

# Modelling the Mechanical Properties of Hydrogel

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## Abstract

The aim of the project for Exeter iGEM 2020 team is to create a new way of producing calcium carbonate using genetically engineered bacteria that take in carbon dioxide from the environment. Using this technique, the calcium carbonate is to be 3D printed into particular shapes using a bio-printer. To accomplish this, the bacteria will be embedded within a hydrogel medium which of a certain shape, and will precipitate calcium carbonate. This will produce an object made of calcium carbonate that is the same shape of the hydrogel. This paper aims to quantify and model some of the physical properties of the hydrogel, specifically its elasticity and viscoelasticity. By understanding these properties we have the capability to model a 3D bioprinter.

## 1 Introduction

Hydrogels are comprised of polymers which are water swollen, cross linked and hydrophilic. The properties of hydrogel are highly important, and the right one must be chosen for a given purpose. Its properties depend on environmental conditions, such as temperature and pressure. The mechanical behaviour of hydrogels is twofold as they show both elasticity and viscoelasticity. At the microscopic level, these can be understood in terms of how the hydrogel polymer matrix changes in response to an applied stress or strain. Unlike other polymers such as plastics, hydrogels are particularly weak materials which don't have a high mechanical strength. However in terms of fluid mechanics they are highly viscous which has effects on certain properties such as the diffusion coefficient, which is important for the analysis of how small molecules and bacteria are able to transmit through the hydrogel. This paper will focus more on the two types of mechanical property.

## 2 Theory of Mechanical Behavior

Hydrogels have two main regimes of mechanical properties, rubber elasticity and viscoelasticity. The determining factor of which type of properties are observed is the degree of swelling of the hydrogels. In a non or little swollen state, the hydrogel exhibits rubber elastic properties. However, in a swollen state the hydrogel is shown to be viscoelastic. This analysis will attempt to quantify mechanical parameters like the shear modulus  $G$  using thermodynamics and statistical physics, and then see how these mechanical properties change depending on the degree of swelling.

### 2.1 Rubber Elasticity

#### 2.1.1 Unswollen State

To derive relationships between the hydrogel characteristics, we use a combination of statistical mechanics and classical thermodynamics. [1] From classical thermodynamics the equation of state for rubber elasticity is (using the general form of a derivative along with the chain rule):

$$f = \frac{\partial U}{\partial L_{T,V}} + T \frac{\partial f}{\partial T_{L,V}} \quad (1)$$

where  $f$  is the retractive force in response to a tensile force,  $U$  is the internal energy  $L$  is the length,  $V$  is the volume and,  $T$  is the temperature. It turns out that 90 percent of the forces in a hydrogel are entropic, rather than energetic [1]. Therefore it's a reasonable approximation to use entropy (the desire of a system to maximise the amount of disorder) as the reason for the elastic behaviour.

Therefore we can write the retractive force from an ideal elastomer as

$$f = -T \frac{\partial S}{\partial L_{T,V}} \quad (2)$$

which can be expressed in terms of the probability  $\Omega$  of the polymer having an end to end distance  $r$  at temperature  $T$ :

$$f = -kT \frac{\partial \ln \Omega(r, t)}{\partial r}_{T,V} \quad (3)$$

For an ideal chain (each monomer is independent from its neighbours), this becomes:

$$f = \frac{3kT}{\langle r_f^2 \rangle} r \quad (4)$$

where  $\langle r_f^2 \rangle$  is the mean squared end to end distance of the chain. If we assume that the hydrogel medium contains  $N$  network chains, then the total change  $\Delta F$  can be calculated by using integration:

$$\Delta F = \int f dr = \frac{3NkT}{\langle r_f^2 \rangle} \int_{\sqrt{\langle r_f^2 \rangle}}^{\sqrt{\langle r^2 \rangle}} r dr \quad (5)$$

After this integration is performed, the statistical thermodynamic equation for the shear stress  $\tau$  is given by

$$\tau = \frac{1}{A} \frac{\partial F}{\partial \lambda_{T,V}} = \frac{\rho RT}{\bar{M}_c} \frac{\langle r_0^2 \rangle}{\langle r_f^2 \rangle} \left( \lambda - \frac{1}{\lambda^2} \right) \quad (6)$$

where  $\rho$  is the density of the hydrogel,  $\bar{M}_c$  is the mean molecular weight of the molecules comprising the hydrogel polymer. The quantity  $\frac{\langle r_0^2 \rangle}{\langle r_f^2 \rangle}$  is known as the *front factor*, and is the ratio between the mean end to end distance in the real network versus the mean end to end distance in the chains.

However in practice chains may contain imperfections such as cycles. This is accounted for by adapting the formula above to:

$$\tau = \frac{\rho RT}{\bar{M}_c} \frac{\langle r_0^2 \rangle}{\langle r_f^2 \rangle} \left( 1 - 2 \frac{\bar{M}_c}{\bar{M}_n} \right) \left( \lambda - \frac{1}{\lambda^2} \right) \quad (7)$$

where  $\bar{M}_n$  is the average molecular weight of the linear chains before cross-linking happens. Using the constitutive relationships, the shear modulus of the hydrogel network can be obtained.

$$G = \frac{\rho RT}{\bar{M}_c} \frac{\langle r_0^2 \rangle}{\langle r_f^2 \rangle} \left( 1 - 2 \frac{\bar{M}_c}{\bar{M}_n} \right) \quad (8)$$

and the stress is hence:

$$\tau = G \left( \lambda - \frac{1}{\lambda^2} \right) \quad (9)$$

From this equation, we can see that the shear modulus depends on the mean molecular weight  $\bar{M}_c$ . When this is compared to experiment, we can see that at low elongations it agrees well at low strains. However, deviates from the theoretical prediction when the strain ratio is above this ( $\lambda = 3$ ). This comparison is shown in Figure 1.

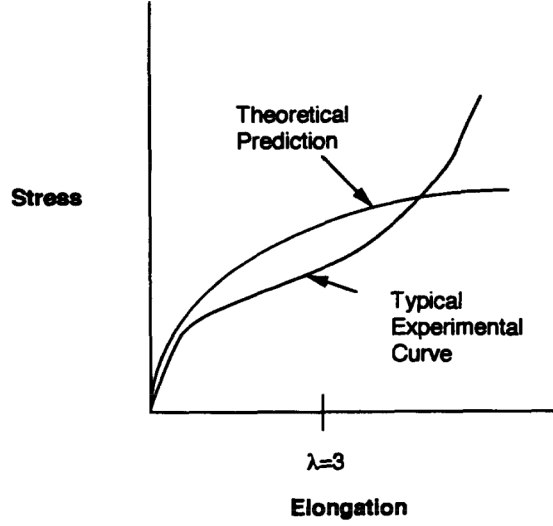


Figure 1: (Extracted from Anseth Et. Al [1]) A stress strain behaviour of a lightly cross linked material compared to statistical and thermodynamic predictions.

### 2.1.2 Swollen State

For the swollen state, assuming a perfect gel network, the relationship between the shear modulus  $G_{sw}$  and the degree of swelling can be modelled as [2]

$$G_{sw} = G_0 Q^{-\frac{1}{3}} \quad (10)$$

where  $Q = \frac{V}{V_0}$  is the ratio between the volume in the unswollen state and the swollen state, and  $G$  is the shear modulus in the unswollen state. It can be shown that even in the swollen state, the shear stress still has the same relationship to the strain:

$$\sigma = G_{sw} \left( \lambda - \frac{1}{\lambda^2} \right) \quad (11)$$

## 2.2 Viscoelasticity

Viscoelasticity is the property of a material to exert both viscous and elastic behaviour when undergoing deformation. Hydrogel is an example of a material that is viscoelastic. This means that it can be stretched, much like an elastic material. However in contrast, it will not return to its original shape when the tensile force is removed. Viscoelastic materials will also expand to fill their container, much like a viscous fluid.

The factor that determines whether a material is viscoelastic or just elastic is whether the rate at

which the deformation occurs matters. In the case of a viscoelastic material, it does, whereas in an elastic material it does not.

## 2.3 Physical Models for Viscoelasticity

Viscoelastic materials exhibit both viscous and elastic behavior. [3] In an elastic material, the stress  $\sigma$  is proportional to the strain  $\varepsilon$ :

$$\sigma = E\varepsilon \quad (12)$$

where the proportionality constant  $E$  is the Young modulus. In contrast, in a viscous material, the stress is proportional to the strain rate:

$$\sigma = \mu \frac{d\varepsilon}{dt} \quad (13)$$

where the proportionality coefficient  $\mu$  is the viscosity of the material. We label these two relationships by drawing an analogy to the spring and dashpot. The spring represents the elastic component, and the dashpot represents the viscous component. Modelling viscoelastic materials requires combining both models, and the way in which they are combined will give unique results for different polymers.

The relationship between stress and strain can be simplified at different time regimes. Over short time periods, the viscous behavior dominates. A dashpot resists change in length, and under a high stress state it can be approximated as a rigid rod. Conversely for long time periods, the viscous components can be effectively removed from the system, and hence it behaves similarly to a spring.

### 2.3.1 Maxwell Model

The Maxwell model consists of a spring and dashpot connected in series. This is shown in Figure 2

This means that the total strain is given as the sum of the individual strains from both the spring and the dashpot.

$$\varepsilon_{tot} = \varepsilon_{spr} + \varepsilon_{das} \quad (14)$$

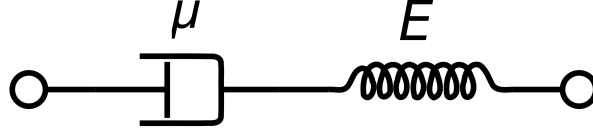


Figure 2: The Maxwell model: A spring and dashpot in series

After differentiating this equation with respect to time, and substituting in each component, the Maxwell model becomes:

$$\mu \frac{d\varepsilon}{dt} = \sigma + \frac{\mu}{E} \frac{d\sigma}{dt} \quad (15)$$

In this model, if the polymer is put under constant strain, the stresses gradually relax. Depending on the rate at which the material is stressed, the response may be elastic or viscous. Experimentally, the elastic component occurs first and then relaxes over time. However, the viscous component grows with time as long as the stress is applied.

### 2.3.2 Kelvin-Voigt Model

Similarly to the Maxwell model, the Kelvin-Voigt model consists of one spring and one dashpot. By contrast however, the spring and dashpot are connected in parallel as shown in 3. In this

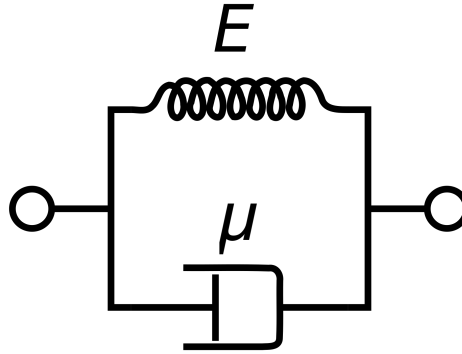


Figure 3: The Kelvin-Voigt model: A spring and dashpot in Parallel.

model, it is the total stress that is given as the sum of the two individual stresses:

$$\sigma_{tot} = \sigma_{spr} + \sigma_{das} \quad (16)$$

After substituting in the expressions for the two stresses, the total stress is given as

$$\sigma = E\varepsilon + \mu \frac{d\varepsilon}{dt} \quad (17)$$

This model represents a material undergoing a reversible, viscoelastic strain. Under constant stress, the material is found to deform at a decreasing rate. When the stress is released, it will return to its original shape again, but again at a decreasing rate. This constant stress model is known as creep behavior. In Section 3, we will attempt to solve this equation.

## 2.4 Creep Behaviour

If a constant stress  $\sigma$  is applied to a viscoelastic material, the strain  $\varepsilon$  is found to depend on time. Creep behaviour in polymer materials such as hydrogels can be modelled using the Kelvin-Voigt model. The creep strain is given by the following convolution integral.

$$\varepsilon(t) = \sigma C_0 + \sigma C \int_0^\infty f(\tau)(1 - e^{-\frac{t}{\tau}})d\tau \quad (18)$$

where

- $\sigma$  is the applied stress
- $C_0$  is the instantaneous creep compliance
- $C$  is the creep compliance coefficient
- $\tau$  is the relaxation time
- $f(t)$  is the distribution of relaxation times

When subjected to a constant stress, viscoelastic materials experience a time-dependent increase in strain. This phenomenon is known as *viscoelastic creep*. When performing the convolution integral, the time dependence on stress and strain can be shown in Figure 4

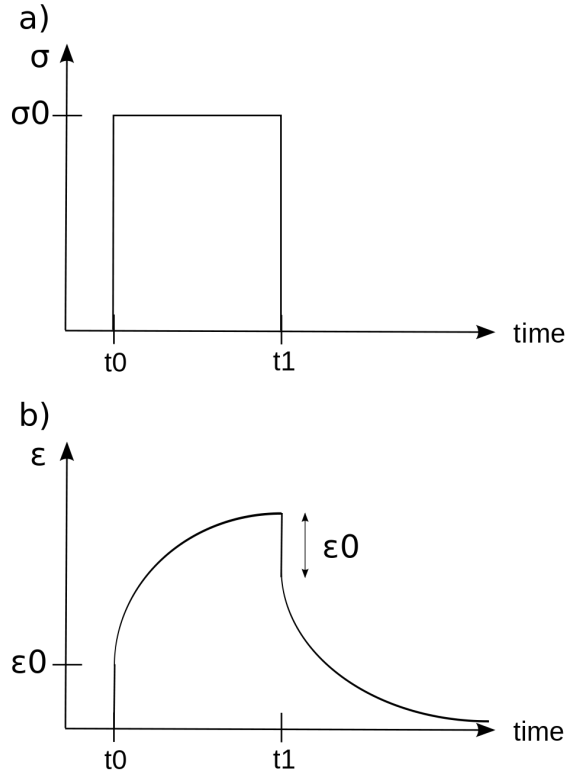


Figure 4: Graphs showing the result of applying (18) to a stress curve, obtaining the resulting strain curve, between two times  $t_0$  and  $t_1$ . This is an example of creep behaviour in viscoelastic polymers.

### 3 Modeling Viscoelasticity

#### 3.1 Maxwell Model

This will require solving the following equation.

$$\mu \frac{d\epsilon}{dt} = \sigma + \frac{\mu}{E} \frac{d\sigma}{dt} \quad (19)$$

In this analysis, we will consider the different types of experiment that are typically performed on viscoelastic materials in the lab, and using the Maxwell model, we will solve the differential equation in each case. This equation can either be solved for stress or strain as a function of time, which will give us several different cases. In each case the parameters  $E = 100\text{kPa}$  and  $\mu = 30\text{ Pa s}$ , which are typical values for the Young's modulus and viscosity respectively. [4] [5]



### 3.1.1 Response to a constant strain

In this case, the material is deformed suddenly and held at a constant strain,  $\varepsilon_0$ . Because the strain does not vary with time, the time derivative term in Equation (19) will be zero. Hence the differential equation becomes

$$\frac{d\sigma}{dt} = -\frac{E}{\mu}\sigma(t) \quad (20)$$

Since the models assume that  $E$  and  $\mu$  are constant, we have a relationship in which the first derivative of stress is directly proportional to the stress itself. This equation can be solved using separation of variables or numerically. For this analysis, a classical fourth order Runge-Kutta method will be used. Full details and code of this are given in Section 3.4. The result of solving this differential equation is shown in Figure 5. The functional solution is given by the equation

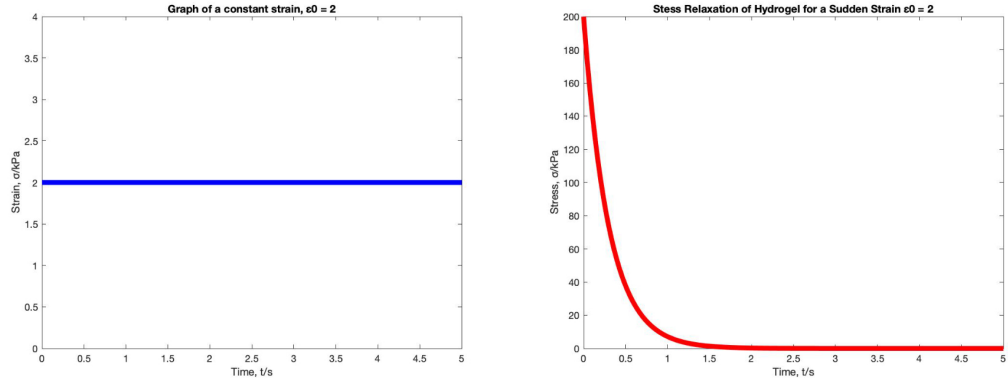


Figure 5: Left: Material held at constant strain  $\varepsilon_0 = 2$  from time  $t = 0$ . Right: Stress response of the material showing exponential decrease over time.

below.

$$\sigma(t) = e^{-\frac{E}{\mu}t} \quad (21)$$

where the quantity  $\frac{\mu}{E}$  has dimensions of time and has the physical interpretation of how long it takes for the material to relax, in other words the relaxation time. Therefore, it is important that we choose a hydrogel which has a relaxation time that isn't too long, otherwise the printer will take a long time to print.

### 3.1.2 Response to constant stress

In this case, the material is placed under a constant stress, and the strain will be solved as a function of time. Under this type of experiment, the time derivative term of the stress vanishes and the differential equation becomes

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\mu} \quad (22)$$

where  $\sigma_0$  is the constant stress level that the material is under. We will now solve this differential equation in a similar manner to before. The solution is shown in Figure 6. As before, the

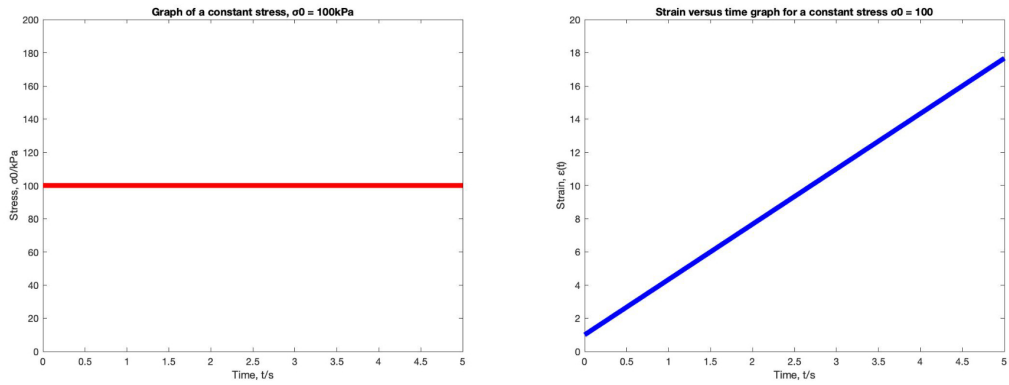


Figure 6: Left: Material held at a constant stress  $\sigma_0 = 100\text{kPa}$  from time  $t = 0$ . Right: Strain deformation response showing a linear increase over time.

strain solution can be expressed as a function of time (which in this case can be easily derived analytically through integration). This is given by

$$\varepsilon(t) = \frac{\sigma_0}{\mu}t + \frac{\sigma_0}{E} \quad (23)$$

From this, we can state that there is a relationship between the viscosity and the strain rate for a given stress. The greater the viscosity, the longer it takes to strain the hydrogel, as one would expect.

## 3.2 Kelvin-Voigt Model

In the case of modelling the hydrogel as a Kelvin-Voigt viscoelastic material, this will require solving the differential equation

$$\sigma(t) = E\varepsilon(t) + \mu \frac{d\varepsilon}{dt} \quad (24)$$

and we will solve this for both the constant strain and constant stress case as before. The parameters  $E = 100\text{kPa}$  and  $\mu = 30\text{Pa}$  will be the same as before.

### 3.2.1 Response to a constant strain

The viscoelastic material will be deformed and held a constant strain  $\varepsilon_0$ . Because the strain is constant, the time derivative term in the equation will vanish, and the equation becomes

$$\sigma(t) = E\varepsilon(t) \quad (25)$$

Hence, if the material is kept at a constant strain, the stress response will also not change with time. The solution is

$$\sigma(t) = E\varepsilon_0 \quad (26)$$

which is simply the equation for elastic response. This is shown in Figure 7.

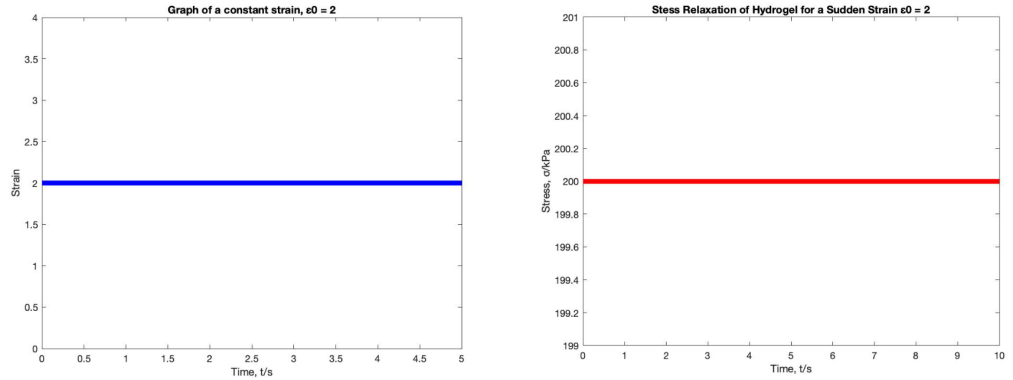


Figure 7: Left: Material held at a constant strain  $\varepsilon_0 = 2$  at time  $t = 0$ . Right: Stress response, showing elastic behaviour in which a constant strain will yield a constant stress.

### 3.2.2 Response to a constant stress

In this case, the material is placed under a constant stress, and the strain dependence on time is measured. The differential equation under these conditions is given by

$$\frac{d\varepsilon}{dt} = \frac{\sigma_0}{\mu} - \frac{E}{\mu}\varepsilon(t) \quad (27)$$

Solving this differential equation numerically yields the following solution, shown in Figure 8, and has the following functional form given by

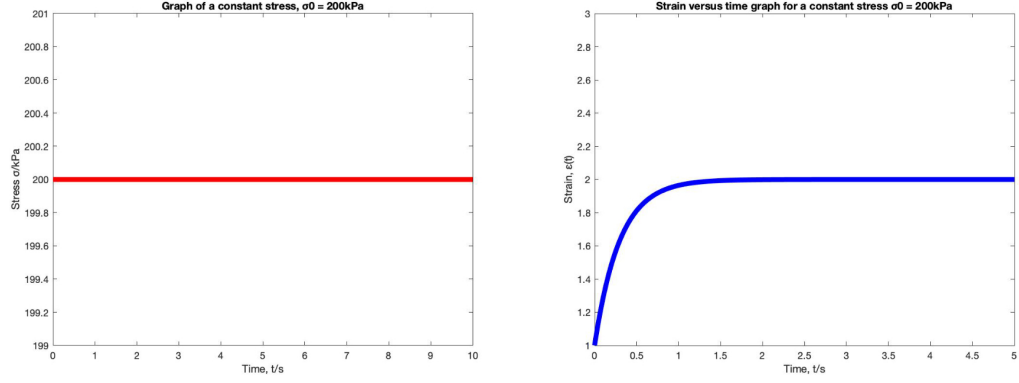


Figure 8: Left: Kelvin-Voigt Material held at a constant stress of  $\sigma_0=200\text{kPa}$ . Right: The strain response over time showing an exponential rise asymptotically approaching the value  $\sigma_0/E$ .

$$\varepsilon(t) = \frac{\sigma_0}{E}(1 - e^{-\frac{E}{\mu}t}) \quad (28)$$

From this, we can deduce that the larger the material behaves elastically, but only over timescales in which  $t \gg \frac{\mu}{E}$ . Therefore, increasing the viscosity  $\mu$  will lead to more of a creep response.

### 3.3 Comparison Between Models

Both models have been shown to realistically model different types of viscoelastic materials. The Kelvin-Voigt model is able to more realistically predict creep behaviour, since unlike the Maxwell model, it approaches a stable value, which is a common observation in these types of materials. However, in the case of small deformations, the Maxwell model is shown to be more successful in modeling small strains and the viscous response. In reality, a viscoelastic material can be modelled by using a combination of both Maxwell and Kelvin-Voigt components. This would generate differential equations that would include further terms in the equation, which could be solved in a similar manner over a specified certain time range.

### 3.4 Numerically Solving the Differential Equation

Although in all of the above cases the solution can be obtained analytically, in practice a more complex model involving extra terms would be difficult to solve. The solution to this problem is to use a numerical differential equation solver. The method to be used is a classical Runge-Kutta [6]. This process relies on discretisation of a continuous differential equation, and evaluating it four times per step. Each step uses the answer to the previous step, and then a weighted average

is taken after this has been carried out. In terms of a function  $f(t, u)$  in which we are to solve for  $u(t)$ , this is given as

$$s_1 = f(t_n, u_n)$$

$$s_2 = f(t_n + \frac{h}{2}, u_n + s_1 \frac{h}{2})$$

$$s_3 = f(t_n + \frac{h}{2}, u_n + s_2 \frac{h}{2})$$

$$s_4 = f(t_n + h, u_n + s_3 h)$$

And the next evaluation of  $y$ ,  $u_{n+1}$  is a weighted average of the four steps in between

$$u_{n+1} = u_n + \frac{h}{6} \left( s_1 + 2s_2 + 2s_3 + s_4 \right) \quad (29)$$

with a heavier emphasis given to the two middle terms as they are fully included in the step, as opposed to being only partially included. With this iterative approach the output is the solution being plotted. This approach will work for all analytical functions as long as both they and their first derivatives are continuous.

### 3.4.1 The Code

This algorithm is translated into code which will be able to generate a plot of the solution for a given input function. The code used is shown in Figure 9.

## 4 Relation to the project

The aim of our project is to model a 3D bioprinter which contains genetically modified bacteria dispersed in a hydrogel medium. The timescale at which a 3D shape can be printed depends highly on its mechanical properties such as viscosity and elastic moduli, which affects both the rate at which different shapes can be formed. In this analysis, we have conducted a brief analysis into both the elastic and viscoelastic properties. It is the viscoelastic property of the hydrogel which makes it an ideal choice of material for use in a bioprinter. We have solved the two differential equations for viscoelasticity to simulate how the hydrogel would respond to a given stress or strain. This has a direct application to the printer as the gel would need to

```

%Mechanical Parameters
E = 100 %Youngs Modulus/kPa
mu = 30 %Viscosity Pa*s
sigma0 = 200 %Constant Stress
epsilon0 = 1 %Initial Strain

F = @(t,epsilon) -(E/mu)*epsilon+ (sigma0/mu)

t0 = 0 %Initial Time
tfinal = 10 %Final Time
h = tfinal/1000 %Step Size

tout = [t0:h:tfinal];

epsilon = epsilon0;
epsilonout = epsilon;
for t = t0 : h : tfinal-h
    s1 = F(t,epsilon);
    s2 = F(t+h/2, epsilon+h*s1/2);
    s3 = F(t+h/2, epsilon+h*s2/2);
    s4 = F(t+h, epsilon+h*s3);
    epsilon = epsilon + h*(s1 + 2*s2 + 2*s3 + s4)/6;
    epsilonout = [epsilonout; epsilon];
end

plot(tout,epsilonout,'b-','LineWidth',5)
xlabel('Time, t/s')
ylabel('Strain,  $\epsilon(t)$ ')
title('Strain versus time graph for a constant stress  $\sigma_0 = 200\text{kPa}$ ')
axis([0 5 1 3])

```

Figure 9: MATLAB Code using a fourth order Runge-Kutta method of solving the Kelvin-Voigt Differential equation. This particular case was taken as an example, same algorithm was used in each different case for solutions to both  $\epsilon(t)$  and  $\sigma(t)$  using both the Maxwell and Kelvin-Voigt models for viscoelasticity.

be moulded into custom 3D shapes, and how it responds is an important physical aspect of the printer. The timescale and ease of how 3D shapes are created play an important part in this project, and is a stepping stone to developing a novel production method of calcium carbonate.

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