

Rubber elasticity

Marc R. Roussel
Department of Chemistry and Biochemistry
University of Lethbridge

February 21, 2009

A rubber is a material that can undergo large deformations (e.g. stretching to five or ten times its original length) and then return to its original shape and size. Many polymeric materials, and not just rubber itself, display rubber elasticity in some range of temperatures. When we characterize these materials, we find that they are made of long chains, with occasional cross-links between the chains. In the resting state, these chains will adopt random coil configurations. As we apply a stress by pulling on a sample of rubber, the chains will tend to align along the stress, which allows the material to stretch. The cross-links pull the material back to its original shape once the stress is removed.

In this note, we will look at a statistical treatment of rubber elasticity. This will allow us to relate the elastic behavior to properties of the polymer.

1 Cross-linking statistics

Figure 1 shows two primary polymer molecules which have formed some cross links. There are both internal cross-links (within a single molecule) and external cross-links (between molecules). Both types can be important to rubber elasticity. The important statistic for rubber elasticity is in fact the number of chains bounded by two cross-link junctions, a quantity called the **number of active chains**, denoted ν_e . Free ends are uninteresting because they can be displaced more-or-less freely. If we have N primary polymers, there will be $2N$ free ends. Let ν be the number of monomers involved in cross-links (two per cross-link). Each cross-link takes two chains and divides them into four, so the number of chains added by making $\nu/2$ cross-links is equal to ν . From this number, we have to subtract the number of chains that end freely. Thus,

$$\nu_e = \nu - 2N = \nu(1 - 2N/\nu).$$

Now let M be the average molar mass of the primary polymers, and M_c be the molar mass per cross-linked monomer, i.e. $M_c = NM/\nu$. Another way to look at M_c is that it's the average molar mass of the active chains. We can then rewrite the last equation

$$\nu_e = \nu(1 - 2M_c/M). \tag{1}$$

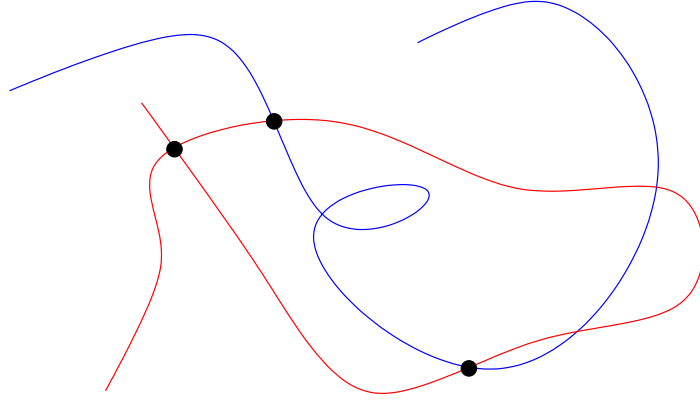


Figure 1: Two primary polymer molecules (i.e. two polymer chains) which have formed some cross-links, shown as bold dots. The chains are colored differently for ease of visualization.

2 Thermodynamics of elasticity

When we write down the differential of U in courses in chemical thermodynamics, we normally only consider pressure-volume work. Here, we need to also consider the extension work. Suppose that f is the externally imposed (equilibrium, i.e. reversible) tension on an elastic body. Then

$$dw = -P dV + f dL,$$

where dL represents a change in the length of the body. You will recognize the new term as a special case of the general definition of mechanical work as force times distance. Then we have

$$dU = dw + dq = -P dV + f dL + T dS.$$

In this form, we have a differential of U in terms of the variables (S, V, L) . Physically, these are not the most convenient variables. We would like to rewrite U as a function of (T, V, L) . To do this, we need to rewrite the differential of S in terms of those variables:

$$dS = \left. \frac{\partial S}{\partial T} \right|_{V,L} dT + \left. \frac{\partial S}{\partial V} \right|_{T,L} dV + \left. \frac{\partial S}{\partial L} \right|_{T,V} dL.$$

If we now substitute this equation into the differential of U , we get

$$\begin{aligned} dU &= \left(T \left. \frac{\partial S}{\partial V} \right|_{T,L} - P \right) dV + \left(T \left. \frac{\partial S}{\partial L} \right|_{T,V} + f \right) dL + T \left. \frac{\partial S}{\partial T} \right|_{V,L} dT. \\ \therefore \left. \frac{\partial U}{\partial L} \right|_{T,V} &= T \left. \frac{\partial S}{\partial L} \right|_{T,V} + f, \\ \text{or } f &= \left. \frac{\partial U}{\partial L} \right|_{T,V} - T \left. \frac{\partial S}{\partial L} \right|_{T,V}. \end{aligned} \tag{2}$$

If we can develop a theory for the thermodynamic properties of rubbers, then equation 2 will give us an equation for the force which must be applied to get a certain extension ΔL from the equilibrium length L .

The elasticity of rubbers is largely due to conformational rearrangements of the chains, which are obtained largely by rotations around σ bonds of the framework. These rotations should take very little energy. If we assume that they take no energy at all, then we get the **ideal rubber** model. In terms of the quantities in equation 2, an ideal rubber is one for which

$$\left. \frac{\partial U}{\partial L} \right|_{T,V} = 0.$$

The elastic force is then due to an entropic effect alone:

$$f = -T \left. \frac{\partial S}{\partial L} \right|_{T,V}. \quad (3)$$

It is worthwhile spending a few minutes thinking about what equation 3 tells us in relation to rubber elasticity. When we pull on a piece of rubber, we straighten out the polymer chains. This decreases the entropy, so $\partial S/\partial L|_{T,V} < 0$. Another way to put this is that there are more microstates associated with the collapsed state than with the stretched state. The random thermal motions of the chains in a stretched state are therefore more likely to be in a direction which would tend to bring the polymer back toward its relaxed state, which generates the resistive force f . This is remarkable: Entropy, which we normally think of as a somewhat abstract statistical quantity, is directly responsible for a macroscopic force!

3 Stress and strain

In materials science, we don't normally talk about the force vs extension relationship, which is what equation 3 would give us. There are two problems:

1. The force depends on the geometry of the sample, in particular its cross-sectional area perpendicular to the applied force. To solve this problem, we define the **stress**

$$\sigma = F/A.$$

2. The actual extension (L) for a given stress depends on the initial length of the sample, L_0 . On the other hand, the **strain**

$$\varepsilon = \Delta L/L_0 = (L - L_0)/L_0$$

only depends on the stress. Equivalently, we can use the **stretch ratio**

$$\lambda = L/L_0 = \varepsilon + 1.$$

We will use λ in these notes, although clearly λ and ε are interchangeable quantities.

Materials scientists thus usually discuss deformation using the **stress-strain** relationship. (The term stress-strain relationship is used even when the strain is described in terms of the stretch ratio.)

From the definition of λ , we have $L = \lambda L_0$. Therefore

$$\frac{\partial}{\partial L} = \frac{1}{L_0} \frac{\partial}{\partial \lambda}.$$

Equation 3 therefore becomes

$$f = -\frac{T}{L_0} \left. \frac{\partial S}{\partial \lambda} \right|_{T,V}. \quad (4)$$

4 Statistical theory of rubber elasticity

To calculate the entropy of a rubber, we will use the Boltzmann equation:

$$S = k \ln W,$$

where W is the number of microstates. The active chains may have different lengths, which affects W . We can compute W by

$$W = \prod_n (W_n)^{\nu_n},$$

where ν_n is the number of chains containing n bonds. This gives

$$S = k \sum_n \nu_n \ln W_n.$$

We need to reinterpret this equation a little: In our case, we can't count the microstates. Suppose that I give you the probability density $p_n(\lambda)$ that a given n -mer has end-to-end is stretched by a factor λ from its resting length. The number of microstates between λ and $\lambda + d\lambda$ is proportional to $p_n(\lambda) d\lambda$. Since we are going to take a logarithm, the proportionality constant, as well as the factor of $d\lambda$, end up in an additive constants:

$$S = k \sum_n (\nu_n \ln p_n(\lambda) + \text{constant}).$$

Our next step will be to take the derivative in equation 4, so the constant will vanish:

$$f = -\frac{kT}{L_0} \sum_n \nu_n \left. \frac{\partial \ln p_n(\lambda)}{\partial \lambda} \right|_{T,V}. \quad (5)$$

Cross-links occur where two primary polymers have come sufficiently close together in the right orientation. Cross-linking should therefore have only a small effect on the locations of the monomers which became cross-linked. The distribution of relative positions of the two

cross-link junctions defining an active chain should therefore obey the Gaussian probability density derived in the last lecture:

$$p_n(x, y, z) = (q/\sqrt{\pi})^3 e^{-q^2(x^2+y^2+z^2)}, \quad (6)$$

where $q^2 = 3/(2n\ell^2)$. We also had $\langle r_0^2 \rangle = n\ell^2 = 3/(2q^2)$, where $\langle r_0^2 \rangle$ is the mean squared end-to-end distance of the *relaxed* polymer.

We now introduce an **affine transformation**: We assume that the deformation of a sample of rubber stretches all the coordinates homogeneously by factors λ_x , λ_y and λ_z in each of the three Cartesian directions. Thus, $(x, y, z) = (\lambda_x x_0, \lambda_y y_0, \lambda_z z_0)$, where (x_0, y_0, z_0) are the initial relative coordinates of the end of a chain. Taking a logarithm of equation 6 and introducing the affine transformation, we get

$$\ln p_n = -q^2 [(\lambda_x x_0)^2 + (\lambda_y y_0)^2 + (\lambda_z z_0)^2] + \text{constant},$$

where again we won't be too concerned with the constants since they won't contribute to the force.

Rubbers are essentially incompressible, so we must have $\lambda_x \lambda_y \lambda_z = 1$. Suppose that we stretch a sample of rubber along the x axis. Let $\lambda_x = \lambda$. We will typically find that $\lambda_y = \lambda_z$.¹ Substituting this relationship into the incompressibility condition, we get $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$. This gives

$$\ln p_n(\lambda) = -q^2 [\lambda^2 x_0^2 + (y_0^2 + z_0^2)/\lambda] + \text{constant}.$$

There is just one more thing: If we have ν_n polymers of length n , then we should average this quantity over all the initial end-to-end distances:

$$\ln p_n(\lambda) = -q^2 [\lambda^2 \langle x_0^2 \rangle + (\langle y_0^2 \rangle + \langle z_0^2 \rangle)/\lambda] + \text{constant}.$$

For the relaxed polymer, there is nothing special about the x axis, i.e. $\langle x_0^2 \rangle = \langle y_0^2 \rangle = \langle z_0^2 \rangle$. Since $\langle r_0^2 \rangle = \langle x_0^2 \rangle + \langle y_0^2 \rangle + \langle z_0^2 \rangle$, this gives $\langle x_0^2 \rangle = \langle y_0^2 \rangle = \langle z_0^2 \rangle = \langle r_0^2 \rangle/3$. We therefore obtain

$$\ln p_n(\lambda) = -\frac{q^2 \langle r_0^2 \rangle}{3} (\lambda^2 + 2/\lambda) + \text{constant} = -\frac{1}{2} (\lambda^2 + 2/\lambda) + \text{constant}.$$

Note that q and $\langle r_0^2 \rangle$ have both dropped out of the non-constant part of this expression. The derivative in equation 5 therefore doesn't depend on n :

$$\left. \frac{\partial \ln p_n(\lambda)}{\partial L} \right|_{T,V} = -(\lambda - 1/\lambda^2).$$

It can therefore be pulled out of the sum, leaving $\sum_n \nu_n = \nu_e$, the number of active chains. Putting it all together, we get the elastic force

$$f = \frac{kT\nu_e}{L_0} (\lambda - 1/\lambda^2).$$

¹Some polymers do deform differently in different directions, but then we would have to orient the sample correctly with respect to any special axes to observe this phenomenon.

To get the strain, we divide this equation by the cross-sectional area. There are actually two slightly different conventions in use here. One is to divide by the cross-sectional area of the relaxed sample, A_0 , giving

$$\sigma_0 = \frac{kT\nu_e}{V_0} (\lambda - 1/\lambda^2). \quad (7)$$

σ_0 is called the **nominal stress**. This is the convention normally used by polymer scientists. The other is to divide by the area corresponding to stretch ratio λ . Since the y and z are transformed by the ratio $\lambda_y = \lambda_z = 1/\sqrt{\lambda}$, $A = A_0/\lambda$. The true stress is therefore

$$\sigma = \frac{kT\nu_e}{V_0} (\lambda^2 - 1/\lambda).$$

We will pursue our analysis with equation 7. Using equation 1, the stress becomes

$$\sigma_0 = \frac{kT\nu}{V_0} (1 - 2M_c/M) (\lambda - 1/\lambda^2).$$

If we define the number of moles of cross-linked monomers $n_c = \nu/N_A$, we get

$$\sigma_0 = \frac{n_c RT}{V_0} (1 - 2M_c/M) (\lambda - 1/\lambda^2).$$

Almost the entire volume is occupied by active chains. The mass of the sample is therefore approximately $n_c M_c$. If we denote by v the specific volume of the relaxed sample, then $V_0 = n_c M_c v$, and therefore

$$\sigma_0 = \frac{RT}{v} \left(\frac{1}{M_c} - \frac{2}{M} \right) (\lambda - 1/\lambda^2).$$

This is our final expression. It predicts two interesting properties of the stress-strain relationship:

1. For a given strain, the stress increases linearly with temperature. Alternatively, if we fix the stress (e.g. by suspending a mass from a piece of rubber), then the extension should decrease as we increase the temperature. This is a well known property of rubber which the statistical theory correctly predicts. Note that this behavior is the opposite of what we observe for normal materials: Typically, heating something up causes it to expand. Putting a stress on normal materials (e.g. metals) as they are being heated does not change this behavior.
2. Increasing the number of cross-links, keeping all other properties constant, decreases M_c , which in turn increases the stress at fixed strain. This is probably intuitively obvious, but it's nice that the statistical theory actually predicts this behavior correctly.