Lecture 16:The Tool-Narayanaswamy-Moynihan Equation Part II and DSC

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First, let's review !

Narayanaswamy assumed that $M_p(t)$ obeys TRS.

$$\xi = \int_0^t \frac{\tau_r}{\tau_P\left[T(t')\right]} dt' = \tau_r \int_0^t \frac{dt'}{\tau_P\left[T(t')\right]}$$

↓

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

↓

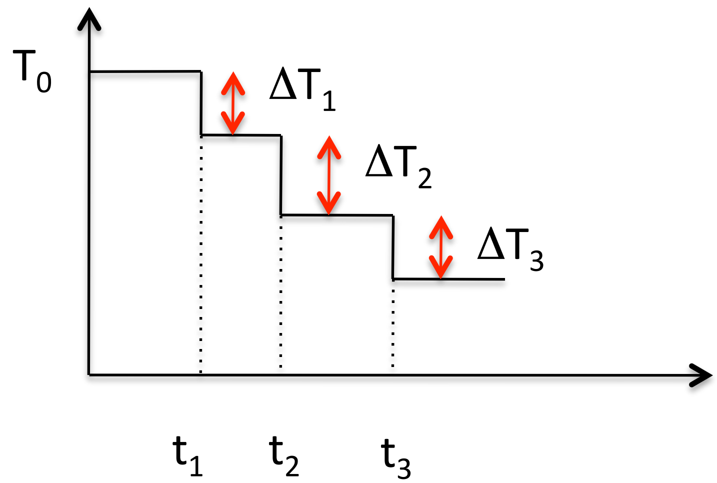
$$M_p(\xi) = \frac{T_f(\xi) - T_2}{T_1 - T_2}$$

↙ ↘

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

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

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



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

↓

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

↓

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

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

↓

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

↓

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

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

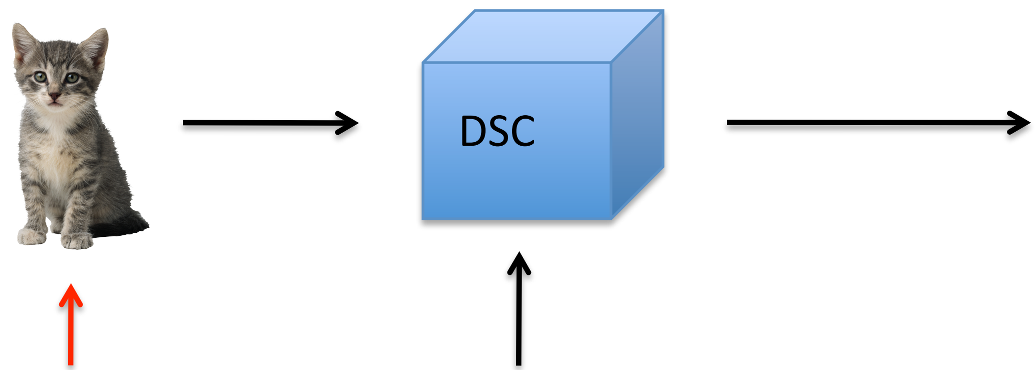
Arrhenius term   A T_f dependence just like Tool !

The Tool-Narayanaswamy-Moynihan equations are

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

and some form for τ_p such as $$\tau_p = \tau_0 \exp\left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f}\right]$$

<u>DSC: Differential Scanning Calorimetry as a "Black Box"</u>. 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.



$Q(t) \quad i.e. \; \frac{dQ}{dt}$

The output is the Q vs. t required to produce the specified T vs. t

Unknown sample

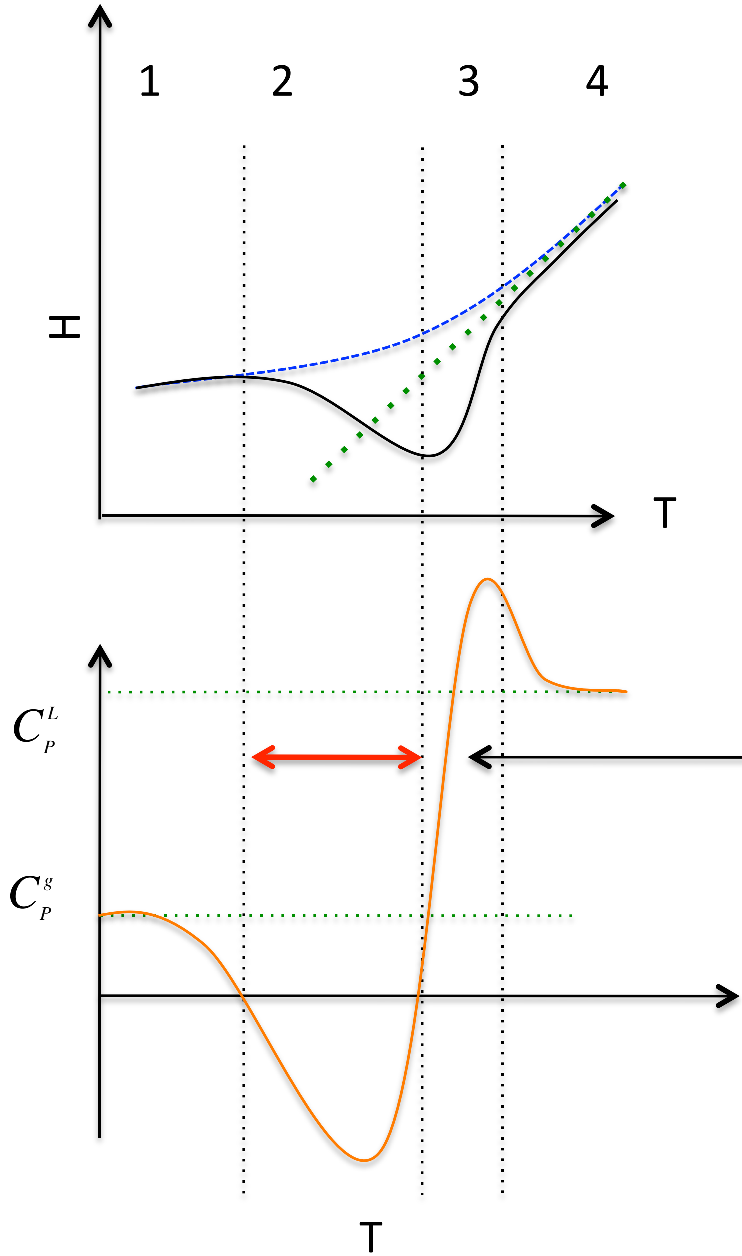
$T(t) \quad i.e. \; \frac{dT}{dt}$

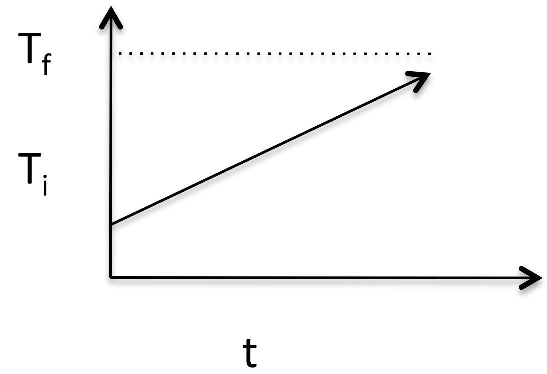
A given T vs. t is specified

The ratio of the output to input is

$$\frac{\frac{dQ}{dt}}{\frac{dT}{dt}} = \frac{dQ}{dT} = C_p$$

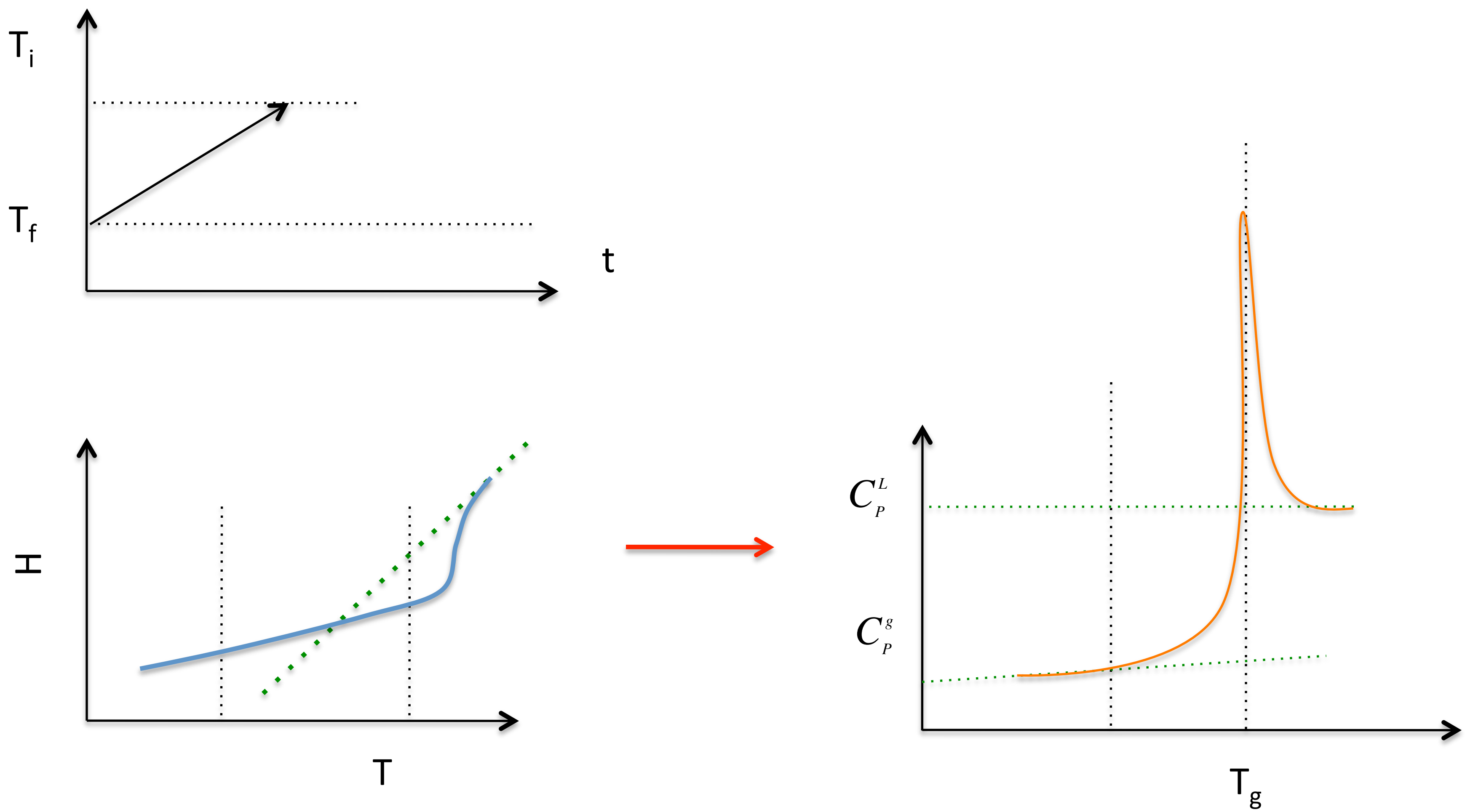
B) Linear heating a glass that was linearly cooled i.e. an " up scan"





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.

D) A linear up scan on an annealed glass

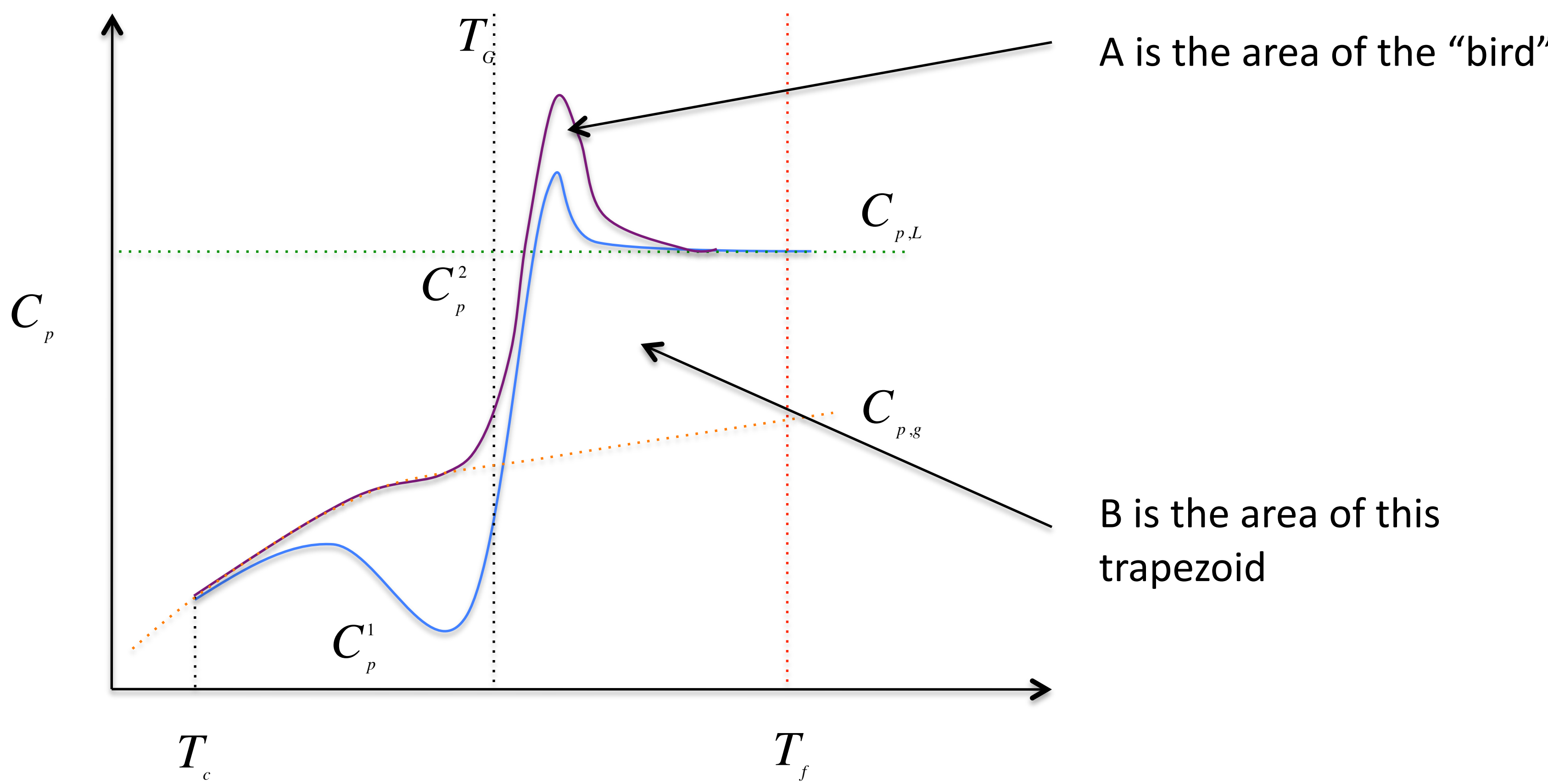


$$A = B$$

Y.Z. Yue Chemical Physics Letters **357** (2002) 20-24

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

Well worth reading !!



Pulling all of the pieces together !

Is there any deeper meaning to $T_f = T - \int_0^{\xi} M_p(\xi - \xi')\frac{dT}{d\xi'}d\xi'$?

What can we use for the response M_p. From experiments, M_p can be fit with a stretched exponent

$$M_p(\xi) = \exp\left(-\frac{\xi}{\tau_r}\right)^b$$

Let's substitute M_p into the T_f expression

$$T_f = T - \int_0^{\xi} M_p(\xi - \xi')\frac{dT}{d\xi'}d\xi' = T - \int_0^{\xi} \exp\left[-\left(\frac{\xi - \xi'}{\tau_p}\right)^b\right]\frac{dT}{d\xi'}d\xi'$$

Using the Prony series approximation to the stretched exponential, we obtain

$$T_f = T - \int_0^{\xi} \exp\left[-\left(\frac{\xi-\xi'}{\tau_p}\right)^b\right]\frac{dT}{d\xi'}d\xi' = T - \int_0^{\xi}\sum_{n=1}^{N} a_n \exp\left(-\left(\frac{\xi-\xi'}{\tau_n}\right)\right)\frac{dT}{d\xi'}d\xi'$$

$$T_f = T - \sum_{n=1}^{N} a_n \int_0^{\xi} \exp\left(-\left(\frac{\xi-\xi'}{\tau_n}\right)\right)\frac{dT}{d\xi'}d\xi' = T - \sum_{n=1}^{N} a_n \int_0^{\xi} e^{-\left(\frac{\xi-\xi'}{\tau_n}\right)}\frac{dT}{d\xi'}d\xi'$$

Recall that the a_n's sum to 1. We can then rewrite the above equation as

$$T_f = T - \sum_{n=1}^{N} a_n \int_0^{\xi} e^{-\left(\frac{\xi-\xi'}{\tau_n}\right)}\frac{dT}{d\xi'}d\xi' = \underbrace{\sum_{n=1}^{N} a_n}_{=1} T - \sum_{n=1}^{N} a_n \int_0^{\xi} e^{-\left(\frac{\xi-\xi'}{\tau_n}\right)}\frac{dT}{d\xi'}d\xi'$$

$$T_f = \sum_{n=1}^{N} a_n \left\{T - \int_0^{\xi} e^{-\left(\frac{\xi-\xi'}{\tau_n}\right)}\frac{dT}{d\xi'}d\xi'\right\}$$

$$T_f = \sum_{n=1}^{N} a_n \left\{ T - \int_0^{\xi} e^{-\left(\frac{\xi - \xi'}{\tau_n}\right)} \frac{dT}{d\xi'} d\xi' \right\}$$

Does this look familiar ?????

Look back at the last lecture

It is just Narayanaswamy's equation for a single τ_n which reduced to Tool's eq !!!!!

We now have N Tool equations. We have come back full circle.

Let's call the fictive temperature associated with each term in the { } $T_{f,n}$, so we now have

$$T_f = \sum_{n=1}^{N} a_n T_{f,n}$$

What is the meaning of this equation ? Each relaxation time τ_n has its own fictive temperature. T_f can be viewed as a weighted sum of the individual fictive temperatures for various relaxation process.

Is there anything else that we can obtain from DSC and compare with theoretical calculation ?

Yes! We can use DSC to measure dT_f/dT . We can then use TNM to T_f vs. t. If we know the cooling rate q = dT/dt then

$$\frac{dT_f}{dT} = \frac{dT_f}{dt}\frac{dt}{dT} = \frac{1}{q(t)}\frac{dT_f}{dt}$$

measure   calculate

How can we measure dT_f/dT from DSC ?

Moynihan was an expert at this !

We can define the fictive temperature in the following fashion

$$H(T) = H_{eq}(T_f) - \underbrace{\int_T^{T_f} C_{P,g}\, dT'}$$

Since $T < T_f$, H decreases by $C_{P,g}$.

In addition, we can write $H(T) = H_{eq}(T_0) + \int_{T_0}^{T} C_P\, dT'$ where T_0 is the initial T

Further, we can write the equilibrium $H_{eq}(T_f)$ as $H_{eq}(T_f) = H_{eq}(T_0) + \int_{T_0}^{T_f} C_{P,L}\, dT'$

Now substitute H(t) and $H_{eq}(T)$ into our top expression yields

$$H_{eq}(T_0) + \int_{T_0}^{T} C_P\, dT' = H_{eq}(T_0) + \int_{T_0}^{T_f} C_{P,L}\, dT' - \int_T^{T_f} C_{P,g}\, dT'$$

So we now have $\int_{T_0}^{T} C_P dT' = \int_{T_0}^{T_f} C_{P,L} dT' - \int_{T}^{T_f} C_{P,g} dT'$

If we now subtract $\int_{T_0}^{T} C_{P,g} dT'$ from both sides we obtain

$$\int_{T_0}^{T} C_P dT' - \int_{T_0}^{T} C_{P,g} dT' = \int_{T_0}^{T_f} C_{P,L} dT' - \int_{T}^{T_f} C_{P,g} dT' - \int_{T_0}^{T} C_{P,g} dT'$$

$$\int_{T_0}^{T} \left(C_P - C_{P,g} \right) dT' = \int_{T_0}^{T_f} C_{P,L} dT' - \int_{T}^{T_f} C_{P,g} dT' - \int_{T_0}^{T} C_{P,g} dT'$$

↑

split this integral into two pieces

Splitting the last integral on the right into two pieces gives

$$\int_{T_0}^{T}\left(C_P - C_{P,g}\right)dT' = \int_{T_0}^{T_f} C_{P,L}\,dT' - \int_{T}^{T_f} C_{P,g}\,dT' - \int_{T_0}^{T} C_{P,g}\,dT'$$

$$\int_{T_0}^{T}\left(C_P - C_{P,g}\right)dT' = \int_{T_0}^{T_f} C_{P,L}\,dT' - \int_{T}^{T_f} C_{P,g}\,dT' - \int_{T_0}^{T_f} C_{P,g}\,dT' - \int_{T_f}^{T} C_{P,g}\,dT'$$

switching the limits

$$-\int_{T_f}^{T} C_{P,g}\,dT' = \int_{T}^{T_f} C_{P,g}\,dT'$$

We now obtain $\displaystyle \int_{T_0}^{T}\left(C_P - C_{P,g}\right)dT' = \int_{T_0}^{T_f}\left(C_{P,L} - C_{P,g}\right)dT'$

Very soon we will see how Moynihan used this expression to find T_f.

But wait there's more !!!!!!!

Recall the fundamental theorem of calculus

$$F(x) = \int_a^x f(x)dx$$ where a is a constant

$$\frac{dF}{dx} = f(x)$$

What happens if F(x) is a composite function, i.e. F(g(x)) ?

$$F(g(x)) = \int_a^{g(x)} f(x)dx$$ Need to use the chain rule

$$\frac{dF(g(x))}{dx} = \frac{dF(g(x))}{dg(x)}\frac{dg}{dx} = f(g(x))\frac{dg}{dx}$$

Apply the fundamental theorem of calculus for a composite function to our expression

$$\int_{T_0}^{T} \left(C_P - C_{P,g}\right) dT' = \int_{T_0}^{T_f} \left(C_{P,L} - C_{P,g}\right) dT'$$

$$\left[C_p(T) - C_{P,g}(T)\right] = \left[C_{p,L}(T_f) - C_{P,g}(T_f)\right] \frac{dT_f}{dT}$$

$$\frac{dT_f}{dT} = \frac{\left[C_p(T) - C_{P,g}(T)\right]}{\left[C_{p,L}(T_f) - C_{P,g}(T_f)\right]}$$

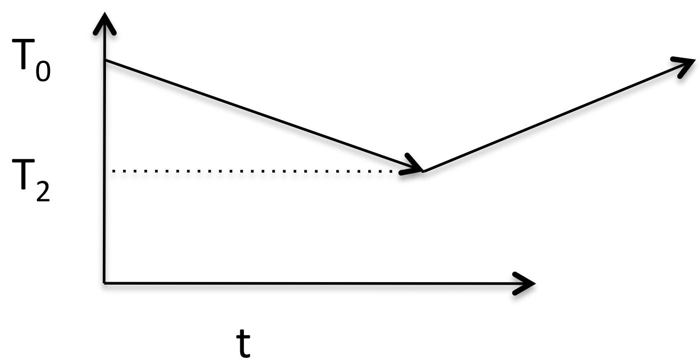
Using DSC you can measure every term on the right side

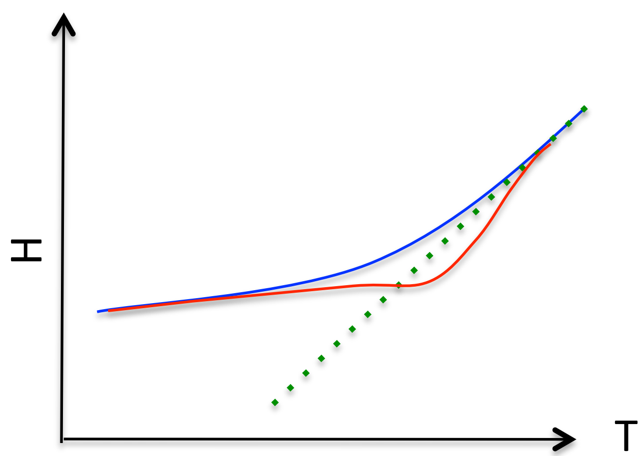
Calculate this with TNM eq.

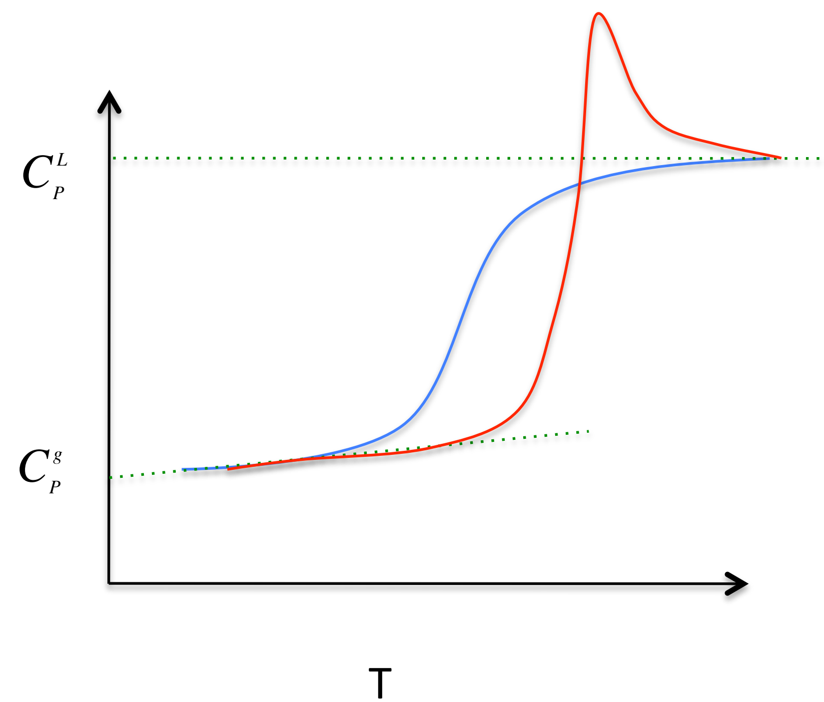
How did Moynihan use this expression to find T_f ?

$$\int_{T_0}^{T}\left(C_P - C_{P,g}\right)dT' = \int_{T_0}^{T_f}\left(C_{P,L} - C_{P,g}\right)dT'$$

Consider the C_p graph for a liquid that is cooled through the glass transition and then reheated through the glass transition. The H vs. T graphs and C_p vs T graphs are



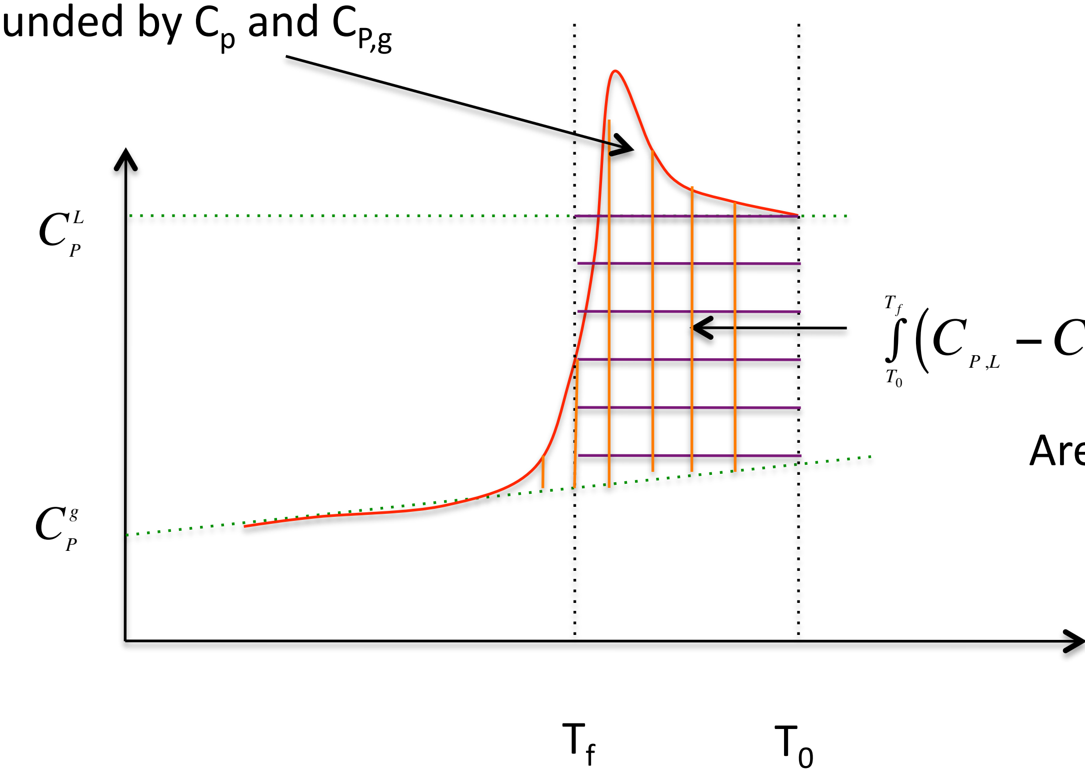




Moynihan's Method

orange $\int_{T_0}^{T}\left(C_P - C_{P,g}\right)dT'$

Area bounded by C_p and $C_{P,g}$



$\int_{T_0}^{T_f}\left(C_{P,L} - C_{P,g}\right)dT'$ *purple*

Area of the trapezoid

In Moynihan's method, T_f approaches a lower limit of T_g

In practice how do you solve the TNM equations

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

Assume some form for τ_P . Typically $\tau_P = \tau_0 \exp\left[\frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f}\right]$

Recall that the reduced time is given by $\xi = \int_0^t \frac{\tau_r}{\tau_P[T(t')]} dt' = \tau_r \int_0^t \frac{dt'}{\tau_P[T(t')]}$

Assume that M_p can be approximated by a stretched exponential $M_p(\xi) = \exp\left(-\frac{\xi}{\tau_r}\right)^b$

Rewrite the reduced time ξ in terms of T and the heating/cooling q = dT/dt

$$\xi = \tau_r \int_0^t \frac{dt'}{\tau_P} \longrightarrow \xi = \tau_r \int_0^t \frac{dt'}{\tau_P(T')}\frac{dT'}{dT'} = \tau_r \int_{T_0}^{T} \frac{dT'}{q\tau_P(T')}$$

If we have a function of ξ – ξ' as we do in M_p then

$$\xi - \xi' = \tau_r \int_{T_0}^{T} \frac{dT'}{q\tau_P(T')} - \tau_r \int_{T_0}^{T'} \frac{dT''}{q\tau_P(T'')}$$

$$\xi - \xi' = \tau_r \int_{T_0}^{T'} \frac{dT'}{q\tau_P(T')} + \tau_r \int_{T'}^{T} \frac{dT'}{q\tau_P(T')} - \tau_r \int_{T_0}^{T'} \frac{dT''}{q\tau_P(T'')} \longrightarrow \xi - \xi' = \tau_r \int_{T'}^{T} \frac{dT''}{q\tau_P(T'')}$$

split the integral

We now break up the T(t) into N section as $$T = T_0 + \sum_{i=1}^{N} \Delta T_i$$

The TNM eq. for T_f can now be written as

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

↓

$$T_f = T - \int_{T_0}^{T} M_p(\xi - \xi') dT$$

→

$$T_f = T - \int_{T_0}^{T} \exp\left[-\left(\frac{\xi - \xi'}{\tau_r}\right)^b\right] dT$$

↙

$$T_f = T - \sum_{i=1}^{N} \Delta T_i \exp\left[-\left(\frac{\xi - \xi'}{\tau_r}\right)^b\right]$$

→

$$T_f = T - \sum_{i=1}^{N} \Delta T_i \exp\left[-\left(\int_{T'}^{T} \frac{dT''}{q\tau_p(T'')}\right)^b\right]$$

$$\xi - \xi' = \tau_r \int_{T'}^{T} \frac{dT''}{q\tau_p(T'')}$$

Finally

$$T_f = T - \sum_{i=1}^{N} \Delta T_i \exp\left[-\left(\int_{T'}^{T} \frac{dT''}{q\tau_P(T'')}\right)^b\right]$$

$$T_f = T - \sum_{i=1}^{N} \Delta T_i \exp\left[-\left(\sum_{j=i}^{N} \frac{\Delta T_j}{q_j \tau_{P,j}}\right)^b\right]$$

The τ_p is tricky since it depends on T_f

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

Use the following cute trick with τ_p

If we break T into temperature steps that are small, it would not be unreasonable to assume that τ_p at temperature step i is very close in value to τ_p at temperature step i-1

So instead of writing t_p at temperature step i as

$$\tau_{P,i} = \tau_0 \exp\left[\frac{x\Delta H}{RT_i} + \frac{(1-x)\Delta H}{RT_{f,i}}\right]$$

We can write $\tau_{p,i}$ as $$\tau_{P,i} = \tau_0 \exp\left[\frac{x\Delta H}{RT_i} + \frac{(1-x)\Delta H}{RT_{f,i-1}}\right]$$

This is fine since we need to know the initial condition of T_f i.e. $T_f(0) \rightarrow T_{f,0}$ = a given.

We need to take smaller and smaller ΔT until this approximation as no effect.

So what do we need to actually do a TNM calculation ?

We need 4 parameters: b for the stretched exponential $M_p(\xi) = \exp\left(-\frac{\xi}{\tau_r}\right)^b$

where $\xi = \tau_r \int_0^t \frac{dt'}{\tau_P[T(t')]}$

and τ_o, x, and ΔH for $\tau_{P,i} = \tau_0 \exp\left[\frac{x\Delta H}{RT_i} + \frac{(1-x)\Delta H}{RT_{f,i-1}}\right]$

We also need the thermal path, T(t), and the initial value $T_f(0)$.

Then use Excel or some other program to iterate $T_f = T - \sum_{i=1}^{N} \Delta T_i \exp\left[-\left(\sum_{j=i}^{N} \frac{\Delta T_j}{q_j \tau_{P,j}}\right)^b\right]$

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

Finally an application !!

It is well known that the index of refraction of glasses, n, varies with the cooling rate. Recall the Ritland and Napolitano and Spinner experiments.

Further, it has been empirically determined that n depends on the prior cooling rate in the following fashion.

$$n_d(h_X) = n_d(h_0) + m_{n_d} \ln\left(\frac{h_x}{h_0}\right)$$

where h_X and h_0 are two different cooling rates and m_{nd} is typically a negative constant.

Can TNM shed any insight into this expression ?

What assumptions did they make ?

Over the visible range, the index of refraction will have a strong density dependence. Assume that the density is a linear function of the fictive temperature T_f. Further, assume that there is only one univerisal T_f for the enthalpy, density and n.

$$n(\lambda) = n(\lambda)_{ref} + \frac{\partial n(\lambda)}{\partial T_f}\left(T_f - T_{f,ref}\right)$$

How can we calculate T_f ?

Ref: U. Fotheringham et al. "*Refractive Index Drop Observed After Molding of Optical Elements: A Quantitative Understanding Based on the Tool-Narayanswamy-Moynihan Model," J. Am. Ceram. Soc.*, [**3**] 780-783 (2008)

Ref: U. Fotheringham et al. "*Evaluation of the Calorimetric Glass Transition of Glasses and Glass Ceramics with Respect to Structural Relaxation and Dimensional Stability," Thermochimica Acta*, **461** [1-2] 72-81 (2007)

Use TNM

$$T_f(t) = T(t) - \int_0^{\varsigma} \frac{dT}{d\varsigma'} \exp\left[-(\varsigma - \varsigma')^b\right] d\varsigma' \qquad \text{where} \qquad \varsigma = \int_0^t \frac{dt'}{\tau(t')}$$

and $$\tau\left[T(t), T_f(t)\right] = \tau_0 \exp \frac{H}{R}\left[\frac{x}{T(t)} + \frac{1-x}{T_f(t)}\right]$$

The parameters used for one glass are

- x =0.789
- t_0 = 1.68 x 10^{-46}s
- H/k = 84396.5
- b = 0.656

The boundary condition they use it T = T_f above the glass transition.

Some results !

Two different glasses. Each glass was taken through two different cooling rates.

glass 1 glass 2

$$\frac{dT_F}{dT}$$

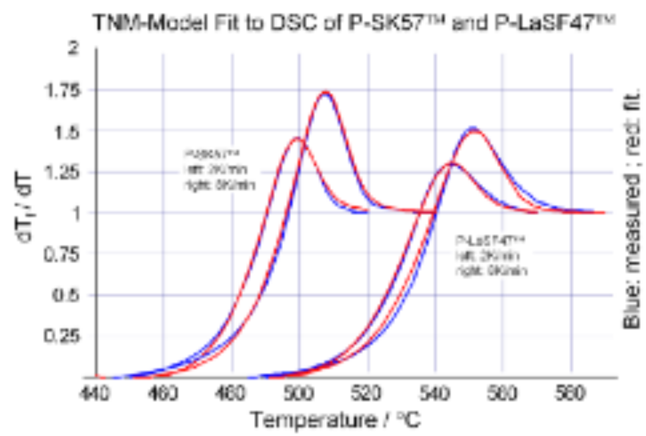


Fig. 3. Differential Scanning Calorimetry (DSC) curves for P-SK57™ and P-LaSF47™ and the fit of the Tool–Narayanaswamy–Moynihan (TNM model) parameters.

A comparison of DSC with TNM. Excellent agreement !!!!

more results

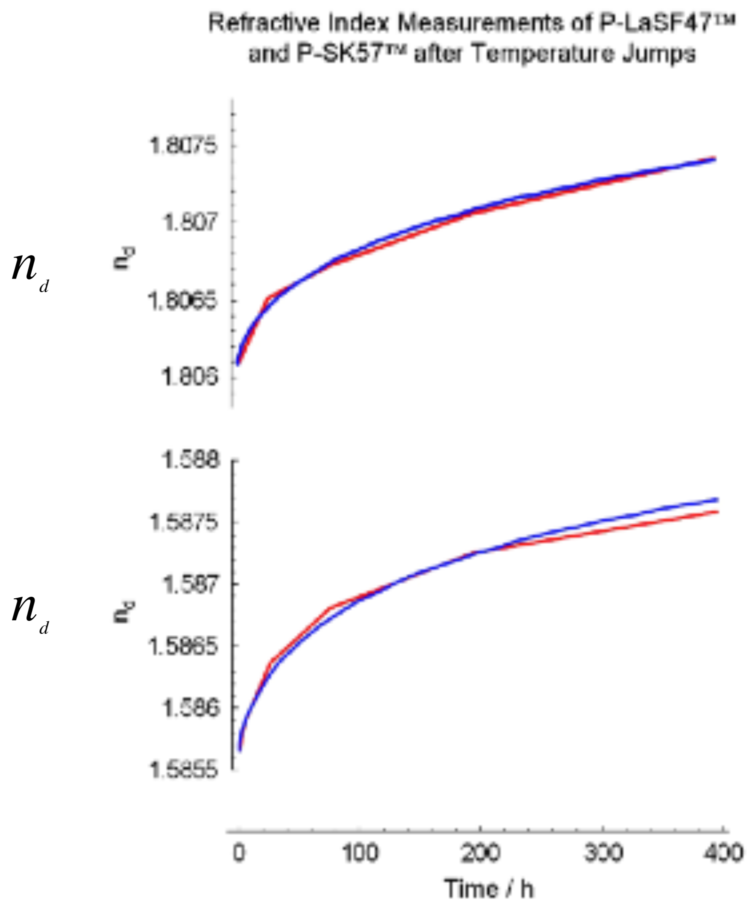


Fig. 4. Measured and simulated refractive indices (n_d) during the temperature jump experiments on P-LaSF47™ (top) and P-SK57™.

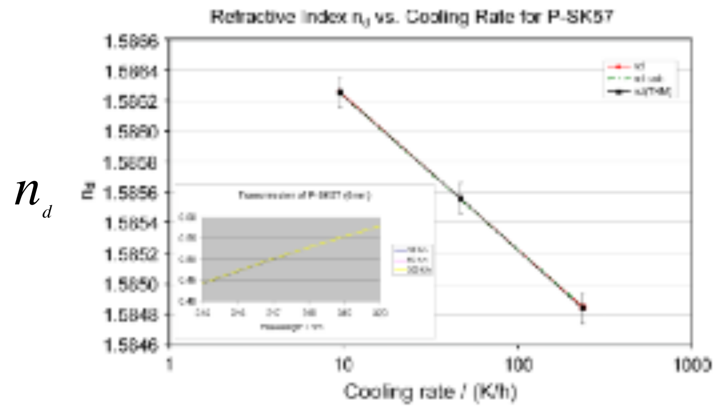


Fig. 6. Results of constant rate cooling experiments for P-SK-57™. Tool–Narayanaswamy–Moynihan (TNM model) parameters.

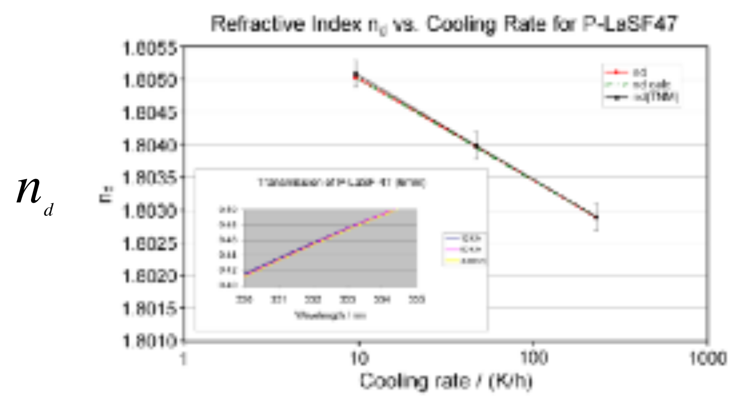


Fig. 5. Results of constant cooling rate experiments on P-LaSF47™. Black: simulated refractive indices. Black error bars: simulation error caused by the $\partial n_d/\partial T_f$ error. Red: measured values. Red error bars: precision of the refractometer used. Green dashed line: best linear fit of measured values on a logarithmic scale. Insertion: position of the UV absorption edge.

Thank You !

Any questions ?