406: Mechanical Properties of Materials

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1 COURSE DESCRIPTION

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1 Course Description

A course on the mechanical properties of materials, designed for first year graduate students in Materials Science and related disciplines.

2 Stress and Strain

The mechanical properties of a material are defined in terms of the strain response of material after a certain stress is applied. In order to properly understand mechanical properties, we have to have a good understanding of stress and strain, so that's where we begin. Some Notes on Notation: There are different ways to represent scalar quan-

tities, vectors and matrices. Here's how we do it in this text:

- ♦ Scalar quantities are straight up symbols, like P_1 , σ_{12} , etc.
- $\diamond\,$ Vectors are indicated with an arrow over the symbol, like P.
- \diamond Unit vectors are indicated with a caret above the symbol, like \hat{n} .
- \diamond Matrices are enclosed in square brackets, like $[\sigma]$

2.1 Tensor Representation of Stress

The stress applied to an object, which we denote as σ_{ij} or $[\sigma]$ is the force acting over an area of an object, divided by the area over which this force is acting. Note note that $[\sigma]$ is a matrix with individual components, σ_{ij} specified by the indices *i* and *j*. These indices have the following significance:

- \diamond i: surface normal (i= x, y, z)
- \diamond j: direction of force (j=x, y, z)

To obtain the **Engineering stress**, $[\sigma^{\text{eng}}]$, we use the undeformed areas of the stress-free object to obtain the stress tensor, whereas the true stress (which is what we generally mean when we write $[\sigma]$) we use the actual areas in the as-stressed state.

The stress matrix is a **tensor**, which means that it obeys the coordinate transformation laws describe below. In two dimensions it has the following form:

$$[\sigma] = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{bmatrix}$$
(2.1)

The stress tensor must be symmetric, with $\sigma_{xy} = \sigma_{yx}$. If this were not the case, the torques on the volume element shown above in Figure 2.1 would not balance, and



Figure 2.1: 2-dimensional stress tensor

the material would not be in static equilibrium. As a result the two dimensional stress state is specified by three components of the stress tensor:

- ♦ 2 normal stresses, σ_{xx} , σ_{yy} . These are referred to as 'normal' stresses because the force acts perpendicular to the plane that it is referred to.
- \diamond A single shear stress, σ_{xy} .

In three dimensions we add a z axis to the existing x and y axes, so the stress state is defined by a symmetric 3x3 tensor. The full stress tensor can be used to define the stresses acting on any given plane. To simplify the notation a bit we label the three orthogonal directions by numbers (1, 2 and 3) instead of letters (x, y and z). The stress tensor gives the components of the force $(P_1, P_2 \text{ and } P_3)$ acting on a given plane. The plane is specified by the orientation of the unit vector, \hat{n} that is perpendicular to the plane. This vector has components n_1 , n_2 and n_3 in the 1, 2 and 3 directions, respectively. It's a 'unit' vector because the length of the vector is $1, \text{ i.e. } (n_1^2 + n_2^2 + n_3^2)^{1/2} = 1$. The relationship between \vec{P} , σ and \vec{n} is as follows:

$$\begin{bmatrix} P_1 \\ P_2 \\ P_3 \end{bmatrix} = A \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \end{bmatrix}$$
(2.2)

or in more compact matrix notation:

$$\vec{P} = A\left[\sigma\right]\hat{n} \tag{2.3}$$

Here A is the total cross sectional area of the plane that we are interested in. (If you need a refresher on matrix multiplication, the Wikipedia page on Matrix Multiplication (https://en.wikipedia.org/wiki/Matrix_multiplication) [?] is very helpful).

In graphical form the relationship is as shown in Figure 2.2. Like the 2-dimensional stress tensor mentioned above, the 3-dimensional stress tensor must also be symmetric in order for static equilibrium to be achieved. There are therefore 6 independent components of the three-dimensional stress tensor:



Figure 2.2: 3 dimensional stress tensor

- \diamond 3 normal stresses, σ_{11} , σ_{22} and σ_{33} , describing stresses applied perpendicular to the 1, 2 and 3 faces of the cubic volume element.
- \diamond 3 shear stresses: σ_{12} , σ_{23} and σ_{13} .

The three dimensional stress tensor is a 3x3 matrix with 9 elements (though only 6 are independent), corresponding to the three stress components acting on each of the three orthogonal faces of cube in the Cartesian coordinate system used to define the stress components. The 1 face has $n_1=1$, $n_2=0$ and $n_3=0$. By setting $\vec{n} = (1,0,0)$ in Eq. 2.2, we get the following for the stresses acting on the 1 face of the volume element:

$$P_{1}/A = \sigma_{11} P_{2}/A = \sigma_{12} P_{3}/A = \sigma_{13}$$
(2.4)

Equivalent expressions can be obtained for the stresses acting on the 2 and 3 faces, by setting $\vec{n} = (0, 1, 0)$ and $\vec{n} = (0, 0, 1)$, respectively.

2.2 Tensor Transformation Law

The stress experienced by a material does not depend on the coordinate system used to define the stress state. The stress tensor will look very different if we chose a different set of coordinate axes to describe it, however, and it is important to understand how changing the coordinate system changes the stress tensor. We begin in this section by describing the procedure for obtaining the stress tensor that emerges from a given change in the coordinate system. We then describe the method for obtaining a specific set of coordinate axis which gives a diagonalized tensor where only normal stresses are present (Section 2.3).

2.2.1 Specification of the Transformation Matrix

In general, we consider the case where our 3 axes (which we refer to simply as axes 1, 2 and 3) are moved about the origin to define a new set of coordinate axes that we refer to as 1', 2' and 3'. As an example, consider the simple counterclockwise rotation around the 3 axis by an angle ϕ , shown schematically in Figure 2.3. In general, the relative orientation of the transformed (rotated) and untransformed coordinate axes are given by a set of 9 angles between the 3 untransformed axes and the three transformed axes. In our notation we specify these angles as θ_{ij} , where *i* specifies the transformed axes (1', 2' or 3') and *j* specifies the untransformed axis (1, 2 or 3). In our simple example, the angle between the 1 and 1' axes is ϕ , so $\theta_{11} = \phi$. The angle between the 2 and 2' axes is also ϕ , so $\theta_{22} = \phi$. The 3 axis remains unchanged in our rotation example, so $\theta_{33} = 0$. The 3/3' axis remains perpendicular to the 1,1', 2,2' axes, so we have $\theta_{31} = \theta_{32} = \theta_{13} = \theta_{23} = 90^{\circ}$. Finally, we see that the angle between the 1' and the 2 axis is $90 - \phi$ ($\theta_{12} = 90 - \phi$) and the angle between the 2' and 1 axis is $90 + \phi$ ($\theta_{21} = 90 + \phi$). The full [θ] matrix in this case is as follows:

$$[\theta] = \begin{bmatrix} \phi & 90 - \phi & 90 \\ 90 + \phi & \phi & 90 \\ 90 & 90 & 0 \end{bmatrix}$$
(2.5)

Note that the $[\theta]$ matrix is NOT symmetric $(\theta_{ij} \neq \theta_{ji})$, so you always need to make sure the first index, i, (denoting the row in the $[\theta]$ matrix) corresponds to the transformed axes, and the second index, j (denoting the column in the $[\theta]$ matrix) corresponds to the original, untransformed axes.

2.2.2 Expressions for the Stress Components

Once we specify all the different components of $[\theta]$, we can use the following general expression to obtain the stresses in the new (primed) coordinate system as a function of the stresses in the original coordinate system:

$$\sigma_{ij}' = \sum_{k,l} \cos \theta_{jk} \cos \theta_{il} \sigma_{kl} \tag{2.6}$$

For each component of the stress tensor, we have to sum 9 individual terms (all combinations of k and l from 1 to 3). For example, σ'_{12} is given as follows:

$$\sigma_{12}' = \cos \theta_{21} \cos \theta_{11} \sigma_{11} + \cos \theta_{21} \cos \theta_{12} \sigma_{12} + \cos \theta_{21} \cos \theta_{13} \sigma_{13} + \cos \theta_{22} \cos \theta_{11} \sigma_{21} + \cos \theta_{22} \cos \theta_{12} \sigma_{22} + \cos \theta_{22} \cos \theta_{13} \sigma_{23} + \cos \theta_{23} \cos \theta_{11} \sigma_{31} + \cos \theta_{23} \cos \theta_{12} \sigma_{32} + \cos \theta_{23} \cos \theta_{13} \sigma_{33}$$

$$(2.7)$$

The calculation is breathtakingly tedious if we do it all by hand, so it makes sense to automate this and do the calculation via computer, in our case with Python. In this example we'll start with a simple stress state corresponding to uniaxial extension in the 1 direction, with the following untransformed stress tensor:

$$[\sigma] = \begin{bmatrix} 5x10^6 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(2.8)

Suppose we want to obtain the stress tensor in the transformed coordinate system obtained from a 45° counterclockwise rotation around the z axis. The rotation matrix is given by Eq. 2.5, with $\phi = 45^{\circ}$. The following Python code solves for the full transformed tensor, with σ_{ij} given by Eq. 2.8 and $[\theta_{ij}]$ given by Eq. 2.5 with $\phi = 45^{\circ}$:



Figure 2.3: Rotation of coordinate system. The coordinate system is rotated by θ about the 3 axis, transforming the 1 axis to1' and the 2 axis to2'.

```
#!/usr/bin/env python3
  # -*- coding: utf-8 -*-
2
3
4
  import numpy as np
  sig=np.zeros((3, 3)) #% create stress tensor and set to zero
  sig[0, 0] = 5e6; # this is the only nonzero component
  sigp=np.zeros((3, 3)) # initalize rotated streses to zero
  phi = 45
10
11
  theta = [[phi,90-phi,90], [90+phi,phi,90], [90,90,0]]
12
13
  theta = np.deg2rad(theta) # trig functions need angles in radians
  for i in [0, 1, 2]:
14
      for j in [0, 1, 2]:
15
           for k in [0, 1, 2]:
16
               for 1 in [0, 1, 2]:
17
                   sigp[i,j]=sigp[i,j]+np.cos(theta[i,k])*np.cos(theta[
18
                     j,1])*sig[k,1]
19
  print(sigp)
                # display the transformed tensor components
20
```

We use Python because it is free, powerful, and quite easy to learn especially if you have experience with a similarly-structured programming environment like MAT-LAB. Various Python code examples are included in this text, and are presented as examples of how to do some useful things in Python.

The output generated by the Python code is shown in Figure 2.4, and corresponds to the following result:

$$[\sigma'] = \begin{bmatrix} 2.5x10^6 & -2.5x10^6 & 0\\ -2.5x10^6 & 2.5x10^6 & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(2.9)

Note the following:

- \diamond The normal stresses in the 1 and 2 directions are equal to one another.
- $\diamond\,$ The transformed shear stress in the 1-2 plane is half the original tensile stress.
- ◊ The sum of the normal stresses (the sum of the diagonal components of the stress tensor) is unchanged by the coordinate transformation

igp =		
1.0e+06 *		
2.5000	2.5000	0
2.5000	2.5000	0
0	0	0

Figure 2.4: Output generated by rotate45.py.

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2.2.3 An Easier Way: Transformation by Direct Matrix Multiplication

A much easier way to do the transformation is to use a little bit of matrix math. The approach we use is described in a very nice web page put together by Bob McGinty[?]. A transformation matrix, Q_{ij} , is obtained by taking the cosines of all of these angles describing the relationship between the transformed and untransformed coordinate axes:

$$[\mathbf{Q}] = \cos\left[\theta\right] \tag{2.10}$$

For the simple case of rotation about the z axis, the angles are given by Eq. 2.5, so that $[\mathbf{Q}]$ is given as:

$$[\mathbf{Q}] = \begin{bmatrix} \cos\phi & \cos(90-\phi) & \cos90\\ \cos(90+\phi) & \cos\phi & \cos90\\ \cos90 & \cos90 & \cos0 \end{bmatrix} = \begin{bmatrix} \cos\phi & \sin\phi & 0\\ -\sin\phi & \cos\phi & 0\\ 0 & 0 & 1 \end{bmatrix}$$
(2.11)

The transformed stress is now obtained by the following simple matrix multiplication:

$$[\sigma'] = [\mathbf{Q}] [\sigma] [\mathbf{Q}]^T$$
(2.12)

where the $[\mathbf{Q}]^T$ is the transpose of $[\mathbf{Q}]$:

$$Q^{T}(i,j) = Q(j,i)$$
 (2.13)

For the rotation by ϕ around the z axis, $[\mathbf{Q}]^T$ is given by the following:

$$\left[\mathbf{Q}\right]^{T} = \begin{bmatrix} \cos\phi & -\sin\phi & 0\\ \sin\phi & \cos\phi & 0\\ 0 & 0 & 1 \end{bmatrix}$$
(2.14)

Equation 2.12 is much easier to deal with than Eq. 2.7. The Python code to take a uniaxial stress state and rotate the coordinate system by 45° about the 3 axis looks like this if we base it on Eq. 2.12:

```
import numpy as np
# create stress tensor with all zero elements
sig = np.zeros((3,3))
# set first one elment to be nonzero (one of the normal stresses)
sig[0][0] = 5e6
# set the rotation angle
phi = 45
# define the rotation matrix in degrees
theta = np.array([[phi,90+phi,90],[90-phi,phi,90],[90,90,0]])
```

```
# now put all the direction cosines in Q
14
  Q = np.cos(np.radians(theta))
15
16
  # claculate the transpose of Q
17
  QT = np.transpose(Q)
18
19
  # now multiply everything together
20
  # note that we use the @ sign to multiply matrices in python
21
  sigp = np.round(Q@sig@QT)
22
23
  # print the result
  print(sigp)
24
```

Running this script gives the output shown in Figure 2.4, <u>i.e.</u> we obtain exactly the same result we obtained by using Eq. 2.7.

2.3 Principal Stresses

Any stress state (true stress) can be written in terms of three principal stresses σ_{1p} , σ_{2p} and σ_{3p} , applied in three perpendicular directions as illustrated in Figure 2.5. Note that we still need 6 independent parameters to specify a stress state: the 3 principal stresses, in addition to three parameters that specify the orientation of the principal axes. The stress tensor depends on our definition of the axes, but it is always possible to chose the axes so that all of the shear components of the stress tensor vanish, so that the stress tensor looks like the following:

$$[\sigma] = \begin{bmatrix} \sigma_{1p} & 0 & 0\\ 0 & \sigma_{2p} & 0\\ 0 & 0 & \sigma_{3p} \end{bmatrix}$$
(2.15)

In order to gain some insight into the points mentioned above, it is useful to consider a range of rotation angles, and not just a singe rotation angle of 45° . One way to do this is to use the symbolic math capability of Python (or your other favorite software) to obtain the full stress tensor as a function of the rotation angle. We'll use the principal axes to define our untransformed state, and transform to a new set of axes by rotating counterclockwise by an angle ϕ around the 3 axis. We want to calculate

 $[\sigma']$ from Eqs.2.11 and 2.12 as we did before, but we leave ϕ as an independent variable. We use the following python script to do this:

1 # mohr_circle.py



Figure 2.5: Principal Stresses

2 STRESS AND STRAIN

```
2 # Mohr's circle derivation
  from sympy import symbols, Matrix, cos, pi, simplify, preview
3
  # specify the principal stressesS
5
  sig1p, sig2p, sig3p = symbols(['sigma_1^p', 'sigma_2^p', 'sigma_3^p'
6
    1)
  sig = Matrix([[sig1p, 0, 0], [0, sig2p, 0], [0, 0, sig3p]])
7
  # now specify the rotation angle
9
10
  phi = symbols('phi')
11
  # specify the theta matrix
12
  theta=Matrix([[phi,pi/2-phi,pi/2], [pi/2+phi,phi,pi/2],[pi/2,pi
13
    /2,0]])
14
  # take the cosine of all the elements in the matrix to get Q
15
  Q=theta.applyfunc(cos)
16
17
  # get the transpose of the matrix
18
  QT=Q.transpose()
19
20
  # now do the matrix multiplication to get the transformed matrix
21
  sigp=Q*sig*QT
22
23
  # now simplify and show the output
24
  exp1 = simplify(sigp)
25
  preview(exp1, filename='../figures/sympy_mohr_exp1.svg')
26
27
  # define the center (C) and radius (R) of the circle
28
  R, C = symbols(['R', 'C'])
29
30
  # now we rewrite in terms of center and radius and simplify again
31
  sigp = sigp.subs([(sig1p, C+R), (sig2p, C-R)])
32
  exp2 = simplify(sigp)
33
34
_{35} # now save the exp1 and exp2 as image files
36 preview(exp1, viewer = 'file', filename = '../figures/
    sympy_mohr_exp1.png')
  preview(exp2, viewer = 'file', filename = '../figures/
37
    sympy_mohr_exp2.png')
```

This results in the following expression for $[\sigma']$ (exp1, generated in line 26 of mohr_circle.py).

$$\begin{bmatrix} C - 2R\sin^2(\phi) + R & -R\sin(2\phi) & 0 \\ -R\sin(2\phi) & C - 2R\cos^2(\phi) + R & 0 \\ 0 & 0 & \sigma_3^p \end{bmatrix}$$

This is not yet a very illuminating result, but it is the basis for the Mohr circle construction, which provides a very useful way to visualize two dimensional stress states. This construction is described in more detail in the following Section.

2.3.1 Mohr's Circle Construction

The Mohr circle is a graphical construction that can be used to describe a two dimensional stress state. A two dimensional stress state is specified by two principal stresses, σ_{1p} and σ_{2p} , and by the orientation of the principal axes. The Mohr circle

is drawn with a radius, R, of $\sigma_{1p} - \sigma_{2p}$, centered at $C = (\sigma_{1p} + \sigma_{2p})/2$ on the horizontal axis. We can use these values of R and C as the independent variables in the expression for σ' that we obtained from our python script. This substitution is made in lines 30-34 of mohr_circle.py, and leads to the following expression for $[\sigma']$:

$$\begin{bmatrix} C - 2R\sin^2\left(\varphi\right) + R & -R\sin\left(2\varphi\right) & 0\\ -R\sin\left(2\varphi\right) & C - 2R\cos^2\left(\varphi\right) + R & 0\\ 0 & 0 & \sigma_3^p \end{bmatrix}$$

Python has taken us almost as far as we need to go, but it doesn't seem to be smart enough to use the following two trigonometric identities:

$$\frac{1 - 2\sin^2 \phi = \cos(2\phi)}{1 - 2\cos^2 \phi = -\cos(2\phi)}$$
(2.16)

Substituting these into the expression for $[\sigma']$ gives our final result:

$$[\sigma'] = \begin{bmatrix} C + R\cos(2\phi) & -R\sin(2\phi) & 0\\ -R\sin(2\phi) & C - R\cos(2\phi) & 0\\ 0 & 0 & \phi_3^p \end{bmatrix}$$
(2.17)

In the Mohr circle construction normal stresses (σ_N) are plotted on the x axis and the shear component of the stress tensor (τ) is plotted on the y axis. For a two dimensional stress state in the 1-2 plane the circle is defined by two points: $(\sigma_{11}, \sigma_{12})$ and $(\sigma_{22}, -\sigma_{12})$. In our current example the stress state in the untransformed axes is represented by the open symbols in Figure 2.6, <u>i.e.</u> by the points $(\sigma_{1p}, 0)$ and $(\sigma_{2p}, 0)$. In the transformed axes the stress state is represented by the solid circles in Figure 2.6. From Eq. 2.17 it is evident that the relationship between the two different representations of the stress state is obtained by a rotation along circle by 2ϕ . Whether this rotation is clockwise or counterclockwise depends on the sign convention in the definition of the shear stress. We're not going to worry about it here, but you can refer to the Mohr's Circle Wikipedia article[?] for the details (see the Section on the sign convention).

The Mohr circle construction can only be applied for a two dimensional meaning that there are no shear stresses with a component in the direction of the rotation axis. There can be a normal stress in the third direction, as in our example above, because this normal stress is simply superposed on the 2d stress state. In general, there are three principal stresses, σ_{1p} , σ_{2p} and σ_{3p} , and we can draw the Mohr circle construction with any combination of these 3 stresses. We end up with 3 different circles, as shown in Figure 2.7. Note that the convention is that σ_{1p} is the largest principal stress and that σ_{3p} is the smallest principal stress, <u>i.e.</u> $\sigma_{1p} > \sigma_{2p} > \sigma_{3p}$. An important result is that the largest shear stress, τ_{max} , is given by the difference between the largest principal stress and the smallest one:

$$\tau_{max} = \frac{1}{2} \left(\sigma_{1p} - \sigma_{3p} \right) \tag{2.18}$$



Figure 2.6: Mohr's circle construction.

This maximum shear stress is an important quantity, because it determines when a material will deform plastically (much more on this later). In order to determine this maximum shear stress, we need to first Figure out what the principal stresses are. In some cases this is easy. In a uniaxial tensile test, one of the principals stresses is the applied stress, and the other two principal stresses are equal to zero.

The individual Mohr's circles in Figure 2.7 correspond to rotations in the around the individual principal axes. Circle C_1 corresponds to rotation around the direction in which σ_{1p} is directed, C_2 corresponds to rotation around the direction in which σ_{2p} is directed, and C_3 corresponds to rotation around the direction in which σ_{3p} is directed. A consequence of this is that is always possible to use the Mohr's circle construction to determine the principal stresses if there is only one non-zero shear stress.

Exercise: Determine the maximum shear stress for the following stress state:

$$[\sigma] = \begin{bmatrix} 3 & 0 & 2 \\ 0 & 3 & 0 \\ 2 & 0 & 5 \end{bmatrix} MPa$$
(2.19)

Solution: We can handle this one without using a computer. There is only one non-zero shear stress (σ_{13}), so we can determine the principals stresses in the following manner:

- 1. One of the three principal stresses is the normal stress in the direction that does not involve either of the directions in the nonzero shear stress. Since the non-zero shear stress in our example is σ_{13} , one of the principal stresses is $\sigma_{22}=3$ MPa.
- 2. Now we draw a Mohr circle construction using the two normal stresses and the non-zero shear stress, in this case σ_{11} , σ_{33} and σ_{13} . Mohr's circle is centered at



Figure 2.7: Three-dimensional Mohr's Circle.

the the average of these two normal stresses, in our case at $C = (\sigma_{11} + \sigma_{33})/2 = 4$ MPa.

3. Determine the radius of the circle, R, is given as:

$$R = \sqrt{(\sigma_{33} - \sigma_c)^2 + \sigma_{13}^2} = \sqrt{(5-4)^2 + \sigma_{13}^2} = 2.24 \text{ MPa}$$

4. The principal stresses are given by the intersections of the circle with the horizontal axis:

$$\sigma_{1p}, \sigma_{2p} = C \pm R = 6.24 \text{ MPa}, 1.76 \text{ MPa}$$

The third principal stress is 3 MPa, as we already determined.

5. The maximum shear stress is half the difference between the largest principal stress (6.64 MPa) and the smallest one (1.76), or 2.24 MPa.



2.3.2 Critical Resolved Shear Stress for Uniaxial Tension

As an example of the Mohr circle construction we can consider the calculation of the resolved shear stress on a sample in a state of uniaxial tension. The Mohr's circle representation of the stress state is shown in Figure 2.8. The resolved shear stress, τ_{rss} , for sample in uniaxial tension is given by the following expression:

$$\tau_{rss} = \sigma_{1p} \cos \phi \cos \lambda \tag{2.20}$$

where σ_{1p} is the applied tensile stress, ϕ is the angle between the tensile axis and a vector normal to the plane of interest, and λ is the angle between the tensile axis and the direction of the shear stress. This shear stress has to be in the plane itself, so for a 2-dimensional sample $\lambda + \phi = 90^{\circ}$. This means we can rewrite Eq. 2.20 in the following way:

$$\tau_{rss} = \sigma_{1p} \cos \phi \cos \left(90^\circ - \phi\right) \tag{2.21}$$

We can use the identities $\cos(90 - \phi) = \sin \phi$ and $\sin(2\phi) = 2\sin \phi \cos \phi$ to obtain the following:

$$\tau_{rss} = \frac{\sigma_{1p}}{2} \sin\left(2\phi\right) \tag{2.22}$$

We can get the same thing from the Mohr's circle construction to redefine the axes by a rotation of ϕ . The shear stress is simply the radius of the circle $(\phi_{1p}/2 \text{ in this}$ case) multiplied by sin (2ϕ) . Mohr's circle also gives us the normal stresses:

$$\sigma_{11} = \frac{\sigma_{1p}}{2} + \frac{\sigma_{1p}}{2} \cos(2\phi) \sigma_{22} = \frac{\sigma_{1p}}{2} - \frac{\sigma_{1p}}{2} \cos(2\phi)$$
(2.23)

The untransformed 2-dimensional stress tensor looks like this:

$$[\sigma] = \begin{bmatrix} \sigma_{1p} & 0\\ 0 & 0 \end{bmatrix}$$
(2.24)

The transformed stress tensor (after rotation by ϕ to give the resolved shear stress) looks like this:

$$[\sigma'] = \begin{bmatrix} \frac{\sigma_{1p}}{2} + \frac{\sigma_{1p}}{2}\cos(2\phi) & \frac{\sigma_{1p}}{2}\sin(2\phi) \\ \frac{\sigma_{1p}}{2}\sin(2\phi) & \frac{\sigma_{1p}}{2} - \frac{\sigma_{1p}}{2}\cos(2\phi) \end{bmatrix}$$
(2.25)

2.3.3 Principal Stress Calculation

Principal stresses can easily by calculated for any stress state just by obtaining the eigenvalues of the stress tensor. In addition, the orientation of the principal axes (the coordinate system for which there are no off-diagonal components in the stress tensor). If you need a refresher on what eigenvalues



Figure 2.8: Mohr's circle construction and calculation of the resolved shear stress for a 2-dimensional sample in uniaxial extension.

and eigenvectors actually are, take a look at the appropriate Wikipedia page (http://en.wikipedia.org/wiki/Eigenvalues_and_eigenvectors). We'll use Python to do this, using the 'eig' command .

To illustrate, we'll start with the stress state specified by Eq. 2.9. which we got by starting with a simple uniaxial extension in the 1 direction, and rotating the coordinate system by 45° about the 3 axis. The Python script to do this is very simple and is as follows:

```
import numpy as np
2
  # write down the stress tensor that we need to diagonalize
3
  sig=1e6*np.array([[2.5,2.5,0],[2.5,2.5,0],[0,0,0]])
  # get the eigen values and eigen vectors
6
  [principalstresses, directions]=np.linalg.eig(sig)
  # the columns in 'directions' correspond to the dot product of the
9
  # principal axes with the orignal coordinate system
10
  # The rotation angles are obtained by calculating the inverse
11
    cosines
  theta=np.arccos(directions)*180/(np.pi)
12
13
  # print the results (or just look at them in the variable explorer
14
    in Spyder)
  print ('theta=\n', theta)
15
  print ('principal stresses=\n', principalstresses)
16
```

Here's the output generated by this script:

3 principal axes returned as column vectors. In this case there is a single normal stress, acting in a direction midway between the original x and y axes. The original uniaxial stress state is recovered in this example, as it should be. To summarize:

- $\diamond\,$ Principal Stresses: Eigenvalues of the stress tensor
- $\diamond\,$ Principal Stress directions: Eigenvectors of the stress tensor

theta =

45.0000 45.0000 90.0000	90.0000 90.0000 0	135.0000 45.0000 90.0000	
principalstr	resses =		
500000)	0	0
0)	0	0
0	0	0	

Figure 2.9: Output generated by principal_stress_calc.py.

2.3.4 Stress Invariants

Some quantities are invariant to choice of axes. The most important one is the

hydrostatic pressure

, p, given by summing the diagonal components of the stress tensor and dividing by 3:

$$p = -\frac{1}{3} \left(\sigma_{11} + \sigma_{22} + \sigma_{33} \right) = -\frac{1}{3} \left(\sigma_{1p} + \sigma_{2p} + \sigma_{3p} \right)$$
(2.26)

The negative sign appears because a positive pressure is compressive, but positive stresses are tensile. The hydrostatic pressure is closely related to a quantity referred to as the 'first stress invariant', I_1 :

$$I_1 = \sigma_{11} + \sigma_{22} + \sigma_{33} \tag{2.27}$$

The second and third stress invariants, I_2 and I_3 , are also independent of the way the axes are defined:

$$I_2 = \sigma_{11}\sigma_{22} + \sigma_{22}\sigma_{33} + \sigma_{33}\sigma_{11} - \sigma_{12}^2 - \sigma_{13}^2 - \sigma_{23}^2$$
(2.28)

$$I_3 = \sigma_{11}\sigma_{22}\sigma_{33} - \sigma_{11}\sigma_{23}^2 - \sigma_{22}\sigma_{13}^2 - \sigma_{33}\sigma_{12}^2 + 2\sigma_{12}\sigma_{13}\sigma_{23}$$
(2.29)

It's not obvious at first that each of these quantities are invariant to the choice of coordinate axes. As a check, we can start with a general tensor, rotate the coordinate system through a full 180 degrees, and plot the value of an invariant as a function of a the rotation angle, ϕ . The following python code does this for I_2 :

```
import numpy as np
import matplotlib.pyplot as plt
4 # create a function that multiplies the transforms a stress
```

```
# tensor sig by a rotation of phi about the Z axis,
  # and returns the vaalue of I2
7
  def I2_calc(phi):
8
      sig = np.array([[3, 5, 4], [5, 2, 9], [4, 9, 6]])
9
      theta = np.array([[phi,90+phi,90],[90-phi,phi,90],[90,90,0]])
10
      Q = np.cos(np.radians(theta))
11
12
      QT = np.transpose(Q)
      sigp = Q@sig@QT
13
      I2 = (sigp[0][0]*sigp[1][1]+sigp[1][1]*sigp[2][2]+sigp[2][2]*
14
        sigp[0][0]-
             sigp[0][1]**2 - sigp[1][2]**2 -sigp[0][2]**2)
15
16
      return I2
17
  # vectorize the function so we can input an array of phi values
18
  vI2 = np.vectorize(I2_calc)
19
20
  # now calculate I2 over a range of phi values
21
  phi = np.linspace(0, 180, 100)
22
  I2vals = vI2(phi)
23
24
  # now make the plot
25
  plt.close('all')
26
  fig, ax = plt.subplots(1,1, figsize=(3,3), constrained_layout=True)
27
28 ax.plot(phi, I2vals, '-')
29 ax.set_xlabel(r'$\phi (deg.)$')
30 ax.set_ylabel(r'$I_2$')
31
32
  # save the plot
  fig.savefig('../figures/I2plot.svg')
33
```

This results in the very boring plot shown in Figure 2.10, indicating that I_2 really is invariant to the definition of the coordinate axes.

2.4 Strain

There are 3 related definitions of the strain:

- 1. Engineering strain
- 2. Tensor strain
- 3. Generalized strain (large deformations, also referred to as 'finite strain')

Each of these definitions of strain describe the way different points an object move relative to one another when the material is deformed. Consider two points P_1 and P_2 , separated initially by the increments x_1, x_2 and x_3 along the 1, 2 and 3 directions. After the deformation is applied, these points move by the following amounts, as illustrated in Figure 2.11:

- $\diamond P_1$ moves by an amount $\vec{u} = (u_1, u_2, u_3)$
- $\diamond P_2$ moves by $\vec{u} + d\vec{u} = (u_1 + du_1, u_2 + du_2, u_3 + du_3)$

2.4.1 Small Strains

Strain describes how much farther point to moved in three different directions, as a function of how far P_2 was from P_1 initially. When P_1 and P_2 are close together so



Figure 2.10: Plot of I_2 as a function of the axis rotation angle for a generic 3d stress state, calculated from I2_invariant_check.py.



Before Deformation

Figure 2.11: Location of two points, P_1 and P_2 , before and after an applied deformation.

:

that dx, dy and dz are small, we can ignore higher order terms in a Taylor expansion for du, dv and dw and maintain only the first, partial derivative terms as follows:

$$du_{1} = \frac{\partial u_{1}}{\partial x_{1}} dx_{1} + \frac{\partial u_{1}}{\partial x_{2}} dx_{2} + \frac{\partial u_{1}}{\partial x_{3}} dx_{3}$$

$$du_{2} = \frac{\partial u_{2}}{\partial x_{1}} dx_{1} + \frac{\partial u_{2}}{\partial x_{2}} dx_{2} + \frac{\partial u_{2}}{\partial x_{3}} dx_{3}$$

$$du_{3} = \frac{\partial u_{3}}{\partial x_{1}} dx_{1} + \frac{\partial u_{3}}{\partial x_{2}} dx_{2} + \frac{\partial u_{3}}{\partial x_{3}} dx_{3}$$
(2.30)

We can write this in matrix form in following way:

$$\begin{bmatrix} du_1 \\ du_2 \\ du_3 \end{bmatrix} = [\mathbf{H}] \begin{bmatrix} dx_1 \\ dx_2 \\ dx_3 \end{bmatrix}$$
(2.31)

where **[H]** is the following tensor representation of the deformation gradient:

$$[\mathbf{H}] = \begin{bmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \frac{\partial u_1}{\partial x_3} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \frac{\partial u_2}{\partial x_3} \\ \frac{\partial u_3}{\partial x_1} & \frac{\partial u_3}{\partial x_2} & \frac{\partial u_3}{\partial x_3} \end{bmatrix}$$
(2.32)

The three normal components of the strain correspond to the change in the displacement in a given direction corresponds to a change in initial separation between the points of interest in the same direction:

$$e_{11} = \frac{\partial u_1}{\partial x_1} \\ e_{22} = \frac{\partial u_2}{\partial x_2} \\ e_{33} = \frac{\partial u_3}{\partial x_3}$$

$$(2.33)$$

The engineering shear strains are defined as follows:

$$e_{23} = \frac{\partial u_3}{\partial x_2} + \frac{\partial u_2}{\partial x_3}$$

$$e_{13} = \frac{\partial u_1}{\partial x_3} + \frac{\partial u_3}{\partial x_1}$$

$$e_{12} = \frac{\partial u_1}{\partial x_2} + \frac{\partial u_2}{\partial x_1}$$
(2.34)

Note: shear strains are often represented by the lower case Greek gamma to distinguish them from normal strains:

$$\gamma_{12} \equiv e_{12}; \, \gamma_{23} \equiv e_{23}; \, \gamma_{13} = e_{13} \tag{2.35}$$

2.4.2 Tensor Shear Strains

Engineering strains relate two vectors to one another $(\vec{x} \text{ and } \vec{u})$, just as a tensor does, but the transformation law between different coordinate systems is not obeyed for the engineering strains. For this reason the engineering strains are NOT tensor strains. Fortunately, all we need to do to change engineering strains to tensor

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strains is to divide the shear components by 2. In our notation we use e to indicate engineering strain and ϵ to indicate tensor strains. The tensor normal strains are exactly the same as the engineering normal strains:

$$\epsilon_{11} = e_{11}$$

$$\epsilon_{22} = e_{22}$$

$$\epsilon_{zz} = e_{zz}$$
(2.36)

Engineering shear strains (e_{23}, e_{13}, e_{12}) are divided by two to give tensor shear strains:

$$\epsilon_{23} = e_{23}/2 \epsilon_{13} = e_{13}/2 \epsilon_{12} = e_{12}/2$$
(2.37)

Note that the tensor strains must be used in coordinate transformations (axis rotation, calculation of principal strains, e_{1p} , e_{2p} , e_{3p}).

2.4.3 Generalized Strain

We can also define the strain by considering a cube of side ℓ that is deformed into a parallelepiped with dimensions of (along principal strain axes). After deformation, the cube has dimensions of $\lambda_{1p}\ell$, $\lambda_{2p}\ell$, $\lambda_{3p}\ell$. Alternatively, a sphere of radius r_0 is deformed into and ellipsoid with principal axes of $\lambda_{1p}r_0$, $\lambda_{2p}r_0$ and $\lambda_{3p}r_0$, as shown in Figure 2.12. The quantities λ_{1p} , λ_{2p} , λ_{3p} are principal stretch ratios, and are related to the principal strains as follows:

$$\lambda_1^p = 1 + e_1^P \lambda_2^p = 1 + e_2^P \lambda_3^p = 1 + e_3^P$$
(2.38)

The true strains, e_1^t , are obtained as by taking the natural log of the relevant stretch ratio. For example, for a uniaxial tensile test, the true strain in the tensile direction (assumed to be the 1 direction here) is:

$$e_1^t = \ln\left(\lambda_1\right) \tag{2.39}$$

This expression for the true strain can be obtained by recognizing that the incremental strain is always given by the fractional increase in length $d\ell/\ell$, where ℓ is the current length of the material as it is being deformed. If the initial length is ℓ_0 and the final, deformed length is ℓ_f , then the total true strain, e_1^{true} is obtained by integrating the incremental strains accumulated throughout the entire deformation history:

$$e_1^{true} = \int_{\ell_0}^{\ell_f} \frac{d\ell}{\ell} = \ln \ell |_{\ell_0}^{\ell_f} = \ln \left(\frac{\ell_f}{\ell_0}\right) = \ln \lambda_1^p$$
(2.40)

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Figure 2.12: Unit sphere deformed into a strain ellipsoid with dimensions $of\lambda_1, \lambda_2, \lambda_3$.

The stretch ratios provide a useful description of the strain for both small and large values of the strain. A material with isotropic mechanical properties has the same coordinate axes for the principal stresses and the principal strains.

A more detailed description of generalized strain, with a lot of relevant matrix math, is provided in the Wikipedia article on finite strain theory (https://en.wikipedia.org/wiki/Finite_strain_theory). If you come across concepts like the

Cauchy-Green deformation tensor

or the

Finger deformation tensor

, this article provides a useful introduction (but be prepared for a lot of matrix math). These concepts appear in a range of useful description of mechanical response, including many in the biomedical field (muscle actuation, deformation of skin, etc).

2.5 Deformation Modes

Now that we've formally defined stress and strain we can give some specific examples where these definitions are used, and begin to define some elastic constants. We'll begin with the two most fundamental deformation states: simple shear and hydrostatic compression. These are complementary strain states - for an isotropic material simple shear changes the shape but not the volume, and hydrostatic compression changes the volume but not the shape. We'll eventually show that for an isotropic material there are only two independent elastic constants, so if we know how an isotropic material behaves in response to these two stress states, we have a complete understanding of the elastic properties of the material.

2.5.1 Simple Shear

Simple shear is a two dimensional strain state, which means that one of the principal strains is zero (or one of the principal stretch ratios is 1).

The stress tensor looks like this:



Figure 2.13: Schematic representation of simple shear.

$$[\sigma] = \begin{bmatrix} 0 & \sigma_{12} & 0\\ \sigma_{12} & 0 & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(2.41)

From the definition of the engineering shear strain (Eq. 2.34) we have:

$$e_{12} = \frac{u}{d} \tag{2.42}$$

We need to divide the engineering shear strains by 2 to get the tensor strains, so we get the following:

$$[\epsilon] = \begin{bmatrix} 0 & e_{12}/2 & 0\\ e_{12}/2 & 0 & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(2.43)

We're generally going to use engineering strains and not tensor strains, so won't often need to worry about the factor of two. The exception is when we want to use a coordinate transformation to find the principal strains. To do this we use a procedure exactly analogous to the procedure described in Section 2.3, but we need to make sure we are using the tensor strains when we do the calculation.

The shear modulus is simply the ratio of the shear stress to the shear strain.

$$G(\text{shear modulus}) = \frac{\sigma_{12}}{e_{12}} \tag{2.44}$$

Note that the volume of the material is not changed, but its shape has. In very general terms we can view the shear modulus of a material as a measure of its resistance to a change in shape under conditions where the volume remains constant.

2.5.2 Simple Shear and the Mohr's Circle Construction for Strains

Mohr's cirlcle for strain looks just like Mohr's circle for stress, provided that we use the appropriate tensor components. That means that we need to plot $e_{12}/2$ on the vertical axis and the normal strains on the vertical axis, as shown in Figure 2.14 (where we have used the common notation for the simple shear geometry, with $e_{xy} = \gamma$). One thing that we notice from this plot is that γ is simply given by the difference between the two principal strains:

$$\gamma = e_{1p} - e_{2p} = \lambda_{1p} - \lambda_{2p} \tag{2.45}$$

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For simple shear this relationship is valid, even for large strains, even though there are other aspects of the Mohr's circle construction that no longer work at large strains. The primary difficulty is that the frame of reference for the strained and unstrained case are not the same. In general, strains rotate the frame of reference by an amount that we don't want to worry about for the purposes of this course. For small strains typically obtained in metals or ceramics (with strain amplitudes of a few percent or less) we don't need to worry about this rotation, but it can become important for polymeric systems that undergo very large strains prior to failure. However, if all we want a measure of the shear strain in the material, we can still use Eq. 2.45, regardless of how large the principal strains (and corresponding stretch ratios) actually are.

Ι

2.5.3 Torsion

An important geometry for characterizing the shear properties of soft materials is the torsional geometry shown in Figure 2.15. In this material a cylindrical or disk-shaped material is twisted about an axis of symmetry. The material could be a long, thin fiber (Figure 2.15a) or a flat disk sandwiched between two plates (Figure 2.15b). We obtain the shear modulus by looking at the torsional stiffness of material, *i.e.*, the Torque, T, required to rotate the top and bottom of the fiber by an angle θ_0 .

We define a cylindrical system with a z axis along the fiber axis. The other axes in this coordinate system are the distance r from this axis of symmetry, and the angle θ around the z axis. The shear strain in the $\theta - z$ plane depends only on r, and is given by:

$$e_{\theta z} = r \frac{d\theta}{dz} = r \frac{\theta_0}{\ell} \tag{2.46}$$

The corresponding shear stress is obtained by multiplying by the shear modulus, G:



Figure 2.14: Mohr's circle construction for SMALL strains.



Figure 2.15: Fiber torsion.

$$\sigma_{\theta z} = Gr\theta_0/\ell \tag{2.47}$$

We integrate the shear stress to give the torque, T:

$$T = \int_0^{d/2} r\sigma_{\theta z} 2\pi r dr = \frac{\pi G \theta_0 d^4}{32\ell}$$
(2.48)

This geometry is commonly used in an oscillatory mode, where θ is oscillated at a specified frequency. In this case the torque response is obtained by using the dynamic shear modulus, G^* (defined in the section on viscoelasticity) in place of G.

2.5.4 Hydrostatic Compression

The

bulk compressive modulus

, K_b , of a material describes its resistance to a change in density. Formally, it is defined in terms of the dependence of the volume of the material on the hydrostatic pressure, p:

$$K_b = -V \frac{dp}{dV} \tag{2.49}$$

The hydrostatic stress state corresponds to the stress state where there are no shear stresses, and each of the normal stresses are equal. Compressive stresses are defined as negative, whereas a compressive pressure is positive, so the stress state for hydrostatic compression looks like this:

$$\sigma = \begin{bmatrix} -p & 0 & 0\\ 0 & -p & 0\\ 0 & 0 & -p \end{bmatrix}$$
(2.50)

where p is the

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hydrostatic pressure

2.5.5 Uniaxial Extension

Uniaxial extension corresponds to the application of a normal stress along one direction, which we define here as the 3 direction so that the stress tensor looks like this:

$$\sigma = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$
(2.51)

We can measure two separate strains from this experiment: the longitudinal strain in the same direction that we apply the stress, and the transverse strain, e_{22} , measured in the direction perpendicular to the applied stress (we'll assume that the sample is isotropic in the 1-2 plane, so $e_{11} = e_{22}$. The strains are given by the fractional changes in the length and width of the sample:

$$e_{33} = \frac{\Delta\ell}{\ell_0} \tag{2.52}$$

$$e_{22} = \frac{\Delta w}{w} \tag{2.53}$$

From these strains we can define

Young's modulus

, E, and

Poisson's ratio

, ν :

$$E = \sigma_{33}/e_{33} \tag{2.54}$$

$$\nu = -e_{22}/e_{33} \tag{2.55}$$



Figure 2.16: Hydrostatic Compression.



Figure 2.17: Uniaxial tensile deformation.

2.5.6 Longitudinal Compression

A final deformation state that we will consider is longitudinal compression. In this state all of the compression is in one direction, which we will specify as the 3 direction. The strains in the other two direction are constrained to be zero, so the strain state is as follows:

$$e = \left[\begin{array}{rrr} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & e_{33} \end{array} \right]$$

Note that the strain state is similar to that of uniaxial extension or compression (Figure 2.17), but in the current case we have a single non-zero strain instead of a single non-zero stress. Finite values of σ_{11} and σ_{22} must exist in order for sample in order for this strain state to be maintained, but we're not going to worry about those for now. Instead, we'll use the following relationship for the longitudinal elastic modulus, E_{ℓ} which is the ratio of σ_{33} to e_{33} for this strain state. Note that this deformation state changes both the shape and volume of the material, so E_{ℓ} involves both G and K_b :

$$E_{\ell} = \frac{\sigma_{33}}{e_{33}} = K_b + \frac{4}{3}G \tag{2.56}$$

2.6 Representative Moduli

A few typical values for G and K are listed in Table 1. Liquids do not have a shear modulus, but they do have a bulk modulus.



Figure 2.18: Longitudinal Compression

Material	G (Pa)	K_b (Pa)
Air	0	$1.0 \mathrm{x} 10^5$
Water	0	$2.2 \text{x} 10^9$
Jello	$\approx 10^4$	$2.2 \text{x} 10^9$
Plastic	$\approx 10^9$	$\approx 2 \mathrm{x} 10^9$
Steel	$8 x 10^{10}$	$1.6 \mathrm{x} 10^{11}$

 Table 1: Representative elastic moduli for different materials.

2.7 Case Study: Speed of Sound

The speed of sound, or **sound velocity**, V_{sound} , is actually a mechanical property. It is related to a modulus, M, in the following way:

$$V_{sound} = \sqrt{\frac{M}{\rho}} \tag{2.57}$$

Here ρ is the density of the material. The modulus that we need to use depends on the type of sound wave that is propagating. The two most common are a shear wave and a longitudinal compressional wave:

- \diamond Longitudinal compressional wave: $M=E_\ell$
- \diamond Shear wave: M = G

In a liquid or gas (like air), G = 0 and shear waves cannot propagate. In this case there is a single sound velocity obtained by setting $M = K_b$. For an ideal gas:

$$P = \frac{n}{V}RT \tag{2.58}$$

If the compression is applied slowly enough so that the temperature of the gas can equilibrate, we have:

$$K_b = -V\frac{dP}{dV} = \frac{n}{V}RT = P \tag{2.59}$$

So we expect that for a gas, the compressive modulus just equal to the pressure. The situation is a bit more complicated for gas, since we need to use the adiabatic modulus, which is about 40% higher than the pressure itself. (For a detailed explanation, see the Wikipedia article on the speed of sound (http://en.wikipedia.org/wiki/Speed_of_sound)[?]. The brief explanation is that for sound propagation, the derivative in Eq. 2.59 needs to be evaluated at constant entropy and not constant temperature, because the sound oscillation is so fast that the heat does not have time to escape). With $\rho=1.2 \text{ kg/m}^3$ and $K = 1.4x10^5$ Pa, we end up with a sound velocity of 344 m/s.

3 Matrix representation of Stress and Strain

As usual, we begin by replacing the directions (x, y, and z) with numbers: $x \to 1$, $y \to 2$, $z \to 3$. Once we do this we have 6 stress components, and six strain components. We then number these components from 1-6, so that 1, 2 and 3 are the normal components and 4, 5 and 6 are the shear components. We do this for both stress and strain as shown in Table 2.

A series of elastic constants relate the stresses to the strains. We can do calculations in either of the following two ways:

- 1. Start with a column vector consisting of the 6 elements of an applied stress, and use the compliance matrix to calculate the strains.
- 2. Start with a column vector consisting of the 6 elements of an applied strain, and use the stiffness matrix to calculate the stresses.

In each case we use a 6×6 matrix to relate two 6-element column vectors to one another. The procedure in each case is outlined below.

3.1 Compliance matrix

In most experimental situations it is more convenient to think of the strains that result from a given applied stress state than to think of the stresses that result from an applied strain. In a simple uniaxial extension experiment, we apply a single known stress along one axis, while also measuring the strain along this same axis. Only one of the stress components is nonzero in this case, but there will be additional non-zero strains because of the changes in the lateral dimensions of the sample as we pull on it. We use the compliance matrix, [S] to obtain the strains from the applied stress state:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = [\mathbf{S}] \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.1)

It is common to use bold symbols to denote matrices, omitting the brackets as we have used here. Most readers of this text do not spend a lot of time thinking

Engineering stress	Matrix Stress	Engineering Strain	Matrix Strain
σ_{11}	σ_1	e_{11}	e_1
σ_{22}	σ_2	e_{22}	e_2
σ_{33}	σ_3	e_{33}	e_3
σ_{23}	σ_4	e_{23}	e_4
σ_{13}	σ_5	e_{13}	e_5
σ_{12}	σ_6	e_{12}	e_6

 Table 2: Definition of the matrix components of stress and strain.

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about the common conventions used for matrix notation, however, so we keep the brackets, since it is more obvious that $[\mathbf{S}]$ is a matrix than it would be if we used the more common notation of \mathbf{S} for this quantity. To clarify things even further and to illustrate the different symmetry requirements that relate components of $[\mathbf{S}]$, we generally include all of the components of $[\mathbf{S}]$, in the following way:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16}\\ S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26}\\ S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36}\\ S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46}\\ S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56}\\ S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.2)

Finally, we note that Eq. 3.2 can also be written in terms of the expression for a given strain component, ϵ_i :

$$\epsilon_i = S_{ij}\sigma_j \tag{3.3}$$

When matrix components are multiplied, the convention is to sum over over all possible values of the indices that are repeated. In Eq. 3.2 the index j appears twice on the right side of the equation, so we need to sum over all possible values of this variable (1-6) for each value of i. For example, we obtain the following for ϵ_3 :

$$\epsilon_3 = S_{31}\sigma_1 + S_{32}\sigma_2 + S_{33}\sigma_3 + S_{34}\sigma_4 + S_{35}\sigma_5 + S_{36}\sigma_6 \tag{3.4}$$

The matrix must be symmetric, with $S_{ij} = S_{ji}$, so there are a maximum of 21 independent compliance coefficients:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16}\\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26}\\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36}\\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46}\\ S_{15} & S_{25} & S_{35} & S_{45} & S_{55} & S_{56}\\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.5)

Note that the compliance coefficients have the units of an inverse stress (Pa^{-1}) .

3.2 Stiffness Matrix

The stiffness matrix (\mathbf{C}) is the inverse of compliance matrix (note the somewhat confusing notation in that the compliance matrix is \mathbf{S} and the stiffness is \mathbf{C} , backwards from what you might expect). The stiffness coefficients have units of stress.

$$\begin{bmatrix} \sigma_{1} \\ \sigma_{2} \\ \sigma_{3} \\ \sigma_{4} \\ \sigma_{5} \\ \sigma_{6} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \begin{bmatrix} e_{1} \\ e_{2} \\ e_{3} \\ e_{4} \\ e_{5} \\ e_{6} \end{bmatrix}$$
(3.6)

3.3 Symmetry requirements on the compliance (or stiffness) matrix.

3.3.1 Orthorhombic symmetry

Extruded polymer sheets, like the one shown schematically in Figure 3.1 have orthorhombic symmetry, with different elastic properties in the extrusion, thickness and width directions. These materials have orthorhombic symmetry.

For materials with orthorhombic symmetry, the principal axes of stress and strain are identical, and all compliance components relating a shear strain (e_4 , e_5 or e_6) to normal stresses ($\sigma_1, \sigma_2 \text{ or } \sigma_3$) or to another shear stress must be zero. The stiffness matrix is as shown in Eq. 3.8 below, and there are 9 independent elastic constants. These 9 elastic constants can be identified as follows:

- $\diamond E_1 = 1/S_{11}, E_2 = 1/S_{22}$ and $E_3 = 1/S_{33}$, Young's moduli for extension in the 1, 2 and 3 directions, respectively.
- $\diamond G_{23} = 1/S_{44}, G_{13} = 1/S_{55}$ and $G_{12} = 1/S_{66}$, Shear moduli for shear in the planes perpendicular to the 1, 2 and 3 directions, respectively.
- ♦ S_{12} , S_{13} and S_{23} , which relate stresses in one direction to strains in the perpendicular direction. These components are related to the corresponding Poisson's ratios, with μ_{ij} giving the ratio of the strain in the i and j directions, for a stress applied in the j direction $(i \neq j)$:

$$\nu_{ij} = \frac{-e_i}{e_j} = \frac{-S_{ij}\sigma_j}{S_{jj}\sigma_j} = -S_{ij}E_j \tag{3.7}$$

Equivalently, we have $S_{ij} = -\frac{\nu_{ij}}{E_j}$.

With these expressions for the different moduli and Poisson's ratios, the full compliance matrix for a material with Orthombic symmetry can be written in the following form:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = \begin{bmatrix} 1/E_1 & -\nu_{12}/E_2 & -\nu_{13}/E_3 & 0 & 0 & 0\\ -\nu_{12}E_2 & 1/E_2 & -\nu_{23}/E_3 & 0 & 0 & 0\\ -\nu_{13}/E_3 & -\nu_{23}/E_3 & 1/E_3 & 0 & 0 & 0\\ 0 & 0 & 0 & 1/G_1 & 0 & 0\\ 0 & 0 & 0 & 0 & 1/G_2 & 0\\ 0 & 0 & 0 & 0 & 0 & 1/G_3 \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.8)

Note that the requirement that [s] be symmetric means that $\nu_{ij}/E_j = \nu_{ji}/E_i (i \neq j)$.



Figure 3.1: Schematic representation of an extruded sheet.

3.3.2 Fiber Symmetry

For a material with fiber symmetry, one of the axes is unique (in this case the 3 axis) and the material is isotropic in the orthogonal plane. We label the identical 1 and 2 axes as transverse axes ('t') and the 3 axis as a fiber axis ('f'). Since the 1 and 2 axes are identical, we have $E_t = E_1 = E_2$, $G_{tf} = G_{13} = G_{23}$ and $\nu_{tf} = \nu_{23} = \nu_{13}$. Additionally, the requirement that all directions in the 1-2 plane be equivalent means that $S_{66} = 2(S_{11} - S_{12})$, or in terms of the moduli:

$$E_t = 2G_{tt} \left(1 + \nu_{tt} \right) \tag{3.9}$$

there are now 5 independent elastic constants and the relationship between the stresses and strains can be written in the following way:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = \begin{bmatrix} \frac{1}{2G_{tt}(1+\nu_{tt})} & \frac{-\nu_{tt}}{2G_{tt}(1+\nu_{tt})} & -\nu_{tf}/E_f & 0 & 0 & 0\\ \frac{-\nu_{tt}}{2G_{tt}(1+\nu_{tt})} & \frac{1}{2G_{tt}(1+\nu_{tt})} & -\nu_{tf}/E_f & 0 & 0 & 0\\ 0 & 0 & 0 & 1/G_{tf} & 0 & 0\\ 0 & 0 & 0 & 0 & 1/G_{tf} & 0\\ 0 & 0 & 0 & 0 & 0 & 1/G_{tf} & 0 \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.10)

Examples of materials with fiber symmetry include the following:

- 1. Many liquid crystalline polymers (e.g. Kevlar).
- 2. Materials after cold drawing (plastic deformation to high strains, carried out below the glass transition temperature or melting temperature of the material.)
- 3. Biological tissue (including muscle fibers, for example) where the function of the material requires unique properties along the fiber axis.

To better understand the significance of the 5 elastic constants for fiber symmetry, it is useful to consider the types of experiment we would need to conduct to measure each of them for a cylindrical fiber. The necessary experiments are described below.

Uniaxial extension along the fiber axis - measurement of E_f and ν_{tf} : We obtain E_f and ν_{tf} by performing a tensile test along the fiber axis (the 3 direction) as shown in Figure 3.2. The strain in the fiber direction, e_f is given by the fractional change in the length of the fiber after application of the load, and the strains in the transverse directions, e_t are is by the fractional changes in the diameter of the fiber:

$$e_f = \Delta \ell / \ell; \ e_t = \Delta d / d_0 \tag{3.11}$$

For E_f we have:

$$E_f = \frac{\sigma_3}{e_3} \tag{3.12}$$

For fiber symmetry we have different Poisson's ratios, depending on the orientation of the applied stress and on the strain component that we are interested in. ν_{tf}

describes the ratio between the transverse strain, e_t and the fiber strain, e_f for a stress applied in the fiber direction:

$$\nu_{tf} = \frac{-e_t}{e_f} \tag{3.13}$$

Note that the symmetry of [s] with $S_{ij} = S_{ji}$ means that the following condition holds:

$$\frac{\nu_{ij}}{E_j} = \frac{\nu_{ji}}{E_i} \tag{3.14}$$

This means that ν_{ft} (the relevant Poisson's ratio used to determine strain in the fiber direction for a uniaxial stress applied in the transverse direction) is given by the following expression:

$$\nu_{ft} = \nu_{tf} \frac{E_t}{E_f} \tag{3.15}$$

Fiber Torsion - Measurement of S_{44} : We obtain the shear modulus by looking at the torsional stiffness of the fiber, *i.e.*, the torque, *T*, required to rotate the top and bottom of the fiber by an angle θ_0 , as illustrated in Figure 3.3

We define a cylindrical system with a z axis along the fiber axis. The other coordinates in this system are the distance r from this axis of symmetry, and the angle θ around the z axis. The shear strain in the $\theta - z$ plane depends on r, and is given by:

$$e_{\theta z} = r \frac{d\theta}{dz} = r \frac{\theta_0}{\ell} \tag{3.16}$$

The corresponding shear stress is obtained by multiplying by the shear modulus, G_{ft} characterizing shear deformation in a plane containing the fiber axis:

$$\sigma_{\theta z} = G_{tf} r \theta_0 / \ell \tag{3.17}$$

We integrate the shear stress to give the torque, T:



Figure 3.2: Fiber extension.



Figure 3.3: Fiber torsion.

$$T = \int_{0}^{d/2} r \sigma_{\theta z} 2\pi r dr = \frac{\pi G_{tf} \theta_0 d^4}{32\ell}$$
(3.18)

So once we know the torsional stiffness of the fiber (the relationship between the applied torque, T, and rotation angle, θ_0) we know the shear modulus, G_{tf} .

Fiber compression in 1-2 plane - determination of E_t and ν_{tt} : The last two elastic constants for a material with fiber symmetry can be determined from an experiment where the fiber is confined between two surfaces and compressed as shown in Figure 3.4. The elastic constants can be determined by measuring the width of the contact region between the fiber and the confining surface. If the confining surfaces are much stiffer than the fiber itself, than this contact width, 2b, is determined by the elastic deformation of the material in the transverse plane. If there is no friction between the fiber and the confining surfaces the fiber is allowed to extend in the fiber direction as it is compressed, the contact width is given by the following expression:

$$b^2 = \frac{2Fd_0}{\ell E_t}$$
(3.19)

where P is the force applied to the fiber, d_0 is its undeformed diameter and ℓ is its length.

A practical situation that is often observed is that friction between the fiber and confining surfaces keeps the fiber length from increasing, so the strain in the three direction must be zero. If we express the stress state in terms of the principle stresses in 1 and 2 directions (both in the transverse plane), we have the following from Eq. 3.10:

$$e_f = \frac{-\nu_{tf}}{E_f} \left(\sigma_1^p + \sigma_2^p\right) + \frac{\sigma_3}{E_f} \tag{3.20}$$

Setting e_3 to zero in this equation gives the following for σ_3 :

$$\sigma_f = \nu_{tf} \left(\sigma_1^p + \sigma_2^p \right) \tag{3.21}$$

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A consequence of this stress is that the frictionless expression for b gets modified to the following:

$$b^2 = \frac{2Fd_0}{\ell} \left(\frac{1}{E_t} - \frac{\nu_{tf}^2}{E_f} \right)$$
(3.22)

The remaining constant, ν_{tt} , is determined from a measurement of d/d_0 , the ratio of the fiber width at the midplane to the original width of the fiber. This relationship is complicated, and involves several of the different elastic constants.

$$\frac{d}{d_0} = f(P, E_1, \nu_{13}, E_3, \nu_{tt}).$$
(3.23)

3.3.3 Cubic Symmetry

For a material with cubic symmetry the 1,2 and 3 axes are all identical to one another, and we end up with 3 independent elastic constants, E, G and ν :

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6\\ \end{bmatrix} = \begin{bmatrix} 1/E & -\nu/E & -\nu/E & 0 & 0 & 0\\ -\nu/E & 1/E & -\nu/E & 0 & 0 & 0\\ -\nu/E & -\nu/E & 1/E & 0 & 0 & 0\\ 0 & 0 & 0 & 1/G & 0 & 0\\ 0 & 0 & 0 & 0 & 1/G & 0\\ 0 & 0 & 0 & 0 & 0 & 1/G \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.24)

Note that cubic systems are NOT isotropic. Elastic constants in the above table correspond either to extension in the directions perpendicular to a cube face, or shear in a plane that is perpendicular to a cube face. In general, moduli for other orientations will be different.

3.3.4 Isotropic systems

For an isotropic material all axes are equivalent, and the properties are invariant to any rotation of the coordinate axes. The requirement that the material properties



Figure 3.4: Transverse deformation of a fiber.
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be invariant with respect to any rotation of the coordinate axes results in the requirement that $S_{44} = 2 (S_{11} - S_{12})$, so there are two independent elastic constants. For isotropic materials there are only two independent elastic constants, with the shear modulus, G, Young's modulus E and Poisson's ratio, ν are related to one another by the following expression:

$$E = 2G(1+\nu)$$
(3.25)

We have only two independent elastic constants for an isotropic material. We can choose which two constants we want to use as the independent ones. Choosing G and ν gives:

$$\begin{bmatrix} e_1\\ e_2\\ e_3\\ e_4\\ e_5\\ e_6 \end{bmatrix} = \begin{bmatrix} \frac{1}{2G(1+\nu)} & \frac{-\nu}{2G(1+\nu)} & \frac{-\nu}{2G(1+\nu)} & 0 & 0 & 0\\ -\nu/E & \frac{1}{2G(1+\nu)} & -\nu/E & 0 & 0 & 0\\ -\nu/E & -\nu/E & \frac{1}{2G(1+\nu)} & 0 & 0 & 0\\ 0 & 0 & 0 & 1/G & 0 & 0\\ 0 & 0 & 0 & 0 & 1/G & 0\\ 0 & 0 & 0 & 0 & 0 & 1/G \end{bmatrix} \begin{bmatrix} \sigma_1\\ \sigma_2\\ \sigma_3\\ \sigma_4\\ \sigma_5\\ \sigma_6 \end{bmatrix}$$
(3.26)

Bulk Modulus for an Isotropic Material : The bulk modulus, K_b , of a material describes its resistance to a change in volume (or density) when we apply a hydrostatic pressure, p. It is defined in the following way:

$$K_b = -V \frac{dP}{dV} \tag{3.27}$$

The stress state in this case is as follows:

$$\sigma = \begin{bmatrix} -p & 0 & 0\\ 0 & -p & 0\\ 0 & 0 & -p \end{bmatrix}$$
(3.28)

From the compliance matrix (Eq. 3.26) we get $e_1 = e_2 = e_3 = -p (S_{11} + 2S_{12})$. The change in volume, ΔV can be written in terms of the three principal extension ratios, λ_1, λ_2 and λ_3 :

$$\frac{\Delta V}{V_0} = \frac{V}{V_0} - 1 = \lambda_1 \lambda_2 \lambda_3 - 1 = (1 + e_1) (1 + e_2) (1 + e_3) - 1 \approx e_1 + e_2 + e_3 \quad (3.29)$$

Now we use the fact that for small x, $(1 + x)^3 \approx 1 + 3x$, so we have:

$$\frac{\Delta V}{V_0} = e_1 + e_2 + e_3 = -\frac{3p}{E} \left(1 - 2\nu\right) \tag{3.30}$$

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Recognizing that the derivative dP/dV in the definition of K_b can be written as the limit of $p/\Delta V$ for very small p allows us to obtain the expression we want for K_b :

$$K_b = \lim_{p \to 0} \frac{-p}{\Delta V/V_0} = \frac{E}{3(1-2\nu)}$$
(3.31)

Relationship between the Isotropic Elastic Constants: Because there are only two independent elastic constants for an isotropic system E and ν can be expressed in terms of some combination of K_b and G. For E the relevant relationship is as follows.

$$E = \frac{9G}{3 + G/K_b} = 2G(1 + \nu)$$
(3.32)

We can also equate the two expressions for G in Eq. 3.32 to get the following expression for ν :

$$\nu = \frac{3 - 2G/K_b}{6 + 2G/K_b} \tag{3.33}$$

Note that if $K_b \gg G$, $E \approx 3G$ and $\nu \approx 0.5$. A summary of various relationships between different moduli is included in Table 3.

One important result that emerges from all of this is that an incompressible isotropic materials has a single independent elastic constant, since Poisson's ratio is constrained to be equal to 0.5. This result has important consequences in the properties of soft materials (like rubber and low-modulus polymer gels), where the linear elastic properties are quantified by a single number.

Relationship between Stiffness Matrix and Compliance Matrix: The stiffness matrix is the inverse of the compliance matrix. The relationships between the individual coefficients is quite complicated, unless there is a lot of symmetry. It's quite straightforward for an isotropic materials, which we handle here using the

Table 3: Relationships between the different elastic constants for an isotropic material. The independent variables are listed in the column at the left, with the other columns containing expressions for the other moduli in terms of these variables (adapted from ref. [?]).

	K_b	E	G	ν	E_{ℓ}
K_b, E			$\frac{3K_bE}{9K_b-E}$	$\frac{1}{2}\left(1-\frac{E}{3K_b}\right)$	$\frac{3K_b(3K_b+E)}{9K_b-E}$
K_b, G		$\frac{9K_bG}{3K_b+G}$		$\frac{\frac{3-2G/K_b}{6+2G/K_b}}{\frac{3-2G}{6+2G}}$	$K_b + 4G/3$
K_b, ν		$3K_b\left(1-2\nu\right)$	$\frac{3K_b(1-2\nu)}{2(1+\nu)}$		$\frac{3K_b(1-\nu)}{1+\nu}$
E, G	$\frac{EG}{3(3G-E)}$			$\frac{E}{2G} - 1$	$\frac{G(4G-E)}{3G-E}$
E, ν	$\frac{E}{3(1-2\nu)}$		$\frac{E}{2(1+\nu)}$		$\frac{E(1-\nu)}{(1+\nu)(1-2\nu)}$
G, ν	$\frac{2\hat{G}(1+\nu)}{3(1-2\nu)}$	$2G\left(1+\nu\right)$			$\frac{2G(1-\nu)}{1-2\nu}$

symbolic math capabilities of Python. The code is shown in Figure 3.5 and the output of this code is shown in Figure 3.6.

```
from sympy import symbols, Matrix, preview
  # specify two independent elements of s for an isotropic material
2
  s11, s12 = symbols(['s_11', 's_12'])
3
4
  # define the matrix
5
  s = Matrix([[s11, s12, s12, 0,0,0],
6
              [s12,s11,s12,0,0,0],
7
8
              [s12,s12,s11,0,0,0],
              [0,0,0,2*(s11-s12),0,0],
9
              [0,0,0,0,2*(s11-s12),0],
10
              [0,0,0,0,0,2*(s11-s12)])
11
12
  # now invert the matrix
13
  c=s.inv()
14
  preview(c, viewer = 'file', filename = '../figures/sympy_c.png')
15
```

Figure 3.5: Symbolic python code to invert the compliance matrix for an isotropic material.



Figure 3.6: Output of the symbolic python code to invert the compliance matrix.

Note that the stiffness matrix has the same symmetry as the compliance matrix, as it must:

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & G & 0 & 0 \\ 0 & 0 & 0 & 0 & G & 0 \\ 0 & 0 & 0 & 0 & 0 & G \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix}$$
(3.34)

Comparison of Eq. 3.34 to the output from symbolic_cmatrix.py gives the following:

$$G = \frac{1}{2(S_{11} - S_{12})}; \quad C_{11} = \frac{S_{11} + S_{12}}{S_{11}^2 + S_{11}S_{12} - 2S_{12}^2}; \quad C_{12} = \frac{-S_{12}}{S_{11}^2 + S_{11}S_{12} - 2S_{12}^2}$$
(3.35)

paragraphMaterial with Fiber Symmetry (transversely isotropic material):

3.3.5 More details on materials with fiber symmetry (transversely isotropic materials)

It is particularly useful to consider the case of fiber symmetry in more detail, particularly because of its relevance to a range of important biology problems, including the behavior of muscle tissue and arterial walls. Here we obtain the stiffness matrix, consider the simplifying assumption of of incompressibility, and consider as an example the case of uniaxial extension in the transverse direction.

Stiffness matrix for a material with fiber symmetry: In some cases it is necessary to work directly with the stiffness matrix. An important example concerns wave propagation in solid materials, a method that is often used to extract the elastic constants of a material. The wave velocities are directly related to the stiffness coefficients, so it useful to have direct expressions for these. For a material with fiber symmetry it is most convenient to write this in the following way:

$$\begin{bmatrix} \sigma_{1} \\ \sigma_{2} \\ \sigma_{3} \\ \sigma_{4} \\ \sigma_{5} \\ \sigma_{6} \end{bmatrix} = \begin{bmatrix} K_{t} + G_{tt} & K_{t} - G_{tt} & 2K_{t}\nu_{tf} & 0 & 0 & 0 \\ K_{t} - G_{tt} & K_{t} + G_{t} & 2K_{t}\nu_{tf} & 0 & 0 & 0 \\ 2K_{t}\nu_{tf} & 2K_{t}\nu_{tf} & E_{f} + 4K_{t}\nu_{f}^{2} & 0 & 0 & 0 \\ 0 & 0 & 0 & G_{tf} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & G_{tf} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & G_{tt} \end{bmatrix} \begin{bmatrix} e_{1} \\ e_{2} \\ e_{3} \\ e_{4} \\ e_{5} \\ e_{6} \end{bmatrix}$$
(3.36)

Here we have introduced the transverse bulk modulus, K_t , given by the following expression:

$$\frac{1}{K_t} = \frac{(1 - \nu_{tf})}{G_{tt} \left(1 + \nu_{tf}\right)} + \frac{4\nu_{tf}^2}{E_f}$$
(3.37)

Substituting this expression for K_t into the expression for the stiffness matrix in Eq. 3.36 and inverting the matrix gives the compliance matrix shown in Eq. 3.10, so everything checks out okay. This can be verified by running the Python code shown in Figure xx.

```
from sympy import symbols, Matrix, simplify
  from IPython.display import display
3 # specify two independent elements of s for an isotropic material
  Kt, Et, Ef, Gtf, Gtt, nutt, nutf = symbols(['K_t','E_t','E_f',
4
   'G_tf', 'G_tt', 'nu_tt', 'nu_tf'])
5
6
7
  # define the compliance matrix
  S = Matrix([[1/Et, -nutt/Et, -nutf/Ef, 0,0,0]])
8
              [-nutt/Et,1/Et,-nutf/Ef,0,0,0],
9
              [-nutf/Ef,-nutf/Ef,1/Ef,0,0,0],
10
11
              [0,0,0,1/Gtf,0,0],
              [0,0,0,0,1/Gtf,0]
12
              [0,0,0,0,0,1/Gtt]])
13
14
  # Substitute for Et
15
  S = S.subs(Et, 2*Gtt*(1+nutt))
16
17
  # Now introduce the proposed version of the stiffness matrix
18
  C = Matrix([[Kt+Gtt, Kt-Gtt, 2*Kt*nutf, 0,0,0],
19
              [Kt-Gtt, Kt+Gtt, 2*Kt*nutf,0,0,0],
20
              [2*Kt*nutf,2*Kt*nutf,Ef+4*Kt*nutf**2,0,0,0],
21
              [0,0,0,Gtf,0,0],
22
              [0,0,0,0,Gtf,0],
23
              [0,0,0,0,0,Gtt]])
24
25
  # substitute for Kt
26
  C=C.subs(Kt, 1/(((1-nutt)/(Gtt*(1+nutt)))-4*nutf**2/Ef))
27
28
29
  # now invert C to get S
  S2 = C.inv()
30
31
_{32} # now compare the two version of S
33 diff= simplify(S-S2)
34 display(diff)
  # diff returns a 6x6 array of zeros, so our version of C is correct
35
```

Figure 3.7: Symbolic python code to validate Eq. 3.36.

Elastic constants for an incompressible material with fiber symmetry: We mentioned above that the condition of incompressibility reduces the number of independent elastic constants for an isotropic material from two to 1, since the condition of incompressibility means that $\nu = 0.5$. Similar considerations reduce the number of independent elastic constants for materials with fiber symmetry (commonly referred to as orthotropic symmetry) as well. For fiber symmetry the incompressibility condition introduces two additional relationships between the the elastic constants, reducing the number of independent elastic constants from 5 to 3. The first condition is obtained from the requirement that the the three normal strains (e_1 , e_3 and e_3) sum to zero for a uniaxial stress applied along the fiber axis (the 3 direction), which gives $\nu_{13} = 1/2$.

The second condition is obtained from the similar requirement that the normal strains sum to zero when a uniaxial tensile stress is applied along the direction perpendicular to the fiber axis (either the 1 or 2 direction), leading to the following

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expression between the elastic constants:

$$\nu_{tt} = 1 - \frac{E_t}{2E_f} \tag{3.38}$$

Of the 5 elastic constants that are commonly reported for an incompressible material with fiber symmetry (G_{tt} , G_{tf} , E_t , E_f and ν_{tt}), only 3 are independent from one another. The 'parallel' shear modulus, G_{tf} is not related to any of the other elastic constants, so must be one of the constants that is specified directly. One is free to choose different combinations of other moduli in order to specify the linear elastic response, using the relationships shown in Table 4.

3.3.6 Transverse Extension of an Incompressible Transversely Isotropic Material (Fiber Symmetry)

An application where these concepts are useful is in the use of a strain energy function to describe the mechanical response of a material with fiber symmetry. The aim here is to express the full strain state of a material as a function of a single variable. This is possible because the different Poisson's ratios relate the different strains to one another. Consider for, example, the uniaxial extension of an incompressible orthotropic material in the 1 direction, which is one on of the transverse directions in our case (with the 3 direction corresponding to the fiber axis). We can use $\nu_{tt} \equiv \nu_{21}$ to obtain e_2 , the strain in the unstressed transverse direction:

$$e_2 = -\nu_{tt}e_1 = e_1 \frac{E_t}{2E_f} - e_1 \tag{3.39}$$

Here we have used $\nu_{tt} = 1 - \frac{E_t}{2E_f}$ from Table 4. We can obtain e_3 , the strain in the fiber direction in either of two ways. The first is to recall that for an incompressible material in limit of small strains, the strains must sum to zero:

$$e_3 = -e_1 - e_2 = -e_1 \frac{E_t}{2E_f} \tag{3.40}$$

We can also write e_3 in terms of e_1 directly, using $\nu_{ft} \equiv \nu_{31}$:

$$e_3 = -\nu_{ft} e_1 = \nu_{tf} \frac{E_t}{E_f},$$
(3.41)

 Table 4: Relationships between the different elastic constants for an incompressible material with fiber (orthotropic) symmetry.

	G_{tt}	E_t	E_f	$ u_{tt} $
G_{tt}, E_t	-	-	$\frac{E_t G_{tt}}{4G_{tt} - E_t}$	$\frac{E_t}{2G_{tt}} - 1$
G_{tt}, E_f	-	$\frac{4E_f G_{tt}}{E_f + G_{tt}}$	-	$\frac{E_f - G_{tt}}{E_f + G_{tt}}$
G_{tt}, ν_{tt}	-	$2G_{tt}\left(\nu_{tt}+1\right)$	$\frac{G_{tt}(1+\nu_{tt})}{1-\nu_{tt}}$	-
E_t, E_f	$\frac{E_t E_f}{4E_f - E_t}$	-	-	$1 - \frac{E_t}{2E_f}$
E_t, ν_{tt}	$\frac{E_t}{2(1+\nu_{tt})}$	-	$\frac{E_t}{2(1-\nu_{tt})}$	-
E_f, ν_{tt}	$\frac{E_f \cdot (1 - \nu_{tt})}{\nu_{tt} + 1}$	$2E_f\left(1-\nu_{tt}\right)$	-	-

where we have used Eq. 3.15 to replace ν_{ft} with ν_{tf} . Eq. 3.40 is recovered by recognizing that $\nu_{tf} = 1/2$ for an incompressible material. The ratio of extension ratios in the 3 and 2 directions (which we define as β) is given by the following (at small strains):

$$\beta \equiv \frac{1+e_3}{1+e_2} = (1+e_3)(1-e_2) \approx 1+e_3-e_2 \tag{3.42}$$

Using the expressions given above for e_2 and e_3 we obtain:

$$\beta \approx 1 + e_1 \left(1 - \frac{E_t}{E_f} \right) \tag{3.43}$$

This expression for β is useful in the the application of strain energy functions for describing transverse deformation of an incompressible transversely isotropic material.

4 Rubber Elasticity

Crosslinked rubbers are unique in that thermodynamic arguments can be used to predict their elastic moduli with remarkable accuracy. Our starting point will be a description of the free energy of an elastomer as a function of its deformation. This free energy is dominated by entropic contributions arising from restrictions on the number of different conformations (or shapes) that polymer strands are able to adopt. The detailed descriptions of polymer chain statistics given earlier were developed so that we would be in a position to describe the mechanical properties of rubbery materials. The description of rubber elasticity given here is proof that statistics and thermodynamics are actually useful!!

4.1 Molecular Deformation

Different types of molecular deformations, and the characteristic lengths and forces, are illustrated in Figure 4.1. In rubber elasticity we are interested in deformations due to changes in the overall shapes of the molecules, with typical molecular forces in the range of 10 pN and deformations in the range of 10 nm. In this force regime we don't need to worry about the specific chemistry of the polymer backbone. All that matters is the distance between the two ends of the molecule. Figure 4.2 shows the situation in this regime of 'entropic elasticity' in more detail.

The origins of entropic elasticity can be understood in terms of the probability density, P_{xyz} , that describes the relative probability that the end-to-end vector has a specific set of x, y and z components. This probability depends on the magnitude of the end-to-end vector normalized by R_0 , the root-mean-squared value of the end-to-end vector . For our purposes here we'll see that we don't actually need the normalization for P_{xyz} - we just need to understand how it depends on $|\vec{R}|$. For simplicity we refer to $|\vec{R}|$ simply as R in our discussion, with P_{xyz} given as follows:

$$P_{xyz} \propto \exp\left(\frac{-3R^2}{2R_0^2}\right) \tag{4.1}$$

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Figure 4.1: Molecular deformation occurring at different force and length scales (from From Osterhelt et al.: http://www.iop.org/EJ/abstract/1367-2630/1/1/006/).



Figure 4.2: Illustration of force, P_d , that must be applied to a single molecule to maintain and end-to-end separation of R.

The value of P_{xyz} is proportional to the number of molecular configurations, Ω , that are consistent with this particular value of R, so we can write:

$$\Omega\left(\vec{R}\right) = C \exp\left(\frac{-3R^2}{2R_0^2}\right) \tag{4.2}$$

where C is some constant that we don't know (and don't need to know). The entropy is obtained from the number of possible molecular shapes:

$$S_d\left(\vec{R}\right) = k_B \ln \Omega\left(\vec{R}\right) = k_B \ln C - \frac{3k_B R^2}{2Na^2}$$
(4.3)

The free energy is assumed to be entirely dominated by this entropic contribution:

$$F_d\left(\vec{R}\right) = -TS_d\left(\vec{R}\right) = -k_B T \ln C + \frac{3k_B T R^2}{2Na^2}$$
(4.4)

In reality, there is a small enthalpic contribution to the stretching free energy as well, because stretching the chain increases the relative proportion of higher energy gauche bonds, but we're not going to worry about that correction here. Because we are only every interested in changes in the free energy, constant terms that don't depend on R are going to drop out when we compare free energies, so the detailed value of this constant is not going to matter.

This expression for the elastic free energy of an individual molecule in terms of its end-to-end distance is remarkably simple. It is one of the most important and widely used results in polymer science. In the following section, we will see how it is used to obtain estimates for the elastic modulus of a crosslinked elastomer.

4.2 Free energy of a stretched rubber

When a rubber is stretched, the free energy increases. In general the free energy increase has enthalpic and entropic contributions ($F_d = H_d - TS_d$). The basic assumption of rubber elasticity theory is that the free energy increase due to deformation is dominated by the decrease in the entropy. In other words $|T\Delta S_d| >> |\Delta H_d|$. The second assumption we will make is that the deformation at a microscopic level mimics the deformation at a macroscopic level. In other words, relative changes in the spacings between crosslink points are identical to relative changes in the overall sample demonstrations. This assumption is referred to as the affine deformation assumption.

4.3 Free energy change due to deformation

Before applying these ideas to calculations of the stress/strain relationships for macroscopic materials, it is useful to bring in the concept of principal axes of deformation. Any general strain state can be obtained by applying normal strains in three mutually perpendicular axes, so that a sphere of radius r_0 is transformed in to an ellipsoid with principal radii of $r_0\lambda_{1p}$, $r_0\lambda_{2p}$ and $r_0\lambda_{3p}$, as illustrate in Figure 4.3. There are still 6 independent components of the strain tensor, but instead of specifying 3 normal strains and 3 shear strains, we specify three normal strains, and 3 parameters that specify the orientation of the principal axes. These principal axes are defined by the appropriate unit vectors, shown as \hat{x}_1, \hat{x}_2 and \hat{x}_3 in Figure 4.3.

What really matters when determining the mechanical properties of a material is the change in free energy resulting from a deformation. For a material that is isotropic in its undeformed state (like the crosslinked rubber discussed here) the orientation of the principal axes does not matter, and free energy is entirely determined by the three principal extension ratios. We will assume that these same principal extension ratios also describe the material at the molecular level as well, an important assumption called the 'affine deformation

assumption'. Prior to deformation, we have $\vec{R} = R_1\hat{x}_1 + R_2\hat{x}_2 + R_3\hat{x}_3$, so that $R^2 = R_1^2 + R_2^2 + R_3^2$. The undeformed free energy, F_0 , is given by using this expression for R^2 in Eq. 4.4:

$$F_0 = -k_B T \ln C + \frac{3k_B T}{2Na^2} \left\{ R_1^2 + R_2^2 + R_3^2 \right\}$$
(4.5)

After deformation, the values of R_1 , R_2 and R_3 are each multiplied by the appropriate extension ratio ($\vec{R} = \lambda_{1p}R_1\hat{x}_1 + \lambda_{2p}R_2\hat{x}_2 + \lambda_3R_3\hat{x}_3$), so that $R^2 = \lambda_{1p}^2R_1^2 + \lambda_{2p}^2R_2^2 + \lambda_{3p}^2R_3^2$. The deformed free energy, F_{def} is:

$$F_{def} = -k_B T \ln C + \frac{3k_B T}{2Na^2} \left\{ \lambda_{1p}^2 R_1^2 + \lambda_{2p}^2 R_2^2 + \lambda_{3p}^2 R_3^2 \right\}$$
(4.6)

The free energy change due to deformation of the molecule is given as follows:

$$\Delta F_d = F_{def} - F_0 = \frac{3k_B T \left\{ (\lambda_{1p}^2 - 1)R_1^2 + (\lambda_{2p}^2 - 1)R_2^2 + (\lambda_{3p}^2 - 1)R_3^2 \right\}}{2Na^2}$$
(4.7)

This result is for the deformation of a single polymer molecule, which for a crosslinked elastomer corresponds to a segment that connects crosslink points.



Figure 4.3: Unit sphere deformed into a strain ellipsoid with dimensions of $\lambda_{1p}, \lambda_{2p}, \lambda_{3p}$.



Figure 4.4: Contrasting free energies before and after deformation

There are a huge number of these segments in a macroscopic chunk of rubber. To get the free energy change for the material as a whole, we need to replace R_1^2 by $n_{el} \langle R_1^2 \rangle$, where n_{el} is the total number of network strands and $\langle R_1^2 \rangle$ is the average value of R_1^2 for these segments. We need to make similar substitutions for R_2^2 and R_3^2 to obtain the following:

$$\Delta F_{d} = \frac{3k_{B}Tn_{el}\left\{\left(\lambda_{1p}^{2}-1\right)\left\langle R_{1}^{2}\right\rangle + \left(\lambda_{2p}^{2}-1\right)\left\langle R_{2}^{2}\right\rangle + \left(\lambda_{3p}^{2}-1\right)\left\langle R_{3}^{2}\right\rangle\right\}}{2Na^{2}}$$
(4.8)

Because the material was isotropic when it was crosslinked there is no difference between the 1, 2 and 3 directions, so that $\langle R_1^2 \rangle = \langle R_2^2 \rangle = \langle R_3^2 \rangle = \langle R^2 \rangle /3$. With this assumption, and with $R_0^2 = Na^2$, we obtain the following result:

$$\Delta F_d = \frac{k_B T n_{el} \left\langle R^2 \right\rangle \left\{ \lambda_{1p}^2 + \lambda_{2p}^2 + \lambda_{3p}^2 - 3 \right\}}{2R_0^2} \tag{4.9}$$

Note that $\langle R^2 \rangle$ is the mean square end-to-end distance of the polymer strands that span the crosslinks, and that R_0^2 is the value of $\langle R^2 \rangle$ when the polymer strands obey random walk statistics. The relationship between these two quantities depends on the conditions of the crosslinking reaction.

It is often useful to work in terms of intensive free energy changes (free energy per unit volume). The free energy of deformation per unit volume Δf_d is obtained very simply from ΔF_d by dividing by V, the volume of a sample. We retain the same expression as shown above, but with the strand concentration, ν_{el} substituted for the number of strands, n_{el} :

$$\Delta f_d = \frac{\Delta F_d}{V} = \frac{k_B T v_s \beta \left\{ \lambda_{1p}^2 + \lambda_{2p}^2 + \lambda_{3p}^2 - 3 \right\}}{2} \tag{4.10}$$

where ν_{el} and β are defined as follows:

$$\nu_{el} = \frac{n_{el}}{V}; \ \beta = \frac{\langle R^2 \rangle}{R_0^2} \tag{4.11}$$

For the most common situation where the crosslinking occurs in an equilibrated polymer in the absence of solvent, $\langle R^2 \rangle = R_0^2$ and $\beta = 1$. Like the intensive free energy, the strand concentration, v_s is useful because it does not depend on the overall size and shape of the elastomer. The assumptions used to develop the free energy expression given above correspond to the simplest model of rubber elasticity, which is often referred to as the

$$\lambda_{1p}\lambda_{2p}\lambda_3 = 1 \tag{4.12}$$

4.4 Shear deformation of an elastomer

For pure shear we need to relate the shear strain, γ , to the extension ratios, λ_{1p} , λ_{2p} and λ_3 . Pure shear is a two dimensional stress state, with $\lambda_3 = 1$ so the Neohookean strain energy function (Eq. 4.10) reduces to the following:

$$\Delta f_d = \frac{k_B T v_s \beta \left\{ \lambda_{1p}^2 + \lambda_{2p}^2 - 2 \right\}}{2} = \frac{k_B T v_s \beta (\lambda_{1p} - \lambda_{2p})^2}{2} = \frac{k_B T v_s \beta \gamma^2}{2} \qquad (4.13)$$

The shear stress is obtained by differentiation of the strain energy function with respect to γ :

$$\sigma_{12} = \frac{d}{d\gamma} (\Delta f_d) = G\gamma \tag{4.14}$$

where G is the shear modulus, given as follows:

$$G = k_B T v_s \beta \tag{4.15}$$

Note that the shear stress is proportional to the shear strain, even for large values of the strain.

At this point we make two changes in the notation to simplify the expression for the strain energy density. First, we refer to this quantity as W instead of Δf_d in order to be consistent with the generally established convention ($W \equiv \Delta f_d$). Also, we use Eq. 4.15 to express W directly in terms of the shear modulus, giving the following expression for the strain energy density function for the Neohookean model (Eq. 4.10):

$$W = \frac{G\left\{\lambda_{1p}^2 + \lambda_{2p}^2 + \lambda_{3p}^2 - 3\right\}}{2}$$
(4.16)

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4.5 Uniaxial deformation of an elastomer

For uniaxial extension or compression the deformation is applied along one axis, which we define as the z axis. We assume that our material is isotropic, so that the extensions in the 1 and 2 directions are identical to one another, i.e. $\lambda_{1p} = \lambda_{2p}$. In addition, the material is assumed to be incompressible, so $\lambda_{1p}\lambda_{2p}\lambda_{3p} = 1$. We therefore have $\lambda_{1p} = \lambda_{2p} = \lambda_{3p}^{-1/2}$. We can therefore write the free energy of a deformed elastomer as a function of the single extension ratio, λ_{3p} :

$$W = \frac{G}{2} \left\{ \lambda_{3p}^2 + \frac{2}{\lambda_{3p}} - 3 \right\}$$
(4.17)

The engineering stress is obtained by differentiating with respect to λ_3 :

$$\sigma_{eng} = \frac{dW}{\partial d\lambda} = G\left\{\lambda_{1p} - \frac{1}{\lambda_{3p}^2}\right\}$$
(4.18)

Young's modulus (E) is defined as the derivative of the stress with respect to strain, evaluated at low strain ($\lambda_3 = 1$):

$$E \equiv \frac{\partial \sigma_{eng}}{\partial \lambda_3} \Big|_{\lambda_3=1} = G \left\{ 1 + \frac{2}{\lambda_{3p}^3} \right\} \Big|_{\lambda_3=1} = 3G = 3v_s \beta k_B T, \quad (4.19)$$

The concentration of network strands (v_s) is the inverse of the volume per strand. This can be calculated from the molecular weight and density. Defining M_s as the number average molecular weight of a network strand (molecular weight between crosslinks) gives:

$$v_s\left(\frac{\text{strands}}{\text{volume}}\right) = \frac{\rho\left(\text{mass/volume}\right)}{M_s\left(\text{mass/mole}\right)} \cdot N_{av}\left(\text{strands/mole}\right)$$
(4.20)

where N_{av} is Avogadro's number ($6.02x10^{23}$). With $R = k_B N_{av} = 8.314 \text{ J/mole} \cdot \text{K}$ the expression

$$E = \frac{3\rho\beta RT}{M_s}$$

Finally, note that 1 J/m $^3 = 1$ Pa. Stresses and elastic moduli have units of force/area or energy/volume.

Exercise: Calculate the expected value of Young's modulus for a crosslinked polyisoprene that has a number average molecular between crosslinks of 4000 g/mole. The density of polyisoprene is 0.9 g/cm^3 . Assume that the polymer was crosslinked under equilibrium conditions in the melt state.

Because the polymer was crosslinked under equilibrium conditions, the network strands obey random walk statistics, with $\beta = 1$. To keep everything in SI units, we need the density in units of kg/m³ (1 g/ cm³ = 1000 kg/ m³), and M_s in kg/mol. In our example, $\rho = 900$ kg/ m³ and $M_s = 4$ kg/mol. We'll also assume that we are interested in the elastic modulus near room temperature (T ≈ 300 K).

$$E = \frac{3(900 \text{ kg/m}^3)(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(300 \text{K})}{4 \text{kg/mol}} = 1.6 \text{x} 10^6 \text{ J/m}^3 = 1.6 x 10^6 \text{ Pa}$$

5 Large Strains

As we know from the previous section on rubber elasticity, with soft materials we are often interested in large strains. The primary complication is that we need to account for changes in the dimensions of the material during deformation. Consider for example the extension of a material during a uniaxial tension test (Figure 5.1). Because of the Poisson contraction, the cross-sectional area decreases during the deformation, so that the actual cross-sectional area, A, is less than the undeformed cross sectional area, A_0 . Both areas can be used to define a stress. The true stress, often referred to as the **Cauchy stress** in the literature and represented as σ in our notation, is obtained by dividing the load by actual cross sectional area:

$$\sigma = \frac{P}{A} \tag{5.1}$$

This is the relevant stress state in the material, and is always what is meant by σ (or $[\sigma]$ when expressed as the full tensor) in this text. The engineering stress, σ_{eng} is obtained by the dividing the load by the undeformed cross-sectional area:

$$\sigma = \frac{P}{A_0} \tag{5.2}$$

If the strain is small, we don't need to worry about the difference between the true stress and the engineering stress, but the distinction becomes much more important at large strains.



Figure 5.1: Uniaxial extension to large strains, illustrating the difference between the true stress (commonly referred to as the Cauchy stress) and the engineering stress.

5.1 Characterizing the Strain

The description here is based largely on the book chapter by Ogden [?], and the Wikipedia article on finite strain theory[?] is also helpful. Our starting point is the **deformation gradient tensor**, [H], which we have encountered before in our definition of the strains:

$$[\mathbf{H}] = \begin{bmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \frac{\partial u_1}{\partial x_3} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \frac{\partial u_2}{\partial x_3} \\ \frac{\partial u_3}{\partial x_1} & \frac{\partial u_3}{\partial x_2} & \frac{\partial u_3}{\partial x_3} \end{bmatrix}$$
(5.3)

Note that in our notation bold quantities in brackets are matrices. Generally we don't see the brackets in discussions of this topic in the literature and in texts, but we use them here in an effort to eliminate confusion about the quantities that are actually matrices. (The target audience for this document includes people who don't spend a lot of time thinking about the details of linear algebra, and are likely not familiar with the commonly used notation conventions involving the fonts used to represent matrices). The next step is to define a transformation tensor, $[\mathbf{F}]$, which is very closely related to $[\mathbf{H}]$, but which gives the identify matrix, $[\mathbf{I}]$, in the unstrained state where all the gradient terms are zero:

$$[\mathbf{F}] = [\mathbf{I}] + [\mathbf{H}] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \begin{bmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \frac{\partial u_1}{\partial x_3} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \frac{\partial u_2}{\partial x_3} \\ \frac{\partial u_3}{\partial x_1} & \frac{\partial u_3}{\partial x_2} & \frac{\partial u_3}{\partial x_3} \end{bmatrix}$$
(5.4)

The transformation tensor transforms the coordinates of a point from an undeformed object, $\overrightarrow{r}(r_1, r_2, r_3)$ to $\overrightarrow{r}^d = (r_1^d, r_2^d, r_3^d)$ the coordinates of the same point on the deformed object:

$$\begin{bmatrix} r_1^d \\ r_2^d \\ r_3^d \end{bmatrix} = \begin{bmatrix} F_{11} & F_{12} & F_{13} \\ F_{21} & F_{22} & F_{23} \\ F_{31} & F_{32} & F_{33} \end{bmatrix} \begin{bmatrix} r_1 \\ r_2 \\ r_3 \end{bmatrix}$$
(5.5)

Consider, for example, simple shear in the 1-2 plane, where the only non-zero component of $[\mathbf{H}]$ is $[\mathbf{H}]_{12} = \partial u_1 / \partial x_2 = \gamma$. For the specific case where $\gamma = 1.2$ we have:

$$[\mathbf{F}] = \begin{bmatrix} 1 & 1.2 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
(5.6)

This value of $[\mathbf{F}]$ transforms a square the the paralellepiped shown in Figure 5.2. Note that any given line segment within the material will be subject to some combination of translation, rotation and stretching, as illustrated by the example line segment in Figure 5.2.

The left Cauchy–Green deformation tensor, [B] is given by the following expression:

$$[\mathbf{B}] = [\mathbf{F}] [\mathbf{F}^T] \tag{5.7}$$

Here $[\mathbf{F}]^T$ is the transpose of $[\mathbf{F}]$, obtained by exchanging the row and column indices, which amounts to 'flipping' the matrix around it's diagonal:

$$F_{ij}^T = F_{ji} \tag{5.8}$$

As a specific example a the transpose of a matrix, we have the following for the transpose of the deformation gradient tensor:

$$\begin{bmatrix} \mathbf{H}^{T} \end{bmatrix} = \begin{bmatrix} \frac{\partial u_{1}}{\partial x_{1}} & \frac{\partial u_{2}}{\partial x_{1}} & \frac{\partial u_{3}}{\partial x_{1}} \\ \frac{\partial u_{1}}{\partial x_{2}} & \frac{\partial u_{2}}{\partial x_{2}} & \frac{\partial u_{3}}{\partial x_{3}} \\ \frac{\partial u_{1}}{\partial x_{3}} & \frac{\partial u_{2}}{\partial x_{3}} & \frac{\partial u_{3}}{\partial x_{3}} \end{bmatrix}$$
(5.9)

Figure 5.2: Deformation of a square region by the transformation tensor given by Eq. 5.6.

Various combinations of the principal stretch ratios, λ_{1p} , λ_{2p} and λ_{3p} are easily obtained from [**B**], which will simplify expressions for the strain energy density. Specifically we have the following for I_1 , I_2 and I_3 , 3 so-called principal strain invariants that commonly appear in expressions for the strain energy density:

$$I_{1} = \lambda_{1p}^{2} + \lambda_{2p}^{2} + \lambda_{3p}^{2}$$

$$I_{2} = \lambda_{2p}^{2} \lambda_{3p}^{2} + \lambda_{3p}^{2} \lambda_{1p}^{2} + \lambda_{1p}^{2} \lambda_{2p}^{2}$$

$$I_{3} = \lambda_{1p} \lambda_{2p} \lambda_{3p}$$
(5.10)

These strain invariants are obtained from $[\mathbf{B}]$ using the following expressions that involve the trace (tr) and determinant (det):

$$I_{1} = \operatorname{tr}[\mathbf{B}] = [\mathbf{B}]_{11} + [\mathbf{B}]_{22} + [\mathbf{B}]_{33}$$

$$I_{2} = \frac{1}{2} \left(I_{1}^{2} - \operatorname{tr} \left([\mathbf{B}]^{2} \right) \right)$$

$$I_{3} = \det \left([\mathbf{B}] \right)$$
(5.11)

5.2 Calculating the Stress from the Strain Energy Function

Stresses are obtained by differentiating the strain energy density with respect to the deformation. Simplified examples have been given previously in the introductory chapter on rubber elasticity. These results can also be obtained from a generalized approach involving the following matrix expression:

$$[\boldsymbol{\sigma}] = \frac{1}{J} [\mathbf{F}] \frac{\partial W}{\partial [\mathbf{F}^T]}$$
(5.12)

Here J is the determinant of $[\mathbf{F}]$, which is equal to 1 for an incompressible material. Differentiation of a scalar with respect to a matrix just means that we differentiate with respect to each of the different components of the matrix. (The Wikipedia page on matrix calculus is useful here.) In expanded form of Eq. 5.12 is

$$[\boldsymbol{\sigma}] = \frac{1}{J} \left[\boldsymbol{F} \right] \begin{bmatrix} \frac{\partial W}{\partial F_{11}} & \frac{\partial W}{\partial F_{21}} & \frac{\partial W}{\partial F_{31}} \\ \frac{\partial W}{\partial F_{12}} & \frac{\partial W}{\partial F_{22}} & \frac{\partial W}{\partial F_{32}} \\ \frac{\partial W}{\partial F_{13}} & \frac{\partial W}{\partial F_{23}} & \frac{\partial W}{\partial F_{33}} \end{bmatrix}$$
(5.13)

A useful method of calculating the derivatives in Eq. 5.13 can be applied if the strain energy depends on some combination of I_1 , I_2 and I_3 . For illustrative purposes we'll consider the case where the strain energy function depends only on I_1 , and where the material is incompressible. In this case we have the following expression for the stress:

$$\left[\boldsymbol{\sigma}\right] = \begin{bmatrix} -p & 0 & 0\\ 0 & -p & 0\\ 0 & 0 & -p \end{bmatrix} + 2\frac{\partial W}{\partial I_1}[\mathbf{B}]$$
(5.14)

Here p is a hydrostatic pressure term, obtained from other constraints on the solution. Use of this equation is illustrated in the following examples.

5.3 Example 1: Deformation of a Neohookean Material

For a Neohookean material, we have $W = \frac{G}{2}(I_1 - 3)$, and Eq. 5.14 becomes:

$$[\boldsymbol{\sigma}] = \begin{bmatrix} -p & 0 & 0\\ 0 & -p & 0\\ 0 & 0 & -p \end{bmatrix} + G[\mathbf{B}]$$
(5.15)

The problem is then reduced to a determination of $[\mathbf{B}]$ from Eq. 5.7. Here we apply it for uniaxial extension and simple shear, obtaining the results already obtained in the introductory chapter on rubber elasticity, and then extend it to more complicated situations.

5.3.1 Uniaxial Extension:

For uniaxial extension for stretch ratio of λ in the x_3 direction (Figure 5.1), we have the following for [**F**] and [**B**]:

$$[\mathbf{F}] = \begin{bmatrix} 1/\sqrt{\lambda} & 0 & 0\\ 0 & 1/\sqrt{\lambda} & 0\\ 0 & 0 & \lambda \end{bmatrix} \begin{bmatrix} 1/\sqrt{\lambda} & 0 & 0\\ 0 & 0 & \lambda \end{bmatrix} \begin{bmatrix} 1/\sqrt{\lambda} & 0 & 0\\ 0 & 1/\sqrt{\lambda} & 0\\ 0 & 0 & \lambda \end{bmatrix} = \begin{bmatrix} 1/\lambda & 0 & 0\\ 0 & 1/\lambda & 0\\ 0 & 0 & \lambda^2 \end{bmatrix}$$
(5.16)

Use of this expression in Eq. 5.15 for the stress gives:

$$[\boldsymbol{\sigma}] = \begin{bmatrix} G/\lambda - p & 0 & 0\\ 0 & G/\lambda - p & 0\\ 0 & 0 & G\lambda^2 - p \end{bmatrix}$$
(5.17)

The pressure, p, is determined from the fact that the stresses in the 2 and 3 directions are zero, so $p = G/\lambda$, giving:

$$[\boldsymbol{\sigma}] = G \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & (\lambda^2 - 1/\lambda) \end{bmatrix}$$
(5.18)

5.3.2 Simple Shear:

For simple shear in the 1-2 plane, with the displacement in the 1 direction (Figure 5.2) we have:

$$[\mathbf{F}] = \begin{bmatrix} 1 & \gamma & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{bmatrix}$$
(5.19)

$$[\mathbf{B}] = \begin{bmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
(5.20)

From Eq. 5.15 we have:

$$[\boldsymbol{\sigma}] = \begin{bmatrix} G(1+\gamma^2-p) & G\gamma & 0\\ G\gamma & G-p & 0\\ 0 & 0 & G-p \end{bmatrix}$$
(5.21)

The boundary conditions here are that the sample is stress free (no normal stresses) in the two and 3 directions, *i.e.*, $\sigma_{22} = \sigma_{33} = 0$. This condition requires that p = G, which in turn gives the following for the stress tensor:

$$[\boldsymbol{\sigma}] = G \begin{bmatrix} \gamma^2 & \gamma & 0\\ \gamma & 0 & 0\\ 0 & 0 & 0 \end{bmatrix}$$
(5.22)

Note that a normal stress of $G\gamma^2$ is generated in the 1 direction, a result that was not evident from our simplified derivation where the concept of a strain energy function was introduced.

5.4 Example 2: Strain Hardening of an Isotropic Elastomer

The following strain energy function accounts for the fact that there is a limit to the extensibility of any material, so the energy increases when I_1 becomes sufficiently large. The following strain energy function is particularly useful:

$$W = \frac{G}{2c_2} \left[\exp\left(c_2 \left(I_1 - 3\right)\right) - 1 \right]$$
(5.23)

For $\partial W/\partial I_1$ we have:

$$\frac{\partial W}{\partial I_1} = \frac{G}{2} \exp\left(c_2 I_1 - 3\right) \tag{5.24}$$

The net result is simply to multiply the stresses obtained from the previous section by $\exp(c_2(I_1-3))$. This strain energy function has been shown to accurately describe the strain-hardening behavior of a series of isotropic synthetic and biobased gels.[?]

5.5 Example 3: Strain Energy Function and Elastic Response of a Strain Hardening Fiber

The strain energy density function can only be written in term of I_1 , I_2 and I_3 if the undeformed material is isotropic, where all directions within the undeformed material are equivalent. If we want to understand the properties of a material where one

of the axes is unique, as with a fiber that is much stiffer in the longitudinal direction along which the fiber is oriented than in the the transverse plane perpendicular to this direction, we need to adjust the strain energy function. This is generally done by including some combination of the fourth and fifth strain invariants, I_4 and I_5 in the strain energy function.[??] These quantities are not formally invariants since they rely on the use of a coordinate system that is tied to the symmetry axis of the material, but they are invariant to rotations of the coordinate system around this axis. They are defined as follows:

$$I_4 = \vec{\mathbf{m}} \cdot \left([C] \vec{\mathbf{m}} \right) \tag{5.25}$$

$$I_5 = \overrightarrow{\mathbf{m}} \cdot \left([\mathbf{C}]^2 \overrightarrow{\mathbf{m}} \right) \tag{5.26}$$

Here $\vec{\mathbf{m}}$ is a unit vector directed along the longitudinal axis. In our coordinate system we fix x_3 to the longitudinal direction, so we have:

$$\vec{\mathbf{m}} = \begin{bmatrix} 0\\0\\1 \end{bmatrix} \tag{5.27}$$

Most proposed strain energy functions for transversely isotropic materials include I_4 but not necessarily I_5 . Feng[?] and Murphy[?] have pointed out that in order to capture the linear elastic properties of the material with independent distinct values for G_L and G_T it is necessary to include both I_4 and I_5 in the strain energy function. Based on a combination of this work and the earlier work of Humphrey and Yin[?], Hegde *et al.* have developed a strain energy function that they refer to as the HYM model.[?] In the incompressible limit the strain energy function can be written in terms of E_L , G_T and G_L , in addition to two parameters, c_2 and c_4 that describe the strain hardening:

$$W = \frac{G_T}{2c_2} \left[e^{c_2(I_1-3)} - 1 \right] + \frac{E_L + G_T - 4G_L}{2c_4} \left[e^{c_4 \left(I_4^{1/2} - 1\right)^2} - 1 \right] + \frac{G_T - G_L}{2} \left(2I_4 - I_5 - 1 \right)$$
(5.28)

Note that the expression for exponential strain hardening for an isotropic material (Eq. 5.23) is recovered for $G_T = G_L = E_L/3$. Hegde *et al.* used the full HYM model to describe the behavior of a range of incompressible, transversely isotropic materials.[?] The appeal of Eq. 5.28 is that it reduces to the appropriate linearized form characterized by three independent elastic constants necessary to describe a transversely isotropic material while including parameters to describe isotropic strain hardening (through c_2) and the much stronger expected strain hardening for deformation along the symmetry axis (through c_4). While the approach we describe below is generalizable to other strain energy functions, we feel that the HYM function used here provides the best combination of accuracy and simplicity. The full Cauchy stress (true stress) tensor, σ , resulting from the deformation of a material with a strain energy function that depends only on I_1 , I_4 and I_5 is obtained from the following expression:[?]

$$\boldsymbol{\sigma} = -p[\mathbf{I}] + 2\frac{\partial W}{\partial I_1}[\mathbf{B}] + \frac{\partial W}{\partial I_4}[\mathbf{F}]\vec{\mathbf{m}} \otimes [\mathbf{F}]\vec{\mathbf{m}} + 2\frac{\partial W}{\partial I_5}\left([\mathbf{F}]\vec{\mathbf{m}} \otimes [\mathbf{B}][\mathbf{F}]\vec{\mathbf{m}} + [\mathbf{B}][\mathbf{F}]\vec{\mathbf{m}} \otimes [\mathbf{F}]\vec{\mathbf{m}}\right)$$
(5.29)

Here $[\mathbf{I}]$ is the identity matrix, \otimes indicates the tensor product and p is a hydrostatic pressure term associated with the incompressibility constraint, obtained from the appropriate boundary conditions. Here the symbol \otimes represents the tensor product. Note that since $[\mathbf{F}]$ is a 2nd rank tensor and $\vec{\mathbf{m}}$ is a vector, $[\mathbf{F}]\vec{\mathbf{m}}$ is also vector, as is $[\mathbf{B}][\mathbf{F}]\vec{\mathbf{m}}$. The tensor product of two vectors $\vec{\mathbf{X}}$ and $\vec{\mathbf{Y}}$ is :

$$\vec{\mathbf{X}} \otimes \vec{\mathbf{Y}} = \vec{\mathbf{X}} \vec{\mathbf{Y}}^T = \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} \begin{bmatrix} Y_1 & Y_2 & Y_3 \end{bmatrix} = \begin{bmatrix} X_1Y_1 & X_1Y_2 & X_1Y_3 \\ X_2Y_1 & X_2Y_2 & X_2Y_3 \\ X_3Y_1 & X_3Y_2 & X_3Y_3 \end{bmatrix}$$
(5.30)

5.6 Example 4: Transverse Extension of a Transversely Isotropic Material (Fiber Symmetry)

The case of transverse extension is more complicated than the case of longitudinal extension because the material is no longer isotropic in the plane perpendicular to the applied extension. By defining β as the ratio of extension in the 3 and 2 directions, and remembering that the product of the three principal extension must be unity for an incompressible material, we obtain the following for the deformation gradient tensor for transverse extension:

$$\mathbf{F} = \begin{bmatrix} \lambda_t & 0 & 0\\ 0 & \sqrt{\frac{1}{\beta\lambda_t}} & 0\\ 0 & 0 & \sqrt{\frac{\beta}{\lambda_t}} \end{bmatrix}$$
(5.31)

For low strains β is determined by the elastic constants of the material:

$$\beta = 1 + (\lambda_t - 1) \left(1 - \frac{4G_T}{E_L + G_T} \right) \tag{5.32}$$

For higher strains the value of β may deviate slightly from the the value given by Eq. 5.32, and is given by the requirement that the lateral stresses vanish. The equations written in this section can be used to obtain expressions for the stress components and the different moduli in terms of the applied deformation, λ_{ℓ} , and the 5 independent parameters appearing in the strain energy function (G_T , G_L , E_L , c_2 c_4). These expressions are rather cumbersome when written out fully, so we do not do this here. Fortunately, the equations can be readily manipulated with the symbolic math capabilities of modern programming tools, in our case Python. A variety of elastic constants have been defined in this section, and it is useful to keep the following features in mind:

5.7 Example 5: Shear Wave Propagation in a Stretched Fiber

This example is given as a more detailed example of the sort of analysis that is relatively simple perform with the strain-energy based approach described in this chapter. The relationship between sound velocity and the elastic modulus can be used to quantify material properties in a non-invasive way. This capability is particularly important in medical diagnostic applications, where tissue stiffness is

may be correlated with disease. These techniques can also be used to measure the stress state of a material. Shear waves are generally used for this, because the shear modulus of a materials is generally more relevant than the longitudinal modulus, which in most biological samples is determined primarily by the very large bulk modulus of water. The technique is illustrated schematically in Figure 5.3, and involve excitation of a shear pulse at one location, with subsequent monitoring of the motion of this shear pulse throughout the material.

Figure 5.4 illustrates three different shear deformation modes for a transversely isotropic material (a material with 'fiber' symmetry), characterized by the shear strains γ_{tt} , $\gamma_{\ell t}$ and $\gamma_{t\ell}$. The two extensional modes characterized by the extension ratios in the longidtdinal (λ_{ℓ}) and transverse (λ_{t}) are also illustrated. The plane-wave velocities for the tt, $t\ell$ and ℓt shear modes illustrated in this figure are given by the following expressions:

$$v_{tt} = \sqrt{\frac{\mu_{tt}}{\rho}}; \quad v_{t\ell} = \sqrt{\frac{\mu_{t\ell}}{\rho}}; \quad v_{\ell t} = \sqrt{\frac{\mu_{\ell t}}{\rho}}$$
(5.33)

where ρ is the material density. In the context of shear wave propagation, the first letter in the mode label describes the polarization (shear displacement) direction and the second describes the propagation direction. For example, $v_{t\ell}$ is the phase velocity for a wave with shear displacement in the transverse direction that propagates in the longitudinal direction.

In some cases we are interested in the behavior of pre-stressed materials (as is often the case with muscle tissue, for example). In these cases the deformation associated with a shear wave is superposed on an existing deformation. We consider the most important case involving a uniaxial deformation along the longitudinal axis (the x_3 direction in our case), quantified by the extension ratio, λ_{ℓ} . For an incompressible material, where the principal extension ratios must multiply to 1, this deformation is described by the following deformation gradient tensor, \mathbf{F}_0 :

$$\mathbf{F}_{0} = \begin{bmatrix} 1/\sqrt{\lambda_{\ell}} & 0 & 0\\ 0 & 1/\sqrt{\lambda_{\ell}} & 0\\ 0 & 0 & \lambda_{\ell} \end{bmatrix}$$
(5.34)

Subsequent to the application of this extension deformation, we apply small incremental shear strains to the material. Experimentally, this shear deformation could be associated with the excitation and propagation of shear waves through the material. Considering the possibility an incremental of all three shear modes, γ_{tt} , $\gamma_{t\ell}$ and $\gamma_{\ell t}$, we have the following gradient tensor for this incremental deformation:

$$\mathbf{F}_{inc} = \begin{bmatrix} 1 & \gamma_{tt} & \gamma_{t\ell} \\ 0 & 1 & 0 \\ 0 & \gamma_{\ell t} & 1 \end{bmatrix}$$
(5.35)

The overall deformation gradient for an extensional deformation described by Eq. 5.34 followed by the shear deformations described by Eq. 5.35 is obtained from the product of \mathbf{F}_{inc} and \mathbf{F}_{0} :

$$\mathbf{F} = \mathbf{F}_{inc} \mathbf{F}_0 = \begin{bmatrix} 1/\sqrt{\lambda_{\ell}} & \gamma_{tt}/\sqrt{\lambda_{\ell}} & 0\\ 0 & 1/\sqrt{\lambda_{\ell}} & \gamma_{t\ell}\lambda_{\ell}\\ 0 & \gamma_{\ell t}/\sqrt{\lambda_{\ell}} & \lambda_{\ell} \end{bmatrix}$$
(5.36)



Figure 5.3: Geometry of a shear wave elastography experiment (from https://en.wikipedia.org/wiki/Shear_Wave_Elastography.



Figure 5.4: Transversely isotropic geometry illustrating the different deformation modes.

The relevant incremental shear moduli are obtained by differentiating the appropriate shear stress with respect to the corresponding applied incremental strain. In this way we define three distinct incremental shear moduli, G_{tt} , $G_{t\ell}$ and $G_{\ell t}$, all of which are functions of the pre-stretch, λ_{ℓ} . In our notation, where the x_3 direction is the longitudinal direction and the $x_1 - x_2$ plane is the transverse plane, we have:

$$G_{tt}(\lambda_{\ell}) = \frac{\partial \sigma_{12} \left(\lambda_{\ell}, \gamma_{tt}\right)}{\partial \gamma_{tt}}$$
(5.37)

$$G_{t\ell}(\lambda_{\ell}) = \frac{\partial \sigma_{23} \left(\lambda_{\ell}, \gamma_{t\ell}\right)}{\partial \gamma_{t\ell}}$$
(5.38)

$$G_{\ell t}(\lambda_{\ell}) = \frac{\partial \sigma_{23} \left(\lambda_{\ell}, \gamma_{\ell t}\right)}{\partial \gamma_{\ell t}}$$
(5.39)

In the calculations for a given shear mode (γ_{tt} for example) the other shear strains ($\gamma_{t\ell}$ and $\gamma_{\ell t}$ in this example) are set to zero in Eq. 5.36. Note that in the unstrained limit, the incremental shear moduli are given by the appropriate shear modulus, either G_T or G_L :

$$G_{tt} (\lambda_{\ell} \to 1) = G_T$$

$$G_{\ell t} (\lambda_{\ell} \to 1) = G_{t\ell} (\lambda_{\ell} \to 1) = G_L$$
(5.40)

As the material is deformed in the longitudinal direction and a tensile stress, σ_{ℓ} , develops in the longitudinal direction, the $t\ell$ and ℓt shear modes are no longer equivalent, so that in general $G_{t\ell} \neq G_{\ell t}$. This result is very useful, providing a method for determining the tensile stress within the material, according to the following equation, derived by Biot[?], and explained more generally by Destrade and Ogden[?] (Eq. 6.21 in Destrade and Ogden):

$$G_{t\ell} - G_{\ell t} = \sigma_{\ell}, \tag{5.41}$$

Note that while the stress dependence of the various incremental moduli depend on the details of the strain energy function, Eq. 5.41 holds more generally.

We also obtain incremental extensional moduli, defined as $E_{\ell\ell}$ in the longitudinal direction and E_{tt} in the transverse direction. Calculation of $E_{\ell\ell}$ is determined in a straightforward way as the derivative of the normal stress in the longitudinal direction with respect to the corresponding extension, λ_{ℓ} , with all shear components in Eq. 5.36 set to zero:

$$E_{\ell\ell}(\lambda_{\ell}) = \frac{\partial \sigma_{\ell}(\lambda_{\ell})}{\partial \lambda_{\ell}}$$
(5.42)

Young's modulus for extension along the longitudinal axis, E_L is simply given by the limiting value of $E_{\ell\ell}$ for $\lambda_{\ell}=1$. A similar expression applies for the determination of E_{tt} , the differential modulus for uniaxial extension of the material in the transverse direction. Defining the 1 axis as the axis of deformation, with $\sigma_t \equiv \sigma_{11}$, we have:

$$E_{tt}(\lambda_t) = \frac{\partial \sigma_t \left(\lambda_t\right)}{\partial \lambda_t} \tag{5.43}$$

The equations written in this section can be used to obtain expressions for the stress components and the different moduli in terms of the applied deformation, λ_{ℓ} , and

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the 5 independent parameters appearing in the strain energy function $(G_T, G_L, E_L, c_2 c_4)$. These expressions are rather cumbersome when written out fully, so we do not do this here. Fortunately, the equations can be readily manipulated with the symbolic math capabilities of modern programming tools, in our case Python. A variety of elastic constants have been defined in this section, and it is useful to keep the following features in mind:

- \diamond Elastic constants with a single subscript (G_T, G_L, E_L) describe the linearly elastic behavior of the undeformed material.
- ♦ Elastic constants with two subscripts $(G_{tt}, G_{\ell t}, G_{t\ell}, E_{tt}, E_{\ell \ell})$ are differential moduli that describe the slope of the stress/strain curve for a specified strain state and deformation mode.

Values of $[\mathbf{F}]$ I_1 and I_4 for some relevant strain states are shown in table 5.

Table 5: Parameters for the different deformation modes shown in Figure 5.4. Values of various moduli obtained from different deformation geometries are expressed in terms of parameters of the bi-exponential strain hardening model (Eq. ??) are listed in the 'modulus' column.

Mode	$[\mathbf{F}]$	I_1	I_4	I_5
$\gamma_{t\ell}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & \gamma_{t\ell} \\ 0 & 0 & 1 \end{bmatrix}$	$3+\gamma_{t\ell}^2$	$1+\gamma_{t\ell}^2$	$\left(1+\gamma_{t\ell}\right)^2+\gamma_{t_{ell}}^2$
$\gamma_{\ell t}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & \gamma_{\ell t} & 1 \end{bmatrix}$	$3+\gamma_{\ell t}^2$	1	$1+\gamma_{\ell t}^2$
γ_{tt}	$\begin{bmatrix} 1 & 0 & 0 \\ \gamma_{tt} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$3+\gamma_{tt}^2$	1	1
λ_t	$\begin{bmatrix} \lambda_t & 0 & 0\\ 0 & \frac{1}{\sqrt{\beta\lambda_t}} & 0\\ 0 & 0 & \sqrt{\frac{\beta}{\lambda_t}} \end{bmatrix}$	$\lambda_t^2 + \frac{\beta}{\lambda_t} + \frac{1}{\beta\lambda_t}$	eta/λ_t	eta^2/λ_t^2
λ_ℓ	$\begin{bmatrix} \frac{1}{\sqrt{\lambda_{\ell}}} & 0 & 0\\ 0 & \frac{1}{\sqrt{\lambda_{\ell}}} & 0\\ 0 & 0 & \lambda_{\ell} \end{bmatrix}$	$\lambda_{\ell}^2 + 2/\lambda_{\ell}$	λ_ℓ^2	λ_ℓ^4

6 Linear Viscoelasticity

6.1 Intro to Time-Dependent Behavior

Many of the concepts of rubber elasticity still apply under certain situations to materials that are not actually crosslinked. Consider, for example, the behavior of Silly-Putty. Silly-putty is based on silicones that are uncrosslinked. Nevertheless, this material still bounces like an ordinary crosslinked rubber ball. This is because over very short times it behaves elastically. The deformation energy stored in the material as it comes into contact with the surface and deforms is available to propel the material back into the air as the deformation relaxes and this strain energy is converted to kinetic energy. If we let the sample sit on a surface for a long period of time, however, it eventually flows and behaves as a liquid.

Before we discuss the way that the properties of viscoelastic materials are characterized, it is useful to discuss the limiting behaviors of purely elastic solids and perfectly viscous liquids. We illustrate this by showing how different materials respond to a shear strain, γ that begins to increase at some constant rate to some final value, and is then fixed at this final value as illustrated in the top panel of Figure 6.3. The response for solids, liquids and viscoelastic materials is as described below.

Solids: In this case the stress is proportional to the strain, and the rate at which the strain is applied does not matter. As a result the time dependence of the stress looks just like the time dependence of the strain. The slopes of the time-dependent stress and strain curves (the top two curves in Figure 6.3) are related to one another by the shear modulus of the material.

Liquids: In liquids the stress is proportional to the rate at which the strain is applied, and is independent of the current strain. Liquids do not store any strain energy, and as soon as the strain stops changing, the stress drops back to zero. The stress for the time dependent strain shown in Figure 6.3 is constant while the stress is increasing and is zero otherwise. The stress is given by the shear viscosity, η , as follows:

$$\sigma_{xy} = \eta \frac{d\gamma}{dt} = \eta \dot{\gamma} \tag{6.1}$$

As a simple illustration of the significance of the viscosity, we can calculate the time it takes for a small sphere of metal to drop to the bottom of pool of water. Suppose we use an iron particle with a radius of 1μ m. The situation is as shown in Figure 6.2. The gravitational force, F, causing the ball to sink is proportional to the volume of the sphere, and the difference in densities between the solid and liquid:

$$F = g \frac{4}{3} \pi R^3 \left(\rho_s - \rho_\ell \right)$$
 (6.2)

Here ρ_s is the density of the solid sphere, ρ_ℓ is the density of the surrounding liquid, *R* is the radius of the sphere and *g* is the gravitational acceleration (9.8 m/s²). This force is balanced by the viscous force exerted by the water on the sphere as the sphere moves the liquid with a velocity, *v*. For a viscous liquid this force is proportional to the velocity. It is also proportional to the viscosity of the liquid and to the radius of the sphere. The specific relationship is as follows:

$$F = 6\pi V \eta R \tag{6.3}$$

At steady state, the velocity reaches a value that is obtained by equating the forces in Eqs.6.2 and 6.3. In this way we obtain:



Figure 6.1: Illustration of viscoelastic behavior. Images of a viscoelastic material behaving elastically as it bounces from a surface (a-c) and the same material spreading over a surface at long times (d-f).



Figure 6.2: Terminal velocity of a sphere descending in a viscous fluid.

$$V = \frac{2}{9} \frac{gR^2}{\eta} \left(\rho_s - \rho_\ell\right) \tag{6.4}$$

Iron has a density of 7.87 g/cm³ (7870 kg/m³) and water has a density of 1000 kg/m³ and a viscosity of 10^{-3} Pa-sec. From this we get a velocity of 16 μ m/s.

Viscoelastic Materials: Viscoelastic materials have characteristics of both solids and liquids. The shear stress depends on both the shear stress and the strain rate, and is not a simple function of either one. The shear stress actually depends on the details of the previous strain history, as described in more detail below.

While the shear geometry is most commonly used to characterize liquid-like materials, solid-like materials are more commonly investigated in a uniaxial tensile geometry, as illustrated in Figure 6.4. Viscoelastic solids will have a value for Young's moduls, E, that depends on the time scale of the measurement. Imagine a tensile experiment where a strain of e_0 is instantaneously applied to the sample. In a viscoelastic material, the resulting stress will decay with time while we maintain the strain at this fixed value. The time dependence of the resulting tensile stress, σ , enables us to define a time-dependent relaxation modulus, E(t):

$$E\left(t\right) = \frac{\sigma\left(t\right)}{e_0}\tag{6.5}$$

We are often interested in the application of an oscillatory strain to a material. Examples include the propagation of sound waves, where wave propagation is determined by the response of the material at the relevant frequency of the acoustic wave that is propagating through the material. In an oscillatory experiment, referred to as a dynamic mechanical experiment in Figure 6.4, the applied shear strain is an oscillatory function with an angular frequency, ω , and an amplitude, <u>eo</u>:

$$e(t) = e_0 \sin(\omega t) \tag{6.6}$$

Note that the strain rate, $\frac{de}{dt}$, is also an oscillatory function, with the same angular frequency, but shifted with respect to the strain by 90°:

$$\frac{de}{dt} = e_0 \omega \cos\left(\omega t\right) = \gamma_0 \omega \sin\left(\omega t + \pi/2\right) \tag{6.7}$$

The resulting stress is also an oscillatory function with an angular frequency of ω , and is described by its amplitude and by the phase shift of the relative to the applied strain:

$$\sigma(t) = \sigma_0 \sin(\omega t + \phi) \tag{6.8}$$

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Figure 6.3: Interactive contrast of elastic, viscous, and viscoelastic response.



Figure 6.4: Tensile geometry for defining the tensile relaxation modulus, E(t), and the frequency- dependent complex tensile modulus, E^* .

Now we can define a complex modulus with real and imaginary components as follows:

$$E^* = E' + iE'' = |E^*| e^{i\phi}$$
(6.9)

There are a couple different ways to think about the complex modulus, E^* . As a complex number we can express it either in terms of its real and imaginary components (E' and E'', respectively), or in terms of its magnitude, $|E^*|$ and phase, ϕ . The magnitude of the complex modulus is simply the stress amplitude normalized by the strain amplitude:

$$|E^*| = \sigma_0 / e_0 \tag{6.10}$$

The phase angle, ϕ , describes the lag between the stress and strain in the sample. Examples for $\phi = 90^{\circ}$ (the maximum value, characteristic of a liquid) and $\phi = 45^{\circ}$ are shown in Figure 6.5.

In order to understand the significance of the real and imaginary components of E^* we begin with the Euler formula for the exponential of an imaginary number:

$$e^{i\phi} = \cos\phi + i\sin\phi, \tag{6.11}$$

where *i* is the imaginary unit (i.e. $i = \sqrt{-1}$). Use of this expression in Eq. 6.9, we see that the **storage modulus**, E' gives the stress that is in phase with the strain (the solid-like part), and is given by the following expression:

$$E' = |E^*| \cos \phi \tag{6.12}$$

Similarly, the **loss modulus**, E'', gives the response of the material that is in phase with the strain rate (the liquid-like part):

$$E'' = |E^*|\sin\phi \tag{6.13}$$



Figure 6.5: Time dependent stress and strain in a dynamic mechanical experiment.

We can combine Eqs. 6.12 and 6.13 to get the following expression for $\tan \phi$, commonly referred to simply as the loss tangent :

$$\tan\phi = \frac{E''}{E'} \tag{6.14}$$

The loss tangent gives the ratio of the energy dissipated in one cycle of an oscillation to the maximum stored elastic energy during this cycle. We can define the complex shear modulus, G^* in a similar way, with G', G'', ϕ and $|G^*|$ related to one another in a way that corresponds to the relationship of the components of E^* . Because the shear geometry is more amenable to the testing of both liquids and solids, we'll use this geometry to illustrate other time dependent quantities in out discussion below.

6.2 Shear Relaxation Modulus

In a shear geometry (Fig. 6.6) we can also conduct relaxation experiments or oscillatory experiments. The shear relaxation modulus is defined as the ratio of the resulting time dependent stress to this initial strain:

$$G\left(t\right) \equiv \frac{\sigma_{xy}\left(t\right)}{\gamma_{0}} \tag{6.15}$$

As with E(t), the shear modulus is independent of γ_0 , provided that γ_0 is sufficiently small. This low strain regime defines the regime of linear viscoelasticity. In the remainder of this section we confine ourselves to this linear regime, assuming a shear geometry so that the relevant time and frequency-dependent property is the shear modulus, G.

6.3 Boltzmann Superposition Principle

In the linear viscoelastic regime the effects of strains applied at different times are additive, a concept known as the Boltzmann superposition principle . A simple example is illustrated in Figure 6.7, where the following step strains are applied to the sample:

- \diamond A strain of $\Delta \gamma_1$ applied at time t_1
- \diamond A strain of $\Delta \gamma_2$ applied at time t_2
- \diamond A strain of $\Delta \gamma_3$ applied at time t_3

The stress contribution from these different strains is obtained by multiplying by the shear relaxation modulus, evaluated at the time that has passed since the strain was applied. If strain was applied at t_1 , for example, the stress at some later time, t, is obtained by multiplying by $G(t - t_1)$. Adding up the contributions from the three different step strains in our example leads to the following:

$$\sigma_{xy} = \Delta \gamma_1 G(t - t_1) + \Delta \gamma_2 G(t - t_2) + \Delta \gamma_3 G(t - t_3) \tag{6.16}$$

This expression can easily be extended to include an arbitrary number of step strains:



Figure 6.6: Shear geometry for defining the shear relaxation modulus, G(t) and the frequency- dependent complex shear modulus G^* .



Figure 6.7: Material response to a series of step strains.

$$\sigma_{xy} = \sum_{i} \Delta \gamma_i G(t - t_i) \tag{6.17}$$

By taking a sum of very small strain increments, we can generalize this expression to account for a continuously changing strain. We begin by writing $\Delta \gamma_i$ in the following way:

$$\Delta \gamma_i = \frac{d\gamma}{dt} (t_i) \Delta t_i = \dot{\gamma}(t_i) \Delta t_i$$
(6.18)

This substitution leads to the following expression for the stress:

$$\sigma_{xy} = \sum_{i} \dot{\gamma}(t_i) G(t - t_i) \Delta t_i \tag{6.19}$$

We can write this in integral form by taking $\Delta t_i \rightarrow 0$ and replacing the summation by an integral over all times less than the current time:

$$\sigma_{xy}(t) = \int_{-\infty}^{t} \dot{\gamma}(t_i) G(t - t_i) dt_i$$
(6.20)

This expression gives the current stress that remains as a result of all of the strains introduced at different times in the past. It is often convenient to change variables so that $s = t - t_i$, $dt_i = -ds$. Note that $s = \infty$ when $t_i = -\infty$, and s = 0 when $t_i = t$. The integral can therefore be rewritten as follows:

$$\sigma_{xy}(t) = \int_{0}^{\infty} \dot{\gamma}(t-s)G(s)ds$$
(6.21)

Note that because s represents time, G(s) and G(t) represent the same timedependent relaxation modulus. We are just using different variables (s and t) to represent time.

The simplest application of Eq. is 'steady shear', where a constant strain rate is applied. Because $\dot{\gamma}$ is independent of time in this case, it can be brought outside the integral, giving the following:

$$\sigma_{xy} = \dot{\gamma} \int_{0}^{\infty} G(t) dt \tag{6.22}$$

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The following expression is obtained for the viscosity:

$$\eta_0 = \frac{\sigma_{xy}}{\dot{\gamma}} = \int_0^\infty G(t)dt \tag{6.23}$$

We refer to this viscosity as the zero shear viscosity, because it assumes that the material is in the linear viscoelastic regime, where the applied stress is low enough so that the stress is proportional to the magnitude of the applied strain. The subscript '0' is a reminder to us that the zero shear viscosity corresponds to a limiting value of the viscosity that is obtained at a very low strain rate.

6.4 Idealized Relaxation Curves

One thing to keep in mind when looking at the viscoelastic properties of materials is that processes occur over a very large range of time scales. To capture all of these time scales we typically plot the time on a logarithmic scale. The same is true for the frequency-domain experiments discussed below. The relaxation modulus can often vary of several orders of magnitude, so that we also plot the relaxation modulus itself on a logarithmic scale.

Three different idealized forms of the relaxation modulus are shown in Figure 6.8. The simplest behavior corresponds to a Maxwell model , where a single relaxation time, τ_g , describes the decay in the modulus from the glassy value of G_g :

$$G(t) = G_q \exp\left(-t/\tau_q\right) \tag{6.24}$$

This relaxation time could, for example, describe the decay in the modulus from a glassy value of $\approx 10^9$ Pa. This relaxation time can be viewed as a 'glass transition time', and its existence is a clue that some equivalence between time and temperature must exist. The relaxation time characterizing the glass transition depends very strongly on the temperature, but is independent of the polymer molecular weight. If the polymer molecular weight is very high, however, the polymers become entangled with one another, and behave elastically for times that are too short for these entanglements (shown schematically in Figure 6.9) to relax by molecular diffusion. In addition to τ_g , there is a second transition time, τ_e , determined by the lifetime of these molecular entanglements. Addition of this second relaxation results in the following expression for the relaxation modulus:

$$G(t) = G_g \exp\left(-t/\tau_g\right) + G_e \exp\left(-t/\tau_e\right) \tag{6.25}$$

Here G_e is the plateau modulus (often referred to as G_N^0 in the literature). Entanglements behave like crosslinks, but they have finite lifetimes as the molecules diffuse and the entanglements are eliminated and reformed elsewhere. The plateau modulus is given by the concentration of entanglements, v_e , or equivalently, by the number average molecular weight between entanglements, M_e (referred to as the entanglement molecular weight):

$$G_e = v_e k_B T = \frac{\rho R T}{M_e} \tag{6.26}$$

The actual relaxation behavior of polymeric materials is complex, and can generally not be described in detail by including only one or two relaxation times. The actual relaxation behavior can always be described with sufficient accuracy by a generalized Maxwell model , where we include a large number of individual exponential relaxation processes:

$$G(t) = \sum_{i=1}^{N_r} G_i \exp(-t/\tau_i)$$
(6.27)

Inclusion of a sufficiently large number of relaxation processes (large N_r) enables very complicated relaxation behavior to be modeled accurately.

6.5 Temperature Dependence

A characteristic of single-component polymeric materials is that the temperature dependence of all of the different relaxation times is the same. The concept is illustrated in Figure 6.10, which shows the relaxation modulus at two different temperatures for an idealized material with two different relaxation times. The relaxation times scale with temperature according to the same temperature dependent shift factor, a_T . The shift factor is equal to one at a reference temperature, T_{ref} , and increases as the temperature is decreased. Because both relaxation times are multiplied by the same factor, the curve is shifted linearly along the logarithmic x axis.

Because all of the relaxation times are multiplied by a_T when the temperature is changed, data obtained at different temperatures superpose when plotted as a function of t/a_T . As a result the relaxation behavior over a large range of times can



Figure 6.8: Characteristic relaxation curves.



Figure 6.9: Schematic representation of a molecular entanglement.



Figure 6.10: Temperature dependence of a material with two relaxation times.

be obtained by measuring the relaxation spectrum at different times, and shifting the data to the reference temperature.

The Vogel-Fulcher-Tamman equation is an empirical equation that is often used to describe the temperature dependence of the shift factor, a_T :

$$\ln(a_T) = A + \frac{B}{T - T_{\infty}} \tag{6.28}$$

The factor A is determined from the requirement that $a_T = 1$ at $T = T_{ref}$:

$$A = -\frac{B}{T_{ref} - T_{\infty}} \tag{6.29}$$

The relaxation times diverge to ∞ at $T = T_{\infty}$, which in free volume theory is the temperature at which the free volume of the equilibrium liquid goes to zero. This divergence is artificial, however, since Eq. 6.70 is only used to express the temperature dependence of a_T for temperatures well above T_{∞} . The quantitative determination of the shift factors is discussed in more detail below in section 6.8 on viscoelastic models.

6.6 Relationship between Frequency-Dependent and Time-Dependent Dynamic Moduli

Experimentally, a wide variation in time scales is accessed by oscillating or vibrating the sample and measuring the frequency response of the material. Consider, for example, an oscillatory shear strain:

$$\gamma = \gamma_0 \sin(\omega t) \tag{6.30}$$

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The strain rate is also sinusoidal:

$$\dot{\gamma}(t) = \frac{d\gamma(t)}{dt} = \omega\gamma_0\cos(\omega t) = \omega\gamma_0\sin(\omega t + \pi/2)$$
(6.31)

Note that the strain and the strain rate are out of phase by $\pi/2$ (90 °). This concept of a phase difference is very important in understanding the frequency dependent dynamic moduli. In this case we use Boltzmann superposition to obtain an expression for the stress:

$$\sigma_{xy}(t) = \int_{0}^{\infty} \dot{\gamma}(t-s)G(s)ds = -\omega\gamma_0 \int_{0}^{\infty} \cos\left\{\omega(t-s)\right\}G(s)ds \qquad (6.32)$$

Now we make use of the following trigonometric identity:

$$\cos(a-b) = \sin(a)\sin(b) + \cos(a)\cos(b) \tag{6.33}$$

We can therefore write the time dependent stress in the following way.

$$\sigma_{xy}(t) = \gamma_0 \omega \left[\int_0^\infty G(s) \sin(\omega s) ds \right] \sin(\omega t) + \gamma_0 \omega \left[\int_0^\infty G(s) \cos(\omega s) ds \right] \cos(\omega t) \quad (6.34)$$

We define G' (storage modulus) and G'' (loss modulus) such that G' describes the component of the stress that is in phase with the strain (the elastic component) and G'' describes the component of the stress that is in phase with the strain rate (the viscous component).

$$\frac{\sigma_{xy}(t)}{\gamma_0} = G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)$$
(6.35)

By comparing Equations 6.34 and 6.35, we obtain the following for G' and G'':

$$G'(\omega) = \omega \int_{0}^{\infty} G(t) \sin(\omega t) dt$$

$$G''(\omega) = \omega \int_{0}^{0} G(t) \cos(\omega t) dt$$
(6.36)

In is useful to consider the behavior of G' and G'' in limiting cases where the system is a perfectly elastic solid with no viscous character, and where the material is a Newtonian liquid with no elastic character:

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Perfectly Elastic System: In this case the shear modulus is independent of both time and frequency. For $\gamma(t) = \gamma_0 \sin(\omega t)$ we have:

$$\sigma_{xy}(t) = G\gamma(t) = G\gamma_0 \sin(\omega t) \tag{6.37}$$

Comparing to Eq. 6.35 gives:

$$\begin{array}{l}
G' = G \\
G'' = 0
\end{array}$$
(6.38)

Perfectly Viscous System: We again have $\gamma(t) = \gamma_0 \sin(\omega t)$, but this time the shear stress depends only on the strain rate:

$$\sigma_{xy}(t) = \eta \frac{d\gamma(t)}{dt} = \eta \omega \gamma_0 \cos(\omega t)$$
(6.39)

Comparing to Eq. 6.35 gives:

$$\begin{array}{l}
G' = 0 \\
G''(\omega) = \omega\eta
\end{array}$$
(6.40)

The

loss tangent

, $\tan(\phi)$, gives the ratio of dissipated and stored elastic energy during a given cycle of deformation. This quantity is maximized when the inverse of the frequency corresponds to a characteristic relaxation time of the material. For a material with two characteristic relaxation times, τ_1 and τ_2 , $\tan(\phi)$ will be maximized at $\omega = 2\pi/\tau_1$ and $\omega = 2\pi/\tau_2$.

6.7 Torsional Resonator

We can now consider the specific example of a **torsional resonator**, shown below in Figure 6.11. The equation of motion for the spring as it is being twisted is[?]:

$$T = K_t \theta + I \frac{d^2 \theta}{dt^2} \tag{6.41}$$

where θ is the rotation angle, T is the torque on the resonator, K_t is the torsional stiffness and I is the moment of inertia of the system, which depends on the details of the inertial bar used in the experiment. For a cylindrical fiber K_t is given by the following expression:

$$K_t \equiv \frac{T}{\theta} = \frac{\pi G d^4}{32\ell} \tag{6.42}$$

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Figure 6.11: Torsional resonator.

The resonant angular frequency of the oscillator, ω_n is given by the following expression:

$$\omega_n = \sqrt{\frac{K_t}{I}} \tag{6.43}$$

The solution to Eq. 6.41 for the case where T = 0 and we just let the fiber move (by twisting to a certain angle and letting it go, for example) is as follows:

$$\theta = \theta_0 \cos\left(\omega_n t\right) \tag{6.44}$$

This analysis assumes that the system is entirely elastic. What if the spring has some viscoelastic character to it? We begin by using Euler's formula (Eq. 6.11) to rewrite Eq. 6.44 in the following way:

$$\theta = \theta_0 \operatorname{Real}\left(\exp\left(i\omega_n t\right)\right) \tag{6.45}$$

Now all we need to do is to replace the modulus, G, with the complex modulus, G^* , and everything works out fine. Here's what happens:

- $\diamond\,$ The torsional stiffness, K_t gets transformed to a complex torsional stiffness K_t^*
- $\diamond~$ The resonant frequency, ω_n gets transformed to a complex resonant frequency, ω_n^*
- ♦ The imaginary part of the complex resonant frequency becomes an exponential damping function

To understand this last point, suppose write ω_n^* in the following way:

$$\omega_n^* = \omega_n' + i\omega_n'' \tag{6.46}$$

Putting this back into Eq. 6.45 gives:

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$$\theta = \theta_0 \operatorname{Real}\left(\exp\left(i\omega_n't\right)\right) \exp\left(-\omega_n''t\right) \tag{6.47}$$

Using the Euler formula (Eq. 6.11) to expande $(i\omega'_n t)$ and taking the real part gives:

$$\theta = \theta_0 \cos\left(\omega'_n t\right) \exp\left(-\omega''_n t\right) \tag{6.48}$$

So the imaginary part of the complex frequency describes the decay of oscillation with time.

6.8 Viscoelastic Models

Models of viscoelasticity can be represented visually by connecting solid-like and liquid-like elements together. In materials science we're used to the solid-like elements. They are simply elastic springs where the force is proportional to the extension of the spring. In terms of stress and strain, the stress, σ is proportional to the strain, e. There is no time-dependence to the behavior of an ideal spring. The stress is proportional to the strain, regardless of how fast or slow the strain is applied. In many real materials the rate at which the strain is applied matters as well, and this is where the dashpots come in. A **dashpot** is a liquid-like element where the stress is proportional to the rate at which the strain is changing, with the viscosity being the ratio between the stress and the strain rate. Schematic representations of springs and dashpots are shown in Figure 6.12. We assume a tensile geometry in our discussion of the viscoelastic models, so the relevant modulus is E as opposed to G, although this same formalism is generally applied to the shear moduli as well.

6.8.1 Maxwell model

The simplest viscoelastic model that contains both liquid-like and solid-like elements is the **Maxwell model** consisting of a linear dashpot with viscosity η_1 in series with a linear spring with a modulus, E_2 (see Figure 6.13). Because the elements are in series the stress is the same in each one of them. This stress can be related to



Figure 6.12: Schematic representations of springs and dashpots used to represent the time-dependent response of viscoelastic materials. Because the geometry here is assumed to be an extensional geometry, we refer to the viscosity as η^{ext} .

the strain e_1 in the dashpot and the strain e_2 in the spring through the following expressions:

$$\sigma = \eta_1 \frac{de_1}{dt} \tag{6.49}$$

$$\sigma = E_2 e_2 \tag{6.50}$$

The total strain, e is $e_1 + e_2$, so the time derivative of the total strain is:

$$\frac{de}{dt} = \frac{de_1}{dt} + \frac{de_2}{dt} = \frac{\sigma}{\eta_1^{\text{ext}}} + \frac{1}{E_2}\frac{d\sigma}{dt}$$
(6.51)

In a stress relaxation experiment the strain instantaneous increased to an initial value of e_0 and we follow the relaxation of the stress at this fixed strain. Because the dashpot cannot respond instantaneously, all of the initial strain is in the spring, i.e., $e_0 = e_2$ and the initial stress, σ_0 is equal to E_0e_0 . The solution to Eq. 6.51 for this initial condition and for de/dt = 0 is:

$$\sigma(t) = Ee_0 \exp\left(-t/\tau\right) \tag{6.52}$$

with the relaxation time, τ , given by the following expression:

$$\tau = \eta_0^{\text{ext}} / E_0 \tag{6.53}$$

We divide by e_0 to obtain the relaxation modulus:

$$E(t) \equiv \sigma(t) / e_0 = E_0 \exp(-t/\tau)$$
(6.54)

We can also obtain the solution for the stress in the case where we apply an oscillatory strain. To get the response of a single Maxwell element in an oscillatory experiment we need to substitute Eq. 6.54 for E(t) into Eq. 6.36 for E' and E''(replacing G^* with E^* , since we are assuming a tensile geometry in this example):



Figure 6.13: a) Maxwell model and b) the exponential stress relaxation function that it represents. Note that for an exponential relaxation, τ is the time at which the stress decays to 37% of its initial value.

$$E'(\omega) = \omega \int_{0}^{\infty} \exp\left(-\frac{t}{\tau}\right) \sin(\omega t) dt$$

$$E''(\omega) = \omega \int_{0}^{\infty} \exp\left(-\frac{t}{\tau}\right) \cos(\omega t) dt$$
(6.55)

We get a bit of help here because these equations now involve **Laplace transforms**, which we can either look up or evaluate with a symbolic math solver (in our case the sympy module of Python). The Laplace transform, $\mathcal{L} \{f(t)\}(s)$, of a function, f(t) is defined in the following way:[?]

$$\mathcal{L}\left\{f\left(t\right)\right\}\left(s\right) = \int_{0}^{\infty} f\left(t\right) \exp\left(-st\right) dt$$
(6.56)

By comparison to Eq. 6.55 we see that E' involves the Laplace transform of the sine function and E'' involves the Laplace transform of the cosine function:

$$E'(\omega) = \omega \mathcal{L} \{ \sin(\omega t) \} (s) E'(\omega) = \omega \mathcal{L} \{ \cos(\omega t) \} (s)$$
(6.57)

with $s = 1/\tau$. Use of symbolic Python (code at msecore.northwestern.edu/331/python/maxwell_Estar.py) results in the following:

$$E^*(\omega) = E'(\omega) + iE''(\omega) = \frac{E_0\omega\tau}{\omega\tau - i}$$
(6.58)

The Python code generates E' and E'' directly, but the expression for E^* contains all the information we need. Once we have this value we can extract E' and E'' by multiplying the top and bottom of Eq. 6.58 by $\omega \tau + i$, remembering that $i^2 = -1$. Taking the real and imaginary components of E^* then gives the following for E'and E'':

$$E'(\omega) = \frac{E(\omega\tau)^2}{1+(\omega\tau)^2}$$
(6.59)

$$E''(\omega) = \frac{E\omega\tau}{1 + (\omega\tau)^2} \tag{6.60}$$

These expressions are plotted in Figure 6.14, along with $\lceil E^* \rceil$ and ϕ . Note the following:

For
$$\omega = 1/\tau$$
 ($\omega \tau = 1$):
 $\diamond E' = E''$
 $\diamond \phi = 45^{\circ}$
 $\diamond E''$ is equal to its maximum value

For $\omega \gg 1/\tau$ ($\omega \tau \gg 1$, high frequency regime): $\diamond E' \approx E_0, E'' \ll E_0$

 $\diamond \ \phi \approx 0$

For $\omega \ll 1/\tau$ ($\omega \tau \ll 1$, low frequency regime):

$$\circ E'' >> E' \diamond E'' \approx \omega \eta_0^{\text{ext}} \diamond E' \propto \omega^2 \diamond \phi \approx 90^{\circ}$$

The fact that $E'' \approx \omega \eta_0^{\text{ext}}$ is generally true for liquid-like materials, even if the behavior at higher frequencies is more complicated. Provided that the viscoelastic phase angle approaches 90° at sufficiently low frequencies, we can define η_0 more generally as a **zero extension rate viscosity** in the following way:

$$\eta_0^{\text{ext}} = \lim_{\omega \to 0} \frac{E''}{\omega} \tag{6.61}$$

The 'ext' superscript is a reminder to us that we are dealing with an extensional geometry. An analogous equation can be used to define a **zero shear rate viscosity**, which we refer to simply as η_0 :

$$\eta_0 = \lim_{\omega \to 0} \frac{G''}{\omega} \tag{6.62}$$

We also note that while the loss modulus, E'', is maximized at an intermediate frequency, the storage modulus, E', and the magnitude of the complex modulus, $\lceil E^* \rceil$, both increase as a function of the frequency (or remain constant with increasing frequency). This increase or constancy in E' and $\lceil E^* \rceil$ with increasing frequency must **always** be true, because any general relaxation for a material can be written as the summation of individual exponential relaxations (the generalized Maxwell model described below).



Figure 6.14: Frequency dependence of the rheological properties for the Maxwell model (plot generated with msecore.northwestern.edu/331/python/maxwell_plot.py.

6.8.2 Standard Linear Solid

For a single Maxwell element the relaxation modulus decays to zero at long times $(t \gg \tau)$. In many real systems we are interested in describing the day of the relaxation modulus from a large value at short times to a much smaller value at larger times. The **standard linear solid** accounts for this by putting an elastic element with a modulus of E_r (the 'relaxed' modulus) in parallel with a single Maxwell element as shown in Figure 6.15. The extra spring adds directly to stress response, so all we have to do is add E_r to the expressions for E(t) and $E^*(w)$ that were obtained from the Maxwell model:

$$E(t) = E_r + E_1 \exp(-t/\tau_1)$$
(6.63)

$$E^*(\omega) = E_r + \frac{E_1 \omega \tau_1}{\omega \tau_1 - i}$$
(6.64)

So we see that the standard linear solid describes the relaxation of the modulus from an initial value of $E_1 + E_r$ at very short times to a relaxed value of E_r at long times. The standard linear solid is the simplest model for describing the transition of an amorphous, crosslinked polymer from glassy polymer behavior to rubbery behavior with typical values of E_1 and E_r being 10⁹ Pa and 10⁶ Pa, respectively.

6.8.3 Generalized Maxwell Model

For real systems, the behaviors of E(t) and $E^*(\omega)$ are usually much more complicated than given by the predictions of the Maxwell model or standard linear solid. To describe the behavior for real materials, we can add an arbitrary number of Maxwell elements in parallel, resulting in the **generalized Maxwell model** shown in Figure 6.16. The stresses for each of the parallel elements are additive, so E(t) and $E^*(w)$ are given by the following expressions:

$$E(t) = E_r + \sum_j E_j \exp\left(-t/\tau_j\right)$$
(6.65)

$$E^*(\omega) = E_r + \sum_j \frac{E_j \omega \tau_j}{\omega \tau_j - i}$$
(6.66)



Figure 6.15: Standard linear solid.

with $\tau_j = \eta_j^{\text{ext}}/E_j$. Any linearly viscoelastic material response can be described by a generalized Maxwell model, provided that we include a sufficient number of Maxwell elements.

6.8.4 Kelvin-Voigt Model

The **Kelvin-Voigt model** consists of a spring and dashpot in parallel, as shown in Figure 6.17. In this case the stresses in two elements are additive and the strains in the two elements are the same:

$$\sigma = \eta_1^{\text{ext}} \frac{de}{dt} + E_1 e \tag{6.67}$$

The Kelvin-Voigt model is the simplest model for the description of a creep experiment, where the stress jumps instantaneously from 0 to $\sigma = \sigma_0$ and we track the strain as a function of time. We have:

$$e(t) = \frac{\sigma_0}{E_1} \left(1 - \exp(t/\tau) \right); \quad \tau = \eta_1^{\text{ext}} / E_1$$
(6.68)

The dynamic modulus for the Kelvin-Voigt element is given by the following expression:

$$E^* = E_0 + i\omega\eta_0 \tag{6.69}$$

So that E' is simply equal to E, and E'' is equal to $\omega \eta_0$.

6.8.5 Viscoelastic Models for Shear Deformation

It is easier to visualize springs and dashpots in an extensional geometry, which is why we used this geometry to illustrate their use in describing the time- and frequency-dependent behavior of viscoelastic materials. The exact same formalism can be used to describe the properties in a shear geometry as well. We just need to replace E^* , E' and E'' with G^* , G' and G''. We also drop the 'ext' superscript from the viscosities, since the viscosity is generally assumed to refer to the shear viscosity. For an incompressible liquid, $\eta^{\text{ext}} = 3\eta$, just as E = 3G for a compressible solid (with Poisson's ratio = 0.5).



Figure 6.16: Generalized Maxwell model.



Figure 6.17: Kelvin-Voigt Model.

6.9 Time-Temperature Superposition of Dynamic Mechanical Data

For many materials we are interested in the dynamic mechanical properties over a very wide range of frequencies, including those for which direct measurements are not possible. Fortunately, in many cases we can use the concept of **timetemperature equivalence** to obtain the response at a very wide range of frequencies by measuring over a much more limited frequency range, but over a range of temperatures. We can do this because for many materials all of the relevant relaxation times have the same temperature dependence. Materials for which this is the case are said to be 'thermorheologically simple', meaning that the temperaturedependence of their linear viscoelastic properties is 'simple'.

As an example of a thermorheologically simple material, we consider here the behavior of poly(t-butyl acrylate) and amorphous polymer with a glass transition temperature near 45 °C. In Figure 6.18 we plot the frequency dependence of $[G^*]$ and ϕ for 5 different temperatures. (The Python code used to generate Figures 6.18) - 6.21 is available at msecore.northwestern.edu/331/python/ptba_master_curve.py, with the raw data available at msecore.northwestern.edu/331/data/ptbadata.xlsx.) The range of angular frequencies extends from 0.1 s^{-1} to 100 s^{-1} . If time temperature equivalence holds, then changing the temperature will change all of the relaxation times by the same temperature-dependent multiplicative factor, a_T . We see from Eq. 6.66 that the response of the material is always determined by the product of ω and a relaxation time. Since all of the relaxation times are proportional to a_T , we would expect the values of E^* to overlap with one another if we plot them as a function of ωa_T . When the scale of the frequency axis is logarithmic, as is generally the case for these sorts of plots, changing the temperature shifts the curves to right or left. Increasing the temperature decreases the relaxation times, and shifts the curves to the left, whereas decreasing the temperature shifts to the curves to the right. The actual shift factors are chosen empirically by seeing what values get the data to actually superpose. When the data from Figure 6.18 is shifted in this way we get the curves shown in Figure 6.19, using the shift factors plotted in Figure 6.20. The reference temperature was chosen as 140 °C.

Master curves for the storage and loss moduli, G' and G'', respectively, are shown in Figure 6.21.

Two equivalent expressions are commonly used to express the temperature dependence of the shift factors. The most straightforward mathematical form is the Vogel-Fulcher-Tamman (VFT) equation introduced above, reproduced here as the



Figure 6.18: Frequency dependence of $|G^*|$ and ϕ for a poly(t-butyl acrylate) polymer at 4 different temperatures.



Figure 6.19: Frequency dependence of $|G^*|$ and ϕ for a poly(t-butyl acrylate) polymer at 4 different temperatures.



Figure 6.20: Shift factors used to generate the temperature-shifted master curves shown in Figure 6.19. The solid line is the VFT equation (Eq. 6.70), using a reference temperature, T_{ref} , of 140 °C and the values of B and T_{∞} shown on the plot.



Figure 6.21: Temperature-shifted master curves for dependence of $|G^*|$ and ϕ for a poly(t-butyl acrylate) polymer at 4 different temperatures.

combination of Eqs. 6.28 and 6.29:

$$\ln\left(a_{T}\right) = \frac{-B}{T_{ref} - T_{\infty}} + \frac{B}{T - T_{\infty}} \tag{6.70}$$

You will often see the temperature dependence of the a_T expressed in a different form, proposed by Williams, Landau and Ferry and known as the WLF equation:

$$\log(a_T) = -\frac{C_1 \left(T - T_{ref}\right)}{C_2 + T - T_{ref}} \tag{6.71}$$

Equation 6.70 reduces exactly to Eq. 6.71 when the following substitutions are made for B and T_{∞} :

$$T_{\infty} = T_{ref} - C_2 \tag{6.72}$$

$$B = 2.303C_1C_2 \tag{6.73}$$

Most polymers have B in the range of 2000K and T_{∞} around 50K below the glass transition temperature.

Measurement of the Entanglement Molecular Weight

It was mentioned above that amorphous polymers with a sufficiently large molecular weight are entangled, with these entanglements acting as temporary crosslinks in the material. These temporary crosslinks produce a 'plateau' in G' at intermediate frequencies, and a corresponding minimum in the phase angle, ϕ , indicating that the behavior of the material has a substantial elastic character in this frequency regime. The modulus in this region is called the plateau modulus, G_N^0 . The specific value of G_N^0 is generally taken as the inflection point in G', or as the value of G'at the frequency at which ϕ is minimized. Once G_N^0 is known, the entanglement molecular weight, M_e can be determined from the relevant expression from rubber elasticity theory:

$$G_N^0 = \frac{\rho RT}{M_e} \tag{6.74}$$

Viscosity from Rheological Data

The zero shear viscosity, η_0 , at the temperature where $a_T = 1$ is determined from the low frequency data, in the regime where G'' is proportional to ω and where $\phi \approx 90^\circ$ a dependence of a_T , since a_T has the same temperature dependence as the viscosity.

7 The Glass Transition

The information presented so far about the structure of amorphous polymers applies both to elastomers like natural rubber, in addition to engineering thermoplastics like polystyrene. The properties of rigid plastics and rubber are obviously quite different, in spite of these similarities. The difference is that below a certain temperature, molecular motion is no longer possible, and the material becomes a relatively hard solid. This transition between "soft" and "hard" behavior occurs at the glass transition temperature, T_q .

7.1 Free volume

A very useful way to think about the glass transition involves the concept of unoccupied space, or 'free volume' in a polymer. This concept is illustrated conceptually in Figure 7.1. The red dots connected together by lines represent polymer molecules. In this lattice model of polymers, the red dots are constrained to fit on a lattice. (The lattice is completely artificial, and does not exist in reality). These dots represent the 'occupied volume' '. Empty lattice sites represent free volume. . The lattice on the left has no free volume, so there is no way for the molecules to move by the 'hopping' of segments into a small region of unoccupied space. The lattice on the right does have free volume, however, so that molecular motion is relatively easy.

The conceptual free volume model of the glass transition makes the assumption that the volume thermal expansion coefficient, α is defined in the following manner:

$$\alpha = \frac{1}{V} \frac{dV}{dT} \tag{7.1}$$

Note that the linear thermal expansion coefficient, defined in terms of the linear dimensions of the sample rather than the volume, is equal to $\alpha/3$. If the fractional change in free volume is small ($\Delta V/V \ll 1$) then α describes the linear relationship between the change in volume in the change in temperature:

$$\frac{\Delta V}{V} = \alpha \Delta T \tag{7.2}$$



Figure 7.1: Conceptual representations of polymers with and without free volume.

In the glassy phase ($T < T_g$), the free volume is assumed to remain constant, so that increases in the volume are governed entirely by increases in the occupied volume:

$$\frac{\Delta V_{occ}}{V} = \alpha \Delta T \tag{7.3}$$

In the liquid phase ($T > T_g$), the free volume and occupied volumes both increase with temperature, and we have:

$$\frac{\Delta V}{V} = \frac{\Delta V_f}{V} + \frac{\Delta V_{occ}}{V} = \alpha_\ell \Delta T \tag{7.4}$$

Combining 7.3 and gives the following expression for the free volume in the liquid state:

$$\frac{\Delta V_f}{V} = (\alpha_\ell - \alpha_g) \,\Delta T \tag{7.5}$$

Now we define a new temperature, T_{∞} which is the theoretical temperature at which the free volume would go to zero, if the material were to continue to follow the liquid behavior below T_g . It is illustrated schematically in Figure 7.2. To determine the fractional free volume at the glass transition, we use Eq. 7.5 with $\Delta T = T_g - T_{\infty}$, recognizing that $V_f/V = 0$ at $T = T_{\infty}$. Typically, T_{∞} is about 50K below the measured glass transition temperature, and the fractional free volume at T_g is in the range of a couple percent.

The concept of free volume can be helpful in sorting out how the glass transition depends on the structure of the polymer, based on the following two guidelines:



Figure 7.2: The glass transition and the free volume concept.

- 1. Changes to the polymer structure that increase the free volume needed in and r for the backbone of the polymer to move will increase T_g . Making the backbone very still (by the incorporation of phenyl groups, as in PET increase T_g . Also, bulky, 'fat' substituents (like methyl or phenyl groups) tend to increase T_g when added to the backbone.
- 2. Changes to the polymer structure that introduce extra free volume will decrease T_g . This is the case for long, thin additions to the backbone, such as alkyl chains $(-(CH_2)_n -)$.

Without experience it's difficult to know which of these effects is greater. If I add something to the backbone for example, does it create more free volume that it needs to move? The best way to get a handle on this is to take a look at the glass transition temperatures of atactic polymers with the general chemical structure shown in Figure 7.3. The glass transition temperatures for these different polymers are listed in Table 6.

Exercise: Polystyrene has a volume thermal expansion coefficient of $6 \times 10^{-4} \text{ K}^{-1}$ for temperatures above T_g , and a thermal expansion coefficient of $2 \times 10^{-4} \text{ K}^{-1}$ for temperatures below T_g . Estimate the ratio of the free volume to the total volume of sample in the glassy state. Assume that T_{∞} is 50K below T_g .

Solution: Since the fractional free volume is assumed to be fixed below T_g , we are looking for the for the fractional free volume at the glass transition, as given by Eq. 7.5. With $\alpha_{\ell} = 6 \times 10^{-4} \,\mathrm{K}^{-1}$, $a_g = 2 \times 10^{-4} \,\mathrm{K}^{-1}$ and $T_g - T_{\infty} = 50 \,\mathrm{K}$, we obtain:

$$\frac{V_f}{V} = (4 \times 10^{-4} \,\mathrm{K}^{-1}) \,(50 \,\mathrm{K}) = 0.02$$

This value of 0.02 is a typical value for the fractional free volume in a glassy polymer.

7.2 Enthalpy and Heat Capacity

The heat capacity (c_p) of the liquid is larger than the heat capacity of the glass. Note that the enthalpy itself is continuous at $T = T_g$. The glass transition is therefore a second order transition - thermodynamic quantities like volume, enthalpy and entropy are continuous at the transition but the derivatives of these quantities with respect to temperature are discontinuous.



Figure 7.3: Structure of the repeat units for the materials listed in Table6.

	$R^{1}=H$	R 1 =CH $_3$
R ² : H	-125	-13
R ² : CH ₃	-13	-75
R ² :-	100	180
R ² :≁	10	105
R ² :Å~~	-54	20

Table 6: Glass transition temperatures (in $^{\circ}$ C) for polymers with the general structure shown in Figure 7.3 (From ref.[?]).



Figure 7.4: A graph of enthalpy vs temperature

7.3 Differential Scanning Calorimetry (DSC)

Glass transition temperatures are most commonly measured by differential scanning calorimetry. The technique can be used to measure the glass transition temperature of a polymer, in addition to the temperature at which a polymer melts or crystallizes. The heat of fusion (heat required to melt a semicrystalline polymer) can also be obtained. Heat flowing into the sample is endothermic, and heat flowing out of the sample is exothermic. We have plotted endothermic heat flow in the positive direction, and exothermic heat flow in the negative direction. Unfortunately, there is no universally followed sign convention for displaying DSC data. Sometimes endothermic direction is commonly indicated on the DSC plot, as we have done in the curve shown in Figure 7.6. Students are encouraged to look at the Macrogalleria web sites on the glass transition[?] and differential scanning calorimetry[?] for discussions at the appropriate level for this class.



Figure 7.5: Simple schematic representation of a calorimeter.



Figure 7.6: Graph of heat flow vs temperature.

8 Creep Behavior

In a creep experiment we apply a fixed stress to a material and monitor the strain as a function of time at this fixed stress. This strain is generally a function of both the applied stress, σ and the time, t, since the load was applied. Much of this section is general, and applicable across different materials classes, although the focus here is on concepts that are particularly relevant to polymeric materials.

8.1 Creep in the Linear Viscoelastic Regime

In the linear viscoelastic regime the strain is linearly dependent on the applied stress, σ , allowing us to define the **creep compliance function**, J(t), in the following way:

$$J(t) \equiv \frac{e(\sigma, t)}{\sigma} \tag{8.1}$$

An example of the sort of spring/dashpot model used to describe creep behavior of a linear viscoelastic material is shown in Figure 8.1. The model consists of a single Kelvin-Voigt element in series with a spring and a dashpot. In this example the strain obtained in response to a jump in the stress from 0 to σ at t = 0 can be represented as the sum of three contributions: e_1 , e_2 , and e_3 :

$$e(\sigma, t) = e_1(\sigma) + e_2(\sigma, t) + e_3(\sigma, t)$$

$$(8.2)$$

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Figure 8.1: Linear creep model.

In this equation e_1 corresponds to an instantaneous elastic strain, e_2 is the recoverable viscoelastic strain and e_3 is the plastic strain, with the three different components illustrated in Figure 8.2, and given by the following expressions:

$$e_1 = \frac{\sigma}{E_1}$$

$$e_2 = \frac{\sigma}{E_2} \left[1 - \exp\left(-t/\tau_2\right)\right]$$

$$e_3 = \frac{\sigma}{\pi_3} t$$
(8.3)

In many cases we are interested in situations where the strain does not increase linearly with the applied stress. The yield point is one obvious example of nonlinear behavior. In ideally plastic system, we only have elastic strains for stresses below the yield stress, but above the yield stress the strains are much larger.

8.2 Nonlinear Creep: Potential Separability of Stress and Time Behaviors

The situation becomes much more complicated in the nonlinear regime, where it is no longer possible to define a stress-independent creep compliance function. In general the strain in the nonlinear regime is a complex function of both the time and the applied stress. In some cases, however, we can separate the stress dependence from the time dependence and write the stress in the following way:

$$\sigma$$

$$e \begin{bmatrix} e_3 \\ e_2 \\ e_1 \end{bmatrix} \qquad t$$

 $e(\sigma, t) = f(\sigma) J(t)$ (8.4)

t

Figure 8.2: Strain contributions in a nonlinear creep model.

If this sort of separability holds, then it is possible to make predictions of creep based on limited experimental data. The procedure is illustrated in Figure 8.3 and involves the following steps:

- 1. Measure e(t) at different different stresses (σ_1 and σ_2) in Figure 8.3. If the ratio $e(\sigma_1, t) / e(\sigma_2, t)$ is constant for all value of t, then the separability into stress dependent and time-dependent functions works (at least for these two stress levels). These experiment enable us to obtain the time dependent function J(t).
- 2. To get the stress-dependent function, $f(\sigma)$, it is sufficient to make a series of measurements at a single, experimentally convenient time.

8.3 Use of empirical, analytic expressions

The procedure outlined in the previous Section only works if the ratio $e(\sigma_1, t) / e(\sigma_2, t)$ is independent of the time. This is not always the case. However, it is often possible to fit the data to relatively simple models. These models are similar to the spring and dashpot models used in linear viscoelasticity, but a linear stress response is not necessarily assumed. One example corresponds to a nonlinear version of the linear model shown in Figure 8.1. As with the linear model, the strain components are assumed to consist of an elastic strain, e_1 , a recoverable viscoelastic strain, e_2 and a plastic strain, e_3 . However, we now use nonlinear elements to describe e_2 and e_3 , with these two strain components given by the following expressions:

$$e_1 = \frac{\sigma}{E_1}$$

$$e_2 = C_1 \sigma^n \left[1 - \exp\left(-C_2 t \right) \right]$$

$$e_3 = C_3 \sigma^n t$$
(8.5)

Not that the material behavior is specified by 5 constants, E, C_1 , C_2 , C_3 , n, that we need to obtain by fitting to actual experimental data. For a linear response (n = 1) we can make a connection to the spring and dashpot models described earlier. In this case the behavior of the material is represented by the model of linear viscoelastic elements shown in Figure 8.4, and the constants appearing in Eq. 8.5 correspond to the following linear viscoelastic elements from Figure 8.1:



Figure 8.3: Creep response of a material with separable dependencies on stress and time.

$$E = E_1
C_1 = 1/\eta_2
C_2 = E_2/\eta_2
C_3 = 1/\eta_3$$
(8.6)

This is just one possible nonlinear model that can be used. An additional nonlinear element is obtained from Eyring rate theory, and is described in the following Section.

8.4 Eyring Model of Steady State Creep

The **Eyring rate model** of creep is a very general model aimed at understanding the effect of the stress on the flow properties of a material. It can be used to describe a very wide range of materials, and is based on the modification of the activation energy for material for flow by the applied stress.

8.4.1 Material Deformation as a Thermally Activated Process

Our starting point is to realize that material deformation is a thermally activated process, meaning that there is some energy barrier that needs to be overcome in order for deformation to occur. The general idea is illustrated in Figure 8.5. The stress does an amount of work on the system equal to σv , where σ is the applied stress and v is the volume of the element that moves in response to this applied stress. The quantity v is typically referred to as an **activation volume**. The net result of the application of the stress is to reduce the activation barrier for motion in the stress direction by an amount equal to $v\sigma/2$ and to increase the activation barrier in the opposite direction by this same amount.

Eyring Rate Law We can develop an expression for the strain rate by recognizing that the net strain rate is given by the net frequency of hops in the forward direction. The frequency of hops in the forward and reverse directions, which we refer to as f_1 and f_2 , respectively, are given as follows:

$$f_1 = f_0 \exp\left(-\frac{Q^* - v\sigma/2}{k_B T}\right) = \exp\left(-\frac{Q^*}{k_B T}\right) \exp\left(\frac{v\sigma}{2k_B T}\right)$$
(8.7)

$$f_2 = f_0 \exp\left(-\frac{Q^* + v\sigma/2}{k_B T}\right) = \exp\left(-\frac{Q^*}{k_B T}\right) \exp\left(\frac{-v\sigma}{2k_B T}\right)$$
(8.8)

The net rate of strain is proportional to $f_1 - f_2$, the net frequency of hops in the forward direction:



Figure 8.4: Nonlinear creep model.



Figure 8.5: Effect of an applied stress on a thermally activated creep process.

$$\frac{de}{dt} = A\left(f_1 - f_2\right) = Af_0 \exp\left(-\frac{Q^*}{k_B T}\right) \left[\exp\left(\frac{v\sigma}{2k_B T}\right) - \exp\left(\frac{-v\sigma}{2k_B T}\right)\right]$$
(8.9)

Where A is a dimensionless constant. Using the following definition of the hyperbolic sine function (sinh):

$$\sinh(x) = \left(e^x - e^{-x}\right)/2$$
 (8.10)

we obtain the following expression for the strain rate:

$$\frac{de}{dt} = 2Af_0 \exp\left(-\frac{Q^*}{k_B T}\right) \sinh\left(\frac{v\sigma}{2k_B T}\right)$$
(8.11)

Before considering the behavior of the Eyring rate equation for high and low stresses, it is useful to consider the overall behavior of the sinh function, which is illustrated in Figure 8.6. Note that for small x, sinh $x \approx x$, and for large x, sinh $(x) \approx 0.5 \exp(x)$.

Low Stress Regime In the low-stress regime we can use the approximation $\sinh(x) \approx x$ to get the following expression, valid for $v\sigma \ll k_B T$.

$$\frac{de}{dt} = \frac{Af_0 v\sigma}{k_B T} \exp\left(-\frac{Q^*}{k_B T}\right)$$
(8.12)



Figure 8.6: Behavior of the hyperbolic sine function.

In this regime the strain rate is linear in stress, which means that we can define a stress-independent viscosity from the following expression:

$$\frac{de}{dt} = \frac{\sigma}{\eta} \tag{8.13}$$

Comparing Eqs.8.12 and 8.13 gives the following for the viscosity:

$$\eta = \frac{k_B T}{A f_0 v} \exp\left(\frac{Q^*}{k_B T}\right) \tag{8.14}$$

So the Eyring theory reduces to and Arrhenius viscosity behavior in the linear, low-stress regime.

High Stress Regime In the high-stress regime, we use the fact that $\sinh(x) \approx \frac{\exp(x)}{2}$ for large x to obtain the following expression for $v\sigma \gg k_B T$:

$$\frac{de}{dt} = Af_0 \exp\left(-\frac{Q^*}{k_B T}\right) \exp\left(\frac{v\sigma}{2k_B T}\right)$$
(8.15)

Equivalently, we can write the following:

$$\frac{de}{dt} = Af_0 \exp\left(-\frac{Q^* - v\sigma/2}{k_B T}\right) \tag{8.16}$$

The effective activation energy decreases linearly with increasing stress, giving a very nonlinear response. In practical terms the activation volume is obtained by plotting $\ln (de/dt)$ vs. σ , with the slope being equal to $v/2k_BT$.

Physical significance of v Eyring rate models are most often used for polymeric systems. In this case the activation volume can be viewed as the volume swept out the portions of a polymer molecule which move during a fundamental creep event, as illustrated schematically in Figure 8.7. A large activation volume means that cooperative deformation of a large region of the material is required in order for the material to flow. Low values of the activation volume indicate that the deformation is controlled by a very localized event, corresponding, for example, to the rupture of a single covalent bond.



Figure 8.7: Illustration of the activation volume.

8.4.2 Additional Nonlinear Dashpot Elements

Nonlinear elements based on the Eyring rate model can also be included in our spring and dashpot models of viscoelastic behavior. For example, we can use an Eyring rate model to describe the stress dependence of the steady state creep of a nonlinear model, in which case Figure 8.4 gets modified to Figure 8.8. The steady state component is specified by the prefactor Af_0 the activation energy Q^* , and the activation volume, v.



Figure 8.8: Nonlinear creep model, including an Eyring rate element for the steadystate creep component.

9 YIELD BEHAVIOR

9 Yield Behavior

The yield point of a material corresponds to the onset of permanent deformation, originating for example from the movement of dislocations. The stress/strain curve for a simple tensile test is shown in Figure 9.1, with the tensile yield stress, σ_y , corresponding to the onset of permanent, irreversible deformation in the material. For most materials this corresponds to the onset of non-linearity in the stress-strain curve (rubber is the exception, and that case is discussed in more detail in 331). What we need is a generalized criterion that can be used to determine the onset of yield for any stress state. These yield criteria all focus on the importance of the shear stress.

9.1 Critical Resolved Shear Stress

The simplest criterion for the yield of a material is that the **resolved shear stress**, τ_{RSS} , exceeds a critical value referred to simply as the **critical resolved shear stress**, τ_{CRSS} . The resolved shear stress is obtained from the applied stress and the orientation of the slip plane as illustrated in Figure 9.2. For a single crystal the relevant resolved shear stress is the shear stress on acting on the slip plane, in the direction of the Burgers vector. In a tensile experiment it is given by the applied tensile stress, σ , the angle ϕ between the slip plane normal and the tensile axis, and the angle λ between the tensile axis and the slip direction:

$$\tau_{RSS} = \sigma \cos \phi \cos \lambda \tag{9.1}$$

In other words, $\tau_{RSS} = \tau_{CRSS}$ when $\sigma = \sigma_y$, where σ_y is the tensile yield strength. Substituting τ_{CRSS} for τ_{RSS} and σ_y for σ in Eq. 9.1 and solving for σ_y gives:

$$\sigma_y = \frac{\tau_{CRSS}}{\cos\phi\cos\lambda} \tag{9.2}$$

The factor $\cos \phi \cos \lambda$ is called the **Schmid factor**, and slip occurs along the slip system that the largest value of this quantity. The sum of ϕ and λ must be at least 90°, and it can be shown that $\cos \phi \cos \lambda$ is maximized when $\phi = \lambda = 45^{\circ}$, in which



Figure 9.1: Tensile testing sample and representative data for a ductile sample.

case the yield stress is twice the critical resolved shear stress. We refer to this value of the yield stress as the minimum value, σ_u^{min} :

$$\sigma_y^{min} = 2\tau_{CRSS} \tag{9.3}$$

Measured values of the critical resolved shear stress for different metals are shown in Table 7.

For polycrystalline materials, the situation is more complicated, since all crystal orientations will have a different value of the Schmid factor. In a polycrystalline material, each grain has a different value of the Schmid factor, so the situation is more complicated. However, we can get a reasonable approximation by using an appropriate average value for the Schmid factor instead of the maximum possible value that this value can have. We actually need the quantity, M, which is the average of the reciprocal Schmid factor for all of the grains in a material:

$$M = \left\langle \frac{1}{\cos\phi\cos\lambda} \right\rangle \tag{9.4}$$

Here the average is taken over all possible grain orientations of the material. The tensile yield stress is given by the following expression:

$$\sigma_y = M \tau_{CRSS} = \frac{M}{2} \sigma_y^{min} \tag{9.5}$$

This value of M is typically between 2.7 and 3, so we end up with a yield stress in a polycrystalline material that is between 35 and 50 percent larger than the minimum possible value given by Eq. 9.3.

9.2 Yield Surfaces

The full stress state of a material is defined by the 3 principal stresses, σ_1^p , σ_2^p and σ_3^p . The stress state of a material can therefore be specified on a 3-dimensional



Figure 9.2: Resolved shear stress.

Material	G (GPa)	τ_{crss} (MPa)
Silver	4.6	0.37
Aluminum	4.2	0.78
Copper	7.2	0.49
Nickel	12.2	3.2 - 7.35
Iron	13.2	27.5
Molybdenum	19	71.6
Niobium	5.8	33.3
Cadmium	3.8	0.57
Magnesium (basal slip)	2.8	0.39
Magnesium (prism slip)	2.8	39.2
Titanium (prism slip)	6.3	13.7
Beryllium (basal slip)	23.4	1.37
Beryllium (prism slip)	23.4	52

Table 7: Shear moduli and values of τ_{crss} for different metals.

space where the values of these 3 principal stresses are plotted on three orthogonal axes. The yield surface is the surface in this space that separates the stress states where yielding will occur from those where it will not occur. Here we describe two of the most common yield surfaces, those defined by the Tresca and Von Mises yield criteria.

9.2.1 Tresca Yield Criterion

The **Tresca yield criterion** is the simplest one in that we just assume that shear occurs whenever the maximum shear stress in the sample exceeds some critical value value τ_c . In mathematical terms, yield occurs under the following conditions:

$$\frac{\left|\sigma_{i}^{p}-\sigma_{j}^{p}\right|_{max}}{2} > \tau_{c} \tag{9.6}$$

where the 'max' subscript indicates that we take the principal stress difference $(\sigma_1^p - \sigma_2^p, \sigma_2^p - \sigma_3^p \text{ or } \sigma_1^p - \sigma_3^p)$ with the largest magnitude. The yield stress, σ_y , is typically measured in a uniaxial tensile experiment, where $\sigma_2^p = \sigma_3^p = 0$, and plastic yielding of the material occurs when $\sigma_1^p > \sigma_y$. In a uniaxial tensile experiment, the maximum shear stress is half the applied tensile stress, so $\tau_{crit} = \sigma_y/2$.

9.2.2 Von Mises Yield Criterion

A more complicated yield criterion is that yield occurs when the **Von Mises stress**, σ_e , exceeds some critical value. The Von Mises stress is given as follows:

$$\sigma_e = \frac{\sqrt{2}}{2} \sqrt{\left(\sigma_2^p - \sigma_1^p\right)^2 + \left(\sigma_3^p - \sigma_1^p\right)^2 + \left(\sigma_3^p - \sigma_2^p\right)^2} \tag{9.7}$$

For uniaxial deformation, as in a simple compression or tensile test, yielding occurs when $\sigma_e > \sigma_y$. The Tresca and Von Mises yield surfaces for a two dimensional

9 YIELD BEHAVIOR

stress state ($\sigma_3^p=0$) are shown in Figure 9.3a. Yielding does not occur inside the surface, but does occur outside the surface. Figure 9.3a is one particular cross section through a 3d yield surface. Another representation is shown in Figure 9.3b, which shows the yield surface viewed along the hydrostatic axis ($\sigma_1^p = \sigma_2^p = \sigma_3^p$).

Exercise: The tensile yield stress of a materials is measured as 45 MPa by a uniaxial tensile test.

- 1. What will the shear stress of the material by if the materials yields at a critical value of the Tresca stress?
- 2. How does your answer change if the material yields at a specified value of the Von Mises stress?

Solution:

- 1. The shear yield strength prediction, according to the Tresca criterion, is simply given by the maximum shear stress, at the yield point, which for a uniaxial tensile test is $\sigma_y/2 = 22.5$ MPa.
- 2. Suppose the stress for the tensile experiment is oriented in the 3 direction, so at the yield point, $\sigma_3^p = \sigma_y$ and $\sigma_1^p = \sigma_1^p = 0$. Substitution of these values into Eq. 9.7 gives $\sigma_e = \sigma_y$, as it should (the prefactor of $\sqrt{2}/2$ was chosen to force this to be the case). Now suppose that we apply a shear stress in the 1-2 plane, so we have $\sigma_1^p = \tau$, $\sigma_2^p = -\tau$ and $\sigma_3^p = 0$. Putting these values into Eq. 9.7 gives $\sigma_e = \sqrt{3}\tau$. Rearranging to give an expression for τ , and taking $\sigma_e = \sigma_y$ gives $\tau = \sigma_y/\sqrt{3} = 26$ MPa.

9.2.3 Coulomb Yield Criterion

The Coulomb yield criterion is a modification of the Coulomb criterion that takes into account that the critical shear stress will be modified by the normal stress acting on the shear plane. We would expect a compressive normal stress to increase the shear stress, whereas a tensile normal stress will decrease the critical shear stress. If the critical shear stress varies linearly with the normal shear stress we have the following:

$$\tau_c = \tau_c^0 - \mu \sigma_N \tag{9.8}$$

Consider a sample that is subjected to a uniaxial compressive stress with a magnitude of σ_1 shown in Figure 9.4. According to the Coulomb yield criterion (Eq. 9.8) yield will occur on the plane for which $\tau + \mu \sigma_N$ is maximized, which means we need to maximize $\sin(2\theta) - \mu \cos(2\theta)$ to determine the plane on which yielding will occur. We have:

$$\frac{d}{d\theta}\left(\sin\left(2\theta\right)\right) = \mu \frac{d}{d\theta}\left(\cos\left(2\theta\right)\right)$$

Solution of this equation gives $\tan (2\theta) = -1/\mu$. After a bit more trigonometry, we get find that the yield condition is first met for $\theta = 45^{\circ} + \phi$ (and the corresponding mirror plane about the y axis), with $\mu = \tan (2\phi)$.



Figure 9.3: Cross sections of the Tresca and Von Mises yield surfaces at the $\sigma_3^p = 0$ plane, and viewed down the hydrostatic line $(\sigma_1^p = \sigma_2^p = \sigma_3^p)$.



Figure 9.4: Normal stress and shear stress on a plane inclined by an angle θ with respect to horizontal.

9.3 Localized Deformation

A material that obeys the strain hardening law of Eq. 9.18 will fail when a portion of the sample becomes thinner than the remainder of the sample. The overall behavior of the sample is a balance between the fact that the strain is larger in this region, and can therefore support a larger true stress, but the cross section is larger, so that a larger true stress is needed just to maintain a constant force along the length of the sample. To understand how to think about this we need to consider the relationship between the true stress and the engineering stress.

Consider a sample that is being deformed in uniaxial extension, as illustrated in Figure 9.5. A sample with an undeformed cross sectional area of A_0 and undeformed length of ℓ_0 is stretched with a force, P. The engineering tensile stress, σ_{eng} , is obtained by dividing the load by the undeformed cross section, and the true tensile stress, σ_t is obtained by dividing the load by the actual cross sectional area of the deformed sample:

$$\sigma_{eng} = P/A_0 \tag{9.9}$$

$$\sigma_{true} = P/A \tag{9.10}$$

In general, the bulk modulus of a material is much larger than its yield stress, so the applied stresses associated with yield phenomena are not large enough to significantly change the volume. As a result, the sample deforms at constant volume, so we have:

$$A\ell = A_0\ell_0 \tag{9.11}$$

The relationship between the true stress and the engineering stress is therefore as follows:

$$\sigma_t = \sigma_{eng} \ell / \ell_0 = \sigma_{eng} \lambda \tag{9.12}$$



Figure 9.5: Uniaxial tensile test.

9.3.1 Considere Construction

The **Considere construction** is a simple construction that can be used to determine the stability of regions in a sample at large tensile deformations. It can be used in to distinguish between unstable and unstable necking of a sample, illustrated schematically in Figure 9.6. We begin by considering a region of the sample that has a slightly thinner cross section than the rest of the sample. The true stress in this region of the sample will be higher than the rest of the sample because we are dividing the applied load by a lower cross section . Two things can happen at this point, the first possibility is that the larger stress in this region of the sample leads to greater deformation, and the sample breaks as the necked region begins to thin down. This is the unstable necking condition illustrated on the left side of Figure 9.6. In this case the maximum force, P, applied to the sample is the force where the neck begins to form.

The second possibility is that the increased strain in the necked region leads to substantial strain hardening, so that this region of the sample is able to support the larger true stress in that region. Under the appropriate conditions the cross section of the necked region will stabilize at a value that is determined by the stress/strain relationship for the material. The sample deforms by 'drawing' new material into this necked region, as illustrated on the right side of Figure 9.6.

To understand when stable or unstable necking occur, we begin by recognizing that the onset of neck formation corresponds to a maximum tensile force that the material is able to sustain. In mathematical terms:

$$\frac{dP}{d\lambda} = 0 \tag{9.13}$$

Since the engineering stress is the load divided by the undeformed cross sectional area, which is a constant, we can write Eq. 9.13 as follows:



Figure 9.6: Schematic representation of stable and unstable necking of a sample under tensile loading conditions.

(9.14)

We can rewrite this expression in terms of the true stress by recognizing that $\sigma_{eng} = \sigma_t / \lambda$ (see Eq. 9.12), from which we obtain:

$$\lambda \frac{d\sigma_t}{d\lambda} - \sigma_t = 0 \tag{9.15}$$

which we rearrange to the following:

$$\frac{d\sigma_t}{d\lambda} = \frac{\sigma_t}{\lambda} \tag{9.16}$$

This condition is met when a line drawn fro the origin of a plot of σ_t vs. λ is tangent to the curve.

9.3.2 Stable and Unstable Necking

Use of the Considere construction is illustrated in Figure 9.7, where we show curves of the true stress vs. extension ratio for a material that does not form a stable neck (part a) and one that does form a stable neck (part b). In part a it is only possible to draw one line originating from the origin that is tangent to the stress-strain curve (point A in Figure 9.7). A necking instability forms when the true stress reaches this value, resulting in a thinned-down region of the sample. This region continues to thin down until the sample breaks. The maximum engineering stress that the sample sees prior to failure is given by the slope of the tangent line in Figure 9.7a.

In Figure 9.7b, it is possible to draw two lines from the origin that are tangent to the curve, with tangent points labeled as A and B. The tangent at point B represents a maximum in the applied force (the stress-strain curve lies below the tangent line) and the tangent at point B represents a minimum in the applied force (the stress-strain curve lies above the tangent line). At point B the neck stabilizes. Additional material is drawn into the necked region with a characteristic draw ratio that given by the value of λ at point B. The engineering stress at which this drawing occurs is less than the engineering stress required to form the neck in the first place. This means that the load during the drawing process to form the stable neck is lower than the stress required to form the neck in the first place. This phenomenon is generally observed in glassy polymeric materials ($T < T_g$) or semicrystalline polymers for which stable neck formation is observed.

$$\frac{d\sigma_t}{d\lambda} = \frac{\sigma_t}{\lambda} \tag{9.17}$$

9.3.3 Case Study - Power Law Strain Hardening

The following equation is often used to describe the behavior of a material after the yield point:

$$\sigma_t = K e_t^n \tag{9.18}$$

where:

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Figure 9.7: Considere construction for a material that does not form a stable neck (a) and a material that does form a stable neck (b).

- $\sigma_t = \text{true stress}$ (force over actual cross sectional area in a tensile test)
- $\diamond e_t = \text{true strain } (\ln (\ell/\ell_0) = \ln \lambda \text{ in a tensile test}).$
- \diamond K = strength coefficient (true stress at true strain of 1)
- \diamond *n*= strain hardening coefficient (dimensionless)

Limiting behavior: n = 1 is perfectly elastic behavior, whereas n = 0 corresponds to perfectly plastic behavior. Actual values of n fall somewhere between these two extremes, and are listed in Table8 for a variety of metals.

9.3.4 Necking Instability in a Power-Law Strain Hardening Material

If we write the true stress appearing in Eq. 9.18 as $\ln \lambda$, we have:

 Table 8: Strain Hardening Coefficients for Various Materials (From Hertzberg, Table 2.8).

Material	Strain Hardening Coefficient
Stainless Steel	0.45-0.55
Brass	0.35-0.4
Copper	0.3-0.35
Aluminum	0.15-0.25
Iron	0.05-0.15

$$\sigma_t = K \left(\ln\left(\lambda\right) \right)^n \tag{9.19}$$

Differentiating with respect to λ gives:

$$\frac{d\sigma_t}{d\lambda} = \frac{nK\left(\ln\left(\lambda\right)\right)^{n-1}}{\lambda} = \frac{nKe_t^{n-1}}{\lambda}$$

and then using Eq. 9.16 to equate $d\sigma_{\lambda}/d\lambda \ to\sigma/\lambda$ gives the following:

$$\frac{nKe_t^{n-1}}{\lambda} = \frac{\sigma}{\lambda} = \frac{Ke_t^n}{\lambda}$$

We can see that this equation is only true when the following condition holds:

$$n = \epsilon_t \tag{9.20}$$

So a measurement of the strain where the necking instability is observed can be used to determine the strain hardening exponent.

10 Deformation of Polymers

The deformation mechanisms in polymeric materials are completely different from those in metals and ceramics, and (almost) never have anything to do with the motion of dislocations. To begin with, we can separate into the polymers that are partially crystalline and those that are not. As one would expect, the structures of these non-crystalline (amorphous) and semicrystalline polymers are very different, as shown schematically in Figure Crystallization and glass formation are the two most important concepts underlying the physical properties of polymers. The ways in which the molecules are organized in non-crystalline (amorphous) polymers and semicrystalline polymers are very different, as illustrated in Figures 10.1 and 10.3. Polymers crystallize at temperatures below T_m (melting temperature) and form glasses at temperatures below T_g (glass transition temperature). All polymers will form glasses under the appropriate conditions, but not all polymers are able to crystallize. The classification scheme shown in Figure Polymers classification scheme divides polymeric materials based on the locations of T_g and T_m (relative to the use temperature, T) and is a good place to start when understanding different types of polymers.

10.1 Case Study: Fracture toughness of glassy polymers

Deformation is significant, but \mathcal{G}_{Ic} is still small compared to other engineering materials.



Figure 10.1: Structure of an amorphous polymer.



Figure 10.2: Structure at different length scales for a semicrystalline polymer.



Figure 10.3: Polymers classification scheme.



Figure 10.4: Load-Displacement and true stress-true strain curves for PVC (polyvinyl chloride) and HDPE (high density polyethylene).



Figure 10.5: Stress-strain curves for PMMA (polymethylmethacrylate) under tensile and compressive loading conditions.



Figure 10.6: Yield surface for PMMA at 20° C and at 90° C. For comparison a map of the Tresca yield criterion (where normal forces do not matter) shown as the dashed line.



Figure 10.7: Molecular weight dependence of fracture toughness for polystyrene (PS) and poly(methyl methacrylate) (PMMA).
10.1.1 Deformation Mechanisms

Suppose we do a simple stress strain experiment on polystyrene. Polystyrene deforms by one of two different mechanisms:

- 1. Shear bands due to strain softening (decrease in true stress after yield in shear).
- 2. **Crazing** requires net dilation of sample (fracture mechanism for PS and PMMA).

Crazes are load bearing - but they break down to form cracks - failure of specimen.

Crazing Fibrils are cold drawn polymer. Extension ratio remains constant as craze widens

Crack propagation:

- 1. 1) new fibrils are created at the craze tip
- 2. 2) fibrils break to form a true crack at the crack tip
- 3. Crazing requires a stress field with a tensile hydrostatic component $\sigma_1 + \sigma_2 + \sigma_3 > 0$ (crazes have voids between fibrils)
- 4. Crazing occurs first for PMMA in uniaxial extension ($\sigma_2 = 0$)
- 5. \mathcal{G}_{Ic} is determined by energy required to form a craze ($\approx 1000 \,\mathrm{J/m^2}$)
- 6. Crazing requires strain hardening of fibrils material must be entangled $(M > M_c), M_c$ typically $\approx 30,000$ g/mol.
- 7. In general, shear yielding competes with crazing at the crack tip

Meniscus instability mechanism (fibril formation at craze tip)

Material near the craze tip is strain softened, and can flow like a fluid between two plates.

http://n-e-r-v-o-u-s.com/blog/?p=1556

Competition between Shear Deformation and Crazing Shear deformation is preferable to crazing for producing high toughness.

Plane stress - shear yielding and crazing criteria (for PMMA)



Figure 10.8



Figure 10.9: Conceptual drawing of fibrils at the interface between the crazed and uncrazed material (from ref.[?])



Figure 10.10: Meniscus instability mechanism for the formation of craze fibrils.



Figure 10.11: Deformation map for the shear yielding and crazing for plane stress conditions ($\sigma_3^p = 0$)

Dugdale model Earlier we considered the maximum stress in front of an eliptical cra

Assumptions:

- 1) Tensile stress throughout plastic zone is constant value, σ_c
- 2) This stress acts to produce a crack opening displacement δ_c

$$\mathcal{G}_{IC} = \delta_c \sigma_c \tag{10.1}$$

The Dugdale zone (the craze in our polystyrene example) modifies the stress field so that it doesn't actually diverge to infinity, since infinite stresses are not really possible.

High Impact Polystyrene: Polystyrene (PS) is a big business - how do we make it tougher? High impact polystyrene (HIPS) is a toughened version of polystyrene produced by incorporating small, micron-sized rubber particles in the material. The morphology is shown in Figure 10.13, and consists small PS inclusions embedded in rubber particles that are in turn embedded in the PS matrix materials. The rubber particles act as stress concentrators that act as nucleation points for crazes.

Tensile Behavior: In Figure 10.15 we compare the tensile behavior of normal polystyrene (PS) and high impact polystyrene (HIPS). The rubber content in the material reduces the modulus but substantially increases the integrated area under the stress/strain curve up to the point of failure, which is a measure of the toughness of the material. We can summarize the differences between PS and HIPS as follows:

- $\diamond\,$ PS is brittle, with E =3GPa and relatively low fracture toughness
- \diamond HIPS is ductile, with a lower modulus, (E=2.1 GPa) and a much larger energy to fracture.

This area under the stress/strain curve is not a very quantitative measure of toughness because we don't have any information about the flaw size responsible for the eventual failure of the material.



Figure 10.12: Crack tip stresses in the Dugdale model.



Figure 10.13: Morphology of high impact polystyrene.

Figure 10.14: Multiple crazes in high impact polystyrene.



Figure 10.15: Schematic stress-strain curves for polystyrene (PS) and high impact polystyrene (HIPS) in the absence of a crack.

deformation via crazing in vicinity of rubber particles (stress concentrators) throughout sample

Samples with Precrack:

(measurement of K_{IC} or G_{IC})

- ♦ Deformation limited to region around crack tip
- $\diamond\,$ Much more deformation for HIPS higher toughness

Impact Tests Impact tests are designed to investigate the failure of materials at high rates. Two common standardized are the **Izod impact test** and the **Charpy impact test**. They both involve measuring the loss in kinetic energy of a swinging pendulum as it fractures a sample. The geometry of a Charpy impact test is illustrated in Figure 10.17 Decrease in pendulum velocity after breaking sample gives impact toughness. For a useful discussion of a Charpy impact test, see https://www.youtube.com/watch?v=tpGhqQvftAo.

For most materials the fracture toughness is rate dependent, but same general features for toughening materials often apply at both high and low fracture rates. For example, high impact polystyrene is much tougher than polystyrene at high strain rates, for the same general reasons outlined in Section 10.1.1.



Figure 10.16: Schematic stress-strain curves for polystyrene (PS) and high impact polystyrene (HIPS) in the presence of a crack.



Figure 10.17: Charpy impact test.



Figure 10.18: Izod impact geometry.

11 Contact Mechanics

In a simple tensile test involving a sample with a uniform cross section, the stresses and strains are both uniform throughout the entire sample. In almost any real application where we care about mechanical properties, this is not the case however. A simple example of this is the case where we press a rigid, cylinder into s soft, compliant material as shown in Figure 11.1.

11.1 Sign conventions

Sign conventions have a tendency to lead to confusion. This issue is particularly problematics in contact mechanics because compressive loads are considered to be positive, but a compressive stress is negative. Here's a summary of the sign conventions relevant to our treatment of contact mechanics:

- $\diamond~P$ (force): a positive force is compressive
- $\diamond~\delta$ (displacement): a positive displacement is compressive
- $\diamond~\sigma$ (stress): a positive stress is tensile
- $\diamond~e$ (strain): a positive strain is tensile



Figure 11.1: Indentation if a soft surface with a rigid, flat-ended cylindrical punch of radius a_0 .

In order not to get too hung up in issues related to the sign, we define P_t and δ_t as the tensile loads and displacements:

$$P_t = -P$$

$$\delta_t = -\delta \tag{11.1}$$

11.2 Flat Punch Indentation

(Note: Many of issues presented here are discussed in more detail in a published review article: see ref.[?]).

Consider a flat-ended cylindrical punch with a radius of a in contact with another material of thickness, h, as shown schematically in Figure 11.2. The material being indented by a punch rests on a rigid substrate. We are interested in the compressive force, P, that accompanies a compressive displacement, δ , applied to the indenter.

11.2.1 Flat Punch: Approximate Result for an elastic half space.

For an elastic half space $(h \to \infty)$, the strain field under the indenter is nonuniform. The largest strains are confined to a region with characteristic dimensions defined by the punch radius, a. We can get a very approximate expression for the relationship



Figure 11.2: Flat punch contact geometry. For an elastic half space, $h \to \infty$.

between the compressive load, P, and the compressive displacement, δ from the following approximate concepts:

♦ The average strain in the highly deformed region of the sample must increase linearly with δ. Because strain is dimensionless we need to divide δ by some length scale in the problem to get a strain. For an elastic half space with $h = \infty$ the only length scale in the problem is the punch radius, a. So the strain fields must depend on δ/a . We'll take this one step further and assume that δ/a is an average in a region of volume ≈ a^3 under the punch:

$$e_{avg} = -\delta/a \tag{11.2}$$

♦ The average contact stress, σ_{avg} under the punch can be quantitatively defined by dividing the compressive load by the stress:

$$\sigma_{avg} = -P/\pi a^2 \tag{11.3}$$

♦ An approximate relationship between *P* and δ is obtained by assuming that the stress and strain are related through the elastic modulus, i.e. $\sigma_{avg} = Ee_{avg}$. Using the equations above for the compliance, *C*₀:

$$C_0 \equiv \frac{\delta}{P} \approx \frac{1}{\pi E a} \tag{11.4}$$

11.2.2 Flat punch - Detailed Result

In a more general situation both of the contacting materials (the indenter and the substrate) may deform to some extent, so the compliance depends on the properties of both materials. If the materials have Young's moduli of E_1 and E_2 and Poisson's ratios of ν_1 and ν_2 , then the expression for C_0 is:

$$C_0 \equiv \frac{\delta}{P} = \frac{\delta_t}{P_t} = \frac{1}{2E_r a} \tag{11.5}$$

where E_r is the following reduced modulus:

$$\frac{1}{E_r} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$
(11.6)

Note that for a stiff indenter, $(E_2 \gg E_1)$ we have $E_r = \frac{E_1}{1-\nu_1^2}$. This is the plane strain modulus that appears in a variety of situations, which we derive below.

11.2.3 Plane strain modulus.

The plane strain modulus, E_r , describes the response of a material when it cannot contract in one of the directions that is perpendicular to an applied tensile stress. It's easy to derive this by using the compliance matrix for an amorphous material, which must look like this;

$$\begin{bmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{bmatrix} = \frac{1}{E} \begin{bmatrix} 1 & -\nu & -\nu & 0 & 0 & 0 \\ -\nu & 1 & -\nu & 0 & 0 & 0 \\ -\nu & -\nu & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2(1+\nu) & 0 & 0 \\ 0 & 0 & 0 & 0 & 2(1+\nu) & 0 \\ 0 & 0 & 0 & 0 & 0 & 2(1+\nu) \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}$$
(11.7)

In writing the compliance matrix this way, we have used the fact that Young's modulus is $1/s_{11}$ and the Poisson's ratio is $-s_{12}/s_{11}$, so we have $s_{11} = 1/E$ and $s_{12} = -\nu/E$. Suppose we apply a stress in the 1 direction, and require that the strain in the 2 direction is 0. This requires that a non-zero stress develop in the 2 direction. If we assume that $\sigma_3 = 0$, we have:

$$e_2 = \frac{-\nu}{E}\sigma_1 + \frac{\sigma_2}{E} \tag{11.8}$$

If e_2 is constrained to be zero, we have:

$$\sigma_2 = \nu \sigma_1 \tag{11.9}$$

Now we can put this value back into Eq. 11.7 and solve for e_1 :

$$e_1 = \frac{1}{E} \left(\sigma_1 - \nu^2 \sigma_1 \right) \tag{11.10}$$

The plane strain modulus relates σ_1 to e_1 , which for the case assumed above ($e_2 = 0$) gives:

$$E_r = \frac{\sigma_1}{e_1} = \frac{E}{1 - \nu^2} \tag{11.11}$$

11.3 Flat Punch Detachment and the Energy Release Rate

If adhesive forces cause the punch to stick to the substrate, we can use fracture mechanics to understand the force required for detachment to occur. The situation is as shown in Figure 12.9 for a flat-ended cylindrical punch with a radius of a_0 . The surface profile of the substrate (assumed in this case to be an elastic half space, i.e., $h = \infty$) is given by the following expression[?]:

$$u_z = (2\delta_t/\pi) \arcsin\left(a/r\right) \tag{11.12}$$

where δ_t is the applied tensile displacement and *a* is the actual radius of the contact area between the punch and the substrate. In Figure 12.9 we compare the shapes of the surface for the following two cases:

 $\diamond a = a_0$: this is the initial contact condition, where the substrate is in contact with the full surface of the indenter.



Compliant Substrate

Figure 11.3: Surface profile under a flat punch, from Eq. 11.12.

 $a = a_0/2$: the contact radius has been reduced to half its initial value.

The decrease in a from a_0 to $a_0/2$ is accompanied by a decrease in the stored elastic strain energy, and this strain energy is what drives the decrease in the contact area. While it may not be immediately obvious from Figure 12.9, the detachment problem is actually a fracture mechanics problem. This is because the edge of the contact can be viewed as a crack, which grows as the contact area shrinks. In the following section we describe a generalized energy based approach to for quantifying the driving force for the contact area to decrease before applying this approach to the specific problem of a flat cylindrical punch.

11.3.1 Energy Release Rate for a Linearly Elastic Material

Specifying the stress field is the same as specifying the stored elastic energy. Fracture occurs when available energy is sufficient to drive a crack forward, or equivalently in our punch problem, to reduce the contact area between the punch and the substrate. To begin we define the following variables:

- \diamond W = work done on system by external stresses
- $\diamond U_{el} =$ elastically stored energy
- $\diamond W U_{el} =$ energy available to drive crack forward.

The **energy release rate**, \mathcal{G} , describes the amount of energy that is used to move a crack forward by some incremental distance. Formally it is described in the following way:

$$\mathcal{G} = \frac{d}{dA_c} \left(W - U_{el} \right) \tag{11.13}$$

where A_c is the crack area. Fracture occurs when the applied energy release rate exceeds a critical value characteristic of the material, defined as the critical energy release rate, \mathcal{G}_C . The fracture condition is therefore:

$$\mathcal{G} = \mathcal{G}_c \tag{11.14}$$

The lowest possible value of \mathcal{G}_c is 2γ where γ is surface energy of the material. That's because the minimal energy to break a material into two pieces is the thermodynamic energy associated with the two surfaces. Some typical values for the surface energy of different materials are listed below (note that $1 \text{ mJ/m}^2 = 1 \text{ erg/cm}^2 = 1 \text{ dyne/cm}$).

- $\diamond\,$ Polymers: 20-50 mJ/m² Van der Waals bonding between molecules
- \diamond Water: 72 mJ/m² Hydrogen bonding between molecules
- \diamond Metals: $\approx 1000 \text{ mJ/m}^2$ Metallic bonding

We can derive a simple expression for the energy release rate if we assume that the material has a linear elastic response. Consider, for example, an experiment where we apply a tensile force, P_t , to a sample, resulting in a tensile displacement, δ_t , as illustrated in Figure 11.4a. If the material has a linear elastic response, the behavior is as illustrated in Figure 11.4. Suppose that the crack area remains constant as the material is loaded to a tensile force P_t . The sample compliance, C, is given by the slope of the displacement-force curve:

$$C = \left. \frac{d\delta_t}{dP_t} \right|_{A_c} \tag{11.15}$$

Now suppose that the crack area is increased by an amount dA_c while the load remains fixed at P_t , i.e. the system moves from point 1 to point two on Figure 11.4b. This increases the compliance by an amount dC, resulting in corresponding increase in the displacement of $P_t \delta C$. If we now unload the sample from point 2 back to the origin, the slope of this unloading curve is given by the enhanced compliance, $C + \delta C$. At the end of this loading cycle be have put energy into the sample equal to the shaded area in Figure 11.4b. This is the total work done on the system by the external stresses (W in Eq. 11.13), and given by the following expression:



Figure 11.4: Derivation of the compliance expression for \mathcal{G} .

$$\delta W = \frac{1}{2} P_t^2 \delta C \tag{11.16}$$

Because the sample at the beginning an end of this process is unstrained, we have $U_{el} = 0$. We can now take the limit where δA_c becomes very small to replace $\delta W/\delta C$ with the derivative, dW/dC to obtain:

$$\mathcal{G} = \lim_{\delta A_c \to 0} \frac{\delta W}{\delta A_c} = \frac{P_t^2}{2} \frac{dC}{dA_c}$$
(11.17)

11.3.2 Stable and Unstable Contact

Two different behaviors are obtained as two contacting materials are separated, depending on the relationship between \mathcal{G} and the contact area A. These behaviors are referred to as stable contact $(d\mathcal{G}/dA > 0)$ and unstable contact $(d\mathcal{G}/dA < 0)$. The difference between these behaviors is illustrated in Figure 11.5, and can be understood by considering two surfaces that are initially brought into contact to establish a contact area, A_0 . We then increase the tensile load, P_t , thereby increasing the applied energy release rate. As the tensile load and the corresponding tensile displacement are increased, \mathcal{G} increases until it reaches the critical value, \mathcal{G}_c . The tensile load at this point is defined as the critical load P_c , and is the load at which A begins to decrease. We fix the tensile load at P_c and observe one of two possible behaviors:

Unstable Detachment: If $d\mathcal{G}/da < 0$, a decrease in A gives rise to an increase in \mathcal{G} , and the contact is unstable, so that the indenter rapidly detaches from the indenter once a starts to decrease.

Stable Detachment: If $d\mathcal{G}/dA > 0$, a decrease in *a* corresponds to a decrease in \mathcal{G} . In this case the contact is stable, and the load (or displacement) must be increased further to continue to decrease the contact area. Detachment in this case occurs gradually as the load continues to increase.

11.3.3 Application of the Griffith Approach to the Flat Punch Problem

The edge of the contact is a crack, which advances as a decreases. We can use Eq. 11.17 for the energy release rate to obtain the following:

$$\mathcal{G} = -\frac{P_t^2}{2}\frac{dC}{dA} = -\frac{P_t^2}{4\pi a}\frac{dC}{da}$$
(11.18)

where we have assumed that the contact area remains circular, with $A = \pi a^2$. Not that A in this expression is the contact area between the indenter and the substrate, and NOT the crack area. The negative sign in Eq. 11.18 emerges from the fact an decrease in contact area corresponds to an equivalent increase in the crack area, so we have:

$$\frac{dC}{dA} = -\frac{dC}{dA_c} \tag{11.19}$$

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Figure 11.5: Illustration of stable contact, where P_t must increase continuously in order for the contact area to continue to decrease, and unstable contact, where the contact area reduces rapidly to zero as soon as a critical tensile load is attained.

With $C = C_0 = 1/2E_r a$ (Eq. 11.5) we obtain the following expression for \mathcal{G} :

$$\mathcal{G} = \frac{P_t^2}{8\pi E_r a^3} \tag{11.20}$$

In some situations it is more convenient to express the energy release rate in terms of the tensile displacement, δ_t . The most general expression is used by using $C = \delta_t/P_t$ to substitute P_t with δ_t/C in Eq. 11.17:

$$\mathcal{G} = -\frac{\delta_t^2}{2C^2} \frac{dC}{dA} = -\frac{\delta_t^2}{4\pi a C^2} \frac{dC}{dA}$$
(11.21)

If the compliance is the value for an elastic half space (Eq. 11.5), then we obtain the following expression for the energy release rate in terms of the displacement:

$$\mathcal{G} = \frac{E_r \delta_t^2}{2\pi a} \tag{11.22}$$

It is useful at this point to make the following general observations:

- \diamond In fracture mechanic terms the contact edge is an interfacial crack. An advancing crack corresponds to a reduction in *a*, and a receding crack corresponds to an increase in *a*.
- \diamond In general, \mathcal{G} is determined by the applied load and the geometry.
- ◇ \mathcal{G}_c is a property of the interface. The crack moves forward (*a* decreases) when the value of \mathcal{G} determined by the loading conditions exceeds \mathcal{G}_c . The detachment criterion is that the energy release rate, \mathcal{G} , is equal to the critical energy release rate, G_c , when the applied tensile force is equal to the critical pull-off force, P_c :

$$\mathcal{G}_c = \frac{P_c^2}{8\pi E_r a^3} \tag{11.23}$$

This equation can be rearranged to give the following for the pull-off force:

$$P_c = \left(8\pi E_r a^3 \mathcal{G}_c\right)^{1/2} \tag{11.24}$$

♦ Detachment from of a flat punch from an elastic half space (a/h = 0) is unstable for load controlled (constant P_t) OR displacement controlled (constant δ_t) conditions. In each of these cases the contact radius, a, is equal to the punch radius, a_0 , at the beginning of an experiment.

11.3.4 Detachment: Size Scaling

An interesting aspect of Eq. 11.24 is that the pull-off force scales with $a^{3/2}$, whereas the punch cross sectional area scales more strongly with a ($A = \pi a^2$). This behavior has some interesting consequences, which we can obtain by dividing P_c by the punch cross sectional area to obtain a critical pull-off stress, σ_c :

$$\sigma_c = \frac{P_c}{\pi a^2} = \left(\frac{8E_r \mathcal{G}_c}{\pi a}\right)^{1/2} \tag{11.25}$$

Note that the detachment stress increases with decreasing punch size.

Let's put in some typical numbers to see what sort of average stresses we end up with:

- ♦ $E_r \approx 10^9$ Pa (typical of glassy polymer)
- $\diamond~\mathcal{G}_c\approx 0.1\,\mathrm{J/m^2}$ (twice the surface energy of a typical organic material)
- $\diamond a \approx 100 \text{ nm}$ (smallest reasonably possible value)
- $\diamond \sigma_c \approx 50 \text{ MPa}$

In order for stresses to be obtained, the pillars must be separated so that the stress fields in substrate don't overlap. This decreases the maximum detachment



Figure 11.6: Electron micrograph of Gecko setae.

stress from the previous calculation by about a factor of 10, so that the largest stress we could reasonably expect is ≈ 5 MPa. That's still a pretty enormous stress, corresponding to 500 N (49 Kg) over a 1 cm² area. This is still difficult to achieve, however, because it requires that the pillar array be extremely well aligned with the surface of interest, a requirement that is very difficult to meet in practice. Nevertheless, improvements in the pull-off forces can be realized by structuring the adhesive layer, and this effect is largely responsible for the adhesive behavior of geckos and other creatures with highly structured surfaces.

11.3.5 Thickness Effects

When the thickness, h, of the compliant layer between a rigid cylindrical punch punch and a rigid, flat substrate decreases, the mechanics change in a way that makes it more difficult to pull the indenter out of contact with the compliant layer. For the geometry shown in Figure 11.8 we can write the compliance of the material in the following way:

$$C = \frac{1}{2E_r a} f_C \tag{11.26}$$

For an elastic half space $(h \to \infty)$ $f_C = 1$. The factor f_C accounts for changes in the compliance due to the decreased thickness of the layer. In general it depends on Poisson's ratio for the compliant layer and the confinement ratio, a/h(the ratio of the punch radius to the thickness of the layer). For an incompressible compliant layer with $\nu = 0.5$ the following expression for f_C provides an excellent approximation to the behavior of the compliance on the aspect ratio, a/h:[?]

$$f_C = \left[1 + 1.33 \left(a/h\right) + 1.33 \left(a/h\right)^3\right]^{-1}$$
(11.27)

The behavior of f_C as a function of a/h is plotted in Figure 11.9. A series of geometric correction factors can be derived from this expression for f_C . The first of these is a correction factor for the compliance of the energy release rate expression with the tensile load, P_t , as the independent variable. In this case we use Eq. 11.18 to get write the expression for the energy release rate in the following form:



Figure 11.7: Schematic representation of an array of pillars in contact with a flat surface.



Figure 11.8: A thin, compliant layer being indented with a rigid, cylindrical punch.

$$\mathcal{G} = -\frac{P_t^2}{4\pi a} \frac{dC}{da} = \frac{P_t^2}{8\pi E_r a^3} f_{\mathcal{G}p} \tag{11.28}$$

Here $f_{\mathcal{G}p}$ accounts for deviations in the compliance derivative due to the confinement effects, in this case determined by the ratio between the actual value of dC/da and the value of this quantity for a/h = 0:

$$f_{\mathcal{G}p} = \frac{dC}{da} / \left. \frac{dC}{da} \right|_{a/h=0} \tag{11.29}$$

Finally, we can use the fact that $P_t = \delta_t/C$ to get a similar expression for \mathcal{G} in terms of the tensile displacement, δ_t :

$$\mathcal{G} = \frac{E_r \delta_t^2}{2\pi a} f_{\mathcal{G}\delta} \tag{11.30}$$

In this case $f_{\mathcal{G}\delta}$ includes the dependence on a/h of both the compliance and it's derivative with respect to a. This dependence is evident from Eq. 11.21, where $\mathcal{G}(\delta_t)$ is seen to be proportional to dC/da and is inversely proportional to C^2 . The a/h dependence of dC/da is accounted for by $f_{\mathcal{G}p}$, and the a/h dependence of C is accounted for by $f_{\mathcal{C}}$, so we obtain the following for $f_{\mathcal{G}\delta}$:

$$f_{\mathcal{G}\delta} = \frac{f_{\mathcal{G}p}}{f_c^2}$$

The confinement functions $f_{\mathcal{G}p}$ and $f_{\mathcal{G}\delta}$ are both equal to one for a/h = 0 and are plotted as a function of a/h for $\nu = 0.5$ in Figure 11.9. A practical consequence of the decrease in $f_{\mathcal{G}p}$ with decreased h is that a larger tensile force is required in order to remove the cylinder from its contact with the compliant layer. With a small value of $f_{\mathcal{G}p}$, a larger tensile load needs to be applied in order for \mathcal{G} to exceed the critical energy release rate, \mathcal{G}_c .



Figure 11.9: Geometric correction factors for the flat punch geometry (generated with python code given as example.

11.4 Contact of Paraboloids

11.4.1 Non-Adhesive Case

Suppose that the indenter is not flat, but has a parabolic profile that can be described by the following expression:

$$z = A_p r^2 \tag{11.31}$$

Here z is the vertical distance from the apex of the parabola, r is the radial distance from symmetry axis for the paraboloid and A_p is a constant that defines the shape of the paraboloid. A sphere has a parabolic shape near the apex, which can be seen by considering the equation for a sphere of Radius R that has it's center at r = 0, z = R (see Figure 11.10):

$$r^{2} + (z - R)^{2} = R^{2}$$
(11.32)

Solving Eq. 11.32 for z gives:

$$z = R\left(1 \pm \sqrt{1 - (r/R)^2}\right)$$
(11.33)

For small $x, \sqrt{1-x} \approx 1-x/2$, so for $r \ll R$ we have:

$$z = \frac{r^2}{2R} \tag{11.34}$$

where we have taken the solution with the smaller value of z, corresponding to the bottom of the sphere. From a comparison of Eqs.11.32 and 11.34, we see the paraboloid is a good approximation for the shape of a sphere, with the sphere radius

given by $1/2A_p$. For this reason we use R instead of A to characterize the parabolic shape, since the results can be applied to contact of spheres, provided that the the contact dimensions are much smaller than R. Generally everything works well as long as r/R < 4.

The compressive a rigid parabolic indenter into the surface of the material (δ_h in Figure 11.10) is given by the following expression:

$$\delta_h = a^2/R \tag{11.35}$$

Note that this is a completely geometric relationship that does not depend on the modulus of the material that is being indented. The compressive force required to establish a contact radius of a is referred to as P_h , and is given by the following expression:

$$P_h = \frac{4E_r a^3}{3R}$$
(11.36)

We can use Eq. 11.35 to substitute for a and obtain a relationship between P_h and δ_h :

$$P_h = \frac{4E_r}{3} R^{1/2} \delta_h^{3/2} \tag{11.37}$$

The assumption here is that there is no adhesion between the indenter and the substrate, <u>i.e.</u>, $\mathcal{G} = K_I = 0$. The fact that there is no stress concentration at the interface is consistent with the fact that the slope of the surface profile of the compliant material is continuous at r = a. This surface profile is plotted in Figure 11.10 and is given by the following expression:[?]

$$u_{z} = \frac{\delta}{\pi} \left\{ \left(2 - \left(r/a \right)^{2} \right) \arcsin\left(a/r \right) + \left(r/a \right) \left(1 - \left(a/r \right)^{2} \right)^{1/2} \right\}$$
(11.38)



Figure 11.10: Non-adhesive contact of a rigid, parabolic indenter into an elastic material.

11.4.2 Effects of Adhesion on Contact

The easiest way to understand the effect of adhesion on the contact between a parabolic is to consider a hypothetical situation where we turn off the adhesion and bring the indenter into contact with the surface, resulting in the deformation illustrated in Figure 11.10. Now we we turn on the adhesion, and begin retracting the indenter from the surface, maintaining a fixed projected contact radius a. The situation for the case where we have retracted the tip to the point where the tip apex is level with the undeformed surface ($\delta_t = 0$) is illustrated in Figure 11.11. The applied compressive load required to reach a given contact radius is less than the value of P_h given by Eq. 11.36 ($P < P_h$). Similarly, the compressive displacement required to reach a given contact radius is less than the value given by Eq. 11.35 ($\delta < \delta_h$). These deviations from δ_h and P_h are related by the system compliance, which for this geometry is C_0 as given by Eq. 11.5:

$$\frac{\delta - \delta_h}{P - P_h} = C_0 = \frac{1}{2E_r a} \tag{11.39}$$

Combination of Eqs. 11.5 and 11.39 gives the following relationship between δ , P and E_r :

$$\delta = \frac{a^2}{3R} + \frac{P}{2E_r a} \tag{11.40}$$

This expression is the one that needs to be used in order to obtain the reduced modulus in situations where adhesive forces between the indenter and the substrate modify the contact radius. It use requires that the contact radius be measured independently. This is easy to do when the contact area is big enough to visualize directly, but is a very difficulty problem for very small contacts (as in atomic force microscopy) where the contact is too small to visualize optically.

Once we know the reduced modulus of the system, we can obtain the energy release rate. The expression for the energy release rate for curved object in contact with surface in a way that is very similar to what we did for the flat punch in Section 11.3. The only difference is that in the absence of adhesion we need to apply a compressive load, P_h (given by Eq. 11.36):



Figure 11.11: An example of the surface profile for adhesive contact for the case where $\delta_t = 0$.

$$\mathcal{G} = -\frac{(P_t + P_h)^2}{2} \frac{dC}{dA} = \frac{(P_t + P_h)^2}{8\pi E_r a^3}$$
(11.41)

This equation can be rearranged to give a^3 as a function of the compressive load, $P(P = -P_t)$, to give an expression that was derived in 1971 by Johnson, Kendall and Roberts [?] and commonly referred to as the **JKR equation**:

$$a^{3} = \frac{3R}{4E_{r}} \left(P + 3\pi \mathcal{G}R + \left(6\pi \mathcal{G}RP + (3\pi \mathcal{G}R)^{2} \right)^{1/2} \right)$$
(11.42)

11.5 Indentation with Berkovich Trips

Parabolic tips are often used in measurements of adhesion or of the elastic properties of materials. For Hardness measurements tips with sharp corners are more commonly used. One example is the **Berkovich tip** shown in Figure 11.12.

The hardness, H, of a material is given by the ratio of the load to the projected contact area of the non-recoverable indent made in the material by the indenter. In our case we obtain the hardness from the maximum load, P_{max} (illustrated in Figure 11.13), and from the corresponding projected area, A, of the hardness impression:

$$H = \frac{P_{max}}{A} \tag{11.43}$$

The projected area is related to the contact depth, δ_c , by a relationship that depends on the shape of the indenter[?]. For a Berkovich tip the appropriate relationship is:

$$A = 24.5\delta_c^2 \tag{11.44}$$



Figure 11.12: Geometry of a Berkovich tip commonly used in indentation experiments. The angle, a, is 65.35° for a standard Berkovich tip.

The procedure for determining the contact depth was developed by Oliver and Pharr, where the following expression is used to estimate the contact depth:

$$\delta_c = \delta_{max} - 0.75 \frac{P_{max}}{S} \tag{11.45}$$

where δ_{max} is the maximum penetration depth of the indenter tip and S is the contact stiffness, determined experimentally as the initial slope of the linear portion of unloading curve (see Figure 11.13). From the measured values of S, P_{max} and δ_{max} , we use Equations 11.44 and 11.45 to determine A. The reduced modulus is then obtained from the following expression for the contact stiffness, assuming a value for the contact stiffness that is the same for a circular contact of the same area:

$$S = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \tag{11.46}$$



Figure 11.13: Typical load-displacement curve for indentation of the polyester resin used to embed the paint samples, labeled to illustrate the values of P_{max} , h_{max} and S.

12 Fracture Mechanics

The stress-strain behavior for a many material can exhibit a range of phenomena, depending on the temperature. This is particularly true of many polymers, which can show the range of behaviors in a uniaxial tensile test shown in Figure 12.1. While not all of these behaviors are necessarily observed in the same material, the following general regimes can often be identified, based on 4 different temperature regimes $(T_1, T_2, T_3 \text{ and } T_4)$.

- $\diamond~T_1$: Brittle behavior. This is generally observed at sufficiently low temperatures.
- \diamond T₂: Ductile behavior (yield before fracture)
- \diamond T₃: cold drawing (stable neck)
- \diamond T₄: uniform deformation

Here we are concerned with brittle behavior(T_1), or in some cases situations where there is a small degree of ductility in the sample (T_2).. There are two equivalent approaches for describing the fracture behavior. The first of these is the energy



Figure 12.1: Typical generic temperature behavior at different temperatures.

based approach described in the previous section, where an existing crack in a material grows when the applied energy release rate is larger than some critical value. In this section we explore the second approach, where characteristic stress field in the vicinity of a crack exceeds some critical value.

12.1 Fracture Modes

Different fracture modes are defined by the relationship between the applied stress and the crack geometry. These are illustrated schematically in Figure 12.2 Fracture of a homogeneous material fracture generally occurs under Mode I conditions, and this is the most important condition. Mode II conditions, where a shear stress is applied in the direction perpendicular to the crack front, is often important for interfacial fracture, including the adhesive bonding of materials with different properties. Mode III is generally not important for our purposes.

12.2 Stress Concentrations

In the previous section on contact mechanics we introduced the concept of the energy release rate, \mathcal{G} , which can be viewed as the driving force for crack propagation. Failure occurs when \mathcal{G} exceeds a critical value, \mathcal{G}_c . was originally formulated by Griffith, and is referred to as the Griffith model for this reason. We can also describe the driving force for crack propagation in terms of the detailed stress field in the vicinity of the tip of a propagating crack. This approach was developed by Irwin, and is referred to here as the Irwin model . The key concept here is that stresses are enhanced, or 'concentrated' in the vicinity of a defect like a crack. The easiest way to start thinking about this is to look at the nature of the stress distribution around a circular hole in a two-dimensional plate (Figure 12.3). A stress is a force per unit area, so we can imagine dividing up the stress into individual force lines, which are equidistant when the stress is uniform. Near a defect the lines of force are closer to one another, indicating that the stress is higher in this area. The maximum tensile stress at the sides of the hole is three times the average applied stress.

For an ellipse of with axis a_c perpendicular to the applied stress and axis b_c parallel to the applied stress (see Figure 12.4), the maximum stress in this case is given by the following expression:



Figure 12.2: Fracture Modes .



Figure 12.3: Force lines around a circular defect.

$$\sigma_{max} = \sigma_0 \left(1 + 2\frac{a_c}{b_c} \right) \tag{12.1}$$

Note that we recover the behavior described above for a circular whole, where $a_c = b_c$ and $\sigma_{max}/\sigma_0=3$. We can also write this in terms of the radius of curvature of the ellipse, ρ_c , at the point of maximum stress:

$$\rho_c = \frac{b_c^2}{a_c} \tag{12.2}$$

Combination of Eqs. 12.1 and 12.2 gives:

$$\sigma_{max} = \sigma_0 \left(1 + 2\sqrt{a_c/\rho_c} \right) \tag{12.3}$$

We are usually interested in very sharp cracks, where $a_c/\rho_c \gg 1$. In this case we can ignore the factor of 1 in Eq. 12.3 and we get the following proportionality:

$$\sigma_{max} \propto \sigma_0 \sqrt{a_c} \tag{12.4}$$

This combination of parameters, with the applied stress multiplied by the square root of the crack length, plays a very important role in fracture mechanics, as we describe in more detail below.

12.3 Stress Intensity Factor

Consider a planar crack in the x-z plane, as shown conceptually Figure 12.5. The stress in the vicinity of the crack tip can be expressed in the following form:

$$\sigma = \frac{K}{\sqrt{2\pi d}} f\left(\theta\right) \tag{12.5}$$

where K is the stress intensity factor, d is the distance from the crack tip and $f(\theta)$ is some function of the angle θ that reduces to 1 for the direction directly in front of a crack ($\theta = 0$). Different functional forms exist for $f(\theta)$ for the different stress components σ_{xx} , σ_{yy} , etc. The detailed stress fields depend on the loading mode (Mode I, II or II, or some combination of these), and the corresponding stress fields



Figure 12.4: Elliptical crack with a crack tip radius of curvature, ρ_c .

are specified by the appropriate value of K (K_I for mode I, K_{II} for mode II or K_{III} for mode III).

Mode I loading

The stresses in the vicinity of a mode I crack are given by the following [?]:

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{pmatrix} = \frac{K_I}{\sqrt{2\pi d}} \cos \frac{\theta}{2} \begin{pmatrix} 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \\ 1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \\ \cos \frac{3\theta}{2} \sin \frac{\theta}{2} \end{pmatrix}$$
(12.6)

This compact notation is used to specify the three relevant values of $f(\theta)$. For example, for σ_{11} we have the following:

$$\sigma_{11} = \left(K_I / \sqrt{2\pi d}\right) \cos\left(\theta / 2\right) \left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) \tag{12.7}$$

These expressions assume that the crack tip is very sharp, with a very small radius of curvature, ρ_c . If *d* is comparable to ρ_c , these equations no longer apply. Consider for example, the presence of an internal crack of length a_c and radius of curvature ρ_c in a thin sheet of material, shown schematically in Figure 12.6. In this case the stress at the crack edge is σ_{max} as given by Eq. 12.3. An assumption in the use of Eq. 12.6 is that the stresses are substantially less than σ_{max} . In other words, *K* describes the stress field close to the crack tip, but still at distances away from the crack tip that are larger than the crack trip radius of curvature, ρ_c .



Figure 12.5: Cartesian (a) and polar (b) coordinate axes use d to define stresses in the vicinity of a crack tip.

The mode I stress intensity factor for this geometry is given by the applied stress, σ_0 and the crack length a_c :

$$K_I = \sigma_0 \sqrt{\pi a_c} \tag{12.8}$$

For values of d that are substantially larger than ρ_c but smaller than a_c , we can determine the stresses from Eq. 12.6, with K_I as given by Eq. 12.8.

Mode II loading

For mode II loading the crack tip stress fields are given by the following set of expressions[?]:

$$\begin{pmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{12} \end{pmatrix} = \frac{K_{II}}{\sqrt{2\pi d}} \begin{pmatrix} -\sin\frac{\theta}{2}\left(2 + \cos\frac{\theta}{2}\cos\frac{3\theta}{2}\right) \\ \sin\frac{\theta}{2}\cos\frac{\theta}{2}\cos\frac{3\theta}{2} \\ \cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right) \end{pmatrix}$$
(12.9)

It is generally difficult to determine K_{II} in a straightforward way, and finite element methods must often be used to determine it for a given loading condition and experimental geometry. Once K_{II} is known, the crack tip stress fields can be obtained from Eq. 12.9.

Mode III loading

While mode III loading is often encountered in practical applications, it is generally avoided in experiments aimed at assessing the fracture behavior of materials, and is not considered further in this text.

12.4 Fracture condition

In the stress-based theory of fracture, the material fails when the stress intensity factor reaches a critical value that depends on the material. For mode I loading, we refer to this critical stress intensity factor as K_{IC} . Setting σ_0 to the fracture stress, σ_f , and setting K_I to K_{IC} in Eq. 12.8 gives:

$$K_{IC} = \sigma_f \sqrt{\pi} a_c \qquad (12.10)$$

Figure 12.6: An internal crack in a homogeneous solid.

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12.5General relationship between stress intensity factor and energy release12FRACTURE MECHANICSrate.

Rearranging gives:

$$\sigma_f = K_{IC} / \sqrt{\pi a_c} \tag{12.11}$$

So the fracture stress decreases as the flaw size, a_c , increases. This is why a material can appear to be fine, even though small cracks are present in the material. The cracks grow very slowly, but when the reach a critical size for which Eq. 12.11 is satisfied, the material fails catastrophically.

The fracture toughness, K_{IC} has strange units - a stress multiplied by the square root of a length. In order to understand where this characteristic stress and the characteristic length actually come from, we need to consider the actual shape of the crack tip. Using Eq. 12.3 we see that the maximum stress in front of the crack tip, σ_{max}^{f} , at the point of fracture is:

$$\sigma_{max}^f \approx 2\sigma_f \sqrt{a_c/\rho_c} \tag{12.12}$$

where we have assumed that $\sqrt{a_c/\rho_c} \gg 1$, so that we can ignore the extra factor of 1 in Eq. 12.3. Now we can use Eq. 12.10 to substitute K_{IC} for σ_f . After rearranging we get:

$$K_{IC} \approx \sigma_{max}^f \frac{\sqrt{\pi}}{2} \sqrt{\rho_c} \approx \sigma_{max}^f \sqrt{\rho_c}$$
(12.13)

This expression is really only valid for a crack tip with a well-defined radius of curvature, which is often not the case. Models that aim to predict and understand the fracture toughness of materials are all based on understanding the details of the yielding processes very close to the crack tip, and the resulting crack shape. We'll return to this issue later. For now we can summarize the stress-based approach fracture mechanics as follows:

- ◊ With the exception of a very small region near the crack tip, all of the strains are elastic.
- \diamond There is a very small plastic zone in the vicinity of a crack tip, with a characteristic dimension, ρ that is determined by the details of the way the material plastically deforms.
- \diamond Fracture occurs when the stress field defined by K_I reaches a critical value.

12.5 General relationship between stress intensity factor and energy release rate.

The stress intensity factor and the energy release rate are related to one another through the following expression:

$$\mathcal{G} = \frac{K_I^2 + K_{II}^2 + K_{III}^2}{E_r} \tag{12.14}$$

Here E_r is the reduced modulus that is slightly different for plane stress and plane strain conditions:

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$$E_r = E \text{ (Plane stress conditions)} \\ E_r = \frac{E}{1-\nu^2} \text{ (Plane strain conditions)}$$
(12.15)

Plane stress conditions generally apply for very thin samples, whereas plane strain conditions apply for thick samples, and also for the axisymmetric punch problems that we have discussed earlier in this text.

The fact that $\mathcal{G} \propto K_I^2$ for a mode I fracture experiment is illustrated in Figure 12.7, which we use to show the relationship between stress and stored elastic energy for an elastically deformed sample. The energy input to the sample up to the point of fracture, which we refer to $\operatorname{as} U_f$, is the area under the stress strain curve:

$$U_f = \frac{1}{2}\sigma_f e_f = \frac{1}{2}\frac{\sigma_f^2}{E_r}$$
(12.16)

The stress intensity factor, K_I at the fracture point is proportional to the stress, σ_f , and the strain energy release rate, \mathcal{G} , at the point of failure is proportional to the total stored elastic energy, U_f . This means that the following proportionality must hold:

$$\mathcal{G} \propto \frac{K_I^2}{E_r} \tag{12.17}$$

This is consistent with Eq. 12.14, but we need to do a more detailed analysis to get the prefactor exactly right.

12.6 Some Specific Geometries

12.6.1 Double cantilever beam geometry

The double cantilever beam geometry illustrated in Figure 12.8 is a common test used to measure crack propagation in materials. It is commonly used to measure the adhesion between two materials that have been glued together. It consists of to beams, each with width, w, and thickness, t. The crack length, a_c in this geometry is the distance between the parts of the beam where the force is applied and the



Figure 12.7: Schematic stress/strain curve for a brittle material in the presence of a crack.

beginning of the region of the sample where the two beams are in contact with one another.

For the double cantilever beam geometry the compliance is given by the following expression:

$$C \equiv \frac{\delta_t}{P_t} = \frac{8a_c^3}{Ewt^3} \tag{12.18}$$

The crack area, A_c is obtained by the crack length, a_c by the width of the sample:

$$A_c = wa_c \tag{12.19}$$

So we have:

$$\frac{dC}{dA_c} = \frac{1}{w} \frac{dC}{da_c} \tag{12.20}$$

We now combine Eqs. 12.18 and 12.20 to obtain the following for the energy release rate:

$$\mathcal{G} = \frac{P_t^2}{2w} \frac{dC}{da_c} = \frac{12a_c^2 P_t^2}{Ew^2 t^3}$$
(12.21)

At fixed load, \mathcal{G} increases as the crack length increases - unstable geometry!

can use We Eq. 12.18 to substitute δ_t for P_t and write the expression for \mathcal{G} in the following way.

$$\mathcal{G} = \frac{3\delta_t^2 t^3 E}{16a_c^4} \tag{12.22}$$

At a fixed displacement, crack will grow until $\mathcal{G} = \mathcal{G}_c$ and then stop. This is a better way to do the experiment.



Figure 12.8: Double cantilever beam geometry.

12.6.2 Flat Punch Geometry: Thick Compliant Layer

For the flat punch case, the following analytic expression exists for the shape of the normal tress distribution directly under the punch (the plane with $z = \delta_t$ in Figure 12.9):

$$\frac{\sigma_{zz}}{\sigma_{avg}} = 0.5 \left(1 - (r/a)^2\right)^{-1/2}$$
(12.23)

Here the average stress, σ_{avg} is defined as follows:

$$\sigma_{avg} \equiv \frac{P}{\pi a^2} \tag{12.24}$$

Note that σ_{zz} diverges at the edge of the punch (r = a). We know that this must be the case because of the stress concentration that exists at the edge of the punch. To get an expression for stress concentration, K_I at this edge, we first defined as the distance from the punch edge:

$$d \equiv a - r \tag{12.25}$$

Substituting d for r in Eq. 12.23 gives:

$$\frac{\sigma_{zz}}{\sigma_{avg}} = \frac{1}{2} \left[2d/a - (d/a)^2 \right]^{-1/2}$$
(12.26)

The stress intensity factor describes the stress field near the contact edge, where a/d is small. We can ignore the term involving the square of a/d to obtain the following expression σ_{zz} that is valid near the contact edge:

$$\frac{\sigma_{zz}}{\sigma_{avg}} \approx \frac{1}{2^{3/2}} \left(\frac{d}{a}\right)^{-1/2} \tag{12.27}$$

by comparing to Eq. 12.6 for K_I we obtain the following:

$$K_{I} = \frac{1}{2} \sigma_{avg} \left(\pi a\right)^{1/2}$$
(12.28)

Now we can use the following equation to obtain the following expression for \mathcal{G} (assuming $K_{II} = K_{III} = 0$):

$$\mathcal{G} = \frac{K_I^2}{2E_r} = \frac{\pi a \sigma_{avg}^2}{8E_r} = \frac{P_t^2}{8\pi E_r a^3}$$
(12.29)

This is the same result that we got previously for a flat-ended cylindrical punch, so everything checks out okay. Note that the extra factor of two in the relationship

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between \mathcal{G} and K_I in Eq. 12.29 comes from the fact the punch is rigid, so it has no stored elastic energy. Because elastic energy is stored only on one side of the interface, the value of \mathcal{G} for crack propagation at the interface with the rigid indenter (Figure 12.9) is half the value of \mathcal{G} for a crack propagating through an elastic material (Figure 12.5, for example).

12.6.3 Flat Punch Geometry: Thin Compliant Layer

Decreasing the thickness of the compliant layer also changes the distribution of normal stresses in contact with the layer. These normal stresses are plotted for different values of a/h in Figure 12.10.

- \diamond Max. stress in center for thin, incompressible layers ($\nu = 0.5$).
- \diamond Decrease in edge stress singularity (decrease K_I) for thin layers.

Since for very thin layers failure does not initiate from the edge because the driving force for this 'edge crack' vanishes as h becomes very thin. Instead, failure initiates from small defects within the central part of the contact zone where σ_{zz} is the highest. The mode I stress intensity factor for a circular, internal crack of radius a_c is given by the following expression:

$$K_I = \frac{2}{\sqrt{\pi}} \sigma_{zz} \sqrt{a_c} \tag{12.30}$$

Note that the prefactor in this expression is slightly different than what is given in Eq. 12.8 because of the different crack geometries. Eq. 12.8 is for a rectangular crack and Eq. 12.30 is for a circular crack. The energy release rate for the circular crack is given by using the relationship between K_I and \mathcal{G} valid for a mode I crack at the interface between compliant and rigid materials (Eq. 12.29):

$$\mathcal{G} = \frac{K_I^2}{2E_r} = \frac{2a_c \sigma_{zz}^2}{\pi E_r} \tag{12.31}$$

12.7 Fracture Toughness of Materials

In the Griffith (energy-based) model of fracture, material fracture occurs when the applied energy release rate, \mathcal{G} , exceeds a threshold value, \mathcal{G}_C , which is characteristic of the material. This value is called the critical strain energy release rate, and is a



Figure 12.9: Comparison of the full solution for the flat punch contact stresses (Eq. 12.23) with the $d^{-1/2}$ singularity obtained from K_I (Eq. 12.28).



Figure 12.10: Dependence of the stress distribution under a flat punch for different values of the confinement ration, a/h.

measure of the fracture toughness of the material, just as the critical stress intensity factor is a measure of the fracture toughness. The critical values of K and \mathcal{G} are related to one another through Eq. 12.14. For mode I fracture, $K_{II} = K_{III} = 0$, and this equation reduced to the following:

$$\mathcal{G}_{IC} = \frac{K_{IC}^2}{E_r} \tag{12.32}$$

Note that we have added the subscript 'I' to \mathcal{G} to remind ourselves that this number corresponds to mode I fracture condition.

Values of \mathcal{G}_C are a bit easier to understand conceptually than values of K_{IC} , since \mathcal{G}_c is simply the energy required to break a sample. We can obtain some estimates of \mathcal{G}_C by making some assumptions about where energy goes. Typical values of \mathcal{G}_c are as follows:

- $\diamond~\mathcal{G}_C=2\gamma~\left(\approx 0.1\,\mathrm{J/m^2}\right)$ if only work during fracture is to break Van der Waals bonds
- ♦ $G_C \approx 1 2 \text{ J/m}^2$ if only work during fracture is to break covalent or metallic bonds across interface
- ♦ $\mathcal{G}_C \gg 1 \,\mathrm{J/m^2}$ if fracture is accompanied by significant plastic deformation of the sample. For the whole fracture mechanics formulation we are using to be valid, the zone of plastic deformation where this energy dissipation is occurring should be small compared to the overall sample size.

Actual values of \mathcal{G}_C are much larger than these values (see Table 9) because a significant amount of plastic deformation occurs near the crack tip.

We can use numbers from Table 9 to say something about the size of the plastically deformed zone in front of a crack tip. We know that in the elastic region directly in front of a propagating crack, the stress scales as $K_I/\sqrt{2\pi d}$, where d is the distance in front of the crack tip. If the maximum stress is equal to the yield stress, σ_y , then

Material	E (GPa)	K_{IC} (MPa $\sqrt{\mathrm{m}}$)	$G_{IC} \mathrm{J/m^2}$
Steel	200	50	12,000
Glass	70	0.7	7
High M polystyrene or PMMA	3	1.5	750
High Impact Polystyrene	2.1	5.8	16,000
Epoxy Resin	2.8	0.5	100
Rubber Toughened Epoxy	2.4	2.2	2,000
Glass Filled Epoxy Resin	7.5	1.4	300

Table 9: Typical fracture toughness values (plane strain) for different material.

this the material must be yielded for values of r that give a stress exceeding σ_y . A propagating crack has $K_I = K_{IC}$, so if the size of the plastic zone is h_p , we have:

$$\sigma_y \approx \frac{K_{IC}}{\sqrt{2\pi h_p}} \tag{12.33}$$

Rearranging gives:

$$h_p \approx \frac{K_I^2}{2\pi\sigma_y^2} \approx \frac{\mathcal{G}_{IC}}{\sigma_y} \frac{E}{2\pi\sigma_y} \tag{12.34}$$

This formula is approximate because it neglects the fact that yielding of the material actually changes the stress distribution. The details of what is going on in the plastic zone depend on the materials system of interest. Below we give a case study for what happens for some common amorphous, glassy polymers (non-crystalline polymers deformed at temperatures below their glass transition temperature).

12.8 Case Studies in Fracture

12.8.1 Case Study: Transformation Toughening of Zirconia

First of all, why do we care about a material like zirconia (ZrO_2) ? It makes a pretty artificial diamond if we can get it in its cubic crystal form, but it is also an important material in a certain class of fuel cells. Fuel cells are classified by the type of electrolyte that enables ions to be transported between the anode and cathode of the fuel cell. In a solid oxide fuel cell, the electrolyte is typically zirconia, heated to a high temperature typically ~ 1000 °C, in order to provide sufficient mobility of the oxygen ions, which move through the electrolyte via a vacancy diffusion mechanism. The electrolyte is part of composite structure, in contact with the anodes and cathodes, and with multiple cells stacked in series to give a structure of the sort shown in Figure 12.11b. Thermal stresses arising as a result of the different thermal expansion coefficients for the different elements can be substantial, and need to be managed appropriately.

An additional problem with the use of zirconia is that different phases are present at equilibrium at different temperatures. In its pure form, zirconia has three different crystal phases: a monoclinic phase at equilibrium at room temperature, a tetragonal



Figure 12.11: a) Schematic of a solid oxide fuel cell utilizing a zirconia solid electrolyte [?]. b) Image of a fuel cell stack, with several fuel cells stacked in series with one another.

phase at equilibrium at between 1170 °C and 2370 °C, and a cubic phase at equilibrium above 2370 °C. These structures are shown schematically in Figure 12.12. The phases have different densities with the cubic phase having the highest density (smallest volume for a given mass of material) and with the monoclinic phase having the lowest density (highest volume per a given mass of material). Volume changes occurring during processing, when the sample is cooled from high temperatures where the cubic phase is stable, give rise to substantial cracking of the material, making pure zirconia unprocessible. A common solution to this problem is to add an alloying element that stabilizes the cubic phase to lower temperatures. Yttrium is a common alloying element, and can be added in its oxidized form (Y₂O₃,or Yttria), to form **yttria stabilized zirconia** (YSZ).

The phase diagram for the Yttria/Zirconia system is shown in Figure 12.13. A typical composition has 8% of the Zr atoms replaced with Y. At room temperature this composition consists of the cubic phase in equilibrium with a substantial volume fraction of monoclinic phase particles. In general, however, the tetragonal phase particles formed at high temperature remain in the material as metastable particles.



Figure 12.12: Crystal structures of Zirconia (from ref. [?]).

When a crack begins to propagate through the material, the tensile stresses in the vicinity of the crack transform these metastable tetragonal particles to the higher-volume, monoclinic particles. The material expansion of associated with this transformation reduces the stress field in front of the crack as illustrated in Figure 12.14, resulting in a substantial toughening of the material.

12.8.2 Tempered Glass

Glass tempering is a process that leaves the external surfaces of the material in a state of compression. This compressive stress acts against the growth of any defects that exist in the material. The net forces on a material at rest must sum to zero, so if the external portion of the sample is in compression, the internal portions of the sample must be in tension. All of these tensile and compressive stresses store a lot of strain energy, so the sample will fracture in dramatic fashion if a crack manages to make into the compressive region of the sample. This effect is illustrated by "Prince Rupert's drops", which are formed by rapidly quenching molten glass droplets by dropping them into water. For an entertaining and useful description of **tempered glass**, see the following video:

https://www.youtube.com/watch?v=xe-f4gokRBs

- 12.8.3 Fiber Composites
- 12.8.4 Nondestructive Testing of a Fiber Laminate Composite



Figure 12.13: ZrO_2/Y_2O_3 Phase Diagram (from ref. [?]).



Figure 12.14: Illustration of the transformation toughening mechanism of Zirconia.


Figure 12.15: Comparison of tempered glass and float glass samples that have been fractured. (from http://www.bharatsafety.com/tempered_glass.html).



Figure 12.16: Laminated safety glass.





Figure 12.18: use of Composites in the Boeing 787 Dreamliner



Figure 12.19: Views of a carbon fiber/epoxy composite perpendicular (left) and parallel (right) to the fiber direction.(from http://www.scielo.br/scielo.php?pid=S1516-14392010000300022&script=sci_arttext).



Figure 12.20: Laminate plies in a carbon fiber composite.



Figure 12.21: SEM image of failure of crack propagation in a carbon fiber composite (left), and a corresponding schematic representation of the crack path (right).



Figure 12.22: Nondestructive evaluation of damage in a carbon fiber composite.

13 Weibull Analysis of Failure

Failure of brittle materials is determined by the largest flaw size, since the largest flaw size will have the largest value of K for a given applied stress. As an example of the use of Weibull statistics, consider the adhesive transfer of a thin layer of a material from a flat, flexible substrate to a rigid, curved indenter as illustrated in Figure 13.1. The basic geometry of the experiment is illustrated in Figure 13.1a, and consists of a thin, viscoelastic film that is coated on an elastomeric substrate. A hemispherical glass indenter is brought into contact with the film and is then pulled away from the surface. The system is designed so that the adhesion of the film to the glass indenter is stronger than the adhesion to the elastomeric substrate, the film will be transfered from the substrate to the indenter. The process occurs by the sequence of steps illustrated in parts b-e of Figure 13.1:

- ◊ b) A crack is nucleated at a defect site at the interface between the film and the substrate at a region where the hydrostatic pressure is maximized.
- $\diamond\,$ c) This crack propagates under the indenter as the material is the indenter is pulled away from the substrate.
- ◊ d) Eventually the entire film in has detached from the substrate over the region where it is contact with the indenter. The remainder of the film begins to peel away from the substrate surface.
- \diamond e) The film breaks at the edge of the area of contact with the indenter.

Details of this experiment can be found in reference[?]. The most important thing to keep in mind is that the whole transfer process is controlled by the initial appearance of a cavity at the indenter/substrate interface (Figure 13.1b). This happens when p_{max} , the maximum hydrostatic tension at the film/substrate interface, reaches a critical value that we refer to as p_{cav} . Qualitatively we find that p_{cav} is close to E_{sub} , the elastic modulus of the substrate, but cavitation occurs for different values of p_{cav} . The **Weibull distribution** for the survival probability, P_s (the probability that cavitation has NOT occurred) is as follows:

$$P_s = \exp\left[-\left(\frac{p_{max}}{p_{cav}}\right)^M\right] \tag{13.1}$$

Here M is the Weibull modulus, which is a measure of the distribution of failure probabilities. We generally want M to be large, so that the distribution stresses is very narrow. For example, if $M \to \infty$, $P_s = 0$ for $p_{max} > p_{cav}$ and $P_s = 1$ for $p_{max} < p_{cav}$.

We can take natural logs of both sides a couple of times to convert Eq. 13.1 to the following:

$$\ln\left[\ln\left(1/P_s\right)\right] = M\ln p_{max} - M\ln p_{cav} \tag{13.2}$$

This means that we can obtain the Weibull modulus as the slope of a plot of $\ln [\ln (1/P_s)]$ vs. p_{max} . The procedure for obtaining P_s as a function of p_{max} is as follows:



Figure 13.1: Adhesive transfer of a thin, viscoelastic film.

- 1. Start with a data set that includes the measured values of the critical stress at which the sample failed. In our example this would be a list of values of p_{max} at the point where the sample failed.
- 2. Organize this list from the lowest value of p_{max} to the highest value.
- 3. Use the list to obtain the survival probability, P_s , for each value of p_{max} . The survival probability is the fraction of samples that did NOT fail for the given value of p_{max} . For example, if our data set has 50 samples in it then the survival probability for the lowest measured value of p_{max} is 49/50. The survival probability for the next highest value of p_{max} is 48/50, etc. We do this for all of the samples except for the one with the highest value of p_{max} , since a value of 0 for P_s would cause problems in the analysis.

In our example the stress is expressed as local maximum in the hydrostatic tension, p_{max} , and p_{cav} is a characteristic value of p_{max} for which a substantial fraction of samples have failed. From Eq. 13.1 we see that the survival probability is 1/e=1/2.72=0.37. A Weibull analysis can be applied in a range of situations, including tensile failure of brittle glass rods. In this case the Weibull analysis applies, with the tensile stress σ as the dependent variable, and with a characteristic tensile stress, σ_{avg} for which the survival probability is 37%:

$$P_s = \exp\left[-\left(\frac{\sigma}{\sigma_{avg}}\right)^M\right] \tag{13.3}$$

The point of the Weibull analysis is to obtain an expression that can be sensibly extrapolated to survival probabilities that are very close to 1. With $\exp(-x) \approx 1-x$ for small x, and with $P_f = 1 - P_f$, we have the following expression for failure probability, assuming P_f is low:

$$P_f \approx \left(\frac{\sigma}{\sigma_{avg}}\right)^M \tag{13.4}$$

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14 TOUGHENING MECHANISMS

14 Toughening Mechanisms

Factors that increase the hardness or tensile strength (σ_{ts}) of a material generally decrease the toughness, K_{IC} , so that the possible values of these two materials lie along a curve like the one shown in Figure 14.1. This type of relationship indicates that a certain degree of yielding is necessary in order to increase the characteristic crack tip radius of curvature, ρ_c (recall that $K_{IC} \propto \sqrt{\rho_c}$ as described by Eq. 12.13). The mode I toughness of a material can be expressed in terms of a critical stress intensity factor, K_{IC} , or a critical energy release rate, \mathcal{G}_C , which are related to one another through the following version Eq. 12.14:

$$\mathcal{G}_C = \frac{\sqrt{K_{IC}}}{E_r} \tag{14.1}$$

It is common to consider the intrinsic toughness and the extrinsic toughness of a material. **Extrinsic toughening** is based on the modification of the stress field in the region of a growing crack. We can describe it by dividing the macroscopic stress intensity factor, K_I , into two parts, K_{tip} and K_s :

$$K_I = \sigma_0 \sqrt{\pi a} = K_{tip} + K_s \tag{14.2}$$

Here K_{tip} describes the stress distribution very close to the crack tip in the usual way. For example, the tensile stress directly in front of a crack tip is given as:

$$\sigma_{zz}(d) = \frac{K_{tip}}{\sqrt{2\pi d}} \tag{14.3}$$

The factor K_s describes a reduction in K_{tip} compared to K_I because of other internal stresses that are applied in some way to the sample in the vicinity of the crack tip. We'll consider two examples: transformation toughening and crack bridging in fiber reinforced composites. In **transformation toughening**, compressive stresses result from a phase transition in front of the crack tip to a lower density (higher volume) phase, thereby accommodating some of the strains in the stress field defined by K_I , so that $K_{tip} < K_I$ ($K_s > 0$). The second example is a conceptually similar crack bridging example, where fibers bridge the crack, (much like craze fibrils in the polymer crazing example discussed above).

14.1 Hydraulic Fracturing (Fracking)

https://www.youtube.com/watch?v=VY34PQUiwOQ



Figure 14.1: Schematic representation of toughness vs. tensile strength.



Figure 14.2: The hydraulic fracturing (fracking) process.

15 Strengthening Mechanisms in Metals

Yield in metals occurs by dislocation motion. This means that if we want to increase the yield stress of a material we have two choices:

- 1. We can make a material with a very low dislocation density, thereby eliminating dislocation as a yield mechanism.
- 2. We can do something to the material to make it more difficult for the dislocations to move.

In almost all cases, we choose option two. This is because mechanisms exist for dislocations to be created during the deformation of a bulk material. More specifically, dislocations multiply when they are pinned in some way, as illustrated by the representation of the operation of a Frank-Read dislocation source in Figure 15.1. (See the 316-1 text to review Frank-Read sources if you don't recall the details.) As a result, even if we manage to create a material with a very low dislocation density, a sufficient number of dislocations will always be created once deformation starts. An exception to this rule is single crystalline whiskers, which are so small that the dislocation density can be reduced essentially to zero. This is because it is energetically favorable for dislocations to move to the free surface of the material, maintaining a very low density of dislocations in the material itself. Many of the details of dislocation structure and the relationship to material deformation was covered in 316-2. Our focus on this section is on the factors that control the stress required for dislocations to move through a material. Our discussion is relatively brief, and should be supplemented by the reading the corresponding Wikipedia articles on the different strengthening mechanisms [????], which are written at an appropriate level of detail for 332.

15.1 Review of some Dislocation Basics

The basics of dislocations are covered in 316-1. Here are the most important concepts to remember and use:

- 1. Dislocations correspond to a discontinuity of the displacement field. This continuity is quantified by the Burgers vector, \vec{b} .
- 2. Dislocations move along slip planes that contain both \vec{b} and the dislocation line.
- 3. When a dislocation exits the sample, portions of the sample on either side of the slip plane are displaced by \vec{b} .
- 4. The energy per length of a dislocation, T_s , is proportional to Gb^2 , where b is the magnitude of \vec{b} . This energy per unit length has the dimensions of a force, and can be viewed as a 'line tension' acting along the dislocation.
- 5. The resolved shear stress required to bend a dislocation through a radius of curvature of r is T_s/rb .
- 6. Dislocations interact with each other through their stress fields ('like' dislocations repel, 'opposite' dislocations attract.

Strengthening schemes based on reducing the mobility of dislocations can be divided into the following general categories, which we will discuss in more detail below:

- \diamond Work hardening
- $\diamond\,$ Grain boundary strengthening
- $\diamond\,$ Solid solution hardening
- ♦ Precipitation hardening



Figure 15.1: Schematic illustration of a Frank-Read source.

15.2 Interactions Between Dislocations

Dislocations interact through the long range strain fields induced by the dislocations. Consider two screw dislocations with Burgers vectors $\vec{b_1}$ and $\vec{b_2}$ that separated by d. The stress at dislocation 2 due to the presence of dislocation 1 is given by the following expression:

$$\vec{\tau} = \frac{G\vec{b}}{2\pi d} \tag{15.1}$$

We use a vector notation for the stress here to remind us that the force associated with the shear stress is directed along \vec{b} .

This stress induces a force on the dislocation, given by the following expression:

$$F_s^{\tau} = \frac{G\vec{b}_2 \cdot \vec{b}_1}{2\pi d} \tag{15.2}$$

If \vec{b}_1 and \vec{b}_2 are pointing in the same direction, the force is positive and the interaction is repulsive. If they are pointing in the opposite direction, the force is negative (attractive). Because the force scales as 1/d it has a very long range.

We can also make a qualitative argument based on the energetics to see what is going on. From Eq. 15.2 we see that $E \propto b^2$. If the dislocations have opposite signs, the dislocation come together and the net b is zero. If they have the same sign, then they form a total Burgers vector with a magnitude of 2b, and an energy of $4b^2$. So the energy is twice as large as it was originally. The energy as a function of separation must look the plot shown in Figure 15.2. If the energy of each individual dislocation is E_1 for $d \to \infty$, then the total dislocation energy at d = 0 is zero for dislocations of opposite sign and $4E_1$ for dislocations of the same sign.

Screw dislocations are easy to think about because the stress field is axially symmetric about the dislocation line, and the stress field is always pure shear. We already know from our previous discussion of stress fields that edge dislocations are more complicated. A simple limiting case involves two edge dislocations on the same slip plane, since within the slip plane we are in a state of pure shear. In this case the discussion from the previous section is still valid, and we get the following expression for the interaction force:

$$F_s^{\tau} = \frac{G\vec{b}_2 \cdot \vec{b}_1}{2\pi \left(1 - \nu\right) d}$$
(15.3)

The expression is the same as the expression for the screw dislocations, with the extra factor of $1 - \nu$.

If the two edge dislocations do not lie on the same slip plane the situation is more complicated, but we can still make some qualitative arguments based on the nature of the strain fields around the dislocations. Consider two edge dislocations on glide planes that are separated by a distance h, as illustrated in Figure 15.3. In this case the Dislocations begin to line up due to cancellation of the strains in the regions where these strain field overlap. The tensile strain induced below the upper dislocation is partially compensated for by the compressive strain above the lower



Figure 15.2: Interactions between screw dislocations of the same sign (solid line) and opposite sign(dashed line).

dislocation. As a result the dislocations move along their respective glide planes so that they lie on top of one another.

Dislocations with the same sign repel each other when they are in the same glide plane (see Figure 15.2), but they move toward each other so that they line up on top of one another when they are in different glide planes (see Figure 15.3). The overall situation is summarized in Figure 15.4, which shows the regions of attractive and repulsive interactions for the dislocations. These interactions can be understood in terms of the edge dislocation stress field. The different regions correspond to the different orientations of the shear stress. The important aspect is the direction of the shear force (right or left, in the blue boxes) acting on the top part of the each diagram showing the shear orientation. This can be viewed as the shear force that is acting on the extra half plane on the second dislocation, as a result of the stress field setup up by the first dislocation. This second dislocation moves to the left or the right in response to this force.

Dislocations can also interact with point defects or other atoms. The reason for this is that point defects also distort the lattice, giving strain fields that overlap with the strain field of a dislocation. This effect is easiest to visualize for edge dislocations, as illustrated in Figure 15.5. Substitutional impurities with different sizes than the majority component atoms can reduce the strain fields surrounding the dislocation



Figure 15.3: Overlapping stress fields for two adjacent dislocations of the same sign.



Figure 15.4: Map showing the regimes where two edge dislocations move toward one another with attractive interaction (-) or apart from one another with a repulsive interaction (+). One of the dislocations is at the origin, with \hat{s} pointing into the plane of the figure. The other dislocation is assumed to have the same value for \hat{s} and \vec{b} . Both dislocations move in glide planes that are perpendicular to the y axis. These dislocations move toward each other if the second dislocation is located within a region that is attractive (-), and apart from one another if the second dislocation is located in a region that is repulsive (+).

by moving to the appropriate region near the dislocation. Large atoms will tend to substitute for atoms in regions where the local strain is tensile, and small atoms will tend to substitute for atoms in regions where the local strain is compressive. Interstitial impurities will segregate to regions of tensile stress as well.

As a result of this impurity segregation, dislocations collect 'clouds' of impurity atoms. For a dislocation to move, it must either break away from this atmosphere or move the impurity atoms along with it. The net result in either case is an increase in the critical resolved shear stress, a process referred to as **solid solution strengthening**.

15.3 Work Hardening

(Required supplementary reading:

Wikipedia article on work hardening[?]).



Figure 15.5: Favored locations the segregation of substitutional impurities to the core of an edge dislocation.

Work hardening originates from interactions between dislocations. Dislocations impede the motion of other dislocations, so the multiplication of dislocations that occurs as a material is deformed results in a harder material. The effect is illustrated in Figure 15.6, which shows the relationship between the shear strength of a material and the dislocation density. In the absence of dislocations, the strength approaches the maximum theoretical shear strength of $\approx G/6$, implying a tensile strength of $\approx G/12$. The introduction of dislocation reduces the strength of the material because the critical resolved shear stress to required to move a dislocation in its slip plan is much less than G/6. As more dislocations become available to introduce a macroscopic plastic strain, the strength of the material goes down as shown in Figure 15.6. Above some critical dislocation density, dislocations interact with each other through their stress fields and the material becomes stronger as the dislocation density increases. The dislocation density at which the strength is minimized is actually quite low. In typical materials the dislocation density is high enough so that the material becomes stronger as it is deformed and the dislocation density increases. In other words, the typical range for actual density is in the increasing part of the strength vs. dislocation density curve, as illustrated in Figure 15.6.

15.4 Grain Boundary Strengthening

(Required supplementary reading:

Wikipedia article on grain boundary strengthening[?]).

Grain boundaries act as barriers to dislocation motion. As a result samples with small grain sizes, which have more grain boundaries in a given volume of sample, have higher yield stresses than samples with large grain sizes (as long as the grain size isn't extremely small - in the range of tens of nanometers). The Hall-Petch equation is commonly used to describe the relationship between the yield strength, σ_y and the grain size, d:

$$\sigma_y = \sigma_i + k_y d^{-1/2} \tag{15.4}$$



Figure 15.6: Qualitative relationship between strength and dislocation density.

Here σ_i and k_y are factors determined by fitting to experimental data. Note that the Hall-Petch equation is based on experimental observations, and is not an expression derived originally from theoretical considerations.

15.5 Precipitation Hardening

(Supplementary reading:

Wikipedia article on precipitation hardening[?]).

When a dislocation encounters a second phase particle it can either cut directly through the particle and continue on its way through the matrix phase, or it can bend around the particle, as shown for example in the illustration of the Frank-Read source in Figure 15.1. We know from 316-1 bending mechanism is going to require the larges shear stress when the particles are small, and close together. If the particles are too close together, however, it may be easier for the dislocation to move through the particle itself. The sheared particle has a slightly larger surface area, and the extra energy required to create this surface gives a contribution to the stress required to move the dislocation through the particle, although this contribution to the stress.

15.6 Solid Solution Strengthening

(Required supplementary reading:

Wikipedia article on solid solution strengthening[?]).

Solid solution hardening is somewhat related to work hardening in that dislocations are interacting by stress fields originating from defects in the material. In work hardening these defects are other dislocations, whereas for solid solutions the stress fields originate from the presence of either substitutional or interstitial impurities in the material.

16 High Temperature Creep in Crystalline Materials

by 'high' temperature for a metal, we generally mean temperatures above half the absolute melting temperature, which we list below in Figure 16.1.



Figure 16.1: Absolute melting temperatures (K) for the elements.

16 HIGH TEMPERATURE CREEP

Typical creep response for a metal is shown in Figure 16.2. The easiest way to do the experiment is under constant load conditions. Because the cross sectional area of the sample decreases as the material deforms, the true stress increases during a constant load creep experiment. If the experiment is done under conditions where the load is reduced to maintain a constant true stress, the creep rate does not increase as fast at the longer times. The increase in the creep rate at long times for the constant load test can be attributed to the increased true stress in the sample at the later stages of the creep experiment. Failure of the sample during a constant load test is referred to as the **creep rupture** point. The creep rupture time decreases with increasing temperature and increasing applied engineering stress, as illustrated by the data for an iron alloy in Figure 16.3.

Different creep regimes during an engineering (constant load) creep rupture test are illustrated in Figure 16.4. At the beginning off the experiment the dislocation density increases with increasing strain, the sample strain hardens, and the strain rate decreases with time. This stage in the experiment is referred to as stage I, or primary creep. Following this there is often a linear regime (stage II in Figure 16.4, referred to as secondary creep) where the strain rate and dislocation density are constant. In this regime dislocations are being created and destroyed at the same rate. The strain rate in this steady state regime is the steady state creep rate, $\dot{\epsilon}_{ss}$. Steady state creep data for TiO₂ at different times and temperatures are shown in Figure 16.5. The final stage in the creep experiment is the tertiary regime, Regime III, where the disloction density is again increasing, ultimately leading to the formation of voids in the sample and to eventual fracture. In many cases the steady state creep regime corresponds to the majority of the experiment. If this is the case, and the failure is independent of the applied stress, then the creep rupture time will be inversely proportional to the steady state creep rate. We'll focus on the secondary, steady-state creep regime in the following discussion.

The data in Figure 16.3 indicate that the effects of stress and temperature are separable, with the same activation energy of 280 J/mol obtained for each of the different stress levels. The overall steady state creep rate in this case can be expressed in the following way:

$$\dot{\epsilon}_{II} = f\left(\sigma\right) \exp\left(-\frac{Q_c}{k_B T}\right) \tag{16.1}$$

For the specific case of power law creep, the stress dependence is given by a simple power law:



Figure 16.2: Qualitative difference between creep behavior under constant load and constant stress conditions.

Figure 16.3: Creep rupture data for an iron-based alloy.

$$f\left(\sigma\right) = A\sigma^{n} \tag{16.2}$$

where n is an empirically determined exponent, with typical values ranging between 1 and 7.

In the high temperature regime, the activation energy for creep, Q_c , is very similar to the activation energy for self-diffusion in the metal (see Figure 16.6), indicating that high temperature creep is controlled by the same processes that control self diffusion. As we describe below, this common process is vacancy diffusion. Vacancy diffusion can contribute to the creep behavior by enabling dislocation climb, or by changing the shapes of individual grains in a manner that does not require the existence of dislocations. These mechanisms are Nabarro-Herring creep and Coble Creep, as described below.



Figure 16.4: Commonly observed creep regimes, illustrating the steady state creep rate, ϵ_{ss} .



Figure 16.5: Creep behavior of TiO₂ (from ref.[?]).



Figure 16.6: Activation energies for creep (for $T/T_m > 0.5$) and atomic diffusion (from ref.[?]).

16.1 Dislocation Glide

The primary deformation mechanism we have talked about so far is dislocation glide, where a dislocation moves laterally in a plane containing the Burgers vector. Dislocation glide can only occur when the resolved shear stress acting on it exceeds some critical value that depends on the curvature of the dislocation. The deformation rate due to dislocation glide is obtained from following relationship between strain rate for dislocation glide, the dislocation density, ρ_d (the total dislocation length per volume, which has units of $1/m^2$), the magnitude of the Burgers vector for the dislocations, b, and the dislocation glide velocity, V_q :

$$\left. \frac{de}{dt} \right|_{glide} = \rho_d V_g b \tag{16.3}$$

Dislocation glide is a thermally activated process, and therefore be described by a model similar to the Eyring model:

$$V_g \propto \sinh\left(\left(\sigma - \sigma_{crit}\right) v/2k_B T\right) \exp\left(-Q_{glide}/k_B T\right)$$
(16.4)

There is a temperature dependence of dislocation glide, since there is a finite activation energy for dislocation motion, which we refer to as Q_{glide} . In most cases however, the stress dependence is much more important than the temperature dependence, and we simply say that the sample deforms plastically for $\sigma > \sigma_{crit}$. Some deformation mechanisms are still available below. These require atomic diffusion and have an activation energy that is larger than Q_{glide} , but become important at high temperatures (greater than about half the absolute melting temperature. These mechanisms are discussed below. The first of these (Nabarro-Herring creep and Coble creep) involve changes in shape of the overall object that mimic the changes shapes of individual grains, with grain shape changing as atoms diffuse between portions of the grain boundaries that are experiencing different stress states. The third mechanism involves dislocation climb.

16.2 Nabarro-Herring Creep: Bulk Diffusion Within a Grain

Nabarro-Herring creep is the mechanism by which vacancies move away from regions of the largest tensile stress in the sample. The mechanism is as illustrated in Figure 16.7. The mechanism is based on the effect that stresses have on the local concentration of vacancies in the system.

In the absence of an applied stress the equilibrium number of concentration of vacancies, C_v^0 is given by the vacancy formation energy, G_v :

$$C_v^0 = \frac{1}{\Omega} \exp\left(-\frac{G_v}{k_B T}\right) \tag{16.5}$$

where Ω is the atomic volume (also equal to the volume of a vacancy). Now suppose we have a grain that is experiencing a tensile stress of magnitude σ at the top and

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Figure 16.7: Conceptual illustration of Nabarro-Herring creep.

bottom, and a compressive force of this same magnitude at the sides. We'll call the vacancy concentrations in the tensile and compressive regions of the sample C_v^t and C_v^c , respectively, so we have:

$$C_v^t = C_v^0 \exp\left(\sigma\Omega/k_B T\right) C_v^c = C_v^0 \exp\left(-\sigma\Omega/k_B T\right)$$
(16.6)

We can now use Fick's first law to to calculate the steady state flux of vacancies, J_v , from the tensile region to the compressive region:

$$J_v = -D_v \frac{dC_v}{dx} \tag{16.7}$$

We approximate the the vacancy concentration gradient, dC_v/dx , as the difference in vacancy concentrations in the tensile and compressive regions of the grain, divided by the grain size, d:

$$\frac{dC_v}{dx} \approx \frac{C_v^t - C_v^c}{d} \tag{16.8}$$

Combining Eqs. 16.7 and 16.8 gives:

$$J_v \approx -D_v \left(\frac{C_v^t - C_v^c}{d}\right) \tag{16.9}$$

In order to relate the flux (units of vacancies/m²·s) to the velocity of the grain edge (in m/s), we need to multiply J_v by the atomic volume, Ω :

$$v = \Omega J_v \approx \Omega D_v \left(\frac{C_v^t - C_v^c}{d}\right) \tag{16.10}$$

Now we get the strain rate by dividing this velocity by d:

$$\frac{de}{dt} = \frac{\Omega J_v}{d} \approx \Omega D_v \left(\frac{C_v^t - C_v^c}{d^2}\right) = \frac{2D_v}{d^2} \sinh\left(\frac{\sigma\Omega}{k_B T}\right) \exp\left(-\frac{G_v}{k_B T}\right)$$
(16.11)

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For real systems the stresses are small enough so that $\sigma \Omega \ll k_B T$, so we can use the fact that $\sinh(x) \approx x$ for small x to obtain:

$$\frac{de}{dt} \approx \frac{2D_v}{d^2} \frac{\sigma\Omega}{k_B T} \exp\left(-\frac{G_v}{k_B T}\right)$$
(16.12)

Vacancy diffusion is a thermally activated process, so we can express the vacancy diffusion coefficient in the following form:

$$D_v = D_0^v \exp\left(-\frac{Q_D^v}{k_B T}\right) \tag{16.13}$$

where Q_v is the activation free energy for vacancy motion. We can define a combined quantity, Q_{vol} that combines the free energy of vacancy formation with the activation free energy for vacancy diffusion:

$$Q_{vol} = Q_v + G_v \tag{16.14}$$

Combination of Eqs. 16.12-16.14 gives the following for the strain rate:

$$\frac{de}{dt} \approx \frac{2D_0}{d^2} \frac{\sigma\Omega}{k_B T} \exp\left(-\frac{Q_{vol}}{k_B T}\right)$$
(16.15)

Here Q_{vol} is the overall activation energy that accounts for the both both the formation and diffusive motion of vacancies diffusing through the interior of the grain.

16.3 Coble Creep: Grain Boundary Diffusion

If diffusion occurs predominantly along the grain boundaries, the mechanisms is slightly different and is referred to as **Coble Creep**. The expression for the strain rate is very similar to the expression for Nabarro-Herring creep, with two difference. First, we replace the bulk vacancy diffusion coefficient, D_v in Eq. 16.7 with the grain boundary diffusion coefficient, D_{gb} , which is generally larger than D_v . In addition, we modify the relationship between J_v to account for the fact that vacancies are not diffusing throughout the entire grain, but only along a narrow grain of width d_{gb} . As a result we need to multiply the velocity in Eq. 16.10 by the overall volume fraction of the grain boundary, which is proportional to d_{gb}/d . The net result is the following expression for the strain rate for Coble creep:

$$\frac{de}{dt} \propto \frac{2D_{gb}d_{gb}}{d^3} \frac{\sigma\Omega}{k_B T} \exp\left(-\frac{G_v}{k_B T}\right)$$
(16.16)

The grain boundary diffusion is also a thermally activated process, so we can combine fold the activation free energy for grain boundary diffusion into an overall activation energy, which we define as Q_{gb} :

$$D_{gb} = D_0^{gb} \exp\left(-\frac{Q_D^{gb}}{k_B T}\right) \tag{16.17}$$

$$Q_{gb} = Q_v + G_v \tag{16.18}$$

$$\frac{de}{dt} \propto \frac{2D_0^{gb}d_{gb}}{d^3} \frac{\sigma\Omega}{k_B T} \exp\left(-\frac{Q_{gb}}{k_B T}\right)$$
(16.19)

Here Q_{gb} is less than Q_{vol} , so Coble creep will be favored over Nabarro-Herring creep at low temperatures.

16.4 Weertman model of Creep by Dislocation Climb

In 1957 Johannes Weertman (one of the early and most important members of the Materials Science and Engineering Department at Northwestern University) developed a creep model that conforms to Eqs. 16.1 and 16.2, but with a specific exponent, n, of 4.5.

In the Weertman model the creep rate is controlled by dislocation climb, illustrated schematically in Figure 16.9. The following relationship for the strain rate was obtained from theoretical considerations:

$$\frac{de}{dt} = A\sigma^3 \sinh\left(B\sigma^{1.5}/k_BT\right) \exp\left(-Q_{vol}/k_BT\right)$$
(16.20)

16.5 Deformation mechanism maps

The different deformation mechanisms discussed above all have different dependencies on temperature and stress. We can put place them all on a deformation map as shown in Figure 16.10. The different regions correspond to combinations of stress and temperature where the indicated mechanism gives the highest deformation rate, and therefore dominates the deformation process. Note the following features:



Figure 16.8: Conceptual illustration of Coble creep.



Figure 16.9: Schematic representation of dislocation climb.

- ◇ Coble creep and Nabarro-Herring (N-H) creep both occur in polycrystalline materials, where the overall shape of the object mimics the change in shape of an individual grain. These mechanisms are suppressed by increasing the grain size, and do not occur at all in large, single crystals.
- ◊ The boundary between Coble creep and Nabarro-Herring creep is a vertical line, since the stress dependence for both measurements is the same.
- ◊ Nabarro-Herring creep occurs at higher temperatures than Coble creep, because diffusion through grains (the Nabarro-Herring mechanism) has a higher activation energy than diffusion at grain boundaries (the Coble mechanism).
- The Coble creep mechanism occurs at grain boundaries, it will be favored for materials with more grain boundaries, <u>i.e.</u>, materials with a smaller grain size. As the grain size decreases, the line separating the Coble and Nabarro-Herring regions will move to the right.
- ♦ The line separating the Nabarro-Herring and Dislocation climb regions is horizontal because these mechanisms have the same temperature dependence, <u>i.e.</u>, the activation energy is the same for both cases (see Figure 16.6).



Figure 16.10: Deformation mechanism map.

A Synthetic Polymers

We include here a very brief introduction to polymeric materials for those who are not already familiar with this class of materials. We begin with a basic introduction to the synthesis of polymeric materials, and the properties of these materials. We conclude with some examples of soft materials made up of building blocks that are held together by relative weak forces.

A.1 What is a Polymer

A polymer is a large molecule made from many small

repeat units

or 'mers'. There is an inherent anisotropy at the molecular level because both strong and weak bonding interactions are important:

- $\diamond\,$ Strong covalent bonds are formed within a molecule (between 'mers').
- ◊ Weak Van der Waals or hydrogen bonding are formed between molecules, and cause the materials to condense into a solid or liquid phase.

A.2 Classification Scheme

Crystallization and glass formation are the two most important concepts underlying the physical properties of polymers. Polymers crystallize at temperatures below T_m (melting temperature) and form glasses at temperatures below T_g (glass transition temperature). All polymers will form glasses under the appropriate conditions, but not all polymers are able to crystallize. The

classification scheme

shown in Figure A.2 divides polymeric materials based on the locations of T_g and T_m (relative to the use temperature, T) and is a good place to start when understanding different types of polymers.

Elastomers

Traditional elastomers are amorphous materials with a glass transition temperature less than the use temperature so that they remain flexible. The are generally crosslinked so that they do not flow over long periods of time. Common examples are shown in Figure A.3.



Figure A.1: Schematic representation of a polymer



Figure A.2: Classification scheme for polymeric materials.



Polychloroprene (Neoprene)







Silicone

Figure A.3: Examples of elastomeric materials.

Glassy Polymers

Glassy polymers are amorphous like elastomers, but their glass transition temperature is above the use temperature. Because of this they behave as rigid solids, with elastic moduli in the range of 10^9 Pa. Glassy polymers do not need to be crosslinked, because below T_g the molecules and flow of the material is suppressed. Also, because the materials are homogenous over length scales comparable to the wavelength of light, they are transparent. Common examples are illustrated in Figure A.4.



Poly(methyl methacrylate) (PlexiGlas)



Polycarbonate



Poly(phenylene oxide)

Figure A.4: Examples of glassy polymers.

Semicrystalline Polymers

Semicrystalline polymers must have molecular structures that are compatible with the formation of an ordered lattice. Most atactic polymers are amorphous (noncrystalline) for this reason (with the exception being examples like poly(vinyl alcohol where the side group is very small). Another requirement is that T_g be less than T_m . If the glass transition temperature is higher than T_m the material will form a glass before crystallization can occur. In the glassy polymer the material is kinetically trapped in the glassy state, even though the crystalline state has a lower free energy below T_m . Examples of some semicrystalline polymers are shown in Figure A.5.

A.3 Understanding Polymer Chemistry

Crystallization and glass formation processes are central to our understanding of polymeric materials, we must eventually address the following question:

◊ How is a polymer's tendency to crystallize or form a glass determined by is molecular structure?

Before we answer this question, however, we must answer the following question:

 $\diamond\,$ What determines this molecular structure, and how are our choices limited?

In order to answer this question properly, we need to study the processes by which polymeric materials are made. Polymer synthesis involves organic chemistry. After familiarizing ourselves with some of the relevant polymer chemistry, we will be in a position to study the physical properties of polymers. For this reason, our discussion of molecular structure in polymers will include some chemistry.

A.3.1 Covalent Bonding

Polymer molecules consist of atoms (primarily carbon, nitrogen, oxygen and hydrogen) which are covalently bound to one another. The fraction of the periodic table that can form strong covalent bonds is relatively small, corresponding to the ten atoms shown in yellow in Figure A.6 (H, C, N, O, F, Si, P, S, Cl, Br). It is useful at this point to recall some of the basic principles governing the bonding between these atoms:

Polyethylene terephthalate.





Spider Web

Poly(tetrafluoroethylene) (Teflon)

Figure A.5: Examples of semicrystalline polymers.

- \diamond Nitrogen, oxygen, carbon and the other covalent bond forming atoms with M>6 (F, Si, P, S, Cl, Br) are surrounded by 8 electrons, included shared electrons.
- $\diamond\,$ Hydrogen atoms are surrounded by 2 electrons, included shared electrons.
- ◊ A single bond involves two shared electrons, a double bond involves 4 shared electrons, and a triple bond involves 6 shared electrons.

A.3.2 Lewis Diagrams

Lewis diagrams (Wikipedia link) provide a convenient way of keeping track of the valence electrons in covalently bonded compounds. Several examples are given here. Note how the rules given on the previous page are followed in each case.

A.3.3 Bonding

The following principles of covalent bonding in organic materials are very helpful:

 $\diamond\,$ Carbon, Silicon: group 14 (4 valence electrons) - 4 more needed to complete shell -

C, Si form 4 bonds with neighboring atoms

•

.

 \diamond Nitrogen, Phosphorous: group 15 (5 valence electrons) - 3 more needed to complete shell -

N, P form 3 bonds with neighboring atoms

 $\diamond\,$ Oxygen, Sulfur: group 16 (6 valence electrons) - 2 more needed to complete shell -

O, S form 2 bonds with neighboring atoms

♦ Hydrogen (group 1) or Fluorine, Chlorine, Bromine (Group 17):

Fl, Cl, Br form 1 bond with neighboring atoms

(The situation for P and S is actually a bit more complicated when either of these atoms are bonded to oxygen, but these general rules serve our purpose for now.) The chemical structures throughout this book can be seen to obey these rules.

A.3.4 Shorthand Chemical Notation

Most of the chemical structures illustrated in this text are relatively simple, consisting of single and double bonds between atoms. We generally don't bother to write all of the carbons and hydrogens into to the structure. We use the following common conventions.



Figure A.6: Periodic table, illustrating the ten atoms that make up the covalentlybonded portion of polymeric materials.



Figure A.7: Examples of Lewis Diagrams

- \diamond If no element is included, element at junctions between different bonds are assumed to be carbon.
- ◊ If atoms are missing, so that the rules given above for the number of bonds attached to each atom type are not satisfied, the missing atoms are hydrogens.

An example of this convention is shown below in the structure for

benzene

::

.

Note the resonance between the two possible ways of drawing the double bonds in the drawing on the left. Molecules with these types of alternating

aromatic compounds



Figure A.8: Examples of Shorthand Notation when drawing chemical structures

B Case Study: Thermoreversible Gels from Triblock Copolymer Solutions

B.1 Introduction

Many of the principles of this course are illustrated by the behavior solutions of acrylic triblock copolymers in higher alcohols. The specific molecular structures of the polymer and the solvent are shown in Figure B.1 and consist of a midblock of poly(n-butyl acrylate) (PnBA) between two blocks of poly(methyl methacrylate) (PMMA). The value of χ for the PnBA/solvent system is less than 0.5 for all temperatures of interest, but the χ for the PMMA/solvent system has the following temperature dependence:

$$\chi = 1.45 - 0.0115T \tag{B.1}$$

with T in °C.

The following points are illustrated by this example:

- 1. Polymers are soluble in solvents when $\chi < 0.5$.
- 2. For $\chi > 0.5$, the solvent content within the polymer can be obtained from the chemical potential expression.
- 3. To understand the temperature dependence of the solubility you need to know the temperature dependence of χ .
- 4. Polymer liquids have higher heat capacities than the corresponding polymer glasses.
- 5. Calorimetry can be used to detect the enthalpy recovery peak from an aged polymer glass.
- 6. Gelation occurs when the average functionality is ≈ 2 .
- 7. Time-temperature superposition works when the structure does not change appreciably with Temperature.
- 8. The viscosity is obtained by integrating G(t) or from the response at very low frequencies.

From Eq. B.1 we see that the value of χ characterizing the PMMA/solvent interaction is greater than 0.5 for T < 83 °C. At temperatures above 83 °C the PMMA and PnBA blocks are both in good solvent conditions, and the polymer behaves as a normal polymer solution. At lower temperatures, however, the PnBA midblock remains in good solvent conditions, but the PMMA endblocks are no longer soluble. As a result these endblocks aggregate to form the micellar structures illustrated schematically in Figure B.2. As a solution is cooled, χ increases and solvent is expelled from these aggregates. When sufficient solvent has been expelled from the PMMA aggregates, they become glassy, and the system behaves as a solid.



Figure B.1: Chemical structure of gel-forming triblock copolymer gels (a), and the alcohols used as the solvents (b).



Figure B.2: Schematic representation of the temperature and concentration dependence of the structure of the triblock copolymer solutions.

B.2 Thermoreversible Gelcasting of Ceramics

The transition from 'liquid-like' to 'solid-like' behavior as the temperature is changes enable these materials to be used in a variety of applications, including the ceramics processing application illustrated in Figures B.3 and B.4. In this application ceramic particles are added to the triblock copolymer at a relatively high volume fraction (around 50% by volume). The thermoreversible nature of the triblock copolymer solution allows the suspension to be poured into a silicone mold at high tempertures (typically ≈ 80 °C). When the system is cooled to room temperature, the triblock copolymer forms a solid gel and the material can be removed from the mold. A ceramic material with the shape of the mold is obtained by letting the solvent evaporate from the suspension, and firing the object at elevated temperature to burn off the polymer and sinter the ceramic particles together.

B.3 Quantifying the Solid/Liquid Transition

The temperature dependence of the mechanical properties of the triblock copolymer solutions are quantified by the frequency dependence of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$. It is conceptually simpler to think in terms of the timedependence of the relaxation modulus, G(t), which can be written as a sum of exponential relaxations:

$$G(t) = \sum_{i} G_{i} \exp\left(-t/\tau_{i}\right)$$
(B.2)

In the frequency domain, the values storage and loss moduli are given by the following expressions:

$$G'(\omega) = \sum_{i} \frac{G_{i}\tau_{i}^{2}\omega^{2}}{1 + \tau_{i}^{2}\omega^{2}}$$
(B.3)
$$Al_{2}O_{3}$$

Gel Matrix (solvent + polymer)



Figure B.3: Schematic representation of the alumina particles dispersed within a thermoreversible triblock copolymer gel.



Figure B.4: Illustration of the thermoreversible geleasting process.

$$G''(\omega) = \sum_{i} \frac{G_i \tau_i \omega}{1 + \tau_i^2 \omega^2} \tag{B.4}$$

The most important thing for us is the viscosity, which we can obtain in terms of the values of G_i and τ_i , or in terms of the loss modulus at very low frequencies:

$$\eta = \sum_{i} G_{i} \tau_{i} = \lim_{\omega \to 0} \frac{G''}{\omega}$$
(B.5)

We generally obtain data as a master plot (where the frequency is multiplied by the temperature shift factor, a_T). In this case we obtain the temperature dependence of the viscosity by multiplying by a_T :

$$\eta = a_T \lim_{a_T \omega \to 0} \frac{G''}{a_T \omega} \tag{B.6}$$

We can also obtain an expression for the limiting modulus at high frequency (or low temperature):

$$G_0 = \sum_i G_i \tag{B.7}$$

Finally, we define an average relaxation time, τ_{av} in the following way:

$$\tau_{av} = \frac{\eta}{G_0} = \frac{\sum G_i \tau_i}{\sum G_i} \tag{B.8}$$

Values of the storage and loss moduli for the triblock copolymer solutions are shown in Figure B.5, along with the values of G_i and τ_i used to fit the data. The temperature dependent viscosity for a solution with $\phi_p = 0.15$ is shown in Figure B.6, and the temperature dependent relaxation times for a variety of solution concentrations are shown in Figure B.7.



Figure B.5: a) Master curves for G' and G'' (symbols) with fits to Eqs.B.3 andB.4. b) Values of G_i and τ_i used to fit the data from part a (the relaxation times, τ_i are referred to by λ_i in the figure). The reference temperature (defined as the temperature where $a_T = 1$) is 65 °C for these data.



Figure B.6: Temperature dependence of the viscosity for a triblock copolymer solution with $\phi_p = 0.15$. in 2-ethyl hexanol. The x's represent the solvent viscosity.



Figure B.7: Values of the average relaxation time, τ_{av} as a function of temperature. Data are included for $\phi_p = 0.05$ (•) $\phi_p = 0.10$ (**II**) $\phi_p = 0.15$ (\bigcirc) $\phi_p = 0.20$ (**A**) $\phi_p = 0.25$ (**V**) $\phi_p = 0.30$ (\bigcirc).

B.4 Characterizing the Glass Transition in PMMA domains

The glass transition is typically observed as step change in heat flow as a sample is cooled through the glass transition. In our case the PMMA domains go through a glass transition during cooling, but the PMMA concentration is so low that the glass transition is not clearly observed during cooling or when when the sample is immediately reheated after cooling (see Figure B.8). However, a large enthalpy peak is observed after the sample has been left to 'age' at room temperature for a long time before reheating the sample. As shown in Figure B.9, the enthalpy peak gets larger and moves to higher temperature as the aging time at room temperature is increased. This peak has the appearance of a melting peak associated with crystallization, but in this case it arises from the glassy PMMA domains.

The origins of the enthalpy peak observed during the aging experiments can be understood by realizing that the glass transition separates an equilibrium, liquid regime at temperatures above T_g from a non-equilibrium, glassy regime at temperatures below T_g . At temperatures below the glass transition, the enthalpy content of the sample is higher than the equilibrium enthalpy content defined by the extrapolation of the liquid behavior (the dashed line in Figure B.10). As a result, the enthalpy slowly decreases toward this equilibrium line as the sample is aged below the glass transition. The decrease in enthalpy during this aging process is labeled as ΔH_a in Figure B.10. When the sample is reheated, the enthalpy increases with temperature according to the glassy heat capacity, C_p^g . As a result the enthalpy content eventually crosses the equilibrium line and becomes less than the equilibrium enthalpy content. At a temperature somewhere just above T_g , the sample is able to equilibrate, and the enthalpy increases by an amount ΔH_r in order to catch up to the equilibrium value. This is the enthalpy corresponding to the peaks in Figure B.9. As the aging time decreases, ΔH_a and ΔH_r both decrease, and the temperature at which the enthalpy is recovered moves closer to T_g . The actual value of the T_g can be estimated by measuring the area of the enthalpy recovery peak and plotting against the location of this peak. Doing this for the data shown in Figure B.9 results in an estimate for T_g of the PMMA domains of 35 °C.

As a final check on all of this, we can see if it makes sense that the glass transition of the PMMA domains should be around 35 °C. The glass transition of PMMA is about 125 °C, which is certainly a lot higher than the value of 35 °C that we are claiming here. However, we need to remember that the PMMA domains contain a lot of solvent, and this solvent will depress T_g significantly. How much solvent do we expect there to be in the PMMA domains? From Eq. B.1 we obtain $\chi=1.05$ at T = 35 °C. The relationship between χ and ϕ_s , the solvent volume fraction in the PMMA cores of the micelles is obtained by setting N_p to ∞ and setting the solvent chemical potential (from Eq??) to 0:

$$\frac{\ln(\phi_s) + 1 - \phi_s + \chi \left(1 - \phi_s\right)^2 = 0}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2 = 0}$$
(B.9)

This equation needs to be solved numerically to obtain ϕ_s (or ϕ_p) from a specified value of χ . A simple MATLAB script used to do this is given in Section??. A value of 1.05 for χ gives $\phi_s=0.289$. Independent measures of the glass transition temperature of bulk PMMA samples with solvent loadings comparable to this do in fact show measured glass transition temperatures close to 35 °C. The relationship between χ and ϕ_p given by Eq. B.9 is plotted in Figure B.11.

B.5 Concentration Dependence of the Gel Modulus

Elasticity of the triblock copolymer solutions at low temperatures arises from the fact that the middle, PnBA blocks of the copolymer can span different PMMA aggregates, thereby linking the whole structure together. The PMMA aggregates behave as physical crosslinks with a functionality given by the number of midblocks that that bridge different aggregates. This functionality is obtained by multiplying the aggregation number, i.e. the number of PMMA endblocks in a single aggregate, by the probability f that a PnBA midblock spans two different PMMA aggregates (we also have to divide by two to account for the fact that there are two PMMA blocks on each triblock copolymer molecule). Aggregation numbers depend on the polymer concentration, and are typically very large, as illustrated in Figure B.12. For high molecular weight polymers the percolation threshold, where the average functionality of a micelle is 2, is quite low, corresponding to $\phi_p \approx 0.035$. Above this percolation threshold, the shear modulus is given by the following expression:

$$G_0 = \nu k_B T \frac{D^2}{R_0^2} \tag{B.10}$$

Here D is the average distance between micelle cores, which can be measured experimentally by x-ray scattering. We also have $R_0 = N^{1/2}a$, where N is the midblock degree of polymerization and a is the statistical segment length for the midblock.



Figure B.8: Measured heat flow during cooling, immediate reheating, and reheating after room temperature storage for 130 days.



Figure B.9: Dependence on the enthalpy recovery peak on the aging time.



Figure B.10: Origins of the enthalpy recovery peak.



Figure B.11: Relationship between ϕ_p and χ obtained from Eq. B.9.

The quantity ν is the conentration of 'load bearing strands', which in this case is the concentration of triblock copolymer chains with bridging midblocks:

$$\nu = \frac{f\phi_p \rho N_{av}}{M}$$

where M is the molecular weight of the triblock copolymer molecule and ρ is the polymer density. The modulus is strongly concentration dependent because of the concentration dependence of the bridging fraction, f, which is shown in Figure B.13. Measured and calculated values of G_0 are shown in Figure B.14.

B.6 Hydrogels: Water as the Solvent

As a final illustration of what can be done with these sorts of triblock copolymer gels, we consider materials where the midblock is replaced with poly(acrylic acid), a polymer that is water soluble at neutral pH. The structure of these polymer is shown in Figure B.15. This figure also shows a scheme for forming gels from these materials. Instead of adjusting χ between the solvent and the PMMA endblocks by changing temperature, we do this by adding a small amount of water to the solvent (which is initially dimethyl sulfoxide). Addition of just a small amount of water increases the effective value of χ characterizing the solvent/PMMA interaction. The result is that the relaxation times for the triblock copolymer solution increase dramatically, as illustrated by the rheological data in Figure B.16. The effects of solvent composition can be illustrated by introducing a shift factor, a_s that depends on the composition of the solvent. It's use is illustrated in Figure B.17. The viscosity at a given temperature is proportional to a_s , so we see that small increases in the water content of the solvent result in an increase in the solution viscosity by several orders of magnitude. This occurs because water induces the aggregation of PMMA blocks in to discrete domains, just as reducing temperature did for the case where alcohol was used as the solvent.

A useful feature of the hydrogels formed from the triblock copolymers with the poly(acrylic acid midblocks) is that the properties can be changed dramatically by immersing the gels in solutions containing divalent cations like Ca ²⁺ or Zn ²⁺. These ions add additional crosslinks to the material, increasing the modulus by a factor of 100 or more (Figure B.18). The materials also have high toughness, and can be extended to several times their original length prior to failure (Figure B.19).


Figure B.12: Concentration dependence of aggregation number for three different PMMA-PnBA-PMMA block copolymer solutions. The three data sets correspond to three different triblock copolymers, with different molecular weights for the PMMA and PnBA blocks.



Figure B.13: Concentration dependence of the network functionality.



Figure B.14: Calculated and experimental concentration dependence of the network functionality.



Figure B.15: Formation and ionic crosslinking of PMMA-PMAA-PMMA triblock copolymer hydrogels (PMAA = poly(methacrylic acid).



Figure B.16: Master plots of storage and loss moduli for PMMA-PMAA-PMMA triblock copolymer gels in DMSO/water mixtures, for water contents within the solvent of 4, 6 and 8 wt. %.

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Figure B.17: 'Super Master' plot of the data from Figure.



Figure B.18: Elastic modulus for triblock copolymer gels that have been ionically crosslinked to varying degrees.



Figure B.19: Tensile stress/strain curves for ionically crosslinked triblock copolymer gels.