

Topic 4

Networks

4.1 Rubber Elasticity

10/21:

- Announcements.
 - Quiz 1 solutions posted to Canvas.
 - Ask Alfredo if you have any questions about the light scattering lecture.
 - 2014 lecture notes are now visible on Canvas for most of the lectures in the course!
- Overview of Topic 4 (by day).
 - Today: Rubbers and networks.
 - Next class: Gels.
 - The following class (as time permits): More on networks or gels.
- **Rubber:** A network of crosslinked chains.
 - The crosslinked chains take many forms: You can have **topological crosslinks**, **loops**, **dangling ends**, etc.
 - Example rubber: A rubber band. Recall that when you heat a rubber band, it tightens up. Today, we will explain this in terms of increasing the entropic spring force!
- **Topological crosslinks:** Two chains that add integrity to the network by looping around each other mechanically, rather than being covalently bonded.
- **Loop:** A chain that connects back with itself without introducing any classical or topological crosslinks, and thus does not carry stress.
- **Dangling ends:** A chain strand in a network that does not bond (classically or mechanically) to any other chain or itself, and thus does not carry stress.
- Recall from Lecture 1: Chichén Itzá (ancient Mayan place) and natural rubber basketball.
 - There were no hoops in this game; rather players tried to get the ball into very small holes in a big wall.
 - Such a tight-fitting target would have necessitated the rubber be crosslinked.
- **Deformation:** A change in the shape of a polymer, without changing the overall volume.
- **Swelling:** Enlarging a polymer network by mixing in a solvent and seeing the resulting increase in volume.
 - Swelling creates a **gel**, the topic of next lecture!

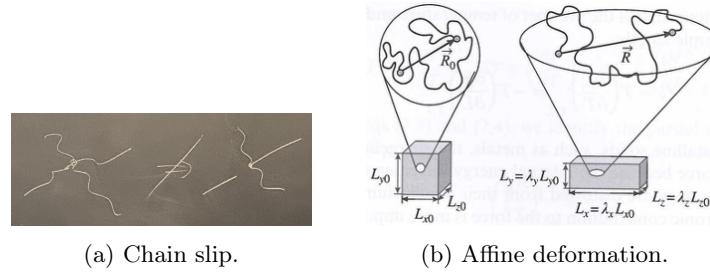


Figure 4.1: Rubber elasticity assumptions.

- Rubber elasticity assumptions.

1. The chains are Gaussian between the permanent crosslinks, and there are no excluded volume effects.
 - It follows that enthalpy/energy considerations are not important, i.e., $U = H = 0$.
 - Thus, basically, $\Delta G \propto \lambda^2 / Nb^2$.
2. The temperature is well above T_g , so no freezing or crystallization occurs.
 - We're living in a liquid state.
3. The chains are flexible, with relatively low backbone bond rotation potential barriers.
 - Changing ϕ from the symmetric hindered rotations model is easy.
4. Chain deformation occurs by conformational changes, *not* bond stretching.
 - l does not change.
5. No relaxation occurs by **chain slip**, i.e., this is a fixed, permanent network (at least on the time scale of the experiment).
 - Crosslinks *cannot* break.
6. Affine deformation.
 - At every length scale, from microscopic subchains to the macroscopic network, the deformation experienced is equivalent.
 - For example, a shear at the surface is the same shear at the microscale. Notice how in Figure 4.1b, the stretch of the entire chunk is mirrored by the stretch in the polymer; we will numerically relate the variables in this diagram shortly.
 - Mathematically, the only permissible deformations are ones that preserve lines and parallelism, but not necessarily Euclidean distances or angles. In other words, these deformations are functions composed of a linear transformation, such as rotation, shear, extension and compression, and a rigid body translation.
7. No crystallization at large strains.
 - In real life, if all chains are fully elongated (trans-trans-trans-etc.), they can pack into crystalline domains. We assume this doesn't happen.
8. No change in volume or density upon deformation.
 - Thus, if we pull it in one direction, it must shrink in the others.

- **Chain slip:** The removal of a covalent or mechanical crosslink via bond cleavage or disentanglement, respectively.
- **Extension ratio** (in the i -direction): One of three ($i \in \{x, y, z\}$) orthogonal extension ratios which depend on the type of loading geometry. Denoted by α_i, λ_i . Given by

$$R_i = \alpha_i R_{i0}$$

$$L_i = \alpha_i L_{i0}$$

where \mathbf{R}_0 is the end-to-end vector of an undeformed subchain in the rubber, \mathbf{R} is the end-to-end vector of the same subchain after deformation, \mathbf{L}_0 is the corner-to-corner vector of the rubber, \mathbf{L} is the corner-to-corner vector of the rubber after deformation, and subscripts denote the i^{th} component of these vectors.

- On notation, Alfredo uses α while the book uses λ . The two notations are completely interchangeable, and we should get used to seeing both.
- More explicit definitions with the above terminology and alternate notations.
 - We assume that the relaxed polymer has root mean square end-to-end distance $\langle R_0^2 \rangle^{1/2}$, and the extended polymer has root mean square end-to-end distance $\langle R^2 \rangle^{1/2}$.
 - These vectors are

$$\mathbf{R}_0 = (R_{x0}, R_{y0}, R_{z0}) = (x, y, z) \quad \mathbf{R} = (R_x, R_y, R_z) = (x', y', z')$$

- Formulating some of the assumptions mathematically in terms of the α_i .
 - Assumption 6, mathematically, is that the macro and micro definitions of α_i are equivalent.
 - Assumption 8 is that $\alpha_x \alpha_y \alpha_z = 1$.
- We now investigate the elastic force with which the polymer tries to restore its original shape after deformation.
- Terminology for describing the rubber's elastic force, which arises entropically.
 - State 1 is relaxed, and State 2 is extended.
 - State 1.
 - Force $F = 0$.
 - Ω_1 possible conformations.
 - Root mean square end-to-end distance (of the average chain) is $\langle R_0^2 \rangle^{1/2}$.
 - Extension coordinates x, y, z .
 - State 2.
 - Force $F > 0$.
 - Ω_2 possible conformations.
 - Root mean square end-to-end distance (of the average chain) is $\langle R^2 \rangle^{1/2}$.
 - Extension coordinates x', y', z' .
 - Sanity check: $\Omega_1 > \Omega_2$.
- Using this terminology, the actual elastic force is derived by considering the change in the conformational entropy of the extended vs. relaxed states.

$$\Delta S = S_2 - S_1 = k_B \ln \Omega_2 - k_B \ln \Omega_1 = k_B \ln \frac{\Omega_2}{\Omega_1}$$

- Let's now look at the scaling of the Ω_i in terms of coordinates and extension ratios.

$$\begin{aligned} \Omega_1 &= \text{const} \cdot \exp\left(-\frac{3R_0^2}{2nl^2}\right) & \Omega_2 &= \text{const} \cdot \exp\left(-\frac{3R^2}{2nl^2}\right) \\ &= \text{const} \cdot \exp\left[-\frac{3(x^2 + y^2 + z^2)}{2nl^2}\right] & &= \text{const} \cdot \exp\left\{-\frac{3[(x')^2 + (y')^2 + (z')^2]}{2nl^2}\right\} \\ &= \text{const} \cdot \exp\left[-\frac{3(1^2x^2 + 1^2y^2 + 1^2z^2)}{2nl^2}\right] & &= \text{const} \cdot \exp\left[-\frac{3(\alpha_x^2x^2 + \alpha_y^2y^2 + \alpha_z^2z^2)}{2nl^2}\right] \end{aligned}$$

- Substituting these definitions of Ω_i into the ΔS equation affords

$$\Delta S = -\frac{3k_B}{2nl^2} [(\alpha_x^2 - 1)x^2 + (\alpha_y^2 - 1)y^2 + (\alpha_z^2 - 1)z^2]$$

- Now averaging over the entire ensemble-like collection of subchains in our rubber, we can assume that the average subchain is isotropic. (This is also consistent with Assumption 1.) Thus,

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{\langle R_0^2 \rangle}{3}$$

- This combined with the fact that $R_0^2 = nl^2$ gives us the final change in entropy per subchain upon deformation in terms of the extension ratios.

$$\begin{aligned} \Delta S &= -\frac{3k_B}{2nl^2} [(\alpha_x^2 - 1)\langle x^2 \rangle + (\alpha_y^2 - 1)\langle y^2 \rangle + (\alpha_z^2 - 1)\langle z^2 \rangle] \\ &= -\frac{3k_B}{2nl^2} \left[(\alpha_x^2 - 1)\frac{\langle R_0^2 \rangle}{3} + (\alpha_y^2 - 1)\frac{\langle R_0^2 \rangle}{3} + (\alpha_z^2 - 1)\frac{\langle R_0^2 \rangle}{3} \right] \\ &= -\frac{3k_B}{2nl^2} \frac{nl^2}{3} [(\alpha_x^2 - 1) + (\alpha_y^2 - 1) + (\alpha_z^2 - 1)] \\ &= -\frac{k_B}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \end{aligned}$$

- It follows that the entropic spring force F_i in the i -direction upon deformation is

$$F_i = \frac{\partial G}{\partial R_i} = \frac{\partial(0 - T\Delta S)}{\partial R_i} = -T \left(\frac{\partial \Delta S(\alpha_i)}{\partial R_i} \right)_{T,P}$$

- Rubber demos.

- Rubber elasticity is of the few times you can experiment with thermodynamics on the fly.
 - Other times: Filling air into tires, and spray-on sunscreen on your back feeling cold.
- Today, we'll “feel” entropy by sensing the change in temperature of a rubber band as we stretch it.
 - Feel temperature of a rubber band, stretch (or release) it very quickly, and feel the temperature again!
 - When you stretch it, the system heats up; when you release it, the system cools down.
 - We need to move quickly so that the change is (approximately) adiabatic, i.e., we do not want to allow the system to exchange heat with the environment to a meaningful extent.

- Let's now analyze the elastic force generated by the simplest type of deformation: Uniaxial deformation.

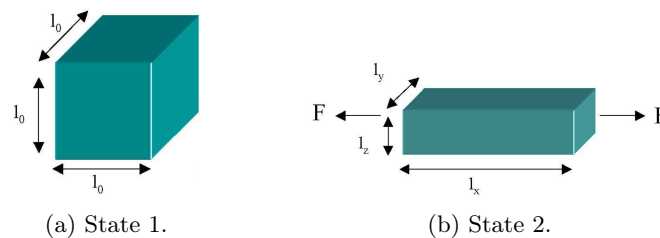


Figure 4.2: Uniaxial deformation of a rubber.

- In this case, α_x is our independent variable. In particular, α_y, α_z depend on it via

$$\alpha_y = \alpha_z = \alpha_x^{-1/2}$$

- This is called a **Poisson contraction** in the lateral directions, and arises from the mathematical formulation of Assumption 8 (i.e., $\alpha_x \alpha_y \alpha_z = 1$).
- It follows that in this case,

$$\Delta S(\alpha_x) = -\frac{k_B}{2} \left(\alpha_x^2 + \frac{1}{\alpha_x} + \frac{1}{\alpha_x} - 3 \right)$$

- Thus, the entropic spring force / restoring force in the x -direction provided by a single chain is

$$\begin{aligned} F_x &= -T \frac{\partial \Delta S}{\partial R_x} \\ &= -T \frac{\partial \Delta S}{\partial \alpha_x} \cdot \frac{\partial \alpha_x}{\partial R_x} \\ &= \frac{k_B T}{2} \frac{\partial}{\partial \alpha_x} \left(\alpha_x^2 + \frac{1}{\alpha_x} + \frac{1}{\alpha_x} - 3 \right) \cdot \frac{\partial}{\partial R_x} \left(\frac{R_x}{R_{x0}} \right) \\ &= \frac{k_B T}{2} \left(2\alpha_x - \frac{2}{\alpha_x^2} \right) \cdot \frac{1}{R_{x0}} \\ &= \frac{k_B T}{R_{x0}} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \end{aligned}$$

- The first term is Hookean ($F \propto \alpha_x$) and corresponds to the penalty for stretching.
- The second term is the correction for compressing the other two dimensions.
- We now seek to scale this microscopic result up to the full macroscopic rubber.
 - Let the full rubber contain z subchains identical to the one we've analyzed, each of which contributes equally to the entropic spring force. Then the total change in entropy upon stretching the rubber is

$$\Delta S_{\text{tot}} = -\frac{z k_B}{2} \left(\alpha_x^2 + \frac{2}{\alpha_x} - 3 \right)$$

- This time, since we have a different system under study, we will need to differentiate with respect to the length of the *rubber* instead of the length of the *polymer*. Analogously to before, this affords

$$F_{x,\text{tot}} = -T \frac{\partial \Delta S_{\text{tot}}}{\partial l_x} = \frac{z k_B T}{l_{x0}} \left(\alpha_x - \frac{1}{\alpha_x^2} \right)$$

- Now the full stress-strain relationship for the rubber is given by a tensor. The entry σ_{xx} , specifically, is the whole rubber's restoring force $F_{x,\text{tot}}$ divided by its cross-sectional area A_0 when unstretched. We now seek to couch the above equation in terms of these new variables.
- To do so, first let V denoted the total volume of the rubber. Then z/V is the number of subchains per unit volume. It follows by dimensional analysis (as in Lecture 3.1) that

$$\frac{z}{V} = \frac{\rho N_A}{M_x}$$

where ρ is the density of the material in g/L and M_x is the number-average molecular weight of the subchains in g/mol.

- Therefore, the stress in terms of observables is

$$\begin{aligned} \sigma_{xx}(\alpha_x) &= \frac{z k_B T}{A_0 l_{x0}} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \\ &= \frac{z k_B T}{V} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \\ &= \frac{\rho N_A k_B T}{M_x} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \end{aligned}$$

- Note that we could also derive the same equation by considering $F_x/(R_{y0}R_{z0})$, as then we would have $1/\langle R^2 \rangle^{3/2} = \rho N_A/M_x$ instead of z/V equals that. This essentially says that the total number of subchains divided by the total volume equals the volume of one subchain divided by its volume.

- **Young's modulus:** The instantaneous stress per strain of a material when you just begin straining it. Denoted by E . Given by

$$E := \lim_{\alpha_x \rightarrow 1} \frac{d\sigma_{xx}}{d\alpha_x}$$

- Let's now investigate the stress σ vs. strain α for the uniaxial deformation case we've been considering.
 - Evaluating the limit, we obtain

$$\begin{aligned} E &= \lim_{\alpha_x \rightarrow 1} \frac{d}{d\alpha_x} \left[\frac{\rho RT}{M_x} \left(\alpha_x - \frac{1}{\alpha_x^2} \right) \right] \\ &= \lim_{\alpha_x \rightarrow 1} \frac{\rho RT}{M_x} \left(1 + \frac{2}{\alpha_x^3} \right) \\ &= \frac{\rho RT}{M_x} \left(1 + \frac{2}{1^3} \right) \\ &= \frac{3\rho RT}{M_x} \end{aligned}$$

- In reality, the prefactor is lower than 3. People like to bring this 3 into an “effective” molecular weight, which is a variant on M_x .
- Notice: The Young's modulus is directly proportional to temperature, and inversely proportional to subchain molecular weight.
- It also follows that to measure the subchain molecular weight M_x , we need only measure the Young's modulus!
- Real-world example: Blowing a hairdryer on an extended rubber band will make it shrink up.
- Comparing our theoretical behavior of elastomers under uniaxial deformation to their real-life behavior.

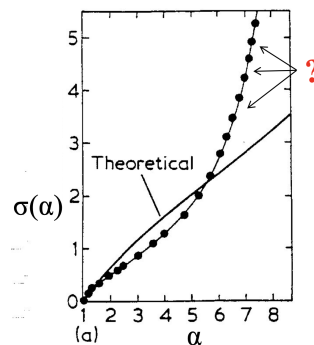


Figure 4.3: Real uniaxial deformation behavior.

- We will not discuss the softening under the curve at low strains α . However, the hardening above the curve at high strains α is something we can discuss.
- Essentially, when a rubber is almost all stretched, we start stretching bonds (violating Assumption 4). This leads to the empirically observed toughening.
- Demonstration: Violating Assumption 7 in real life.

- Two students at the front of class stretch a rubber band as far as they can without breaking it, and then Alfredo starts making a small cut in the middle with a pair of scissors. The crack does not propagate. However, when the students let the rubber band relax, wait a little while, and then try to restretch it, the crack propagates further and it breaks then. Why does this happen?
- When everything's in the trans conformation (stretched rubber band), you start getting crystallization which will add more effective crosslinks. This is why the stretched rubber band won't break even as Alfredo cuts it.
- However, when the students release the strain and then stretch it again, crystallization cannot occur quick enough and the rubber band breaks.
- Now instead of using entropy alone, let's look at a more realistic derivation for the length of a subchain as a function of the stretching force applied to it.

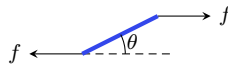


Figure 4.4: Stretching a single bond in a subchain.

- Consider a single bond defined by the vector \mathbf{l} , which is being stretched by a force f in each direction at both ends (Figure 4.4).
- We still assume that $\mathbf{R} = \sum \mathbf{l}$.
- How much work W do we do by rotating the bond an angle θ away from equilibrium?

$$W(\theta) = f \Delta d = f \cdot l \sin \theta$$

- We get the above from the definition of work as force times distance (for constant forces), and a bit of trigonometry to get the distance moved in terms of θ .
- We now bring in partition functions from thermodynamics.
 - The probability that a chain link will be at angle θ from the ideal is $e^{-U(\theta)/k_B T}$, where $U(\theta) = W(\theta)$.
 - Then we average over all possible lengths of this bond ($-l$ to l , indexed by θ), weighted by the Boltzmann probability of the length occurring.

$$\langle l \rangle = \frac{1}{\int_0^\pi e^{-U(\theta)/k_B T} d\theta} \int_0^\pi l \cos \theta e^{-U(\theta)/k_B T} d\theta = l \left(\coth \beta - \frac{1}{\beta} \right)$$

- Sum over all N bonds affords

$$\langle R \rangle = Nl \left(\coth \beta - \frac{1}{\beta} \right)$$

where $\beta = fl/k_B T$ is the **relative force**.

- Thus, putting everything together, we can consider two approximate behavioral regimes for stretching a chain.
 - Up until about 20% stretching ($\beta \ll 1$), everything is pretty linear and Hookean. We can use our purely entropic model here.
 - Note that by 20% stretching, we mean stretching the chain to 20% of its maximum length. Symbolically, we mean stretching from $\langle R_0^2 \rangle^{1/2}$ up to $0.2R_{\max}$.
 - But as the force becomes very large ($\beta \gg 1$), we cannot extend beyond the total length of the system. Here, we need the Figure 4.4 derivation.
 - Force rises faster in these more stretched regimes because we don't have so much "rope to give." In other words, we have very few conformations left available to us.

- Note that if N is large, 20% elongation may be a pretty substantial stretch. This is because $R_0 = N^{1/2}b$ and $R_{\max} = Nb$ collectively imply that

$$\frac{R_0}{R_{\max}} = N^{-1/2}$$

- Let's now see how well our two-regime model matches empirically obtained data.
 - Ortiz and Hadziioannou (1999) used atomic force microscopy (AFM) to stretch a single chain of PMMA.
 - Back in the '90s, people were using AFM for everything.
 - The data they found matched the entropic FJC model really well up to about 20%, and then matched the Figure 4.4 one past that pretty well!
 - Note that the stretching force they applied to the single polymer was on the scale of nanonewtons
 - A nanonewton of force is *not* a small quantity of force on a molecular scale.
 - For context, ligand-receptor bindings are on the scale of high femptonewtons to low piconewtons. van der Waals forces are on the scale of femptonewtons.
 - Thus, a nanonewton is a really strong force; that's about when we start breaking covalent C–C bonds! In other words, they had to put enough force on the polymer that it was about to break in order to get it past 20% elongation!
- Next time.
 - Gels (probs the whole class and a bit of the next one). These get more complicated, and there are more factors.