Rubber Elasticity

(Indented text follows Strobl, other follows Doi)

Elasticity of A Single Chain:

The spring constant associated with a single polymer chain is of importance in a wide range of situations from the development of a simple description of rubber elasticity to understanding flow behavior and other physical deformations of the chain. The basis of rubber elasticity is the Gaussian chain and most descriptions are limited by this framework. Despite this limitation the description of the elasticity of a polymer chain is one of the major success stories of polymer science. Elasticity in polymers is based on thermal motion of the chain units. Consider a jump rope that is being swung. The ends of the rope are pulled inward due to the kinetic energy of the rope. Similarly, the thermal kinetic energy of a polymer chain tends to oppose stresses applied to the random coil. Put differently, the chain seeks to maintain a random state and any force applied to deform the chain acts to reduce the randomness of the chain. This can be a compressive, tensile or shear force.

For a chain of length N and $W_0(\mathbf{r})$ conformational states the free energy can be written as a sum of the entropic and enthalpic contributions,

$$A = -kT \ln W_0(\mathbf{r}) + C = 3kT\, \mathbf{r}^2/(2Nl_p^2) + C$$

where C is a constant associated with the enthalpy of the chain. The free energy is a function of the chain extension, **r**. Changes in this free energy with respect to **r** result in a force, **-f**,

$$\mathbf{f} = -\delta A/\delta \mathbf{r} = -3kT\, \mathbf{r}/(Nl_p^2)$$

Thermal motion of the chain is the source of this force just as thermal motion of atoms in a gas give rise to pressure. Generally, we can speak of a spring constant $\mathbf{f} = K\, \mathbf{r}$, where $K = 3kT/(Nl_p^2)$, for an ideal chain.

> For an ideal chain the free energy associated with deformation in the "y"-direction comes solely from entropy changes.
> Force = $\delta f/\delta y = -T\, \delta s/\delta y$
> The entropy is given by the partition function Z from $s = k \ln Z(y)$, where Z is the number of conformations available to the chain when the two ends are separated by a distance "y". The Gaussian distribution describes the probability of a given end to end distance,

$$p(x, y, z) = (2\pi R_0^2/3)^{-3/2} \exp\{-3(x^2+y^2+z^2)/(2R_0^2)\}$$

This reflects the number of conformations for a given end to end distance. For x = 0, z = 0 and y having a value,

$$Z(y) \sim \exp(-3y^2/(2R_0^2))$$

and the entropy is

$$s(y) = K + k(-3y^2/(2R_0^2))$$

Then the force associated with deformation of a single chain is force = $3kT/(R_0^2)\ y$

Free Energy of a Network (Rubber):

Consider a bulk sample of rubber composed of tens of millions of single chains connected by crosslink sites. For such systems it is appropriate to consider a continuum view and define a deformation by the displacement of a material element at position **R** in the unstressed state to a position **R'** in the stressed state. The deformation gradient tensor, $E_{i\phi}$, describes the defomation in terms of a tensor expression $E_{i\phi} = \delta R'_i/\delta R_j$, where i and j are any combination of Cartesian coordinates 1,2,3. Then E_{ij} is a 3x3 matrix describing the relative positions of material elements on deformation.

Consider that the position of a material element in the deformed state R' is a function of the initial , undeformed position R, R'(R). This is the displacement function. Not all deformations dR'(R)/dR lead to stress. Rigid body rotations and translations, for example, do not lead to the development of stress. Then the question is how can we consider only deformations that lead to stress. Take R' and R' + dR', two neighboring positions in the deformed state. Then release stress so the two positions go to R and R+dR. The relative change in position is given by the square root of dR'•dR' - dR•dR, and this must have a value different from 0 for the development of stress. We have that dR = (dR/dR') dR' and $(dR/dR')_{ij} = (dR_i/dR_j)$. If you substitute in these expressions you obtain,

$$dR_i' \bullet dR_i' - dR_i \bullet dR_i = dR'_j\ (C_{jk} - \delta_{jk})\ dR'_k$$

where C_{jk} is the Cauchy tensor that gives deformations that lead to stress. $C_{jk} = (dR_i/dR'_j)(dR_i/dR'_k)$

As noted above, the free energy of a chain between crosslinks of N units with end to end vector **r** is

$f = (3kT/(2Nl_p^2))\mathbf{r}^2$

In the network chains of variable end to end distance exist so the free energy, A, must be integrated over **r**. If the rubber contains n_c chains, and the probability of a chain of molecular weight N and end to end distance **r** is $\Psi(N, \mathbf{r})$ then,

$$A = n_c \int dr \int_0^\infty dN \Psi(r, N) \frac{3kT}{2Nl_p^2} r^2 + K$$

where K is a constant. This expression is simplified by the following assumptions:
1) The chains are Gaussian in the deformed and undeformed states.

$$\Psi(r, N) = \left(\frac{3}{2\pi N l_p^2}\right)^{3/2} \exp\left(\frac{-3r^2}{2Nl_p^2}\right) \Phi(N)$$

2) Deformation is affine so **r**' = **E** • **r** where **E** is the deformation gradient tensor. Then the free energy for the deformed state is,

$$A = n_c \int dr \int_0^\infty dN \Psi(r, N) \frac{3kT}{2Nl_p^2} (E \cdot r)^2 + K$$

Integrating leads to,

$$A = n_c 3kT \left(E_{\alpha\beta}\right)^2 + K$$

Deformation of a Real Rubber:

Under isothermal conditions the change in free energy, δA, due to an infinitesimal strain, $\delta\varepsilon$, is,

$\delta A = V \sigma_{\alpha\beta} \delta\varepsilon_{\alpha\beta}$

The infinitesimal change in the deformation gradient tensor, $\delta E_{\alpha\beta}$, is given by,

$\delta E_{\alpha\beta} = \Sigma \delta\varepsilon_{\alpha\mu} \delta E_{\mu\beta}$

and the change in volume, δV, is,

$$\delta V = \Sigma V \delta\varepsilon_{\mu\mu}$$

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

$$\delta A = \Sigma\Sigma\Sigma \{n_c kT \delta\varepsilon_{\alpha\mu} E_{\mu\beta} E_{\alpha\beta} + (\delta K/\delta V)_T V \delta\varepsilon_{\mu\mu}\}$$

where the summations are over α, β and μ. From this an expression for the stress, $\sigma_{\alpha\beta}$ can be obtained,

$$\sigma_{\alpha\beta} = \Sigma(n_c/V) kT E_{\alpha\mu} E_{\beta\mu} - P\delta_{\alpha\beta}$$

where the summation is over μ.

Finger Tensor:

The deformation gradient, $E_{i\phi} = \delta R'_i/\delta R_j$, relates the position in the stressed (prime) to the unstressed state. The Finger tensor is expressed by,

$$B_{ij} = \Sigma E_{i\mu} E_{j\mu} = \Sigma\, \delta R'_i/\delta R_\mu\, \delta R'_j/\delta R_\mu$$

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 **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 does not consider translation and rotation as leading to a change in free energy. Then we can write for incompressible elastic bodies,

$$\sigma = G\bullet\mathbf{B} - P\,\mathbf{1}$$

and for a rubber,

$$\sigma_{\alpha\beta} = (n_c/V) kT B_{\alpha\beta} - P\delta_{\alpha\beta}$$

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,

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

Simple Shear Deformation:

For simple shear deformation, x'=γy+x; y'=y; z'=z

$$E_{\alpha\beta} = \begin{pmatrix} 1 & \gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and B_{ij} is given by,

$$B_{\alpha\beta} = \begin{pmatrix} (\gamma^2 + 1) & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

so,

$\sigma_{xy} = (n_c/V)\, kT\, \gamma$
$\sigma_{xx} = (n_c/V)\, kT\, (1+\gamma^2) - P$
$\sigma_{yy} = \sigma_{zz} = (n_c/V)\, kT - P$

The shear modulus is given by,

$$G = \lim_{\gamma \to 0} \frac{\sigma_{xy}}{\gamma} = \upsilon_c kT$$

where ν_c is the number density of network chains.

1) There is a linear relationship between shear stress and shear strain.

2) The first normal stress difference for an ideal rubber, $\sigma_{xx} - \sigma_{zz} = (n_c/V)\, kT\, \gamma^2$ is non-linear depending on γ^2.

3) The second normal stress difference is 0 for an ideal rubber.

Pure Shear:

For pure shear (Strobl p. 319) the y coordinate is held constant and $z' = \lambda^{-1} z$; $x' = \lambda x$; $y' = y$ under deformation, so,

$$E_{\alpha\beta} = \begin{pmatrix} \lambda & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1/\lambda \end{pmatrix}$$

$$B_{\alpha\beta} = \begin{pmatrix} 1/\lambda^2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}$$

All three normal stress differences have values:

1) $\sigma_{zz} - \sigma_{xx} = G(\lambda^2 - \lambda^{-2})$
2) $\sigma_{zz} - \sigma_{yy} = G(\lambda^2 - 1)$
3) $\sigma_{yy} - \sigma_{xx} = G(1 - \lambda^{-2})$

Uniaxial Extension:

For uniaxial extension, $z' = \lambda z$; $x' = x\lambda^{-1/2}$; $y' = y\lambda^{-1/2}$,

$$E_{\alpha\beta} = \begin{pmatrix} 1/\sqrt{\lambda} & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

and B_{ij} is given by (depending on the definition of λ), (as given by Strobl p. 318)

$$B_{\alpha\beta} = \begin{pmatrix} 1/\lambda & 0 & 0 \\ 0 & 1/\lambda & 0 \\ 0 & 0 & \lambda^2 \end{pmatrix}$$

so,

$\sigma_{xy} = (n_c/V)\, kT\, \gamma$
$\sigma_{zz} = \nu_c\, kT\lambda^2 - P$
$\sigma_{xx} = \sigma_{yy} = \nu_c\, kT/\lambda - P$

for $\sigma_{xx} = \sigma_{yy} = 0$, $P = \nu_c\, kT/\lambda$, and

$\sigma_{zz} = \nu_c\, kT(\lambda^2 - 1/\lambda)$

The latter equation is the basis of the Mooney-Rivlin Plot (Strobl p. 323) of reduced tensile stress, $\sigma/(\lambda - 1/\lambda^2)$, versus the inverse of strain, $1/\lambda$. This approach does not work for compression as shown by Strobl on page 323.