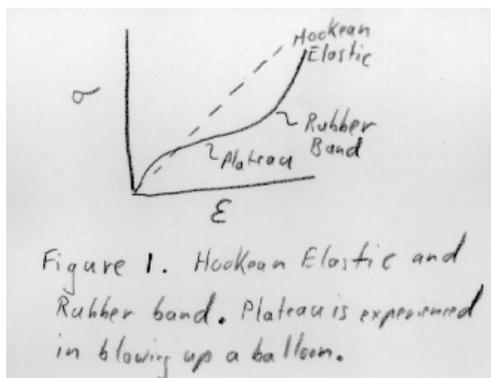


Chapter 2. Rubber Elasticity:

The mechanical behavior of a rubber band, at first glance, might appear to be Hookean in that strain is close to 100% recoverable. However, the stress strain curve for a rubber band does not approximate what is expected from Hookean behavior,



For a rubber the initial modulus diminishes with elongation with a pseudo plateau region followed by and increase in the stress at high elongations. The curve is completely different from a Hookean elastic. Despite the complexity of the deformation curve for a rubber, the curve can be well described with a simple model based on the random arrangement of mer units in a polymer chain. A hint at the relationship between the randomness (entropy) of a polymer chain and the mechanical properties is seen when a stressed rubber is subject to changes in temperature. A rubber band stretched by a fixed weight will shorten with increasing temperature, reflecting a net thermal contraction rather than expansion! One simple way to understand this is to consider the polymer chains as jump ropes that swing faster with higher temperature. In a rubber the jump ropes are connected into a network. As temperature rises the ropes swing faster drawing the ends of the rope inward towards the center of mass of the chain. Then higher temperature leads to a contraction of the chains and the sample as a whole.

The thermally driven random state of a polymer chain in a rubber leads to a random distribution function (Gaussian function) that describes the probability of the chain having two ends separated by a distance "R" if the chain is composed of "n" units,

$$P(R,n)dR = 4 R^2 \frac{2 nb^2}{3}^{\frac{3}{2}} \exp -\frac{3}{2} \frac{R^2}{nb^2} dR \quad (1)$$

From this probability we can calculate the mean $\langle R \rangle = 0$, and the second moment, $\langle R^2 \rangle = nb^2$. The average distance of this random walk chain is proportional to the square root of the number of steps, n. For an ideal chain, where there are no enthalpic interactions between chain units, we can consider the number of states, $\Omega(R)$, as a function of end-to-end-distance, R,

$$\Omega(R)dR = Z^n P(R,n)dR \quad (2)$$

where Z is the number of configurations a chain unit can take, i.e. the coordination number for a lattice site in Flory's approach. The ideal chain has no enthalpic considerations and the entropy is calculated from $S = k \ln \Omega$,

$$A = -TS = -\frac{3kTR^2}{2nb^2} \quad (3)$$

The force, F , associated with deformation of the chain (change in length R) is equal to the derivative of the free energy, dA/dR ,

$$F = \frac{3kT}{nb^2} R \quad (4)$$

which follows Hook's Law with the spring constant $3kT/(nb^2)$. The spring constant increases linearly with temperature, i.e. stress increases. The spring constant decreases with n in an inverse relationship, i.e. higher molecular weight chains are more easily deformed.

Elasticity of a Rubber (Fixed Junction Model):

We can calculate the modulus tensor for an ideal rubber network of ideal polymer chains (no enthalpy of interaction) if we consider:

- 1) chains joined at fixed junction points in the rubber
- 2) molecular weight of all chains is the same, n .
- 3) the sample deforms affinely, that is the individual chains are strained in an identical fashion to the entire sample
- 4) deformation is a perturbation to the Gaussian state, i.e. we can use the Gaussian equation for the strained and unstrained chains

For a cube sample subject to a tensile load we can write the excess entropy for one chain within the cube as,

$$s' - s_0 = -\frac{3k}{2R_0^2} (x_1'^2 + x_2'^2 + x_3'^2) = -\frac{3k \frac{R_0^2}{3}}{2R_0^2} \left(\frac{2}{1} + \frac{2}{2} + \frac{2}{3} \right) = -\frac{k}{2} \left(\frac{2}{1} + \frac{2}{2} + \frac{2}{3} \right)$$

where λ_i is the extension ratio for the direction i . λ_i is 1 for the undeformed state and for an incompressible system $\lambda_1 \lambda_2 \lambda_3 = 1$. For tensile deformation $\lambda_2 = \lambda_3$ so,

$$s = -\frac{k}{2} \left(\frac{2}{1} + \frac{2}{2} + \frac{2}{3} - 3 \right) = -\frac{k}{2} \left(\frac{2}{3} + \frac{2}{3} - 3 \right)$$

where s is the tensile strain for an affine single chain. Integrating over all chains in the system (which are all identical) yields,

$$S = \frac{kV}{2} \left(\frac{2}{x_{1o}} + \frac{2}{x_{1o}^2} - 3 \right)$$

The derivative of the free energy yields the force as discussed above for a single chain,

$$F = \frac{T}{x_{1o}} \frac{dS}{dx_{1o}} = \frac{V kT}{x_{1o}} \left(-\frac{2}{x_{1o}^2} + \frac{4}{x_{1o}^3} \right)$$

conversion to true stress yields,

$$\sigma_{11} = kT \left(\frac{2}{\lambda} - \frac{1}{\lambda^3} \right) \quad \text{True Stress}$$

and for engineering stress,

$$\sigma_{11} = kT \left(\frac{2}{\lambda} - \frac{1}{\lambda^3} \right) = kT \frac{(\lambda + 1)^3 - 1}{(\lambda + 1)^2} \quad \text{Engineering Stress}$$

For large strains the function is linear but at low strains the behavior is non-Hookean. The tangential slope at $\lambda = 1$ is given by,

$$\frac{d\sigma_{11}}{d\lambda} (\lambda = 1) = kT \left(-\frac{2}{\lambda^3} + \frac{3}{\lambda^4} \right) \Big|_{\lambda=1} = 3 kT$$

The chain density, ν , is related to the effective molecular weight between crosslinks by,

$$\nu = \frac{\text{mass}}{M_{eff}} N_A$$

Chains are arranged randomly in a rubber (elastomer or gel) network. That is the directions of the end-to-end vectors are randomly distributed in 3-d space. Then we must consider an arbitrary direction for the applied stress to chains of the network. The resulting deformation gradient tensor, e_{ij} , will certainly contain a rotational component for some (most) network chains. Simply considering the vorticity and the strain tensors for the bulk sample does not account for this arbitrary distribution of strain on the molecular level. Additionally, strains are not infinitesimally small but are generally quite large for elastomers. Consider that a typical rubber band can reversibly stretch to 3 times its initial length. The low strain approach considered in chapter 1 is not sufficient for elastomers. A general treatment of large strain deformations and deformations where local volume elements are subject to arbitrary strain is not unique to elastomers or gels. In fact, the continuum-mechanics approach to this problem was worked out in the 1890's by Cauchy, Green and Finger among others prior to Goodyear's discovery of crosslinking processes for elastomers.

Large Deformations, Complete Tensoral Material Functions:

There are two approaches which are closely related, one using the Cauchy tensor, C_{ij} , and the other using the Finger Tensor, B_{ij} . The Cauchy tensor and the Finger tensor are related by,

$$\underline{B} = \frac{1}{\underline{C}}$$

This nomenclature is somewhat confusing in that we have used C for the modulus tensor and for the Cauchy tensor. (This is, however, consistent with the literature.)

Two points in the *deformed* rubber separated by the vector $d\mathbf{r} = (dx_1, dx_2, dx_3)$ can be uniquely related to the separation vector $d\mathbf{r}'$ in the relaxed rubber. Then rather than considering the sample as a whole we consider a collection of material points that can deform in an arbitrary manner within the sample. This differs from the description used for small strains where only the bulk sample is considered. In this context we can consider the presence of stress as being related to a change in this separation distance for *internal points* on removal of the stress. The separation distance, independent of rotations and translations, can be determined by considering the square of the vector, $d\mathbf{r} \cdot d\mathbf{r}$. The change in this separation distance on relaxation from the stressed state (unprimed) to the relaxed state (primed) is given by,

$$\text{Change in Sep. Dist.} = d\mathbf{r}' \cdot d\mathbf{r}' - d\mathbf{r} \cdot d\mathbf{r}$$

Consider that the vector $d\mathbf{r}'$ is the derivative of a function $\mathbf{r}'(\mathbf{r})$ called the *mapping function* or the *displacement function*. This function relates each point in the relaxed state (prime) to each point in the stressed state (unprimed). The vector gradient of the mapping function, \mathbf{r}' / \mathbf{r} , determines the relationship between $d\mathbf{r}'$ and $d\mathbf{r}$,

$$d\mathbf{r}' = \frac{\mathbf{r}'}{\mathbf{r}} \cdot d\mathbf{r}$$

Using,

$$\frac{\mathbf{r}'}{\mathbf{r}} = \frac{r'_i}{r_j}$$

the change in separation distance can be written,

$$d\mathbf{r}' \cdot d\mathbf{r}' - d\mathbf{r} \cdot d\mathbf{r} = \frac{r'_i}{r_j} dr_j \frac{r'_i}{r_k} dr_k - dr_i dr_i = dr_j (C_{jk} - \delta_{jk}) dr_k$$

which defines the *Cauchy strain tensor* as,

$$C_{jk} = \frac{r'_j}{r_j} \frac{r'_k}{r_k}$$

The Cauchy tensor can describe any deformation, large strain, inhomogeneous strain, or small strain and homogeneous strain.

The Cauchy tensor can be compared with the discussion of strain given previously. Particularly, for a diagonal strain tensor (principle axes),

$$C_{ij} = \lambda_i^2 \delta_{ij}$$

The *Eulerian strain tensor* is defined by,

$$2E_{ij} = C_{ij} - \delta_{ij}$$

For the limit of very small strains the Eulerian strain tensor and the *strain tensor* (defined in chapter 1), ϵ_{ij} , are the same. This is because at small strains the reference frame can be interchangeably the deformed or the relaxed state.

The Finger tensor, B_{ij} , is useful for some material constitutive equations and is defined as,

$$B_{ij} = \frac{r_i}{r'_k} \frac{r_j}{r'_k} = C_{ij}^{-1}$$

The Finger tensor uses the undeformed state as the reference state. This is of use in rubber elasticity where the entropy function is written in the unperturbed state, i.e. it is based on the Gaussian chain. For a diagonal Cauchy tensor, the Finger tensor is just the inverse of the cross values (diagonal values). A more complicated relationship exists for non-diagonal Cauchy tensors and the simplest approach is to calculate the Finger tensor independently.

A Strain Energy Function:

Under isothermal conditions the change in free energy, ΔA , due to an infinitesimal strain, e , is,

$$\Delta A = V e$$

The infinitesimal change in the deformation gradient tensor, e , is given by,

$$e = \frac{1}{2} \left(\frac{r'_1}{r_1} + \frac{r'_2}{r_2} + \frac{r'_3}{r_3} \right) - \frac{3}{2}$$

where e is the strain tensor defined above and the primed terms are after deformation. The change in volume, ΔV , is,

$$V = V_{\mu\mu}$$

where the summations are over the indicies μ . From the expression for the free energy for an elastomer,

$$A = \{n_c kT \sum_{\mu} e_{\mu} e_{\mu} + (K/V)_T V_{\mu\mu}\}$$

where the summations are over μ , and μ . From this an expression for the stress, can be obtained,

$$= (n_c/V) kT e_{\mu} e_{\mu} - P = (n_c/V) kT B - P$$

where the summation is over μ . This expression shows the importance of the Finger tensor, B_{ij} for rubber elasticity.

Finger Tensor:

The deformation gradient, $e = R'_i / R_j$, relates the position in the unstressed (prime) to the stressed state. The Finger tensor is expressed by,

$$B_{ij} = e_{i\mu} e_{j\mu} = r'_i / r_{\mu} r'_j / r_{\mu}$$

where the summation is over the index μ . The Finger tensor describes the deformation in the absence of rotations and translations that do not lead to a change in the material position \mathbf{r} relative to a coordinate system based in the material, i.e. a *codeformational coordinate system*. This tensor is necessary since the Flory expression for rubber elasticity is based on the unstressed chain and perturbations to the end to end distance distribution function. From above, we can write,

$$= (n_c/V) kT B - P$$

The Cauchy tensor, C_{ij} , is related to the Finger tensor by,

$$C_{ij} = 1/B_{ij}$$

The Eulerian strain tensor, e_{ij} (the strain for linear response), is related to these tensors by,

$$2e_{ij} = \dots - C_{ij}$$

Meaning of Cauchy Tensor Components:

Cross terms in Cauchy tensor, C_{ij} , describe the length change on relaxation of stress for the major Cartesian axes. The cross terms describe the angle change from the orthogonal state for the Cartesian coordinate system,

$$\cos \theta_{ij} = \frac{C_{ij}}{(C_{ii}C_{jj})^{1/2}}$$

The Cauchy tensor is symmetric and can be converted to a diagonal form. In diagonal form it refers to a Cartesian volume element with orthogonal form in the deformed and undeformed states. The volume element can translate and rotate on relaxation from the stressed state. In diagonal form the Cauchy tensor is given by the three Cartesian extension ratios,

$$C_{ij} = \lambda_i^2 \delta_{ij}$$

The Cauchy tensor is directly related to the Eulerian strain tensor, \mathbf{E} ,

$$2E_{ij} = C_{ij} - \delta_{ij}$$

This is consistent with the relationship between the extension ratio and the strain but does not rely on infinitely small strains. In the limit of infinitesimal deformation the Eulerian strain tensor is identical to the total strain tensor e_{ij} previously defined in chapter 1.

Generalized Constitutive Equations for a “Hyperelastic” Material:

A generalized hyperelastic material is a material that responds to stress in a predictable way and returns to the original state after deformation, that is there is no hysteresis (loss or permanent set) in mechanical response.

The Cauchy (or Finger) tensor describes all local deformations that can lead to stress. Then the stress tensor can be described by the Cauchy (or Finger) strain tensor alone. Finger proposed that for a hyper elastic material, the stress-strain relationship depends on the relationship between the strain invariants and the free energy density. The three invariants are defined as,

$$\begin{aligned} I_C &= C_{ii} \\ II_C &= C_{11}C_{22} + C_{22}C_{33} + C_{33}C_{11} \\ &\quad - C_{12}C_{21} - C_{13}C_{31} - C_{23}C_{32} \\ III_C &= |C| \end{aligned}$$

For a diagonal Cauchy strain matrix, $C_{ij} = \lambda_i^2 \delta_{ij}$, and,

$$\begin{aligned}
I_C &= \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} \\
II_C &= \lambda_1^{-2} \lambda_2^{-2} + \lambda_2^{-2} \lambda_3^{-2} + \lambda_3^{-2} \lambda_1^{-2} \\
III_C &= \lambda_1^{-2} \lambda_2^{-2} \lambda_3^{-2}
\end{aligned}$$

Under the assumption that the free energy is a function only of these invariants, i.e. it depends only on local strain, Finger obtained the following general constitutive equation for a hyperelastic body,

$$\begin{aligned}
\mathbf{T} &= c_{-1} \mathbf{C}^{-1} + c_0 \mathbf{1} + c_1 \mathbf{C} \\
c_{-1} &= 2III_C^{3/2} \frac{f}{II_C} \\
c_0 &= -2III_C^{1/2} II_C \frac{f}{II_C} + III_C \frac{f}{III_C} \\
c_1 &= -2III_C^{1/2} \frac{f}{I_C}
\end{aligned}$$

If the strain dependence of free energy for a local element can be determined, then the stress for any deformation can be obtained. For many cases an equation based on the Finger tensor, \mathbf{B} , is more directly applicable. For a diagonal Finger tensor, $B_{ij} = \lambda_i^2 \delta_{ij}$, and,

$$\begin{aligned}
I_B &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\
II_B &= \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \\
III_B &= \lambda_1^2 \lambda_2^2 \lambda_3^2 \\
\mathbf{T} &= b_1 \mathbf{B} + b_0 \mathbf{1} + b_{-1} \mathbf{B}^{-1} \\
b_1 &= 2III_B^{-1/2} \frac{f}{I_B} \\
b_0 &= 2III_B^{-1/2} II_B \frac{f}{II_B} + III_B \frac{f}{III_B} \\
b_{-1} &= -2III_B^{1/2} \frac{f}{II_B}
\end{aligned}$$

For an ideal rubber the Finger tensor expression is most natural because the force can be written,

$$F = \frac{G}{2} (I_B - 3)$$

Because this expression does not include II_B and III_B the ideal rubber can be described with only the derivative term involving the first invariant, i.e. for an ideal rubber incompressibility removes

dependence on the third invariant and the equation of state precludes a derivative associated with the second invariant.

For an incompressible system $III_B = 1$. For a macroscopically isotropic, incompressible system,

$$\begin{aligned} \lambda_2 &= \lambda_3 = \lambda_1^{-1/2} \quad \text{where } \lambda_1 = \\ I_B &= \lambda_1^2 + 2 \\ II_B &= \lambda_1^{-2} + 1 \\ III_B &= 1 \end{aligned}$$

For a general hyperelastic material we have,

$$\underline{\underline{\sigma}} = 2 \frac{f}{I_B} \cdot \underline{\underline{B}} - 2 \frac{f}{II_B} \cdot \underline{\underline{B}}^{-1} - P \underline{\underline{1}}$$

and for an ideal rubber,

$$\underline{\underline{\sigma}} = G \cdot \underline{\underline{B}} - P \underline{\underline{1}}$$

We can consider several simple deformations and apply the Finger tensor approach to determine the constitutive equation describing deformation.

Shear Deformation:

For simple shear deformation, we can write in Cartesian coordinates the relationship between the deformed and undeformed (primed) states,

$$\begin{aligned} x' &= x - z \\ y' &= y \\ z' &= z \end{aligned}$$

The Eulerian strain tensor (total strain tensor, \mathbf{e} , at small strains) is given by,

$$E_{ij} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

and B_{ij} is given by $B_{ij} = e_{i\mu} e_{j\mu} = r'_i / r_\mu r'_j / r_\mu$. For the xx component $B_{11} = 1x1 + 0x0 + x$. The xz component is $B_{13} = 1x0 + 0x0 + x1$.

$$B_{ij} = \begin{pmatrix} 1 + \lambda^2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This is used in the Finger Equation, $\underline{\underline{\sigma}} = G \cdot \underline{\underline{B}} - P\mathbf{1}$, to yield,

$$\sigma_{xy} = (n_c/V) kT$$

$$\sigma_{xx} = (n_c/V) kT (1 + \lambda^2) - P$$

$$\sigma_{yy} = \sigma_{zz} = (n_c/V) kT - P$$

The shear modulus is given by,

$$G = \lim_{\gamma \rightarrow 0} \frac{\sigma_{xy}}{\gamma} = n_c kT$$

where n_c is the number density of network chains. Shear deformation of an elastomer leads to a simple linear Hookean expression for the modulus in contrast to the tensile expression given above.

Uniaxial Extension:

For uniaxial extension, we can write in Cartesian coordinates the relationship between the deformed and undeformed (primed) states,

$$x' = x / \lambda$$

$$y' = y / \lambda$$

$$z' = z$$

the Eulerian strain tensor is given by,

$$E_{e,d} = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

and B_{ij} is given by $B_{ij} = \mathbf{e}_{i\mu} \mathbf{e}_{j\mu} = \mathbf{r}'_i / r_\mu \mathbf{r}'_j / r_\mu$. For the xx component $B_{11} = x^{-1/2} x^{-1/2} + 0x0 + 0x0$. The xz component is $B_{33} = 0x0 + 0x0 + x^2$.

$$\underline{B} = \begin{pmatrix} 1/\lambda & 0 & 0 \\ 0 & 1/\lambda & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}$$

so, using the Finger Equation, $\underline{\sigma} = G \cdot \underline{B} - P\mathbf{1}$,

$$\sigma_{xy} = 0$$

$$\sigma_{zz} = c kT (\lambda^2 - 1) - P$$

$$\sigma_{xx} = \sigma_{yy} = c kT (\lambda^{-2} - 1) - P$$

for $\sigma_{xx} = \sigma_{yy} = 0$, $P = c kT (\lambda^{-2} - 1)$, and

$$\sigma_{zz} = c kT (\lambda^2 - 1)$$

Mooney-Rivlin Plots:

The expression for tensile deformation of an ideal rubber, $\sigma_{zz} = c kT (\lambda^2 - 1)$ suggests that a plot of tensile stress versus strain is not appropriate. Typically tensile data from elastomers is plotted using the Mooney-Rivlin plot which accounts for the non-linearity of the ideal rubber function. A Mooney-Rivlin plot can be done in several ways, one popular way is to divide the tensile stress by $\lambda^{-2} - 1$ and to plot this function against the inverse of extension. The Mooney expression for tensile stress is given by,

$$\frac{\sigma_{zz}}{\lambda^{-2} - 1} = 2 c_1 + \frac{2 c_2}{\lambda^2}$$

This is obtained by considering the normal stress difference, $\sigma_{zz} - \sigma_{xx}$,

$$\sigma_{33} - \sigma_{11} = 2 c_1 (\lambda^2 - \lambda^{-2}) - 2 c_2 (\lambda^{-2} - \lambda^2)$$

This function includes the derivative of the free energy with respect to the second invariant of the Finger tensor, $\underline{\sigma} = 2 \frac{f}{I_B} \cdot \underline{B} - 2 \frac{f}{II_B} \cdot \underline{B}^{-1} - P\mathbf{1}$. By considering the normal stress difference the pressure term drops out. c_1 and c_2 are sometimes called the Mooney constants. Algebra yields the Mooney-Rivlin equation.

