

Lecture 15: The Tool-Narayanaswamy-Moynihan Equation Part II and DSC

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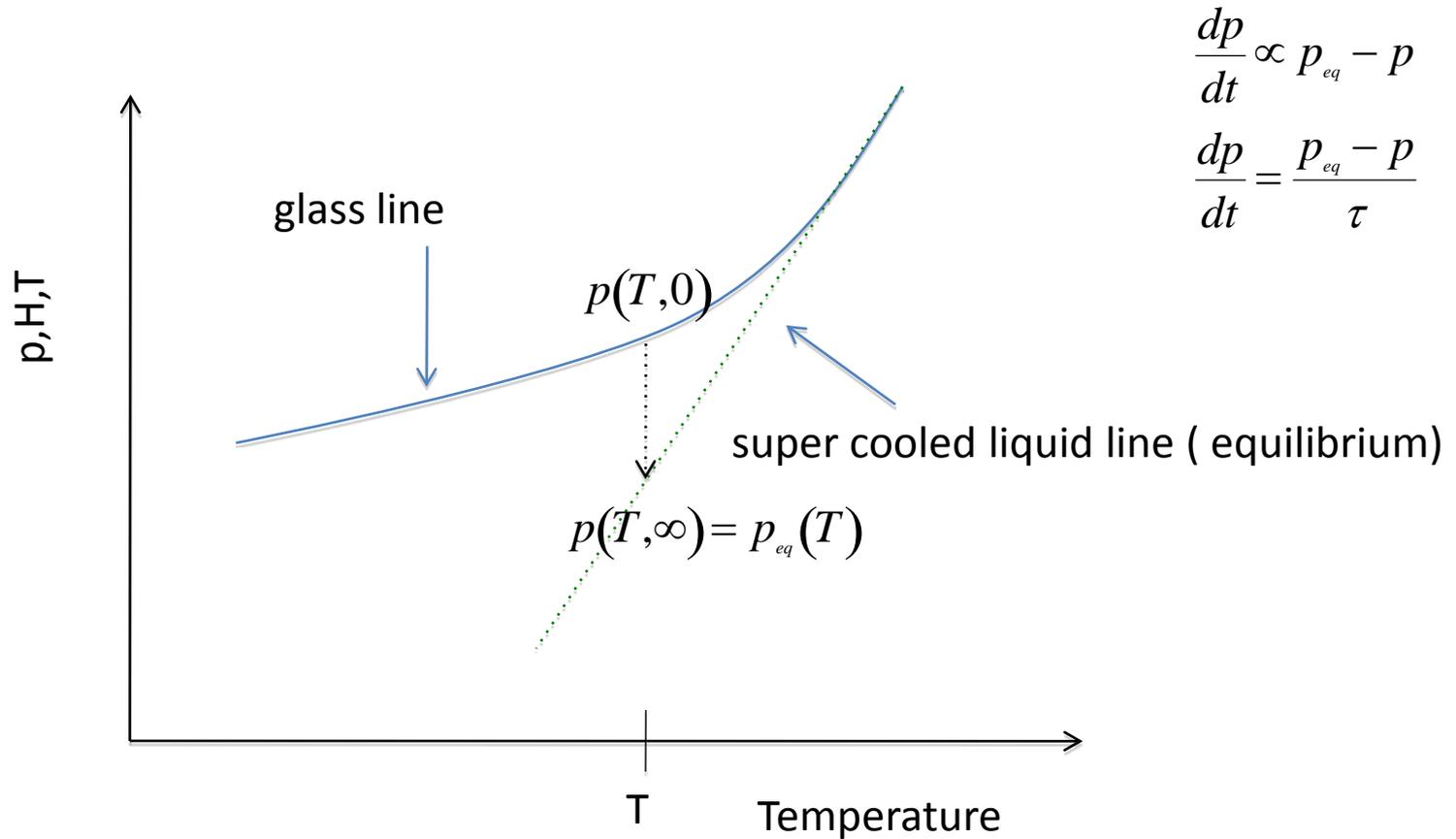
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Thank you for taking me home !
My eyes are completely open
now ! I understand the glass
transition very well !!!!



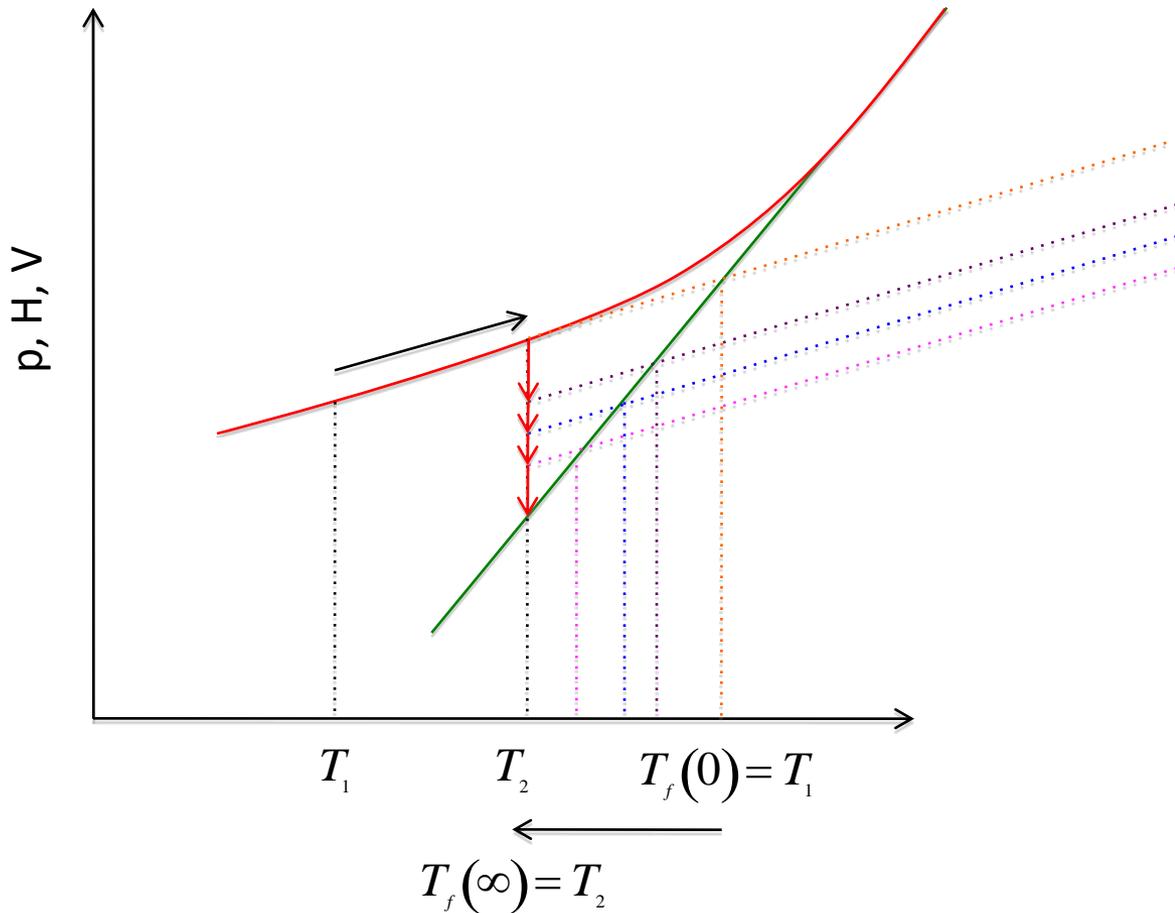
First Let's Review



We used these three equations.

$$\begin{aligned}
 p(T,t) &= p_v(T) + p_s(T,t) \\
 p(T) &= p_{eq}(T_0) + \alpha_L(T_f - T_0) + \alpha_g(T - T_f) \\
 \frac{dp}{dt} &= \frac{p_{eq} - p}{\tau}
 \end{aligned}
 \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} \longrightarrow \frac{dT_f}{dt} = \frac{T_f - T}{\tau}$$

Tool's eq.



Initially Tool used $\tau = K\eta = \tau_0 e^{-AT}$ 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 .

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

$$\eta = \eta_0 e^{-(A_1 T + A_2 T_f)} \longrightarrow \tau = \tau_0 e^{-(A_1 T + A_2 T_f)} \quad \text{where } \eta_0 \text{ and } A_1 \text{ and } A_2 \text{ are constants.}$$

Tool's equation becomes

$$\frac{dT_f}{dt} = \left(\frac{T_f - T}{\tau_0} \right) e^{(A_1 T + A_2 T_f)}$$

As clever as Tool's equation is, it can not account for the cross over experiments of Ritland. The reason for this lack of agreement is the single relaxation time.

Thermorheological Simplicity

Define the relaxation response 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 $t = \infty$, $R = 0$.

The response R can typically be described by the stretched exponential

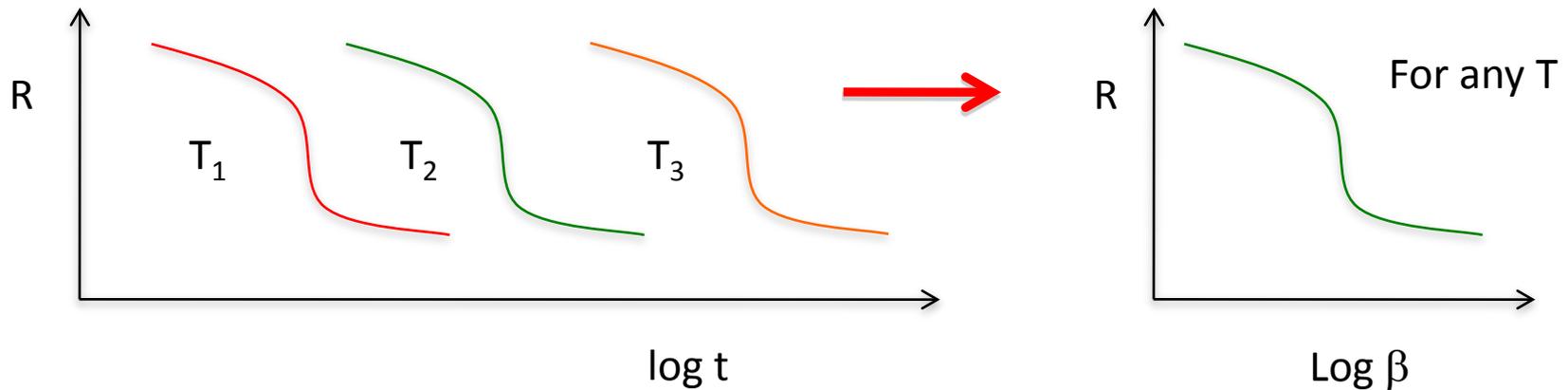
$$R = e^{-\left(\frac{t}{\tau_{\text{exp}}}\right)^b} \approx \sum_{n=1}^N a_n e^{-\frac{t}{\tau_n}}$$

where τ_{exp} is an experimentally determined parameter, $0 < b < 1$. Stretched exponentials can be approximated by the Prony series where the a_n 's sum to 1.

If all the τ_n 's have the same mathematical dependence on temperature then TRS results. To see this, rewrite the τ_n R in the Prony series as τ/λ_n so R becomes

$$R = \sum_{n=1}^N a_n e^{-\frac{\lambda_n t}{\tau}} = \sum_{n=1}^N a_n e^{-\lambda_n \beta} \quad \text{where} \quad \frac{t}{\tau} \equiv \beta$$

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, define a reference temperature T_r at which the Master graph would be measured. Call the time associated with this reference temperature ξ . Since the same graph would result at any temperature T, we can conclude that

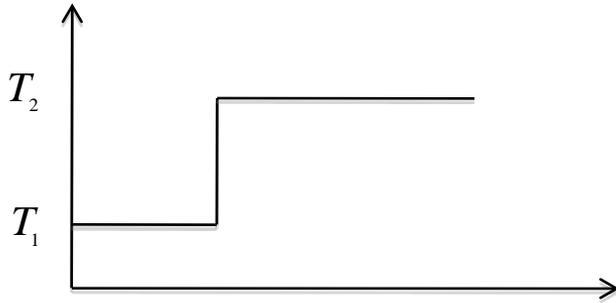
$$\beta = \frac{\xi}{\tau_r} = \frac{t}{\tau} \quad \text{or more simply} \quad \xi = \frac{\tau_r}{\tau} t \quad \text{where } \xi \text{ is called the reduced time.}$$

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.

$$R(t, T) = R(\xi, T_r) \longrightarrow R = \sum_{n=1}^N a_n e^{-\frac{\lambda_n t}{\tau}} = \sum_{n=1}^N a_n e^{-\lambda_n \beta} = \sum_{n=1}^N a_n e^{-\lambda_n \frac{\xi}{\tau_r}}$$

How can we extend this to temperature changes ?

Defining a new response function $M_p(t) \equiv \frac{p(T_2, t) - p(T_2, \infty)}{p(T_2, 0) - p(T_2, \infty)}$ for T changes



M has the same range as R, i.e. $t = 0$, $M_p = 1$ and if $t = \infty$, $M_p = 0$.

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

And the conditions: $t = 0$, $T_f(0) = T_1$ and $T_f(\infty) = T_2$ M_p we becomes

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

Narayanaswamy assumed that $M_p(t)$ obeys TRS ! How ?

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

M_p in terms of the reduced time ξ

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

$$\downarrow$$

$$T_f(\xi) - T_2 = -M_p(\xi)\Delta T$$

While

$$p(T, t) = p_{eq}(T) + \alpha_s (T_f(t) - T) \longrightarrow p(T, \xi) = p_{eq}(T) + \alpha_s (T_f(\xi) - T)$$

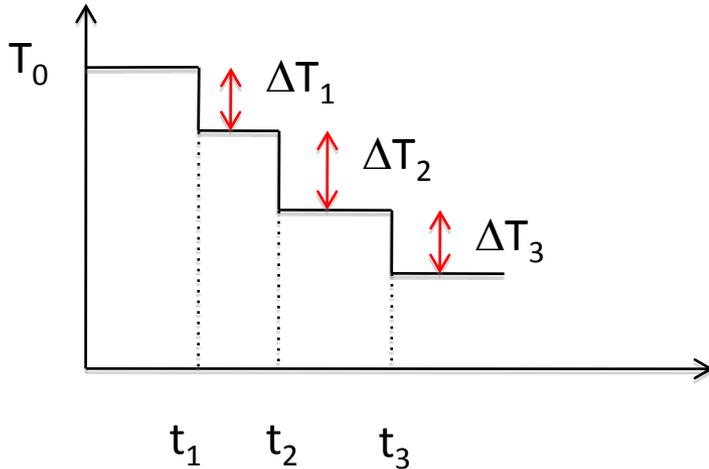
$$\downarrow$$

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

Episode III: Revenge of the ξ

To complete the derivation, imagine that the temperature is changed from some initial value of T_0 to some final value T in a series of N steps, i.e.

$$T = T_0 + \Delta T_1 + \Delta T_2 + \dots + \Delta T_N = T_0 + \sum_{i=1}^N \Delta T_i$$



How can be extend $T_f(\xi)$ and $p(T, \xi)$ to multiple temperature steps ?

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



$$p(T, \xi) = p(T, \infty) - \alpha_s \Delta T_1 M_p(\xi - \xi_1) + \dots - \alpha_s \Delta T_N M_p(\xi - \xi_N)$$

$$p(T, \xi) = p(T, \infty) - \sum_{i=1}^N \alpha_s \Delta T_i M_p(\xi - \xi_i)$$

Using the chain rule and rewriting ΔT_i in terms of ξ yields

$$\Delta T_i = \frac{\Delta T(\xi)}{\Delta \xi_i} \Delta \xi_i \rightarrow dT = \frac{dT}{d\xi} d\xi$$



$$p(T, \xi) = p(T, \infty) - \sum_{i=1}^N \alpha_s \Delta T_i M_p(\xi - \xi_i)$$

$$p(T, \xi) = p(T, \infty) - \sum_{i=1}^N \alpha_s M_p(\xi - \xi_i) \frac{\Delta T(\xi)}{\Delta \xi_i} \Delta \xi_i$$



$$p(T, \xi) = p(T, \infty) - \int_0^{\xi} \alpha_s M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi'$$

Likewise, the equation for fictive temperature becomes

$$T_f(\xi) - T_2 = -M_p(\xi)\Delta T$$



$$T_f = T - \sum_{i=1}^N \Delta T_i M_p(\xi - \xi_i)$$

$$T_f = T - \sum_{i=1}^N M_p(\xi - \xi_i) \frac{\Delta T(\xi)}{\Delta \xi_i} \Delta \xi_i$$



$$T_f = T - \int_0^{\xi} M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi'$$

Recall in the last lecture, we stated that the fundamental flaw in Tool's equation is that it only has one relaxation time. Let's pretend that $M_p(\xi)$ is given by only one relaxation time, i.e.

$$M_p(\xi) = e^{-\frac{\xi}{\tau_r}}$$

Substituting this M into Narayanaswamy's equation for the evolution of T_f yields

$$T_f = T - \int_0^{\xi} M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi' = T - \int_0^{\xi} e^{-\frac{(\xi - \xi')}{\tau_r}} \frac{dT}{d\xi'} d\xi'$$

or

$$T - T_f = \int_0^{\xi} e^{-\frac{(\xi - \xi')}{\tau_r}} \frac{dT}{d\xi'} d\xi'$$

Taking the derivative with respect to ξ gives

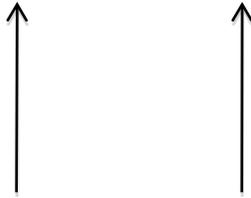
$$\frac{dT_f}{d\xi} = \frac{1}{\tau_r} \int_0^{\xi} e^{-\frac{(\xi - \xi')}{\tau_r}} \frac{dT}{d\xi'} d\xi'$$

$$\frac{dT_f}{d\xi} = \frac{T - T_f}{\tau_r}$$

Tool's eq.

What did Narayanaswamy use for τ ?

$$\tau_p = \tau_0 \exp \left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f} \right] \quad \text{where } 0 < x < 1$$



Arrhenius term A T_f dependence just like Tool !

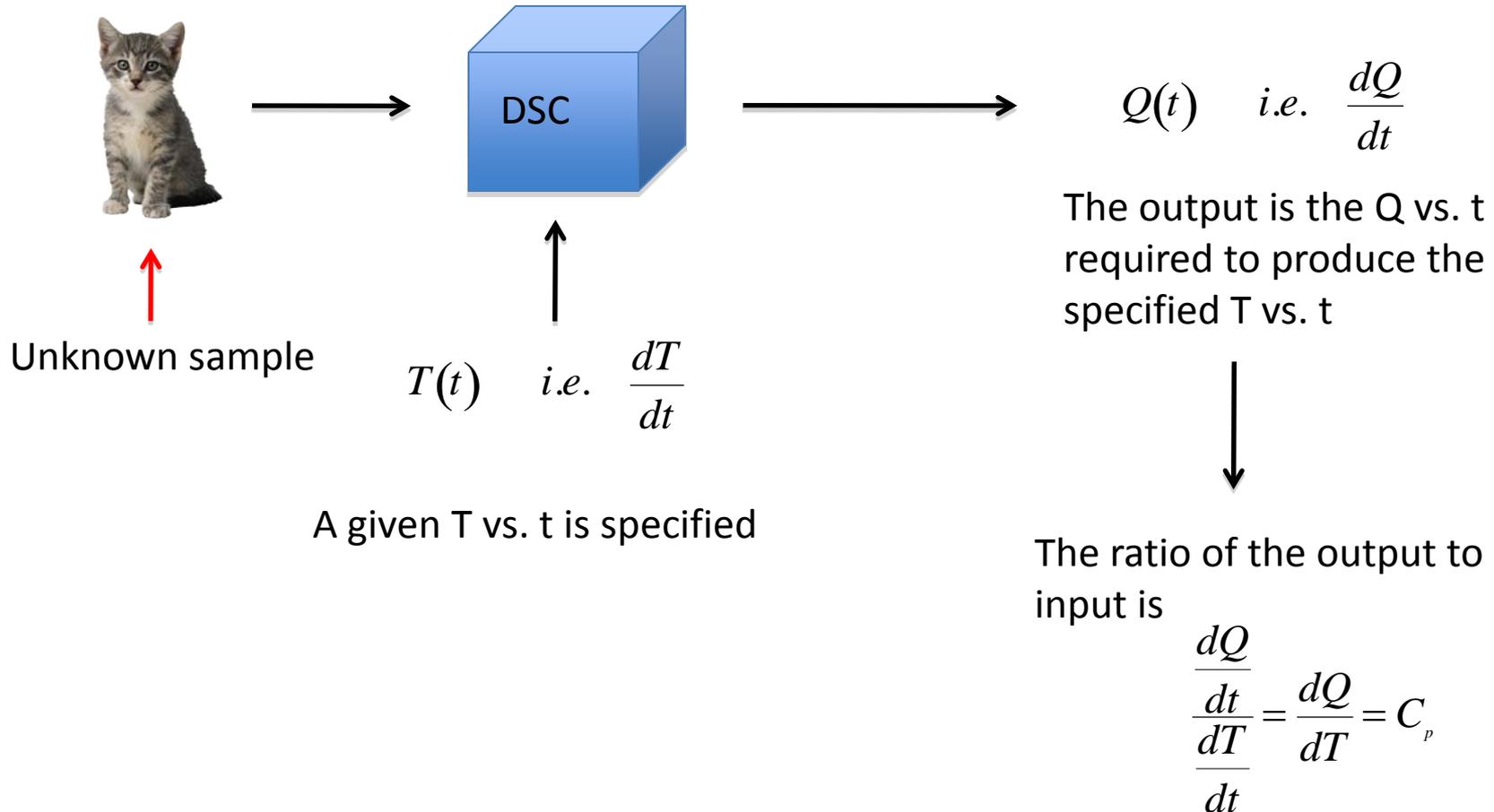
The Tool-Narayanaswamy-Moynihan equations are

$$p(T, \xi) = p(T, \infty) - \int_0^\xi \alpha_s M_p (\xi - \xi') \frac{dT}{d\xi'} d\xi' \quad \text{and} \quad T_f = T - \int_0^\xi M_p (\xi - \xi') \frac{dT}{d\xi'} d\xi'$$

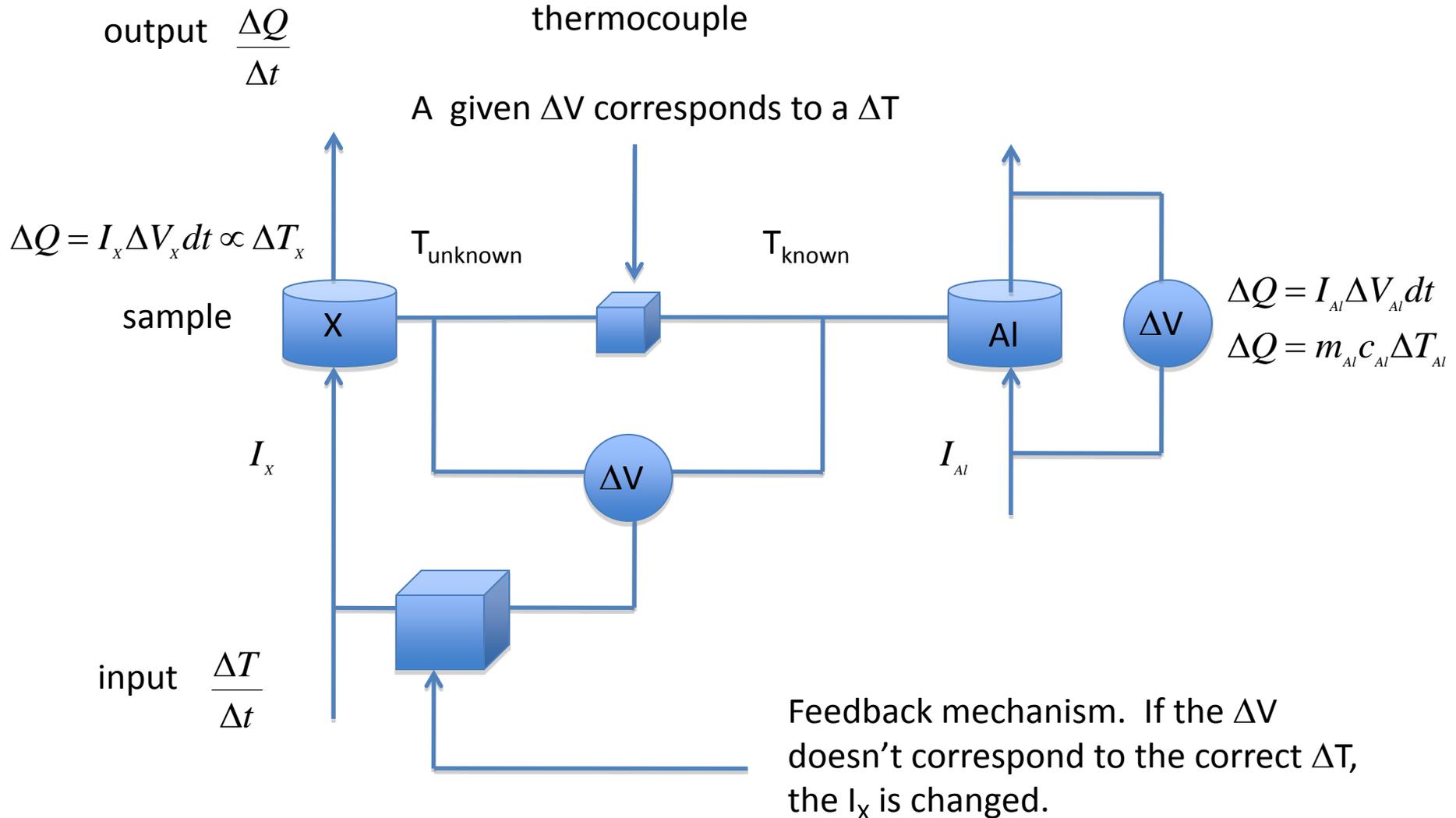
and some form for t_p such as

$$\tau_p = \tau_0 \exp \left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f} \right]$$

DSC: Differential Scanning Calorimetry as a “Black Box”. By a “black box”, I mean 1) what are the inputs and 2) what is the output. Ignore the details of how the apparatus works.



How does a DSC work ? The “philosophy” of the device.





Starting the Q100

1. Turn the power switch OFF. Do not touch the sample pan lid or the sample pan. Do not touch the sample pan lid or the sample pan. Do not touch the sample pan lid or the sample pan.
2. Turn the power switch ON. Do not touch the sample pan lid or the sample pan. Do not touch the sample pan lid or the sample pan.
3. Turn the power switch OFF. Do not touch the sample pan lid or the sample pan. Do not touch the sample pan lid or the sample pan.
4. Turn the power switch ON. Do not touch the sample pan lid or the sample pan. Do not touch the sample pan lid or the sample pan.

DSC Q100

Temperature Range

Temperature Range	Sample Pan	Reference Pan
0 to 300 °C	Aluminum	Aluminum
0 to 300 °C	Aluminum	Aluminum
0 to 300 °C	Aluminum	Aluminum

Sealed Al pans containing the samples



The Empty Al pan
acts as the reference
sample



Temperature Range

- ⊗ **WARNING!** Do not exceed 100 °C with the DSC cooling heat sinkset and the crucator heater cell. Serious damage and/or injury may occur.
- ⚠ **CAUTION:** Do not use the DSC when running isothermal experiments above 500 °C. Damage to the unit can occur if used at high temperatures for extended periods.
- ⚠ **CAUTION:** Damage to the unit may result if cooling fluid with a temperature below -25 °C is used.

Pans go in here

DSC Q100



2300	James
2301	James
2302	James
2303	James
2304	James
2305	James
2306	James
2307	James
2308	James
2309	James
2310	James
2311	James
2312	James
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2349	James
2350	James



Starting the CCS

Once the CCS has been properly installed, follow the steps below to set up the instrument pressure and condition the CCS system for optimum performance.

1. Verify that the correct model type (e.g., CCS) and the system, under the secondary stage when set-up, are both selected on the **Tube Treatment Parameters** sub-page of the DSC instrument control software.
2. Verify that a small bit of dry nitrogen is connected to the flow loop, if using the CCS Plug-in, and that it ports to the top of the DSC instrument.
3. Dry the CCS system by following step 1 of the conditioning procedure found in the user manual. This includes setting the CCS.
4. Verify that the gas inlet conditions (pressure through the Flowmeter Page by checking the **Flow Rate** value) are set to desired. A temperature sensor should be used to verify the gas inlet flow, using a wet-bulb temperature sensor (e.g., **Wet Bulb** value on the CCS). Once these conditions are verified, select the **Go To Standby** button from the Control menu to display the standby equipment screen.

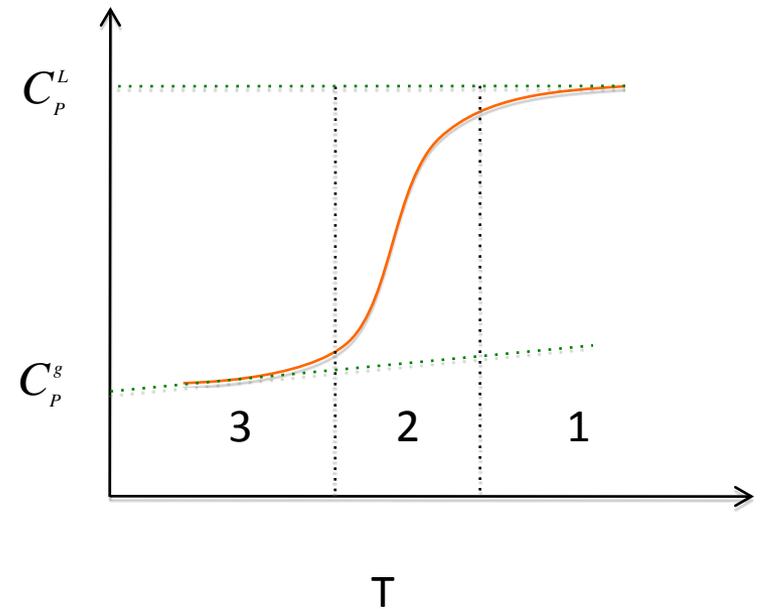
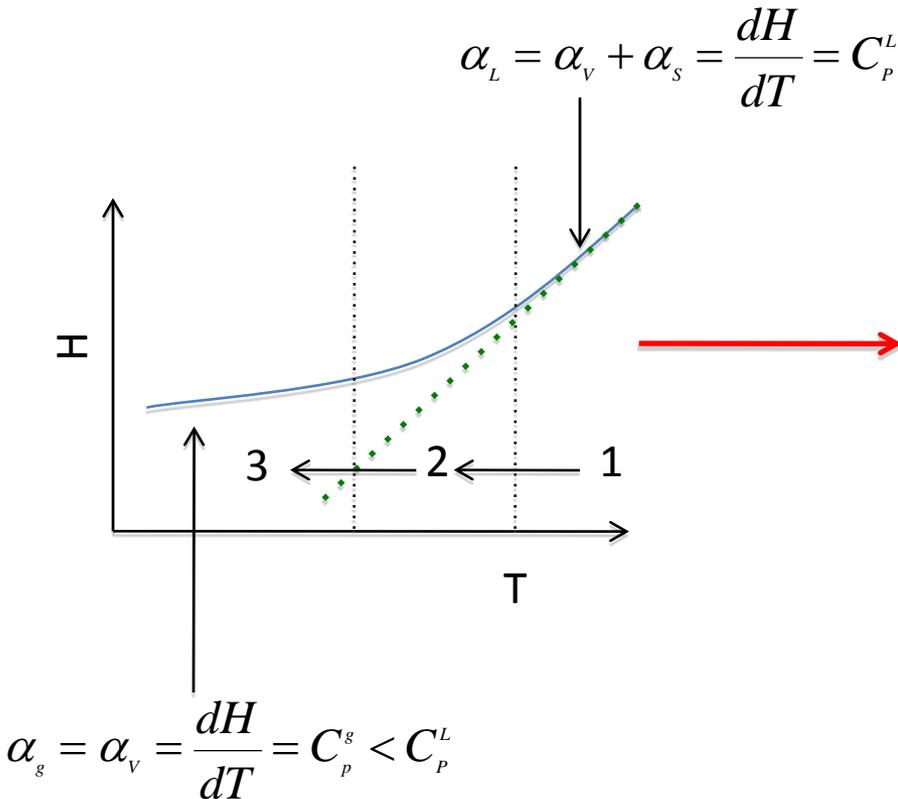
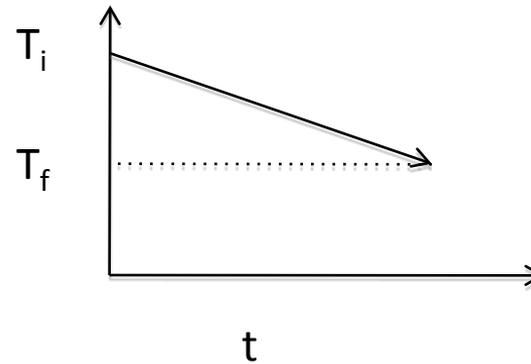
NOTE: The CCS will always be in a standby state when the instrument is powered on. The CCS will not start until the instrument is powered on.

5. Proceed to Step 2, "Conditioning the System," in the conditioning procedure found in the user manual. "Conditioning the CCS" includes verifying the DSC CCS system later in the manual. This step is required before the DSC CCS system is available for operation, resulting in optimal results and efficiency.
6. Reconfigure the DSC after conditioning the system.

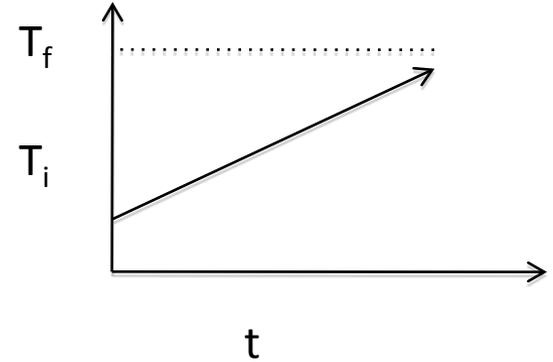
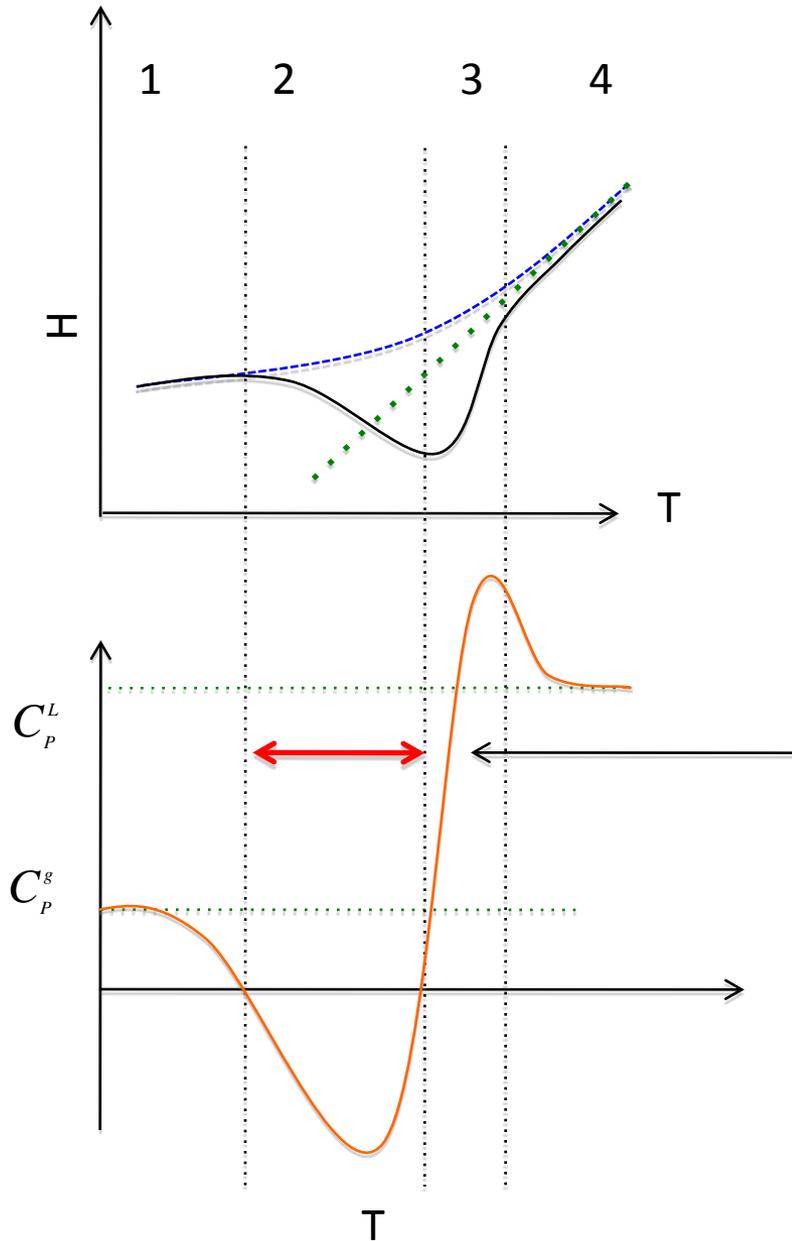
THIS SERIAL NO. IS THE PROPERTY OF THE MANUFACTURER. IT IS THE RESPONSIBILITY OF THE USER TO MAINTAIN AN ACCURATE RECORD OF THIS DATE.

Before we explain how to measure T_f and T_g using a DSC, let's first examine some typical C_p vs T results

A) C_p vs. T for a linear cooled liquid
i.e. a "down scan"

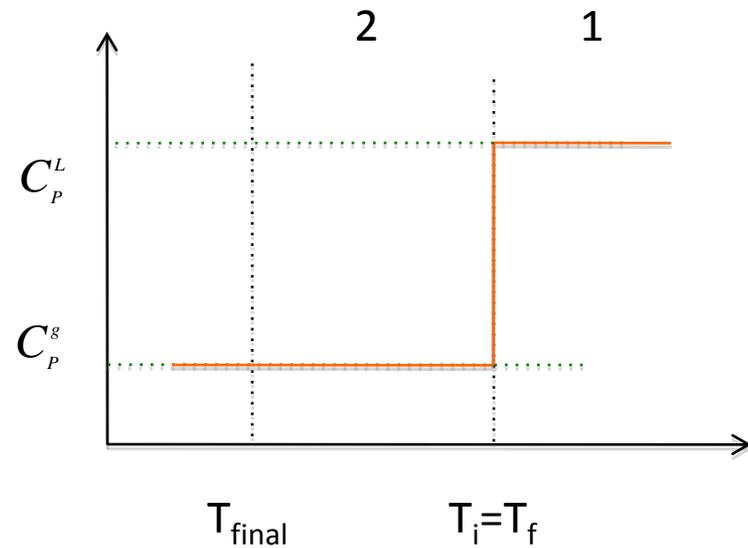
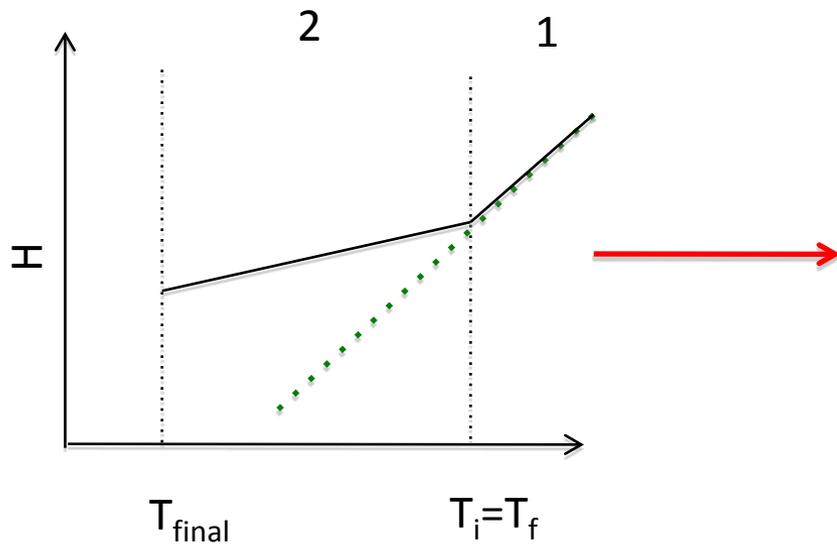
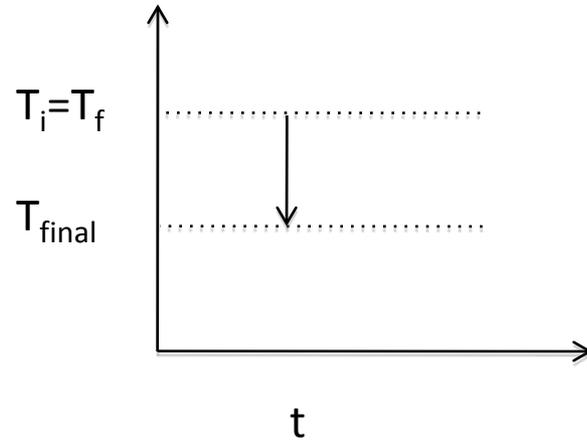


B) Linear heating a glass that was linearly cooled i.e. an “up scan”

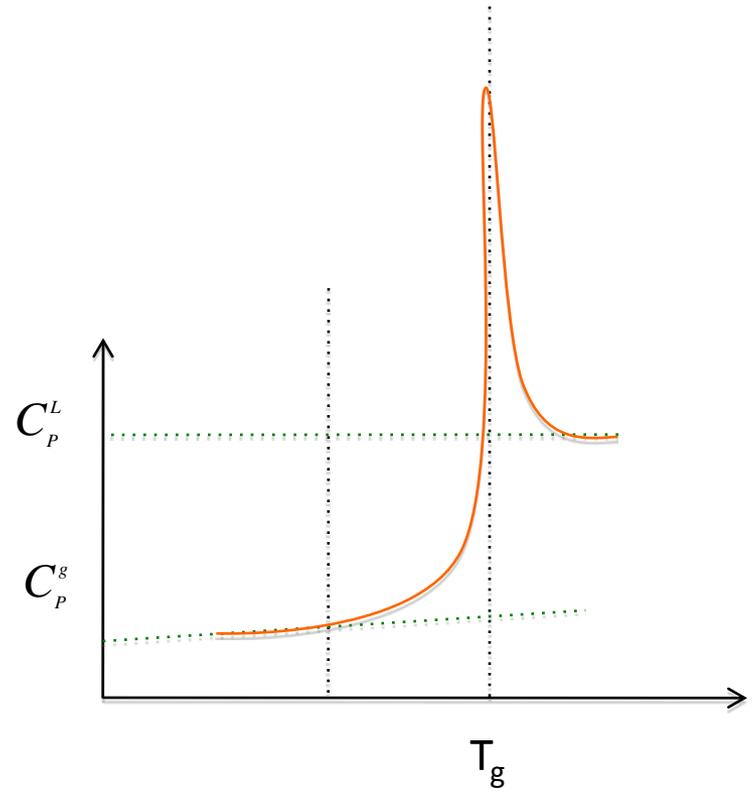
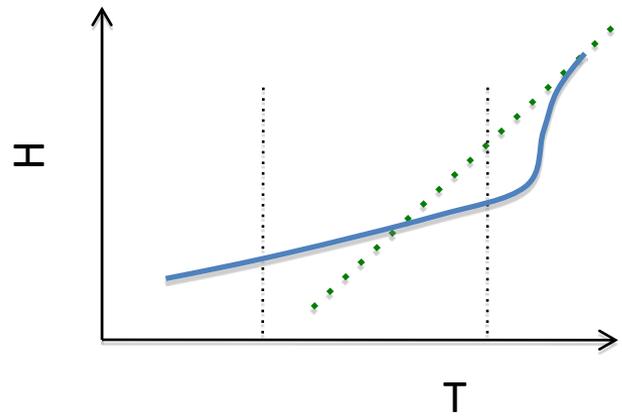
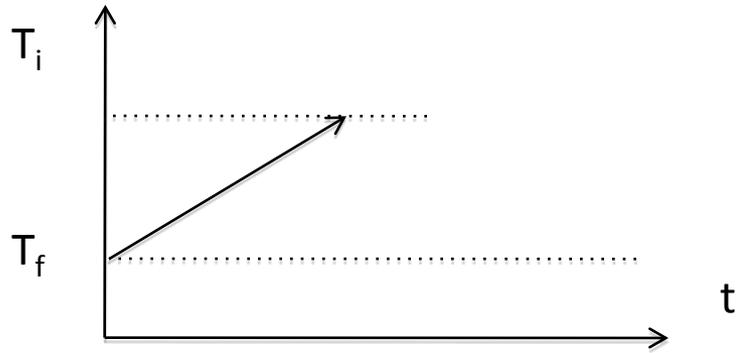


As the glass is relaxing toward the super cooled equilibrium line, heat is given off i.e. H is decreasing so this region is exothermic.

C) A liquid cooled by a down quench



D) A linear up scan on an annealed glass



What information does a C_p vs T graph provide ?

Recall that $C_p = \frac{dH}{dT}$ \longrightarrow $\left\{ \begin{array}{l} C_p dT = dH \\ \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} dH = H_2 - H_1 = \Delta H \end{array} \right.$

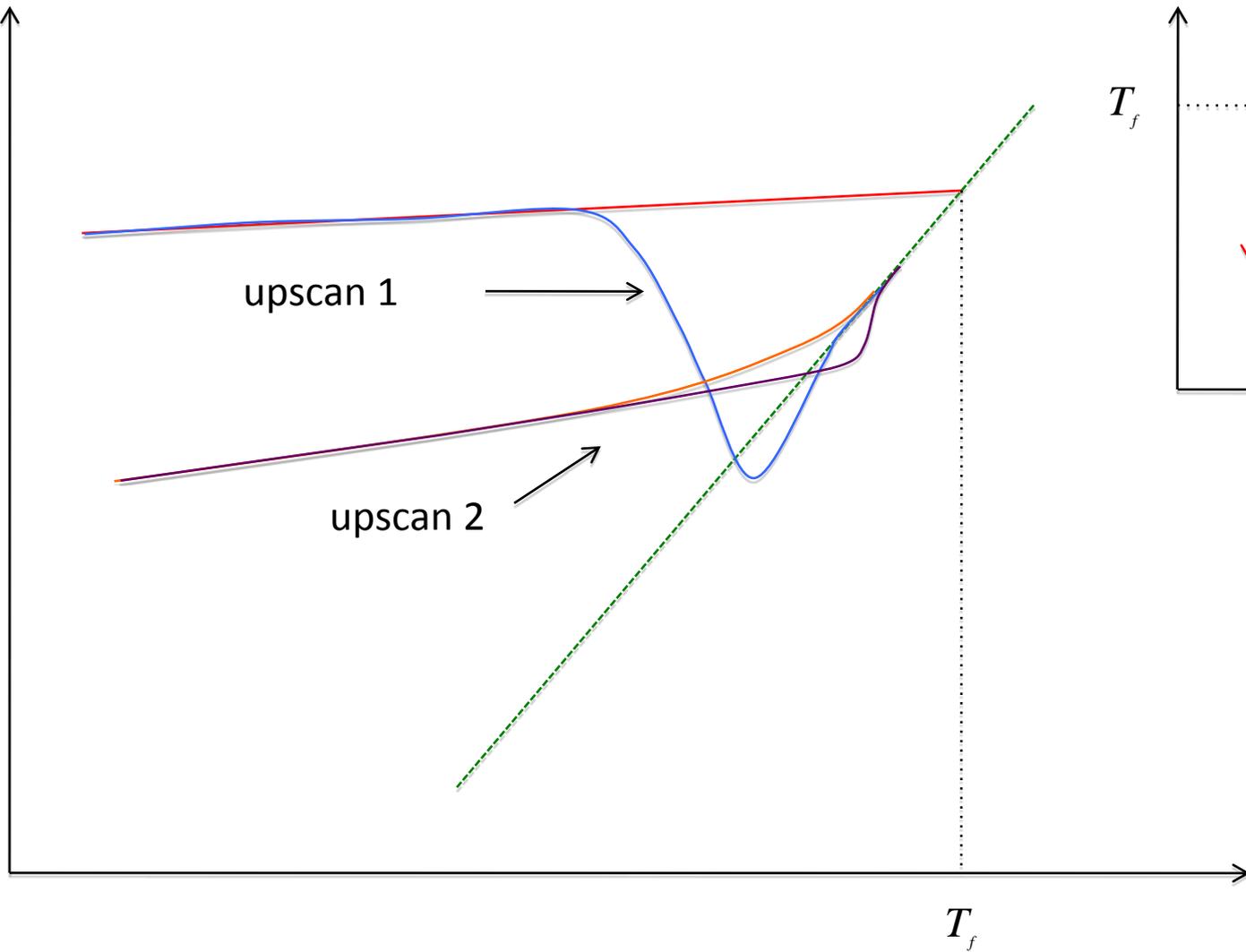
If the system is a glass at T_1 and a liquid at T_2 , then $\Delta H = H_L - H_g$.

How can we use this to find T_f and T_g ? For example, how do you measure the T_f and T_g of a quenched glass ?

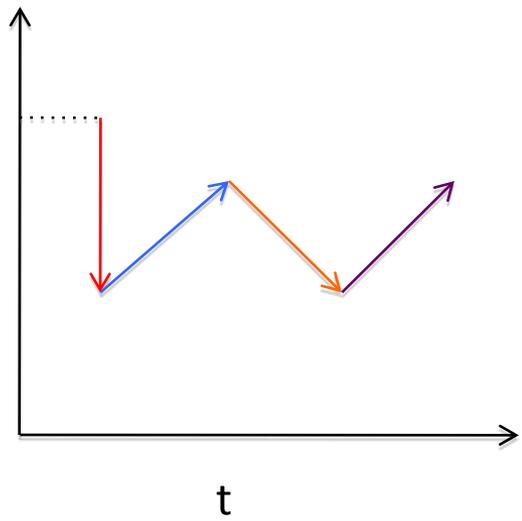
Yuanzheng Yue's Enthalpy-Matching Method

- 1) Make a glass and quench it. The cooling rate and T_f are unknown. What is the T_f of this quenched glass ?
- 2) Place a sample of the quenched glass into a DSC and heat the sample up to the liquid state at some fixed linear rate say $20^{\circ}\text{C}/\text{min}$ or $10^{\circ}\text{C}/\text{min}$. Call the C_p for this first "upscan" C_p^1 .
- 3) Cool the liquid at the the same linear rate, i.e. say $20^{\circ}\text{C}/\text{min}$, to room temperature.
- 4) Reheat the cooled glass sample using at the same linear rate of $20^{\circ}\text{C}/\text{min}$ back up to the liquid state. Call the C_p for this second "upscan" C_p^2 . The graph for C_p^2 will not have a severe of a "dip" since the glass has relaxed.
- 5) Graph of C_p^1 and C_p^2 vs. T curves.

H



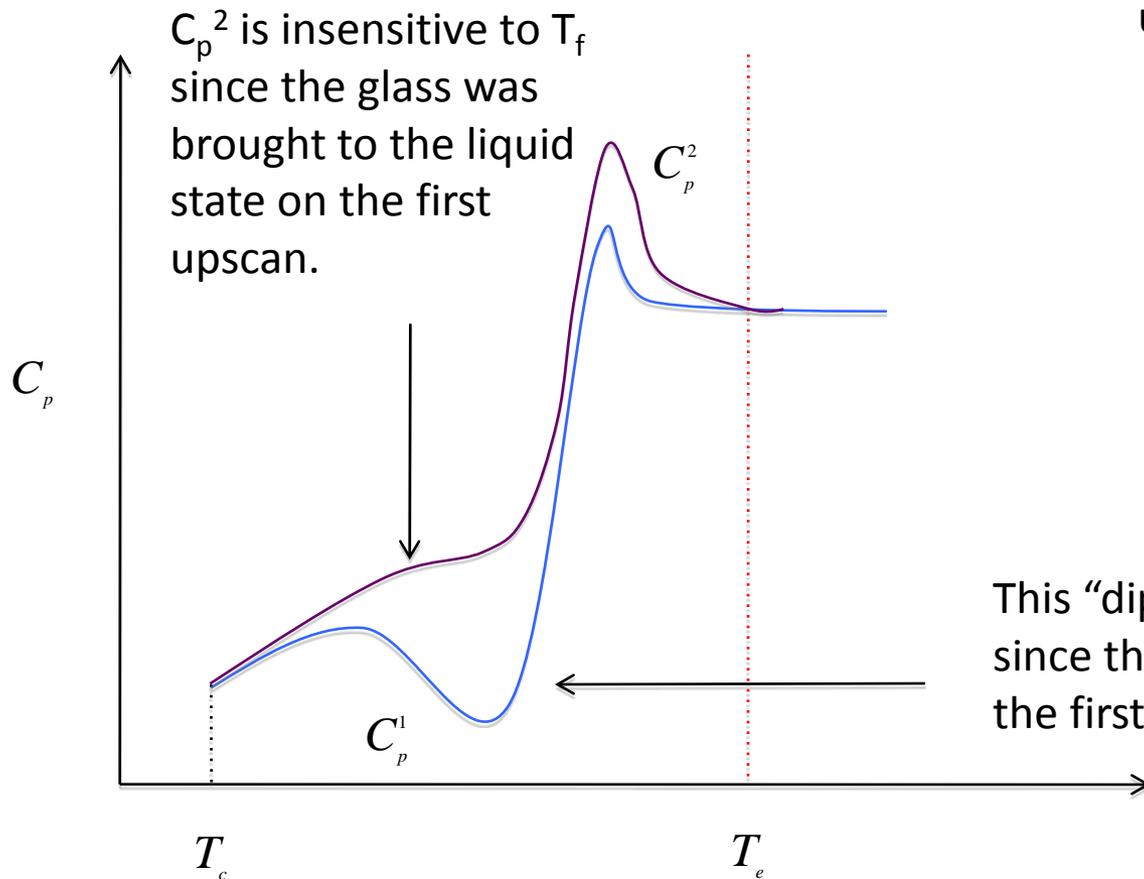
T_f



Applying Yue's technique is easy in practice. We'll set it up in steps. Why the technique works requires more effort. I'll explain what to do first before I give the explanation.

First, calculate the integral $A \equiv \int_{T_c}^{T_e} (C_p^2 - C_p^1) dT$

Clearly, this is just the area between the second and first upscans.



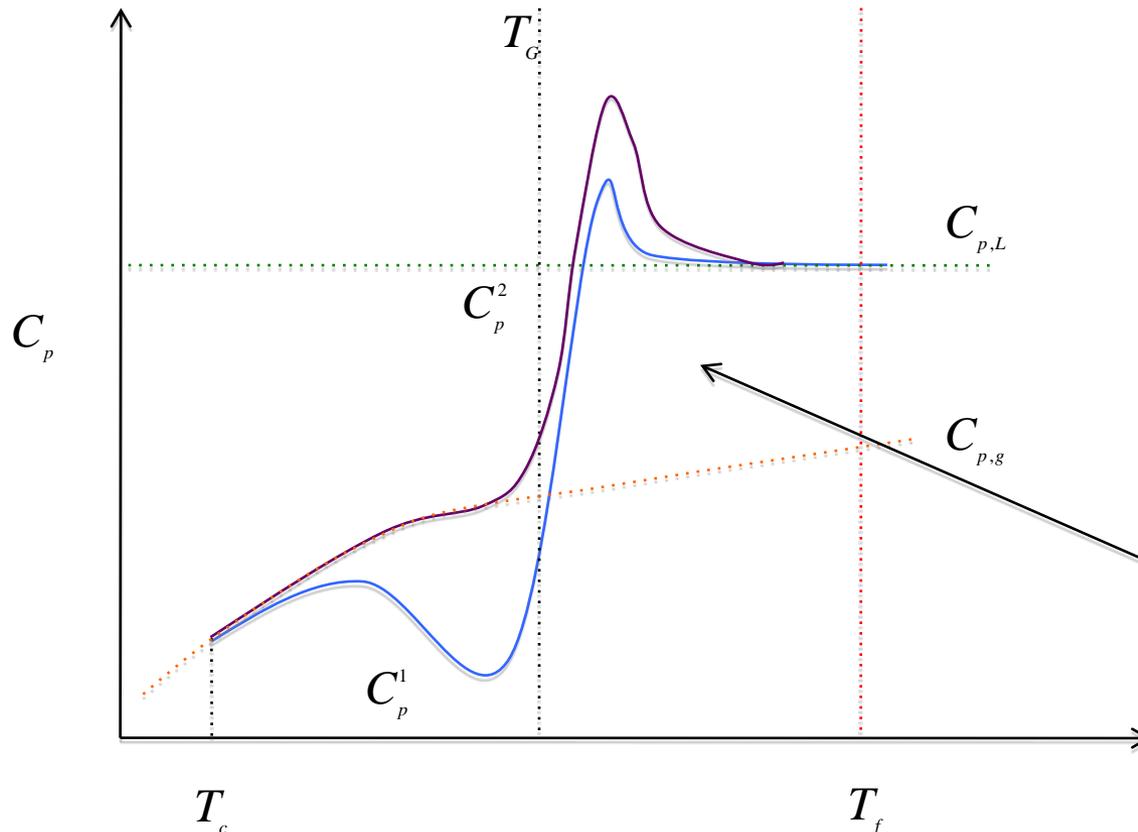
This "dip" will deepen if T_f is higher since the glass will relax more on the first upscan.

Second, calculate the integral $B \equiv \int_{T_g}^{T_f} (C_{p,L} - C_{p,g}) dT$

The $C_{p,g}$ is the C_p curve for the glass. It is found by extrapolating the C_p^2 curve before T_g . To extrapolate the $C_{p,g}$ curve use the following fit

$$C_{p,g} = a + bT + \frac{c}{T^2} + \frac{d}{T^{0.5}}$$

where the a, b, c and d are constants that must be determined experimentally



T_G is given by the following method. Find the inflection point on the C_p^2 curve and draw a tangent. The T at which it intercepts $C_{p,g}$ is T_g .

B is the area of this trapezoid

It turns out that integrals A and B are equal

$$A = B$$

$$\int_{T_c}^{T_f} (C_P^2 - C_P^1) dT = \int_{T_g}^{T_f} (C_{P,L} - C_{P,g}) dT$$

To find T_f , change the upper limit in the right integral until the two integrals are equal.
When they equal, that value is T_f !

WHY ????

To understand why these two integrals are equal, let's examine each integral separately. Start with B.

$$B \equiv \int_{T_g}^{T_f} (C_{P,L} - C_{P,S}) dT$$

Recall from previous lectures that $\alpha_p - \alpha_g = \alpha_s$ where $\alpha_p = C_p$ and $\alpha_g = C_g$ in our case. The structure/configuration of the liquid that is quenched will change from T_f to the T_g . Past T_g the relax times are too large for any appreciable relaxation to occur. Above T_f the liquid is still in equilibrium.

$$B \equiv \int_{T_g}^{T_f} C_{P,S} dT = \Delta H_{structure}$$

Further, $\Delta H = \Delta E + p\Delta V$ and most of ΔH comes from ΔE since ΔV is small compared so

$$\Delta H_{structure} \cong \Delta E_{structure}$$

Now let's consider the left integral A.

$$A \equiv \int_{T_c}^{T_f} (C_p^2 - C_p^1) dT$$

Below T_c both C_p^1 and C_p^2 are identical. Recall that the slopes of p vs T graphs for low T were all identical ! Above T_e , both C_p^1 and C_p^2 are identical since they are in the both liquids.

The vibrational contribution to C_p^1 and C_p^2 are identical at a given T. Therefore, the vibrational contributions cancel and all that is left is the contribution from structural changes. Note that if the upper limit of this integral was extended to T_f , the integral would not since $C_p^1 = C_p^2$ in the liquid region.

Therefore, A is also equal to $\Delta H_{\text{structure}}$.

$$\therefore A = B$$

Yue is very clever !

This is an active area of work !!!!!!!