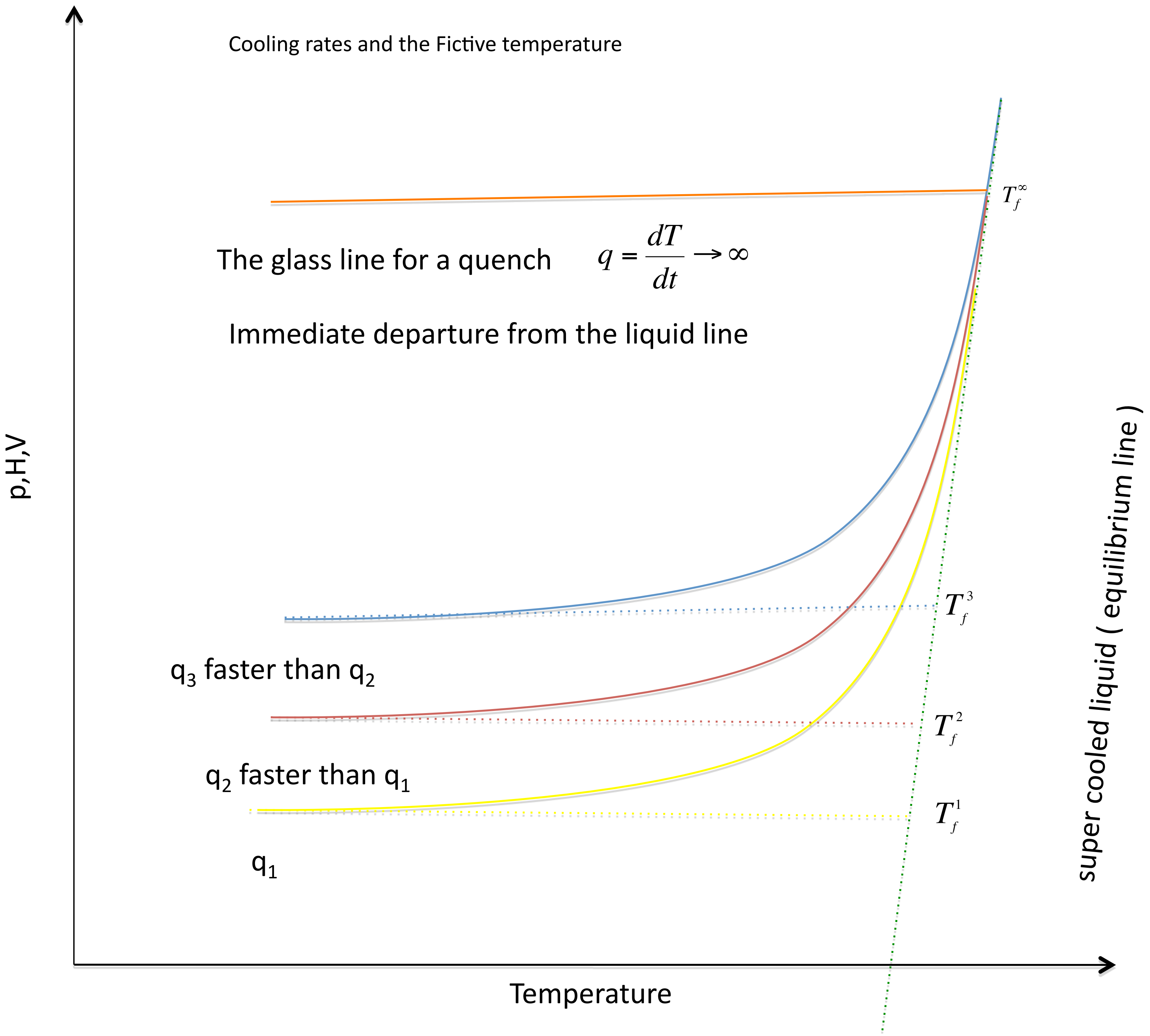
$$\tau^{glass-transition}_{relaxation} \approx t_{observation}$$

Definition of the Fictive temperature



Tool viewed a glass at temperature T_2 as having the same structure as a super cooled liquid at temperature T_f, i.e. T_f acts almost as a map between a nonequilibrium glass and an equilibrium liquid.

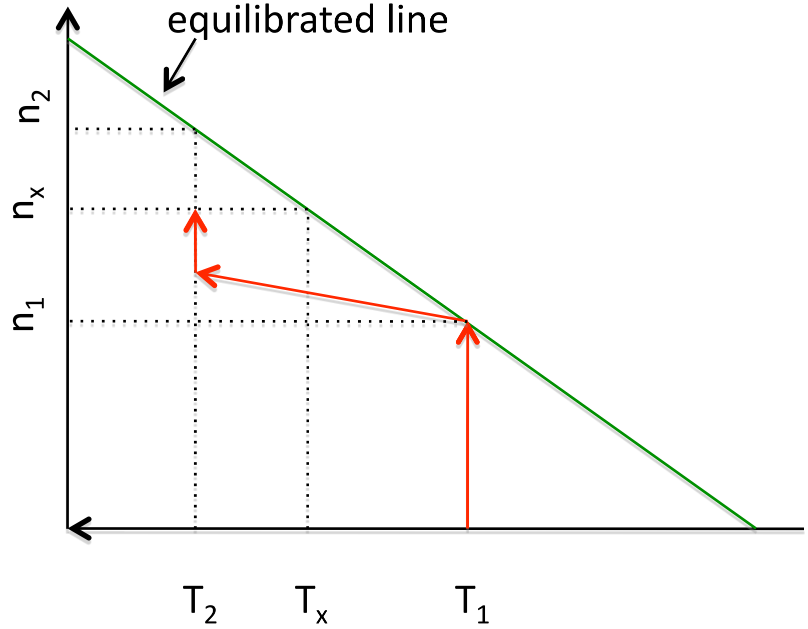
Cooling rates and the Fictive temperature

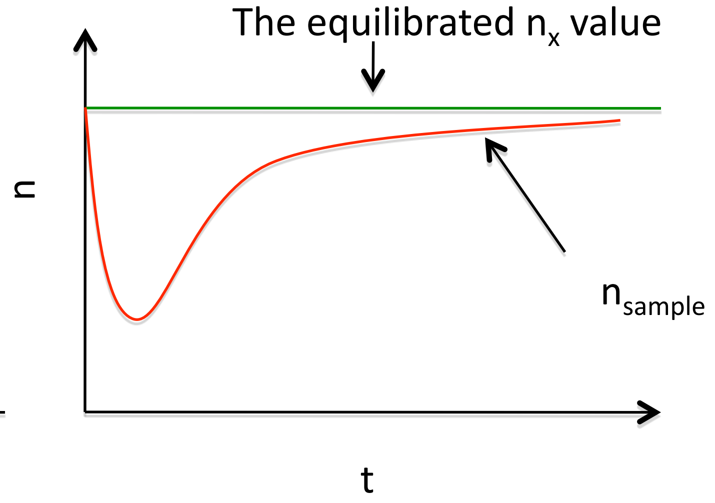


The glass line for a quench $q = \frac{dT}{dt} \rightarrow \infty$

Immediate departure from the liquid line

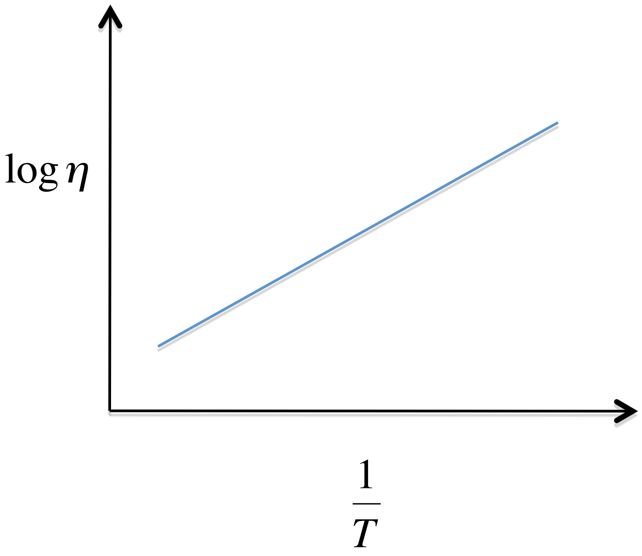
The Ritand and Napolitano and Spinner experiments





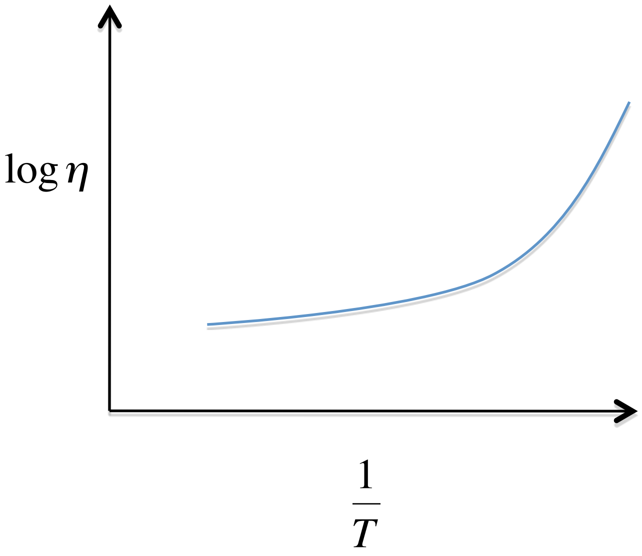
A single Fictive temperature is insufficient.

Liquids can be classified as either “strong or “fragile”



A Strong **Liquid**
(Arrhenius Behavior)

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



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

Almost all liquids are fragile.

$$\log\eta_{VFT} = \log\eta_o + \frac{A}{T - T_o}$$

or

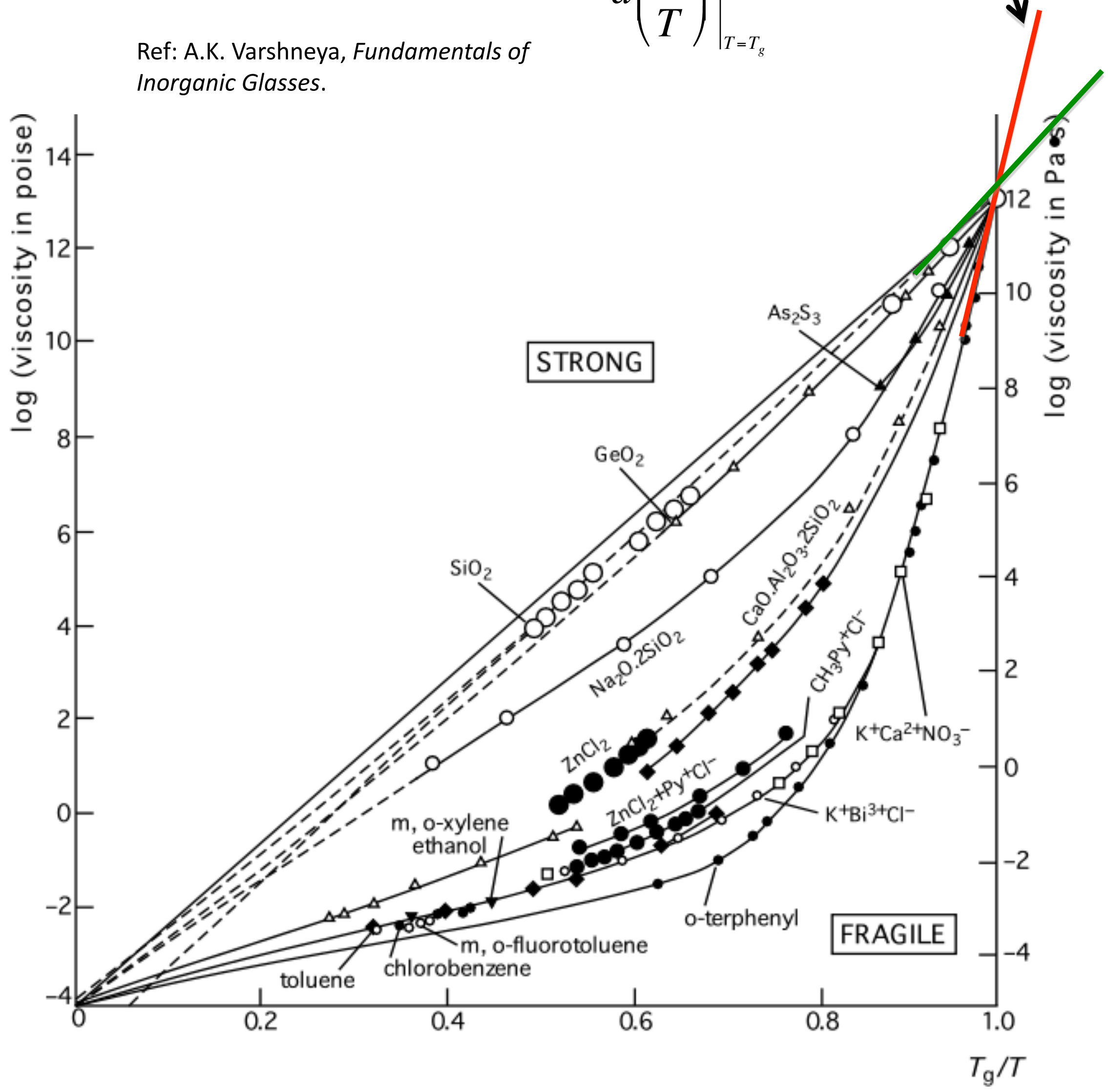
$$\tau_{AG} = \tau_o e^{-\frac{\Delta H}{S_c T}}$$

Definition of Fragility:

$$m = \left. \frac{d \log \eta}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g}$$

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

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



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

What does relaxation mean ?

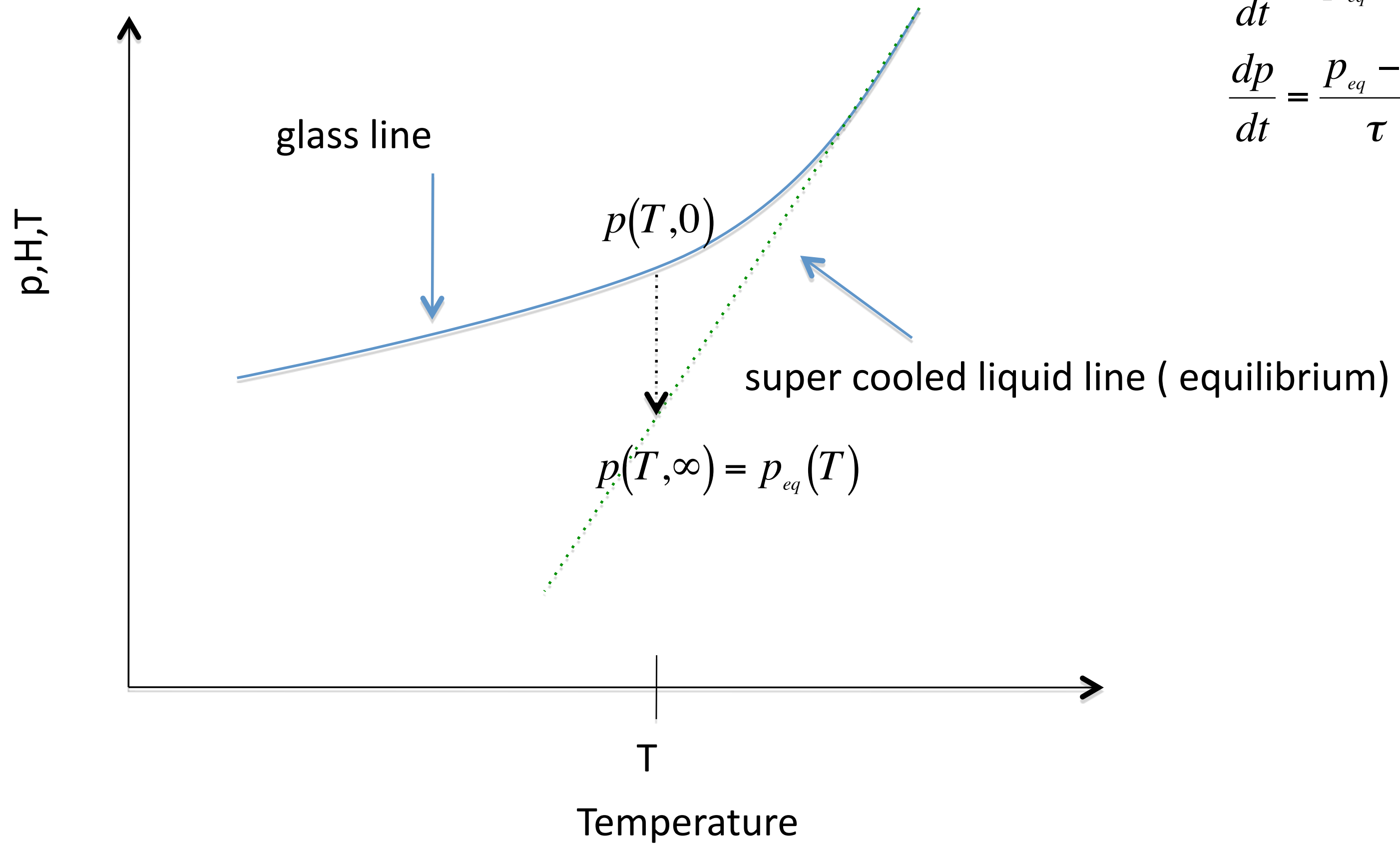
or

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

Recall from Lecture xxx that the rate of change is directly proportional to the “distance” from equilibrium.

$$\frac{dp}{dt} \propto p_{eq} - p$$

$$\frac{dp}{dt} = \frac{p_{eq} - p}{\tau}$$



Derivation of Tool's equation

(The derivation will only seem painful. It isn't.)

Recall from lecture 13, that A)

$$p(T) = p_{eq}(T_0) + \Delta p_L + \Delta p_g$$

$$p(T) = p_{eq}(T_0) + \alpha_L(T_f - T_0) + \alpha_g(T - T_f)$$

The vibrational contribution to p(T) is B) $p_V(T) = p_V(T_0) + \alpha_g(T - T_0)$ *Recall that $\alpha_g = \alpha_V$*

Subtracting A) from B) yields

$$p(T) - p_V(T) = \left[p_{eq}(T_0) + \alpha_L(T_f - T_0) + \overbrace{\alpha_g(T - T_f)\right] - \left[p_V(T_0) + \alpha_g(T}^{\text{these terms cancel}} - T_0)\right]$$

$$\underbrace{p(T) - p_V(T)}_{p_s(T)} = \underbrace{p_{eq}(T_0) - p_V(T_0)}_{p_s(T_0)} + (\underbrace{\alpha_L - \alpha_g}_{\alpha_s \equiv \alpha_L - \alpha_g})T_f - (\alpha_L - \alpha_g)T_0$$

C) $p_s(T) = p_{eqs}(T_0) + \alpha_s(T_f - T_0)$ The structure can not change past the Fictive temperature.

Taking the time derivative of C) yields

D) $$\frac{dp_s(T)}{dt} = \alpha_s \frac{dT_f}{dt}$$

Recall on slide 9 that we stated E) $$\frac{dp}{dt} = \frac{p_{eq} - p}{\tau}$$

p is the sum of the both vibrational and structural contributions as F) $p(T,t) = p_V(T) + p_s(T,t)$

When t →∞, we obtain G)

$$p(T,\infty) = p_V(T) + p_s(T,\infty)$$
$$p_{eq}(T) = p_V(T) + p_{eqs}(T)$$

Further, we can rewrite eq. A) as $$p(T) = p_{eq}(T_0) + \alpha_L(T_f - T_0) + \alpha_g(T - T_f)$$

add and subtract the same term

$$p(T) = p_{eq}(T_0) + \alpha_L(T_f - T_0) + \alpha_g(T - T_f) + \overbrace{\alpha_L T - \alpha_L T}$$

Exchange these terms

$$p(T) = p_{eq}(T_0) + \alpha_L(T - T_0) + \alpha_g(T - T_f) + \alpha_L T_f - \alpha_L T$$

H) $$p(T) = \underbrace{p_{eq}(T_0) + \alpha_L(T - T_0)}_{p_{eq}(T)} + (\alpha_L - \alpha_g)(T_f - T) = p_{eq}(T) + \alpha_s(T_f - T)$$

Substituting F) $p(T,t) = p_V(T) + p_s(T,t)$ and G) $p_{eq}(T) = p_V(T) + p_{eqs}(T)$ Into E) $\frac{dp}{dt} = \frac{p_{eq} - p}{\tau}$

yields $$\frac{d\left(p_V(T) + p_s(T,t)\right)}{dt} = \frac{\left(p_V(T) + p_{eqs}(T)\right) - \left(p_V(T) + p_s(T,t)\right)}{\tau}$$

I) $$\frac{dp_s(T,t)}{dt} = \frac{p_{eqs}(T) - p_s(T,t)}{\tau}$$

Recall p_V has no time dependence.

Now rewriting H) $p(T) = p_{eq}(T) + \alpha_s(T_f - T)$ as $p(T) - p_{eq}(T) = \alpha_s(T_f - T)$ and substituting

F) $p(T,t) = p_V(T) + p_s(T,t)$ and G) $p_{eq}(T) = p_V(T) + p_{eqs}(T)$ yields

$$\left(\cancel{p_V(T)} + p_s(T,t)\right) - \left(\cancel{p_V(T)} + p_{eqs}(T)\right) = \alpha_s(T_f - T)$$

J) $$p_s(T,t) - p_{eqs}(T) = \alpha_s(T_f - T)$$

Please stop !!!!!! When will this be over !!!!!!

Equating D) $\frac{dp_s(T)}{dt} = \alpha_s \frac{dT_f}{dt}$ and I) $\frac{dp_s(T,t)}{dt} = \frac{p_{eqs}(T) - p_s(T,t)}{\tau}$

and substituting in eq. J) $p_s(T,t) - p_{eqs}(T) = \alpha_s(T_f - T)$

Tool's eq.

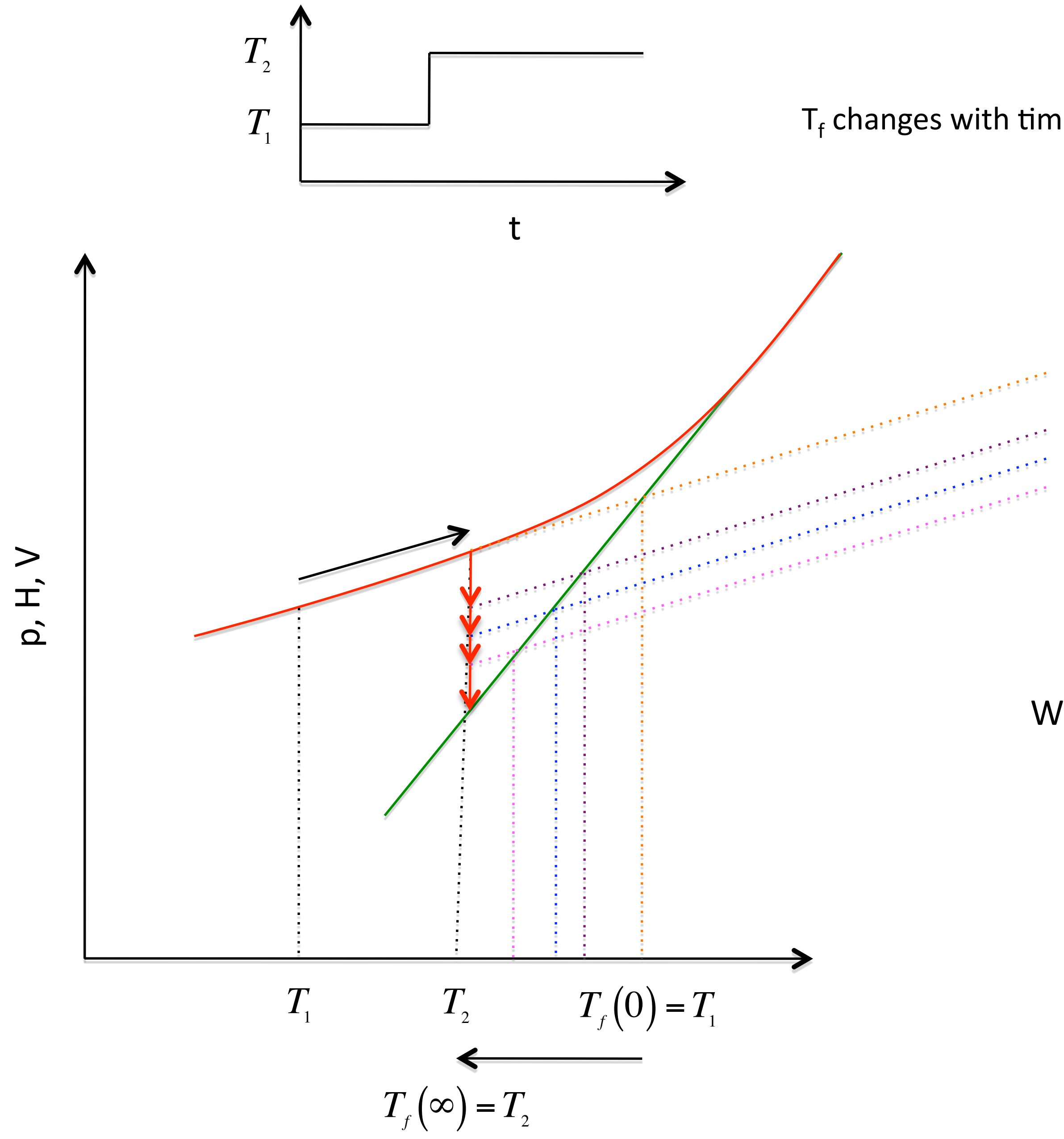
finally gives

$$\frac{dp_s(T)}{dt} = \alpha_s \frac{dT_f}{dt} = \frac{p_{eqs}(T) - p_s(T,t)}{\tau} = \frac{\alpha_s(T_f - T)}{\tau} \longrightarrow \frac{dT_f}{dt} = \frac{T_f - T}{\tau}$$

What is the graphical meaning of Tool's equation ?

What happens to T_f, when a glass is changed T_1 to T_2 ?

In particular, what happens when an up quench from T_1 to T_2 followed by an isothermal hold at T_2 ?



T_f changes with time according to Tool's equation.

$$\frac{dT_f}{dt} = \frac{T_f - T}{\tau}$$

What did Tool use for τ ?

What is a good choice for τ ?

We recall that $\eta = G\tau$. So $\tau = \eta/G = K\eta$. This makes perfect sense. If the system is more viscous, the relax time should be larger ?

Tool assumed that over a small region of T, η could be approximated as $\eta = \eta_o e^{-AT}$ where η_0 and A are constants.

Tool quickly realized that this did not account for the data. He postulated that η must depend on the Fictive temperature T_f.

His argument goes as the following. If a liquid were cooled quickly, it would have a larger T_f than a slower cooled liquid. This larger T_f would correspond to a more "open" structure which would reduce the η. If the liquid were cooled slower, then the T_f would be smaller and the structure is "closer" together and would have a larger η. To account for this, Tool (1946) assumed that a better choice of η would be

$$\eta = \eta_0 e^{-(A_1T + A_2T_f)}$$

So we can finally write $\tau = K\eta = K\eta_0 e^{-(A_1T + A_2T_f)} = \tau_0 e^{-(A_1T + A_2T_f)}$

where η_0 and A_1 and A_2 are constants.

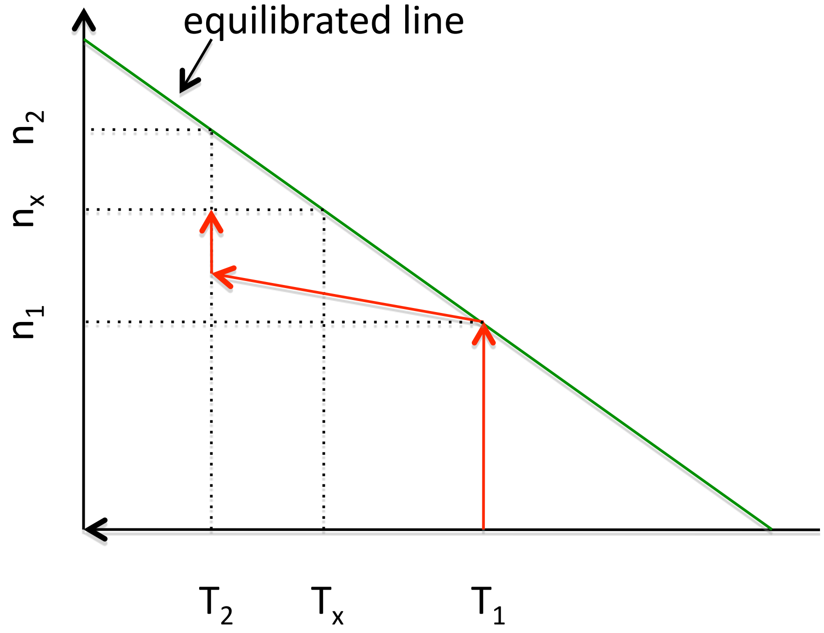
Tool's equation becomes

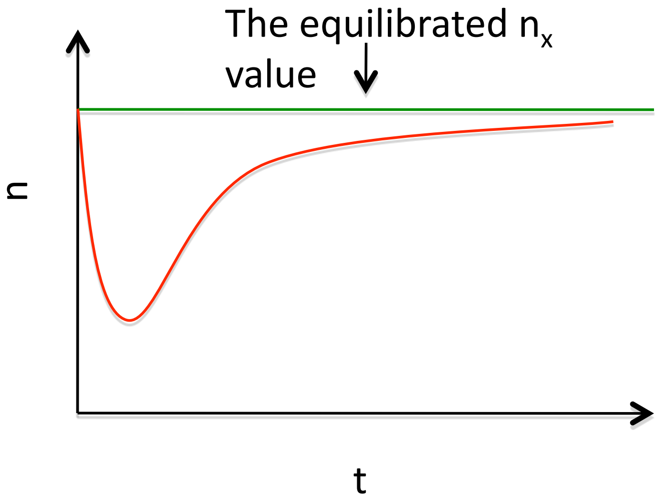
$$\frac{dT_f}{dt} = \left(\frac{T_f - T}{\tau_0}\right) e^{(A_1T + A_2T_f)}$$

However, this equation is incorrect. Why ? Problems with Tool's equation.

Tool's eq. $\frac{dT_f}{dt} = \frac{T_f - T}{\tau}$ can not describe Ritand's or Napolitano's and Spinner's experiment.

If a glass is equilibrated at T_x then $T_f = T_x$. Recall that when the index of refraction of the sample equals n_x, it is placed in a furnace at temperature T_x. The same index of refraction implies the same structure and according to Tool the same T_f. Since $T = T_x$ and $T_f = T_x$, the right side of Tool's equation equals zero, so T_f = a constant = T_x. n_{sample} should remain fixed. It doesn't !





What is the fundamental problem with Tool’s equation ?

Tool’s equation only has <u>one</u> relaxation time.

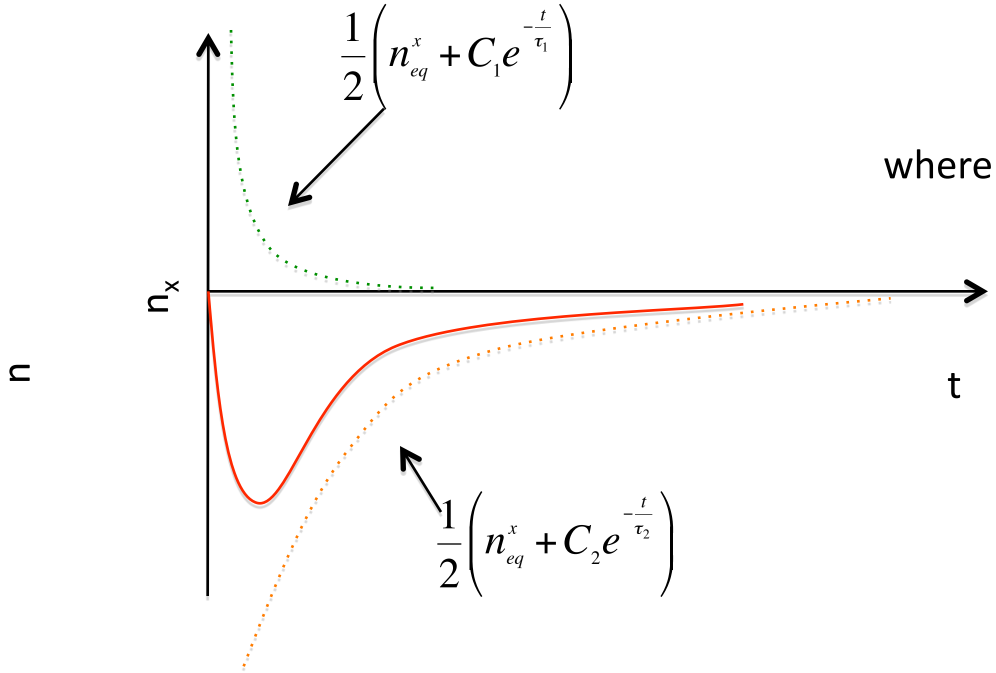
$$\frac{dT_f}{dt} = \frac{T_f - T}{\tau}$$

Napolitano and Macedo assumed that there were two relaxation times, one fast the other slow.

They assumed that n(t) must have the mathematical form

$$n(t) = n^x_{eq} + \frac{1}{2}\left(C_1 e^{-\frac{t}{\tau_1}} + C_2 e^{-\frac{t}{\tau_2}}\right)$$

where C_1 and C_2 are constants and $\tau_1 << \tau_2$.



In some sense this result is not too surprising. Recall from lecture xxx, that a stretched exponential often fit the data better. Further, stretched exponentials can be approximated by the Prony series.

$$\tau = e^{-\left(\frac{t}{\tau_{\exp}}\right)^{b}} \approx \sum_{n=1}^{N} a_n e^{-\frac{t}{\tau_n}}$$

where $\tau_{\exp}$ is an experimentally determined parameter, $0 < b < 1$, and the a_n's sum to 1.

Can we do any better ? Yes! The Narayanaswamy Model.

In order to fully comprehend the Narayanaswamy model, we first need to understand the concept of thermorheological simplicity (TRS).

What is Thermorheological Simplicity ?

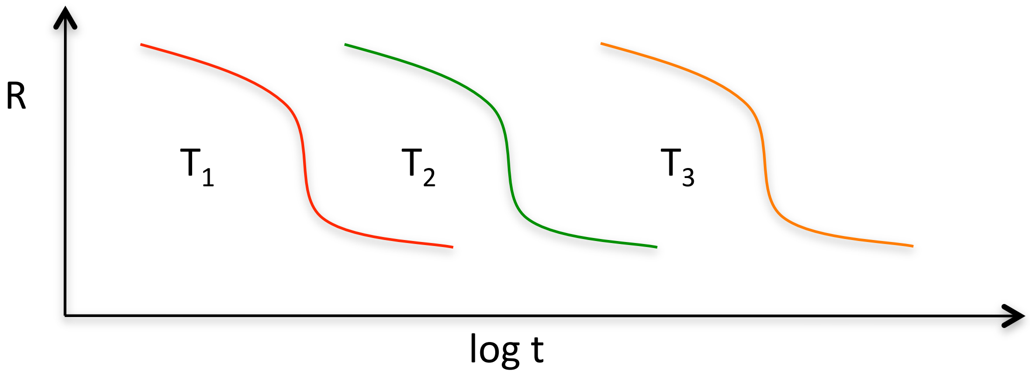
We can define the relaxation respond at a temperature T as

$$R \equiv \frac{p(T,t) - p(T,\infty)}{p(T,0) - p(T,\infty)}$$

The range of R is 1 to 0, i.e. if t = 0, R = 1 and if t = ∞, R = 0.

Suppose the relaxation response of some property p of a glass has been measured at some temperature $T_{1.}$ This same relaxation experiment is then carried out at two new temperatures T_2 and $T_{3.}$ such that $T_1 > T_2 > T_3$.

A graph of R versus log t, might look like the following



In certain cases, the form of the response R is identical in shape but only shifted. At a temperature $T_2 < T_1$, the response R is delayed in time since the kinetics are slower. Likewise for T_3 , since $T_3 > T_2 > T_1$. This is called TRS. What are the mathematical implications of TRS ?

As stated earlier, often the response function R can be fit to a stretched exponential. Further the stretched exponential can be approximated by a Prony series as shown below.

$$R = e^{-\left(\frac{t}{\tau_{\exp}}\right)^{b}} \approx \sum_{n=1}^{N} a_n e^{-\frac{t}{\tau_n}}$$

where $\tau_{\exp}$ is an experimentally determined parameter, $0 < b < 1$, and the a_n's sum to 1.

The temperature dependence comes from the τ_n. In order for TRS to occur, the temperature dependence in all of the τ_n's must be the same. To see this, suppose that the Prony series of R is composed of only two terms. Let's assume that τ_1 has an Arrehinus dependence,

$\tau_1 = a_1 e^{-\frac{\Delta H}{RT}}$ on T while τ_2 has an exponential dependence, $\tau_2 = a_2 e^{-kT}$

Clearly, if the temperature T were doubled to 2T, then the response function would look radically different at the two temperatures and R would not exhibit TRS.

However, if all of the τ_n's of a system had the same temperature dependence, then the system would exhibit TRS. If a system exhibits TRS, then all the τ_n's can only differ from one another by some temperature independent multiplicative constant. If we call this constant λ_n for the relaxation τ_n, then mathematically we have

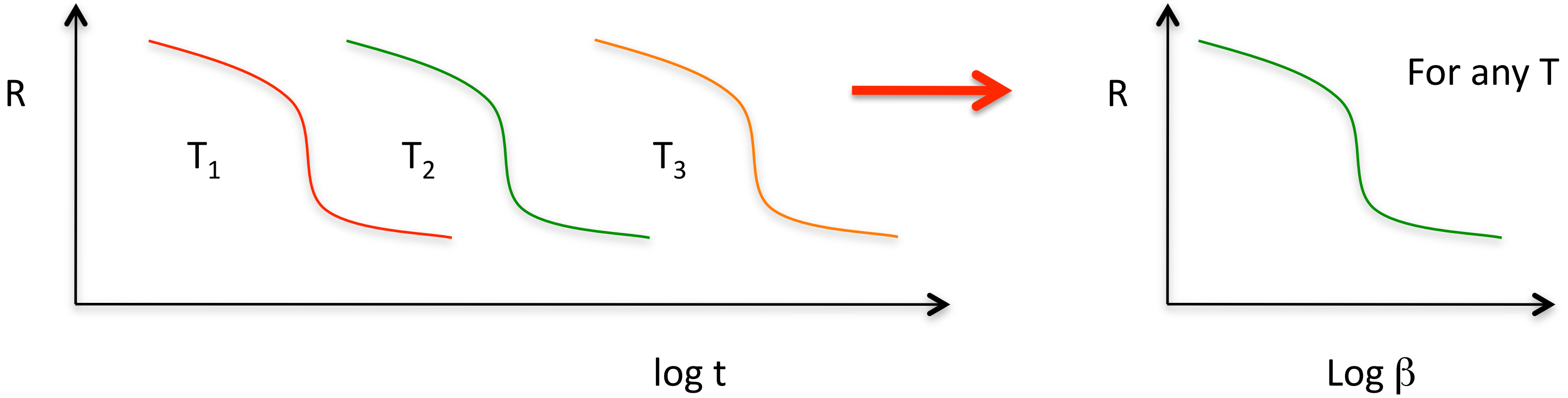
$$\tau_n = \frac{\tau}{\lambda_n}$$

where the τ contains all of the functional dependence on the temperature T.

We can now write the response function R as $R = \sum_{n=1}^{N} a_n e^{-\frac{\lambda_n t}{\tau}}$

The response function R is only a function of the ratio $\frac{t}{\tau} \equiv \beta$ $\longrightarrow$ $R = \sum_{n=1}^{N} a_n e^{-\frac{\lambda_n t}{\tau}} = \sum_{n=1}^{N} a_n e^{-\lambda_n \beta}$

If the R for a system were measured at any value of T and then graphed as R vs. β, all of the R's at various T's would lie on top of one another, i.e. there would be one Master graph.



Since there is one Master graph of R, let's define a reference temperature T_r at which the Master graph would be measured. Further, let's call the time associated with this reference temperature ξ . Since the same graph would result at any temperature T, we can conclude that

$\beta = \dfrac{\xi}{\tau_r} = \dfrac{t}{\tau}$ or more simply $\xi = \dfrac{\tau_r}{\tau} t$ where ξ is called the reduced time.

When $T = T_r$, x = t. We can view ξ in the following way. If a system relaxes by some amount at temperature T in a time t, ξ is the time that is needed for the system to relax the same amount at temperature T_r, i.e.

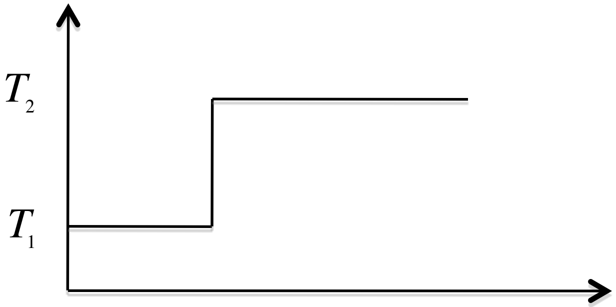
$$R(t,T) = R(\xi,T_r)$$

We may now write R as $R = \sum_{n=1}^{N} a_n e^{-\frac{\lambda_n t}{\tau}} = \sum_{n=1}^{N} a_n e^{-\lambda_n \beta} = \sum_{n=1}^{N} a_n e^{-\lambda_n \frac{\xi}{\tau_r}}$

Today's Quiz Stops Here !

What would be the relaxation response if we changed the temperature from T_1 to T_2 ? Or in other words, what is the generalization of the isothermal relaxation response R ?

$$R \equiv \frac{p(T,t) - p(T,\infty)}{p(T,0) - p(T,\infty)}$$



We call this response M and it is defined as $M_p(t) \equiv \frac{p(T_2,t) - p(T_2,\infty)}{p(T_2,0) - p(T_2,\infty)}$

This has the same range as R. When t = 0, M_p = 1 and if t = ∞, M_p = 0.

Using eq. H) on slide 10, we have

$$p(T) = p_{eq}(T) + \alpha_s(T_f - T) = \underbrace{p(T_1) + \alpha_L(T - T_1)} + \alpha_s(T_f - T)$$

Now at t = 0, $T_f(0) = T_1$ and $T_f(\infty) = T_2$, so substituting H) into our expression of M_p we obtain

$$M_p(t) \equiv \frac{p(T_2,t) - p(T_2,\infty)}{p(T_2,0) - p(T_2,\infty)}$$

$$M_p(t) = \frac{\left[\cancel{p_{eq}(T_1)} + \alpha_L(\cancel{T_2 - T_1}) + \alpha_s(T_f(t) - \cancel{T_2})\right] - \left[\cancel{p_{eq}(T_1)} + \alpha_L(\cancel{T_2 - T_1}) + \alpha_s(T_f(\infty) - \cancel{T_2})\right]}{\left[\cancel{p_{eq}(T_1)} + \alpha_L(\cancel{T_2 - T_1}) + \alpha_s(T_f(0) - \cancel{T_2})\right] - \left[\cancel{p_{eq}(T_1)} + \alpha_L(\cancel{T_2 - T_1}) + \alpha_s(T_f(\infty) - \cancel{T_2})\right]}$$

J) $$M_p(t) = \frac{T_f(t) - T_2}{T_1 - T_2}$$

Can one assume that the stretched exponential solution for R is valid for M, i.e.

Is $M = e^{-\left(\frac{t}{\tau_{\exp}}\right)^{b}}$ correct ?

The ability to write M as a stretched exponential isn't obvious ! Why ? τ_{exp} is a function of T(t) and T_f(t). This non-trvial temperature dependence needs to be taken into account. This was the problem facing Narayanaswamy !

What was Narayanaswamy's solution ?????

He invoked TRS on M_p ! How did he do this ?

Recall that for TRS the reduced time is given by $\xi = \frac{\tau_r}{\tau(T)} t$

How can ξ be modified to account for a temperature that is changing with time ?

If we assume that during an infinitesimal change in time, dt, that τ doesn't vary much, we can write the differential of the reduced time as

$d\xi = \frac{\tau_r}{\tau[T(t)]} dt$ Integrating this from 0 to t yields $\xi = \int_0^t \frac{\tau_r}{\tau[T(t')]} dt' = \tau_r \int_0^t \frac{dt'}{\tau[T(t')]}$

Rewriting eq. J) , $M_p(t) = \frac{T_f(t) - T_2}{T_1 - T_2}$ we obtain M_p in terms of the reduced time ξ $M_p(\xi) = \frac{T_f(\xi) - T_2}{T_1 - T_2}$

We can rewrite eq. H), $p(T,t) = p_{eq}(T) + \alpha_s(T_f(t) - T)$ in terms ξ as $p(T,\xi) = p_{eq}(T) + \alpha_s(T_f(\xi) - T)$

Rewrite M_p as $T_f(\xi) - T_2 = -M_p(\xi)\Delta T$ where $\Delta T = T_2 - T_1$

and substituting, we obtain

$$p(T_2,\xi) = p(T_2,\infty) - \alpha_s \Delta T M_p(\xi)$$

To Be Continued ……..

We will answer such questions as ……

Will Lassie save Timmy in the well ?????