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.

\[
\xi = \int_0^r \frac{\tau}{\tau_p[T(t')]} dt' = \tau \int_0^r \frac{dt'}{\tau_p[T(t')]} 
\]

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

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

\[
p(T_2, \xi) = p(T_2, \infty) - \alpha \Delta TM_p(\xi) \\
T_f(\xi) - T_2 = -M_p(\xi)\Delta T
\]
\[ T = T_0 + \Delta T_1 + \Delta T_2 + \ldots + \Delta T_N = T_0 + \sum_{i=1}^{N} \Delta T_i \]

\[ p(T_2, \xi) = p(T_2, \infty) - \alpha s \Delta T M_p(\xi) \]

\[ p(T, \xi) = p(T, \infty) - \sum_{i=1}^{N} \alpha s M_p(\xi - \xi_i) \frac{\Delta T(\xi)}{\Delta \xi_i} \Delta \xi_i \]

\[ p(T, \xi) = p(T, \infty) - \int_{\xi_i}^{\xi} \alpha s M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi' \]

\[ T_f(\xi) - T_2 = -M_p(\xi) \Delta T \]

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

\[ T_f = T - \int_{\xi_i}^{\xi} M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi' \]
\[ \tau_p = \tau_0 \exp \left[ \frac{x\Delta H}{RT} + \frac{(1-x)\Delta H}{RT_f} \right] \quad \text{where } 0 < x < 1 \]

Arrhenius term \quad A T_f \text{ dependence just like Tool !}

The Tool-Narayanaswamy-Moynihan equations are

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

and some form for \( \tau_p \) 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.

![Diagram of DSC process]

- **Unknown sample**
- **$T(t)$** (i.e. $\frac{dT}{dt}$)
- **A given $T$ vs. $t$ is specified**

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

The ratio of the output to input is

$$\frac{dQ}{dt} = \frac{dQ}{dT} = C_p$$
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
\[ A = B \]

\[
\int_{T_c}^{T_f} (C_p^2 - C_p^1) dT = \int_{T_c}^{T_f} (C_{p,L} - C_{p,g}) dT
\]


Well worth reading !!

A is the area of the “bird”

B is the area of this trapezoid
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

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

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

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

\[
T_f = T - \sum_{n=1}^N a_n \int_0^\xi e^{-\frac{\xi - \xi'}{\tau_n}} d\xi = \sum_{n=1}^N a_n T - \sum_{n=1}^N a_n \int_0^\xi e^{-\frac{\xi - \xi'}{\tau_n}} d\xi
\]

\[
= 1
\]

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

Does this look familiar ????

Look back at the last lecture

It is just Narayanaswamy’s equation for a single \( \tau_n \) 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 \( \tau_n \) 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

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

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

\[
H(T) = H_{eq}(T_f) - \int_{T}^{T_f} C_p \, dT'
\]

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

\[
\int_{T_0}^{T} C_p \, dT' - \int_{T_0}^{T_f} C_{p,g} \, dT' = \int_{T_0}^{T_f} C_{p,L} \, dT' - \int_{T}^{T_f} C_{p,g} \, dT' - \int_{T_0}^{T} C_{p,g} \, dT'
\]

\[
\int_{T_0}^{T} (C_p - C_{p,g}) \, dT' = \int_{T_0}^{T_f} C_{p,L} \, dT' - \int_{T}^{T_f} C_{p,g} \, dT' - \int_{T_0}^{T} C_{p,g} \, dT'
\]

split this integral into two pieces
Splitting the last integral on the right into two pieces gives

\[ \int_{T_0}^{T_f} \left( C_p - C_{p,g} \right) dT' = \int_{T_0}^{T_f} C_{p,L} dT' - \int_{T_0}^{T_f} C_{p,g} dT' - \int_{T_0}^{T_f} C_{p,g} dT' \]

Switching the limits

\[ -\int_{T_f}^{T_0} C_{p,g} dT' = \int_{T_f}^{T_0} C_{p,g} dT' \]

We now obtain

\[ \int_{T_0}^{T_f} \left( C_p - C_{p,g} \right) dT' = \int_{T_0}^{T_f} \left( C_{p,L} - C_{p,g} \right) dT' \]

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

\[ F(x) = \int_a^x f(x) \, dx \quad \text{where a is a constant} \]

\[ \frac{dF}{dx} = f(x) \]

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

\[ F(g(x)) = \int_a^{g(x)} f(x) \, dx \quad \text{Need to use the chain rule} \]

\[ \frac{dF(g(x))}{dx} = \frac{dF(g(x))}{dg(x)} \frac{dg}{dx} = f(g(x)) \frac{dg}{dx} \]
Apply the fundamental theorem of calculus for a composite function to our expression

\[
\int_{T_0}^{T_f} \left( C_p - C_{p,g} \right) dT' = \int_{T_0}^{T_f} \left( C_{p,l} - C_{p,s} \right) dT'
\]

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

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

Using DSC you can measure every term on the right side

Calculate this with TNM eq.
How did Moynihan use this expression to find $T_f$?

$$\int_{T_0}^{T_f} (C_P - C_{P,g})dT' = \int_{T_0}^{T_f} (C_{P,L} - C_{P,g})dT'$$

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

\[ \int_{T_0}^{T_f} (C_p - C_{p,g}) \, dT' \]

Area bounded by \( C_p \) and \( C_{p,g} \)

In Moynihan’s method, \( T_f \) approaches a lower limit of \( T_g \)
In practice how do you solve the TNM equations

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

Assume some form for \( \tau_p \). 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 \( \xi = \int_0^r \frac{\tau_r}{\tau_p [T(t')]} dt' = \tau \int_0^r \frac{dt'}{\tau_p [T(t')]} \)

Assume that \( M_p \) can be approximated by a stretched exponential \( M_p (\xi) = \exp \left( -\frac{\xi}{\tau} \right)^b \)
Rewrite the reduced time $\bar{\xi}$ in terms of $T$ and the heating/cooling $q = dT/dt$

$$\bar{\xi} = \tau_r \int_0^{\tau_r} \frac{dt'}{\tau_p(T')} \frac{dT'}{dT'} = \tau_r \int_0^{\tau_r} q \tau_p(T')$$

If we have a function of $\bar{\xi} - \bar{\xi}'$ as we do in $M_p$ then

$$\bar{\xi} - \bar{\xi}' = \tau_r \int_0^{\tau_r} \frac{dT'}{q \tau_p(T')} - \tau_r \int_0^{\tau_r} \frac{dT''}{q \tau_p(T'')}$$

$$\bar{\xi} - \bar{\xi}' = \tau_r \int_0^{\tau_r} \frac{dT'}{q \tau_p(T')} + \tau_r \int_0^{\tau_r} \frac{dT'}{q \tau_p(T')} - \tau_r \int_0^{\tau_r} \frac{dT''}{q \tau_p(T'')}$$

split the integral

$$\bar{\xi} - \bar{\xi}' = \tau_r \int_0^{\tau_r} \frac{dT''}{q \tau_p(T'')}$$
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

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

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

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

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

$$T_f = T - \sum_{i=1}^{N} \Delta T_i \exp \left[ -\left( \int_{T_0}^{T} \frac{dT''}{q\tau_p(T''')} \right)^b \right]$$

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

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

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

The \( \tau_p \) 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 $\tau_p$

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

So instead of writing $t_p$ at temperature step $i$ as

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

We can write $\tau_{p,i}$ as

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

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

We need to take smaller and smaller $\Delta T$ 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 \( \tau_0, x, \) and \( \Delta H \) for

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

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

\[
p(T, \xi) = p(T, \infty) - \int_0^\xi \alpha M_\cdot (\xi - \xi') \frac{dT}{d\xi'} d\xi'
\]

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.

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

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 universal $T_f$ for the enthalpy, density and $n$.

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

How can we calculate $T_f$?


Use TNM

\[ T_f(t) = T(t) - \int_0^t \frac{dT}{d\zeta'} \exp \left[ -(\zeta - \zeta')^b \right] d\zeta' \]

where \( \zeta = \int_0^t \frac{dt'}{\tau(t')} \)

and

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

The parameters used for one glass are:

\[
\begin{align*}
\text{x} &= 0.789 \\
\text{t}_0 &= 1.68 \times 10^{-46} \text{s} \\
\text{H/k} &= 84396.5 \\
\text{b} &= 0.656
\end{align*}
\]

The boundary condition they use is \( T = T_f \) above the glass transition.
Some results!

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

```
glass 1        glass 2
```

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. 5. Results of constant cooling rate experiments on P-LaSF47™. Black: simulated refractive indices. Black error bars: simulation error caused by the $\bar{\sigma}_o(\bar{\sigma}_T)$ 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. Inset: position of the UV absorption edge.

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

Any questions?