Project Report

Modelling non-monotonic relaxation behaviour in biopolymers

RRI

Submitted By

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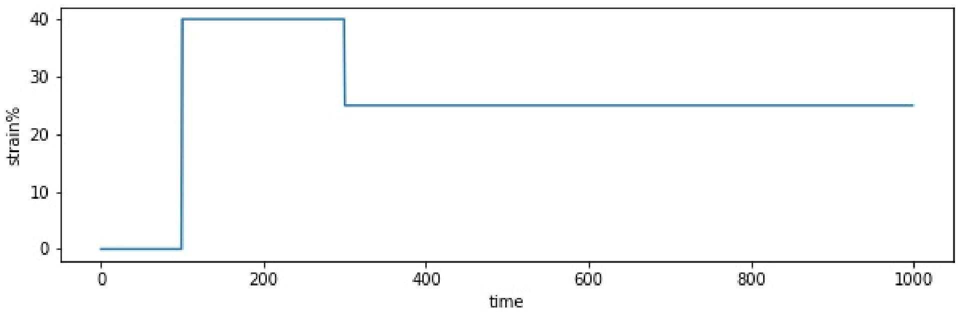
Contents

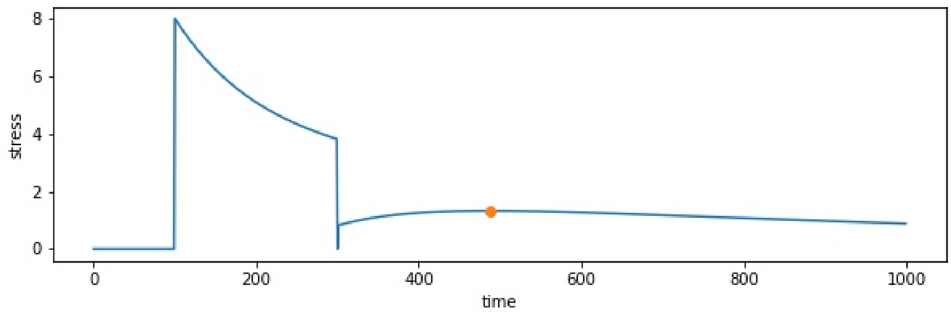
1 Working of system

1.1 Stress Relaxation

We begin our simulation experiments by subjecting a viscoelastic sample (like collagen) to a mechanical strain of value γ. After time *tw*, the strain is decreased by an amount $\Delta\gamma$ to get a resultant strain of $\gamma - \Delta\gamma$. The first graph, strain v/s time, demonstrates how strain is applied to the system.
The second graph shows how the stress response is built up in the sample. The stress tends to slowly reach an equilibrium value when the system is left undisturbed.



Applied strain with time



Resultant stress relaxation with time

In the above plots, we have applied a strain of 40% for a wait time of 200s. The strain is then reduced by 15% to a resultant strain of 25%.
The simulation is modelled using viscoelastic parameters. When the strain of 40% is first applied at 100s, the elastic part tries to reach maximum stress instantaneously, but the viscous part slowly brings the stress down exponentially (to approach an equilibrium value). When the strain is reduced after a waiting time of 200s, we see at 300s the elastic part decreases instantaneously but the viscous parts are slower to respond. Depending on their value before the strain drop, we may observe a peak as shown, after which the system relaxes to equilibrium.
This behaviour of the sample to slowly return to an equilibrium value after a sudden strain change is known as relaxation, and is a result of its viscoelastic properties. We call this plot a relaxation curve. However, the relaxation is not monotonic in nature - it seems to sometimes show an increase in stress and then a subsequent decrease to equilibrium. This deviation from the expected exponential behaviour to form a peak is counter-intuitive and will be explored in this report.

1.2 Parameters

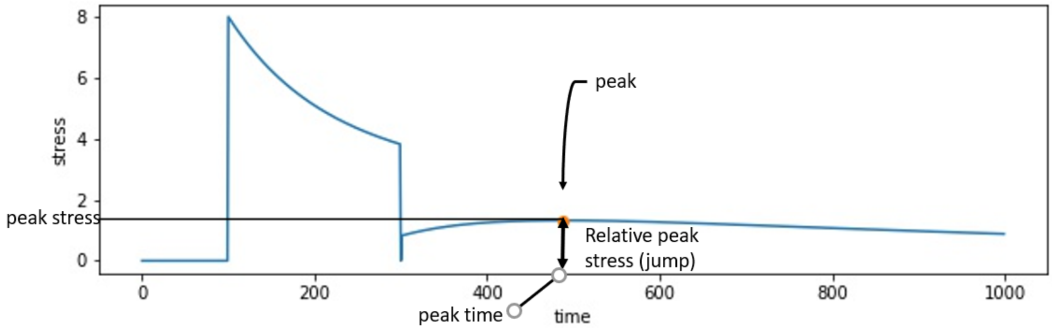
From the obtained relaxation curve, we can point out certain observed parameters of relaxation.

1. **Peak time** The time taken from the drop in strain to form a peak

2. **Peak stress** The absolute value of shear stress at the top of the formed peak

3. **Relative peakstress** The relative value of shear stress at the top of the peak, measured from the base value of stress (at the time the strain is dropped). This is the net value of the *jump*.

These parameters are pointed out in the plot below.



Parameters in peak formed during stress relaxation

2 Relaxation of collagen

2.1 Memory effect in collagen

In our analysis, we notice that if we strain the system for a longer time, the peak takes longer to form as well.The relationship between peaktime (tp) and waittime (tw) seems to be proportional. The system behaves like it ”remembers” for how long the strain had been applied. Thus, we explore the memory effects in collagen.

Kovacs effect

In the 1960s, Kovacs and group noticed that certain polymeric materials, when heated to a high temperature and then cooled to an intermediate temperature, allowing the volume to pass to an equilibrium value, the volume would instead increase to a maximum above the equilibrium value to form a peak, and then relax. This non-monotonic relaxation behaviour was striking because it indicates that the system is composed of several different states (or modes) which all relax with different relaxation times. *[1]*
It is also known as the crossover effect since the dependent quantity (volume) crosses above the equilibrium value before returning back.
We observe similar effects in our experiments with collagen, which is also a polymer. In our case, we apply strain and reduce it to an intermediate value. The resultant stress relaxes to equilibrium after increasing to a maximum and forming a peak.
This is typical of ”memory effects” of a system, wherein the subsequent behaviour depends not only on the present state, but also its history (in our case, waittime). *[2]*
Kovacs effect is a memory of ”duration”. The time-dependent evolution of the system depends on a single parameter of the history. *[3]*

Memory effect in other systems

The Kovacs effect can be observed in different types of systems, where a certain parameter is changed and in the short term, the system behaves in the opposite manner to what is expected. This is due to the ”memory” of the previous state of the system. Non-monotonic effects of relaxation as result of different modes can be observed in the behaviour of other systems.

- A crumpled sheet of Mylar is one such system. When the sheet is compressed to a small volume and allowed to expand slightly, the force that the sheet exerts on the compressing lid first increases and then decreases. It was also found that the time taken to reach peak force is proportional to the amount of time the sheet was compressed for (waiting time). ‘
- Frictional surfaces demonstrate relaxation behaviour similar to Kovacs effect. The area of contact between two materials first decreases before increasing when a constant load is dropped, thus indicating that a frictional surface may exhibit glassy dynamics.*[4]*
- When a system comprised of a granular material is set to a vibrational intensity which is then decreased, exhibits a rise in the packing fraction (unexpectedly becomes denser) before relaxing to a lower value at equilibrium. *[5]*

2.2 Non-monotonicity

The peak formation in our sample goes against intuition, wherein we expect the system to relax exponentially towards an equilibrium value. However, in several cases, we observe a peak that forms before an exponential relaxation.
This peak is attributed to the system having several ”modes” of relaxation. That is, the system is comprised of different modes which all relax at different rates. The observed relaxation curve is the resultant of all such modes of the system. Thus, when some modes are increasing in stress and others are decreasing, we might find a peak in the value of stress.

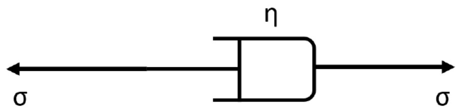
3 Theory

This section explains the theory that drives the simulation algorithm.
When a material under a deforming force exhibits properties of both viscous and elastic materials, it is known as a viscoelastic material. The samples used experimentally are viscoelastic in nature, hence as a starting point we explore basic models of viscoelasticity.

3.1 Viscoelastic models

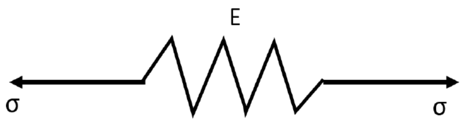
We discuss one-dimensional linear viscoelastic models. Each model has two main components.

1. **Viscous part** - We use a perfectly viscous dashpot, with a viscosity coefficient η. An applied stress of σ causes the strain ϵ to increase linearly by the relationship $\dot{\epsilon} = \frac{1}{\eta}\sigma$.



Viscous dashpot

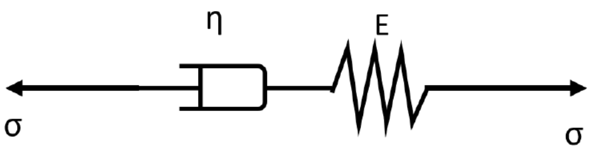
2. **Elastic part** - We use a perfectly elastic spring, with an elasticity modulus G. An applied stress of σ will cause the strain ϵ to respond instantaneously, by the relation $\epsilon = \frac{1}{G}\sigma$



Elastic spring

3.2 Maxwell model

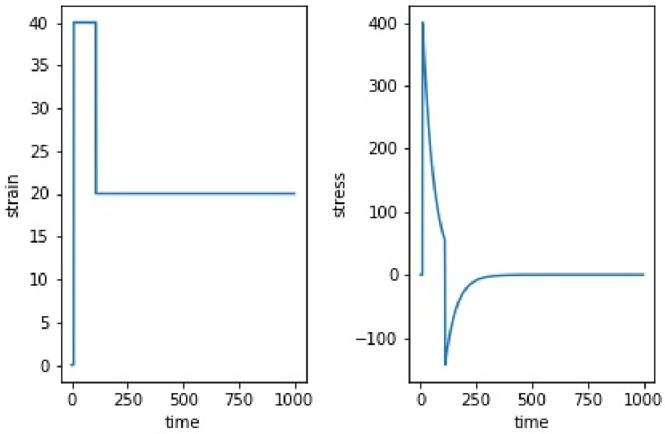
A linear combination of spring and a dashpot is called a Maxwell element. The viscoelastic equation of a Maxwell element is $\sigma + \frac{\eta}{E}\dot{\sigma} = \eta\dot{\epsilon}$.
A Maxwell element is shown below.



Single Maxwell element

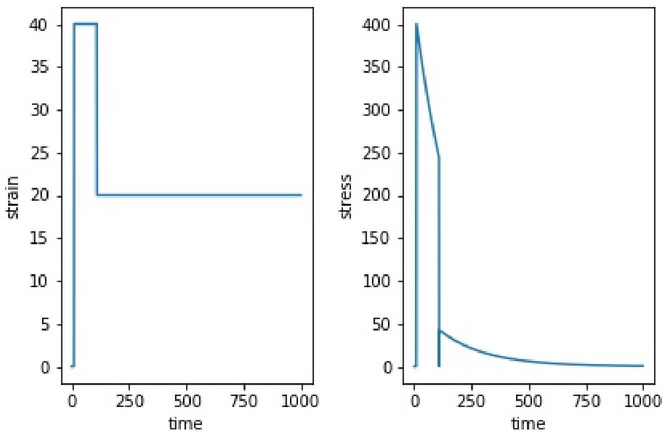
Since a Maxwell element responds to an applied strain by relaxing exponentially, with a relaxation time $T = \frac{\eta}{G}$, we use Maxwell elements as the basis for our model. We use two or three elements with different relaxation times, so that the combination may result in a non-monotonic relaxation curve and consequently, a peak.
Each Maxwell element represents a "mode" of the system.
Here we see how a Maxwell element responds to a decrease in the applied strain, which is applied for a particular wait time tw. Depending on the value of relaxation time, we can have two cases.

- $T < tw$ - If the relaxation time T is small, the element has already relaxed by the time the strain is reduced. Here tw = 100s and T = 50s.



One element model, $T < tw$

- $T > tw$ - If the relaxation time T is large, the element has not yet relaxed by the time the strain is reduced. Hence it continues to relax. Here tw = 100s and T = 200s.

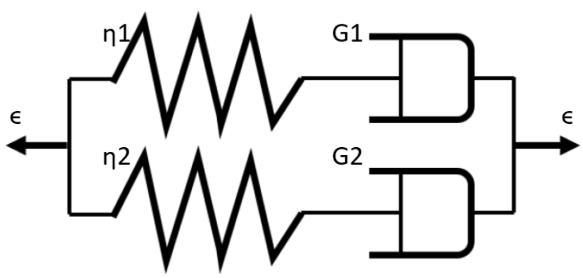


One element model, $T > tw$

However, neither of these cases gives rise to a peak.
Since a peak is formed due to non-monotonicity, we require Maxwell elements with stresses in different directions - at least one increasing and one decreasing. Hence we begin with two Maxwell elements to observe a peak.

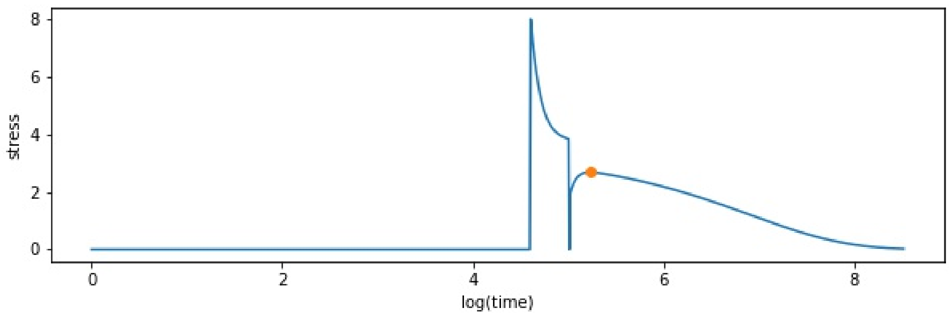
3.3 Two element Maxwell model

Two Maxwell elements kept in parallel form a two element Maxwell model. A strain of ϵ is applied to the system. Each Maxwell element has a different relaxation time, T1 = η1/G1 and T2 = η2/G2 respectively. Hence each element, called a mode of the system, relaxes at different speeds.

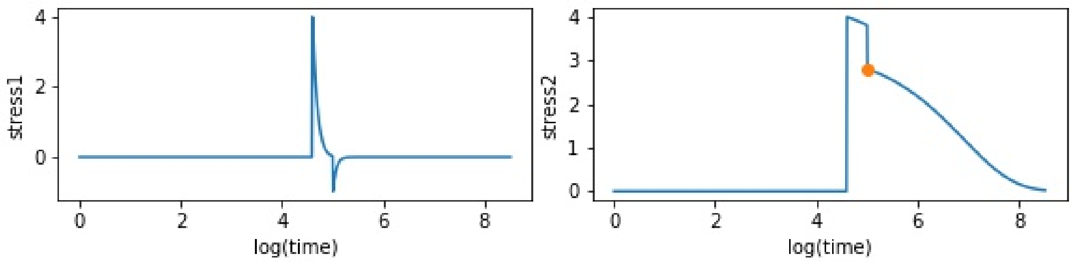


Two element Maxwell model

We can obtain a peak formation if T1 < tw and T2 > tw (or vice versa). We assume $T1 < tw < T2$. We would expect T1 to completely relax before the wait time is over.
Below we can see the relaxation of the individual elements and how they give rise to the peak. The figures are in logarithmic scale of time to view the peaks more clearly.



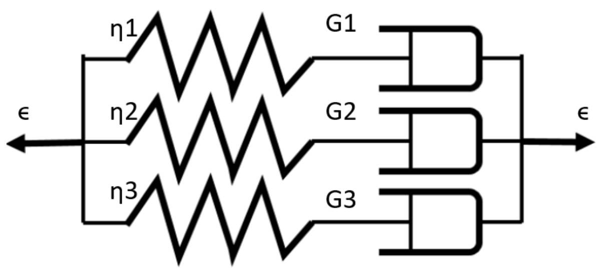
Two element model peak formation, tw = 50s



T1 is 10s and T2 is 1000s

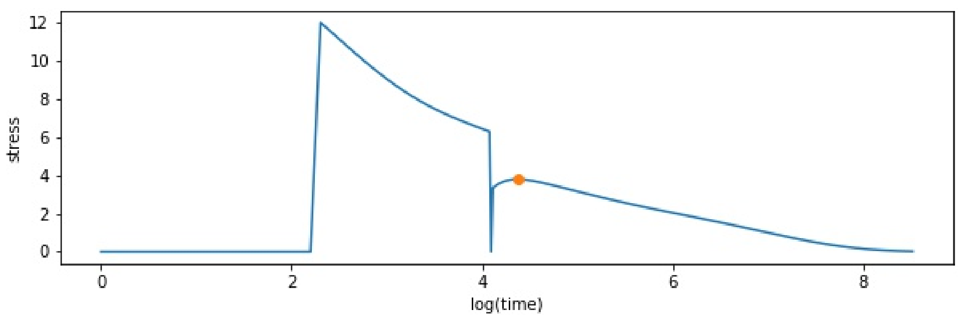
3.4 Three element Maxwell model

Three Maxwell elements in parallel are used as shown.

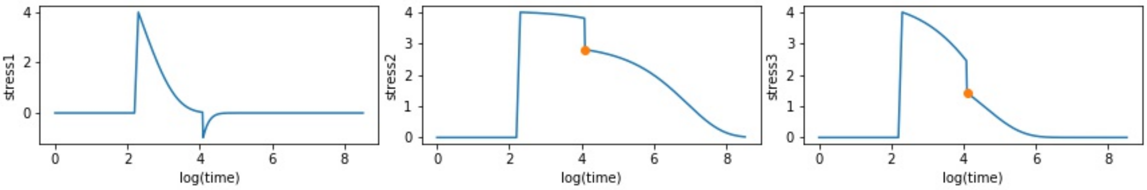


Three element Maxwell model

Once again, we keep $T1 < tw < T2$ and any value of T3 between T1 and T2 and observe the peak formation.



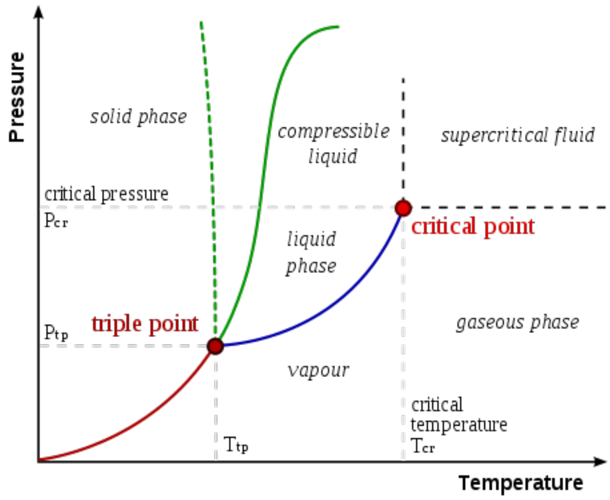
Three element model peak formation, tw = 50s



T1 is 10s, T2 is 1000s and T3 is 100s

4 Phase Diagrams

Phase diagrams are graphical representations of the parameter space of a system. Moving in a particular direction within the phase diagram, we will be able to observe how the state of the system varies.
A popular example of a phase diagram is that of the physical state of water, as shown.



Phase diagram of water (Wikipedia)

Here, the parameters that are controlled are pressure and temperature. One can find the value of the dependent parameter, volume, for each combination of pressure and temperature by simply looking at the diagram.
To construct our phase diagram, we list out parameters that can be controlled by an experimenter and the parameters that change as a result.

- Independent Parameters
  1. Wait time
  2. Applied strain
  3. Change in strain
  4. Relaxation time of third element
- Dependent Parameters
  1. Peaktime
  2. Peakstress
  3. Relative peakstress (jump)

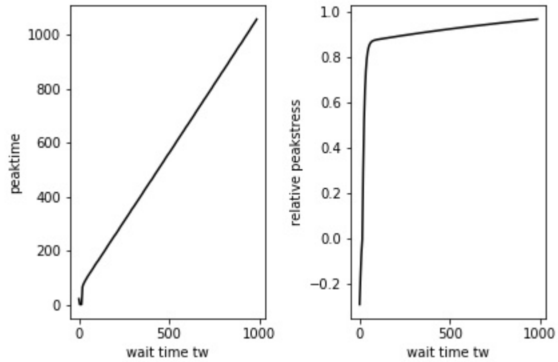
To construct phase diagrams based on the relaxation curves, we select two independent parameters that we can vary and find how a specific dependent parameter (either peaktime or relative peakstress) varies with respect to the other two parameters.

4.1 Varying strain drop

In this case, for a particular value of change in strain $\Delta\gamma$, we find how the dependent parameters vary with the wait time. This is done for both two and three element models.
In either case, we expect the peaktime to be proportional to the wait time. That is, if we hold the strain for a longer amount of time, we expect the peak formation to be delayed as well.
The relative peakstress represents the jump. We also look at how the jump value varies with the wait time.

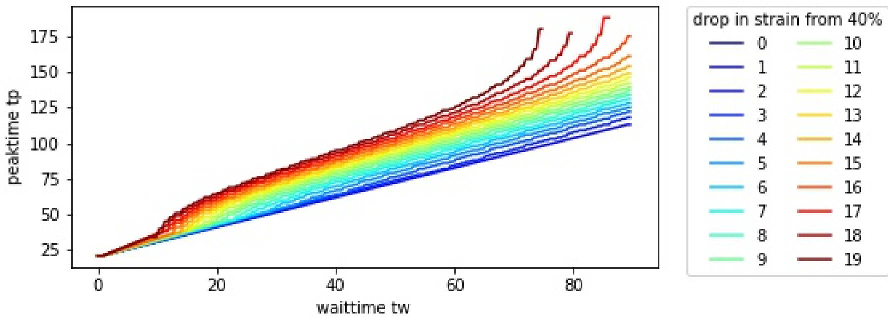
Two element case

First we look at how peaktime and relative peakstress vary with wait time, at a particular value of strain (from 40% to 30%).

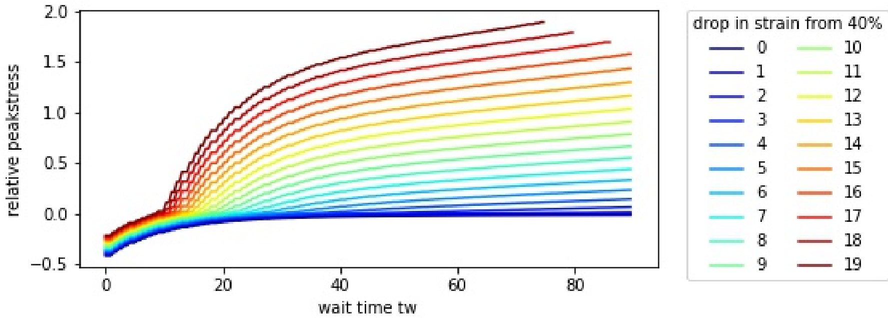


Single value of

Now, we take several values of change in strain, $\Delta\gamma$ to plot our phase diagram using several similar curves. For each $\Delta\gamma$ value (a different colour), we take a range of wait time values and find the corresponding peaktime and jump value of the relaxation curve.



Peaktime - waittime graph for two element model

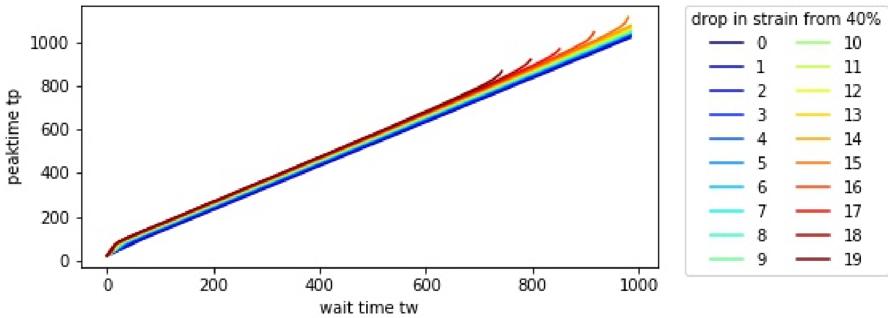


Relative peakstress - waittime graph for two element model

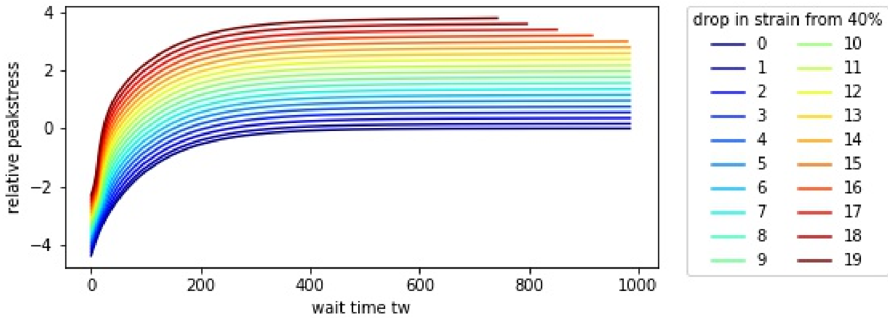
We can see that the peaktime-waittime graph has curves that are fairly linear. (Deviations from linearity occer when the change in strain is higher.) The relative peakstress, or jump value, increases slowly as the waittime increases and then remains fairly constant.

Three element case

We first look at the variation for different values of change in strain, $\Delta\gamma$ from an initial value of 40%. We see that the peaktime increases almost linearly with wait time, whereas the relative peakstress increases rapidly and then saturates.



Peaktime - waittime graph for three element model

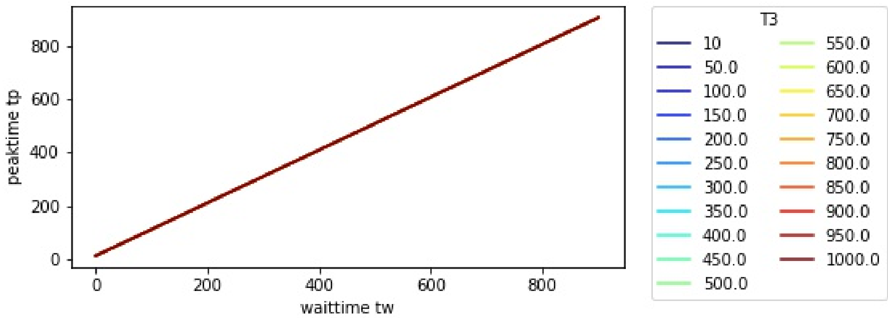


Relative peakstress - waittime graph for three element model

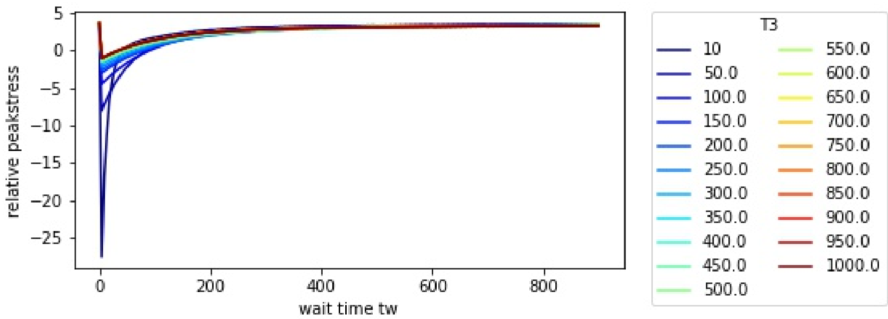
We see similar curves as seen in the two-element case.

4.2 Varying relaxation time of a single mode

For the three element model, we can also keep the relaxation times of two of the modes fixed (T1 and T2), and vary the third relaxation time T3 between T1 and T2.
Here, T1 = 10s and T2 = 1000s. Each curve represents a value T3 between 10s and 1000s.



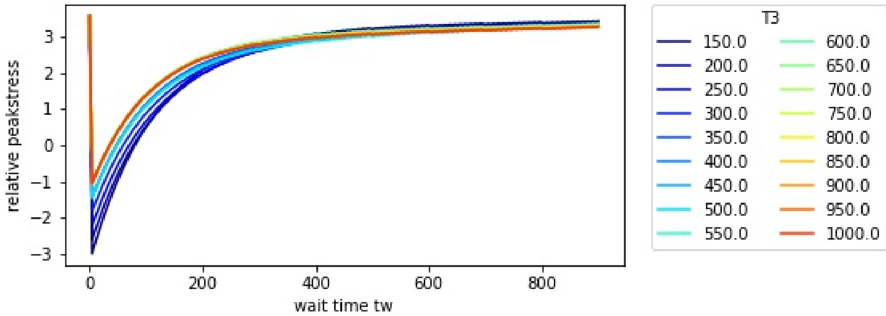
Peaktime - waittime graph for three element model



Relative peakstress - waittime graph for three element model

Once again, we observe that the peaktime is proportional to waittime. The curves all have the same value because the peak is determined by the slowest and fastest mode, in this case T1 and T2, which is the same

for all cases. However, the stress value of the third mode may determine the value of the jump (relative peakstress).
We can see that the relative peakstress saturates to a constant value as waittime increases. The figure below shows the same curve, but without the outlier cases.



Relative peakstress - waittime graph for three element model

Appendices

1 Basic algorithm

The algorithm outlined below works for a general n-element Maxwell model. We have used 2 and 3 element models so far. This can be extended to accommodate a larger number of modes with a distribution of relaxation times T.

Input G, η values for each element
T = $\frac{\eta}{G}$
Input initial strain γ
Input change in strain $\Delta\gamma$
Final strain = $\gamma - \Delta\gamma = \gamma'$
Input start time t0
Input wait time tw
Time at strain drop = $t0 + tw$
for all values of time **do**
  if $time < t0$ **then**
    $strain \leftarrow 0$
    $stress \leftarrow 0$
  end if
  if $t0 < time < t2$ **then**
    $strain \leftarrow \gamma$
    $stress \leftarrow (G * \gamma) * \exp(-(time - t0)/T)$
  end if
  if $time == t2$ **then**
    $strain \leftarrow \gamma'$
    $stress \leftarrow G * (\gamma * \exp(-tw/T) - \Delta\gamma)$
  end if
  if $time > t2$ **then**
    $strain \leftarrow \gamma'$
    $(G * (\gamma * \exp(-tw/T) - \Delta\gamma)) * \exp(-(time - t2)/T)$
  end if
end for

2 Working of algorithm

The algorithm used is based on an analytical solution of two and three element models. The implementation of a generalised Maxwell model is hence slightly cumbersome, but the algorithm works well for 2 or 3 modes.
The program is first set to specific values of input parameters, namely strain γ, drop in strain $\Delta\gamma$ and the time for which strain has been applied (wait time, tw). These parameters can be manipulated in laboratory settings as well.
Then we iterate over values of time, t. There are three possibilities, chronologically:

1. **Strain has not been applied yet** ($0 < t < t0$) - Then we set stress 0. System is at rest.

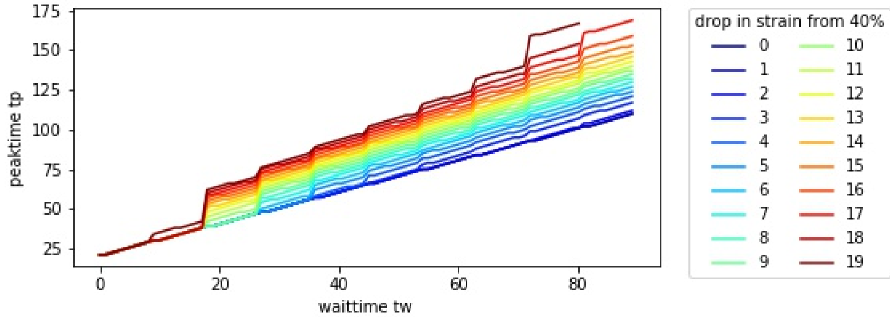
2. **Initial value of strain is applied (for time tw)** ($t0 < t < t0 + tw$) - Elasticity makes the stress jump to its maximum value, but the viscosity slowly starts bringing the system to equilibrium. Each mode is exponentially relaxing from its respective maximum stress.

3. **Strain value is decreased** ($t > t0 + tw$) - Modes continue to relax if relaxation time is high. Otherwise, if relaxation time is low, they jump to a new value of maximum and relax to equilibrium once again.

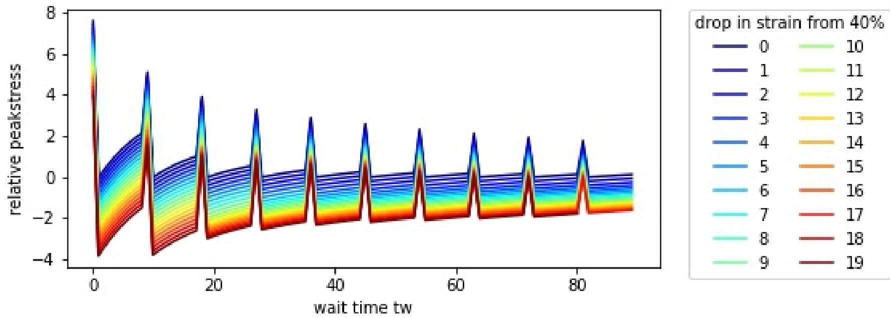
We must note that at each instant of time, the stress is calculated seperately for each Maxwell element based on its specific parameter values (T, η, γ). The net value of stress at a particular instant of time is the sum of stresses of all Maxwell elements.

3 Error encountered: Unexpected peaks in phase diagrams

Initially when plotting the phase diagrams, we encountered sudden peaks where we would expect smooth curves.



Peaktime-waittime graph for various changes in strain



Relative peakstress-waittime graph for various changes in strain

The peaks are due to the time values being integer numbers, but wait time values being a non-integer. Thus, the value of time at strain drop was a non-integer as well. Upon attempting to extract out the value of the stress when strain is dropped, we might not get the correct value.
2 possible solutions have been implemented, which may be kept in mind while writing the code.

Solutions

1. Use only integer values of wait time Our wait time values are between T1 and T2 (relaxation times). We take only the integer values in consideration.
However, we compromise on the resolution of wait times, we can use only a limited number of values.

2. Take the closest integer value of t0+tw Instead of calling the stress value during the drop and coming up with zero value, we instead take the closest integer value of t0+tw and take the stress at this instant. Hence the peaks significantly reduce.
It is not an ideal solution since we still use a closest integer instead of the absolute value but the solution suffices for our purposes.

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