

# 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 0.1: Chichén Itaá (ancient Mayan place) and natural rubber basquetbol.
  - 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!

- Rubber elasticity assumptions.

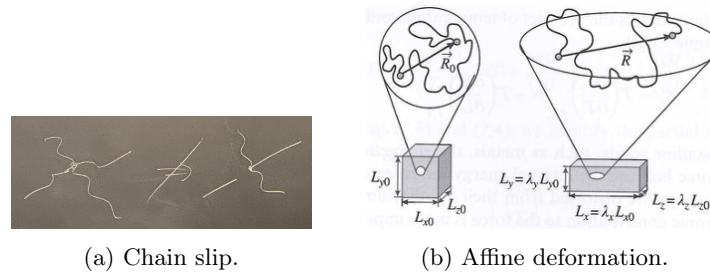


Figure 4.1: Rubber elasticity assumptions.

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  $\phi$  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  $\alpha_i, \lambda_i$ . 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  $i^{\text{th}}$  component of these vectors.

- On notation, Alfredo uses  $\alpha$  while the book uses  $\lambda$ . 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  $\alpha_i$ .
  - Assumption 6, mathematically, is that the macro and micro definitions of  $\alpha_i$  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  $F = 0$ .
    - $\Omega_1$  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  $F > 0$ .
    - $\Omega_2$  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  $\Omega_i$  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  $\Omega_i$  into the  $\Delta S$  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.

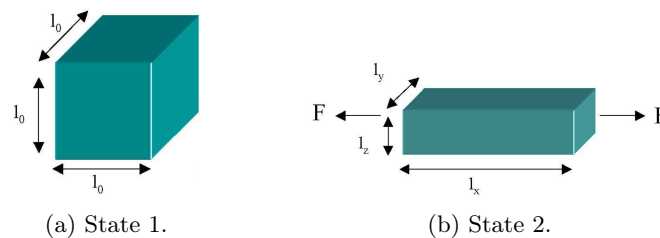


Figure 4.2: Uniaxial deformation of a rubber.

- In this case,  $\alpha_x$  is our independent variable. In particular,  $\alpha_y, \alpha_z$  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  $\sigma_{xx}$ , 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  $\rho$  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  $\sigma$  vs. strain  $\alpha$  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.

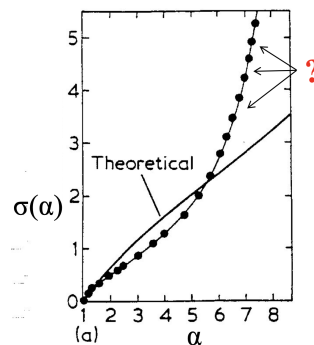


Figure 4.3: Real uniaxial deformation behavior.

- We will not discuss the softening under the curve at low strains  $\alpha$ . However, the hardening above the curve at high strains  $\alpha$  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.

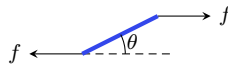


Figure 4.4: Stretching a single bond in a subchain.

- 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  $\theta$  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  $\theta$ .
- We now bring in partition functions from thermodynamics.
  - The probability that a chain link will be at angle  $\theta$  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  $\theta$ ), 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.

## 4.2 Neutral Gels

- 10/23: • Most gels we think about are water-based, e.g., diapers, Jello, and contact lenses.

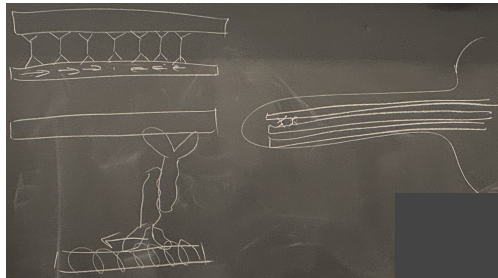


Figure 4.5: The flagellar motion of a sperm's tail is driven by polymer physics!

- Diapers absorb *a lot* of water.
  - Over the course of lecture, Alfredo will pour about 2 liters of water into a standard diaper.
  - Note, however, that this maximum swelling does take time — when your kids pee all at once, the diaper will not absorb it all instantly!
- Biological gels: Mucus.
  - Home chemistry: Take a booger out, put it in water, and see what happens.
  - This happens because boogers' heavily glycosylated (sugar) chains expand significantly.
- Active biological gels (ABGs): Cells!
  - Cells contain many (typically living) polymers.



- Examples (from stiffest to least stiff): Microtubules, actin, peptides or ssRNA.
  - Recall these from Lecture 1.2 on persistence length.
- Example cellular motion controlled by an active gel: The tail of a sperm (Figure 4.5).
  - These contain molecular motors (e.g., dyneins and kinesins) that walk along a microtubule filament.
  - Motor proteins know which direction to walk along a microtubule because microtubules are helical, and the helix has an orientation!
  - Flagellar motion of the tail occurs by the walking of kinesins both toward the same part of the membrane, which induces buckeling.
- Example: Nature-inspired ABG.
  - Self-propagating Belousov-Zhabotinsky reaction.
  - Reference: Chen et al. (2011).
- This concludes the introduction; we now begin the lecture content in earnest.
- **Gel:** A highly swollen network.
- Several ways to form a gel.
  - Start with a monomer melt and link the monomers into a 3D network (e.g., S-*co*-DVB), then swell it with a solvent.
    - S-*co*-DVB is hydrophobic (swell it with an organic solvent).
    - PEG is hydrophilic (swell it with water).
  - Start with a polymer-solvent solution and induce network formation, e.g., crosslink the polymer via...
    - Radiation (UV, electron beam);
      - Induces covalent bonds.
    - Chemical means (e.g., S-*co*-DVB);
      - Induces covalent bonds.
    - Physical associations (e.g., noncovalent bonds induced by lowering the temperature or adding a nonsolvent).
      - Example: Collagen forms triple helices when it cools.
- Some gels are classified as responsive molecules.
- Example responsive molecule class: Polyelectrolytes.
  - These undergo a collapse transition in response to solvent quality.
  - Essentially, when the  $pH$  is tuned one way or the other, a polyelectrolyte will either swell or collapse into a globule.
  - Benefits: Tunable polarity, potential for self-assembly, cheap and easy to synthesize.
  - Example: Poly(methacrylic acid).
    - Hydrophilic solvent / high  $pH$  leads to expansion.
    - Hydrophobic solvent / low  $pH$  induces collapse to globules.
- Flory-Rehner theory of gel swelling.

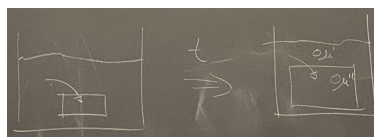


Figure 4.6: Gel swelling schematic.

- Key assumption: The energetic contributions of elasticity and mixing are linearly additive. That is,

$$\Delta G_{\text{tot}} = \Delta G_{\text{mix}} + \Delta G_{\text{elastic}}$$

- We assume a (basically infinite) reservoir of solvent, and we look at how much solvent goes in or out of the system. Solvent will go in until the chemical potential of the solvent is equal both outside and inside the polymer ( $\mu' = \mu''$ ).
- Parameters to consider.
  - A thermodynamically good solvent swells rubber. This involves a favorable  $\chi$  interaction (i.e.,  $\chi < 1/2$ ) and a favorable entropy of mixing.
  - Entropic elasticity of the network (as discussed last lecture) exerts a retractive force to oppose swelling.

- Variables to be aware of in Flory-Rehner theory.

- $\alpha_x = x'/x$  is the linear swelling ratio.
  - We assume extension ratios for swelling are isotropic (the same in every dimension). Thus, we only have one extension ratio  $\alpha_s$  for swelling, defined by

$$\alpha_s := \alpha_x = \alpha_y = \alpha_z$$

- $\phi_2 = V_0/V$  is the volume fraction of the polymer in its swelled volume.
  - $V_0$  is the volume of the polymer globule (containing no solvent, volume is all polymer).
  - $V$  is the final, swelled volume.
- $z = N = \rho N_A V_0 / M_x$  is the number of subchains in the network, i.e., degree of crosslinking.
- $\mu_i = (\partial G_{\text{tot}} / \partial n_i)_{T,P,n_j}$  is the chemical potential of component  $i$ .
- $\mu_1 - \mu_1^\circ$  is the chemical potential difference between the solvent in the gel and the pure solvent.

- Useful mathematical relations between said variables.

- The swelled volume  $V$  scales from the polymer volume via the swelling ratio.

$$V = V_0 \alpha_s^3$$

- An important consequence (we will see why shortly) is that  $\alpha_s^3 = 1/\phi_2$ .
- It follows from the chemical potential equations that

$$\begin{aligned} \mu_1 - \mu_1^\circ &= \left( \frac{\partial \Delta G_{\text{tot}}}{\partial n_1} \right)_{T,P,n_2} \\ &= \left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right)_{T,P,n_2} + \left( \frac{\partial \Delta G_{\text{elastic}}}{\partial n_1} \right)_{T,P,n_2} \\ \mu_1 - \mu_1^\circ &= \left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right)_{T,P,n_2} + \left( \frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha_s} \right) \left( \frac{\partial \alpha_s}{\partial n_1} \right)_{T,P,n_2} \end{aligned}$$

- PSet 2, Q1a evaluated the left term above.
  - Today, we will calculate the right term above.
- In particular, recall from Lecture 2.2 that for a polymer-solvent solution,

$$\left( \frac{\partial \Delta G_{\text{mix}}}{\partial n_1} \right)_{T,P,n_2} = RT(\ln \phi_1 + \phi_2 + \chi_{12} \phi_2^2)$$

- We've gotten rid of the  $-\phi_2/N_2$  term because network crosslinking implies  $N_2 \rightarrow \infty$ .
- Evaluating the  $\Delta G_{\text{elastic}}$  term.

- Recall from last class that the change in entropy per subchain is

$$\frac{\Delta S_{\text{elastic}}}{z} = -\frac{k_B}{2} \left\{ [(\alpha_x^2 + \alpha_y^2 + \alpha_z^2) - 3] - \underbrace{\ln \frac{V}{V_0}}_{\text{new term}} \right\}$$

- The new term corresponds to an additional entropy increase per subchain upon swelling, due to the increased volume that swelling makes available to each subchain.
- The new term turns about to be unimportant, but it isn't that negligible when you get into the details. More precisely, it is the major term when the polymer is dry, but it is not the major term when the polymer is already wet / partially swollen.
- It follows that the whole network's change in Gibbs free energy upon swelling is

$$\Delta G_{\text{elastic}} = -T \Delta S_{\text{elastic}} = \frac{z k_B T}{2} \left( 3\alpha_s^2 - 3 - \ln \frac{V}{V_0} \right)$$

- Now we take derivatives.
- Invoking the chain rule as above, we first investigate

$$\begin{aligned} \frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha} &= \frac{z k_B T}{2} \frac{\partial}{\partial \alpha_s} \left( 3\alpha_s^2 - 3 - \ln \frac{\alpha_s^3 V_0}{V_0} \right) \\ &= \frac{z k_B T}{2} \left( 6\alpha_s - \frac{3\alpha_s^2}{\alpha_s^3} \right) \\ &= \frac{3}{2} z k_B T \left( 2\alpha_s - \frac{1}{\alpha_s} \right) \end{aligned}$$

- To solve other derivative, we must first express  $\alpha$  in terms of  $n_1$  as follows.

$$\alpha_s^3 = \frac{V}{V_0} = \frac{V_0 + n_1 \hat{V}_1}{V_0}$$

- $n_1$  is the number of moles of solvent.
- $\hat{V}_1$  is the molar volume of the solvent.
- Then, using implicit differentiation,

$$\begin{aligned} \frac{\partial}{\partial n_1} (\alpha_s^3) &= \frac{\partial}{\partial n_1} \left( \frac{V_0 + n_1 \hat{V}_1}{V_0} \right) \\ 3\alpha_s^2 \frac{\partial \alpha_s}{\partial n_1} &= \frac{\hat{V}_1}{V_0} \\ \frac{\partial \alpha_s}{\partial n_1} &= \frac{\hat{V}_1}{3\alpha_s^2 V_0} \end{aligned}$$

- Putting everything together, we obtain

$$\begin{aligned} \left( \frac{\partial \Delta G_{\text{elastic}}}{\partial n_1} \right)_{T,P,n_2} &= \left( \frac{\partial \Delta G_{\text{elastic}}}{\partial \alpha_s} \right) \left( \frac{\partial \alpha_s}{\partial n_1} \right)_{T,P,n_2} \\ &= \frac{3}{2} z k_B T \left( 2\alpha_s - \frac{1}{\alpha_s} \right) \cdot \frac{\hat{V}_1}{3\alpha_s^2 V_0} \\ &= \frac{z k_B T \hat{V}_1}{2V_0} \left( \frac{2}{\alpha_s} - \frac{1}{\alpha_s^3} \right) \end{aligned}$$

- We reexpress this in terms of  $\phi_2$  and  $M_x$  using the useful mathematical relations from earlier.

$$\begin{aligned} \left( \frac{\partial \Delta G_{\text{elastic}}}{\partial n_1} \right)_{T,P,n_2} &= \frac{\rho N_A}{M_x} \cdot \frac{k_B T \hat{V}_1}{2} \left[ \frac{2}{(1/\phi_2)^{1/3}} - \frac{1}{1/\phi_2} \right] \\ &= \frac{\rho R T \hat{V}_1}{M_x} \left( \phi_2^{1/3} - \frac{\phi_2}{2} \right) \end{aligned}$$

- It follows that the overall change in chemical potential upon swelling is

$$\frac{\mu_1 - \mu_1^\circ}{RT} = [\ln(1 - \phi_2) + \phi_2 + \chi_{12} \phi_2^2] + \frac{\rho \hat{V}_1}{M_x} \left( \phi_2^{1/3} - \frac{\phi_2}{2} \right)$$

- This is the famous Flory-Rehner theory of gel swelling.

- Once the optimal swelling has been achieved,  $\mu_1 = \mu_1^\circ$  (that is,  $\mu_1 - \mu_1^\circ = 0$ ). Let's plug this into the Flory-Rehner theory and solve for  $\phi_2$ .

- First, let's assume  $\phi_2 \ll 1$  and expand the logarithm in the Flory-Rehner equation to two terms, as in Lecture 2.2. This affords

$$-\phi_2 - \frac{\phi_2^2}{2} + \phi_2 + \chi \phi_2^2 = -\frac{\rho \hat{V}_1}{M_x} \left( \phi_2^{1/3} - \frac{\phi_2}{2} \right)$$

- If  $\phi_2 \ll 1$ , then  $\phi_2^{1/3} \gg \phi_2/2$ . Thus, we may neglect the rightmost term above to obtain

$$\phi_2^2 \left( \chi - \frac{1}{2} \right) = -\frac{\rho \hat{V}_1 \phi_2^{1/3}}{M_x}$$

- The right term above is negative, so for the left term above to be negative, we must have  $\chi < 1/2$ ! This is how the math expresses our intuition that the polymer must be soluble in the solvent in order for swelling to occur.

- Knowing  $\chi < 1/2$ , we may write

$$\begin{aligned} \phi_2^2 \left| \chi - \frac{1}{2} \right| &= \frac{\rho \hat{V}_1 \phi_2^{1/3}}{M_x} \\ \phi_2^{5/3} &= \frac{\rho \hat{V}_1}{M_x} \cdot \frac{1}{\left| \chi - \frac{1}{2} \right|} \end{aligned}$$

- It follows that the variables we can tweak to control swelling are (1) the subchain molecular weight  $M_x$  and (2) making  $|\chi - 1/2|$  large.

➤ Moreover, since  $\chi$  can't be changed that much, it's really down to  $M_x$ .

- If you want the material to swell by 2x, you need  $M_x$  to grow by almost 4x because of the 3/5 exponent.

- Remember that doubling the volume is equivalent to changing the lateral parameters by  $\alpha = 2^{1/3}$ . Thus, to double the lateral parameters, you will need to *octuple* the volume.

- $\phi_2 = \alpha^{-3}$ , so

$$\begin{aligned} \frac{1}{\alpha^3} &= \left( \frac{\rho \hat{V}_1}{M_x f(\chi)} \right)^{3/5} \\ \alpha &\propto M_x^{1/5} f(\chi)^{1/5} \end{aligned}$$

where  $f(\chi) = 1/|\chi - 1/2|$  shorthands the relevant function of  $\chi$ .

- Implication: You have to change the molecular weight by *a lot* in order to affect the swelling.

- Applications of gels: Contact lenses.

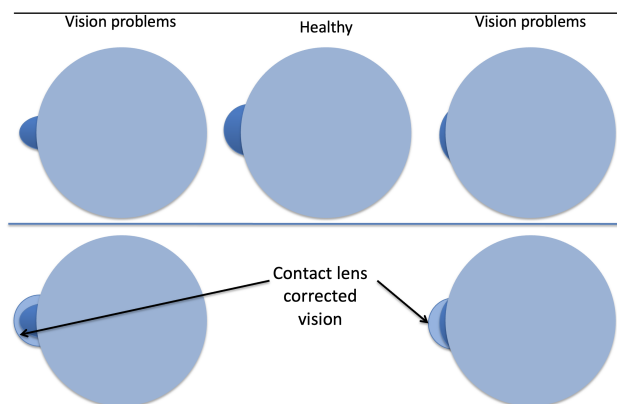


Figure 4.7: Contact lenses' mechanism of action.

- These are crosslinked hydrogels.
- How contact lenses work.
  - Different eye shapes give different refractions that need to be neutralized.

### 4.3 Ionic Gels

10/28:

- Lecture outline.
  - Estimate swelling with Flory-Rehner theory.
  - Compute charged interactions.
  - Evaluate swelling of charged gels.
- We begin by estimating the extent of swelling for gels we're likely to encounter.
  - Recall from last time that if  $\phi_2 \ll 1$ , then the equilibrium swelling is

$$\phi_2 = \left( \frac{\rho \hat{V}_1}{M_x} \cdot \frac{1}{|\chi - \frac{1}{2}|} \right)^{3/5}$$

- Approximations of the quantities.
  - $1/f(\chi) \approx 2$  is a constant on the order of 1, so we'll neglect it outright.
  - $\rho \approx 1 \text{ g/mL} = 10^3 \text{ kg/m}^3$  for most polymers (i.e., pretty close to that of water).
  - $\hat{V}_1 \approx N_A \cdot 100 \text{ \AA}^3$ .
  - $M_x \approx 10^3\text{-}10^5 \text{ g/mol}$ .
- Let's now put all the approximations together, first assuming relatively short subchains.

$$\phi_2 \approx \left[ \frac{(10^3 \text{ kg m}^{-3})(6 \times 10^{23} \text{ mol}^{-1})(100 \times 10^{-30} \text{ m}^3)}{1 \text{ kg mol}^{-1}} \right]^{3/5} = (6 \times 10^{-2})^{3/5} \approx 0.18$$

- Increasing  $M_x$  two orders of magnitude yields 0.01 as our approximation.
- Thus, we range from about 80% of the volume being solvent to almost 99%.
- We now move onto charged gels.
  - Recall that the  $\text{p}K_a$  is the pH at which a group becomes charged.

- What groups are useful for creating charged gels?
  - Carboxylic acids.
    - Deprotonate to contribute an anionic group to the gel.
    - $pK_a \approx 4-5$ .
  - Amines.
    - Protonate to contribute a cationic group to the gel.
    - $pK_a \approx 10-12$ .
  - Sulfonates.
    - Deprotonate.
    - $pK_a \approx 0$ .
- What is the  $pK_a$  of a polyelectrolyte, e.g., polyacrylic acid?
  - The  $pK_a$  of the polyelectrolyte is *higher* than that of a monoelectrolyte.
  - This is because the like charges generated don't want to be in close proximity; rather, they have to pay an electrostatic (energetic) penalty to be so close.
  - The  $pK_a$  of a given polyelectrolyte will depend on the rigidity of the chain, how far apart all of the ionizable monomers are, etc.
- Now consider a charged gel.

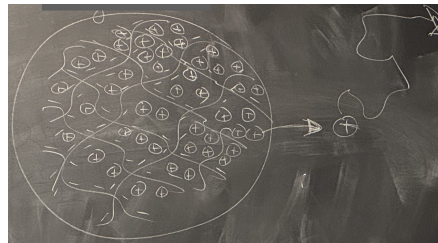


Figure 4.8: A negatively charged gel.

- Since the gel is negatively charged along its backbones, it will have intercalating positive charges.
- Since there is no wall at the edge of the gel, the counterions are not trapped; rather, they can move out into the rest of solution! What we are interested in understanding is how many leave the gel.
- To address this question, let's begin by calculating the energy of a pair of charges.

$$U_{\text{elec}} = \frac{q_+ q_-}{4\pi\epsilon r}$$

- $\epsilon$  is the permittivity of the solvent (as in Lecture 3.5).
- This expression allows us to define the **Bjerrum length**.
- Let's now return to the gel. How much energy does it take to move a charge from the border of the gel to just outside of it?
  - Let  $Q_{\text{macro}}$  denote the charge of the gel *after* the one charge leaves it, and let  $R$  denote the radius of the gel.
    - Since a single positive charge is leaving the gel (as in Figure 4.8), the gel will have a net negative charge afterwards. In other words,  $Q_{\text{macro}}$  is equal to the opposite of the charge on the one leaving charge.

- Once the single charge leaves, what we essentially have is two charges of equal magnitude separated by a distance equal to (just over) the radius of the gel. Symbolically,

$$U_{\text{elec}} = \frac{Q_{\text{macro}}^2}{4\pi\epsilon R}$$

- Dividing through by  $k_B T$ , we obtain

$$\frac{U_{\text{elec}}}{k_B T} = \frac{Q_{\text{macro}}^2}{4\pi\epsilon R k_B T} = \frac{\ell_B}{R}$$

- If  $Q_{\text{macro}} \cdot \ell_B / R > 1$ , then “no” charges will leave the gel?? So  $Q_{\text{macro}} > R/\ell_B$ .
- Let  $Q_{\text{tot}}$  denote the original number of charges in the gel. What is the ratio  $Q_{\text{macro}}/Q_{\text{tot}}$ ?
  - Let  $v$  denote the volume of a monomer (assumed to be the same for polymer and solvent). Additionally, let’s expand our definition of  $Q_{\text{macro}}$  to mean the total charge of the gel after many potential departures.
  - If the gel is dry, it will contain  $V_0/v$  monomers.
  - It follows that the number of *ionized* monomers in it is  $fV_0/v$ , where  $f$  is the **degree of ionization**.
  - Multiplying by  $V/V = 1$  and simplify using  $V_0/V = 1/\phi_2$  ( $V_0/V = \phi_2$ , as defined last lecture??), we obtain

$$Q_{\text{tot}} = \frac{fV_0}{v} \cdot \frac{V}{V} = \frac{fV}{v\phi_2}$$

- This combined with the fact that  $Q_{\text{macro}} \propto \ell_B/R$  yields

$$\frac{Q_{\text{macro}}}{Q_{\text{tot}}} = \frac{R/\ell_B}{fV/v\phi_2} \propto \frac{R/\ell_B}{fR^3/v\phi_2} = \frac{\phi_2 v}{f\ell_B R^2}$$

where we have invoked  $V \propto R^3$ .

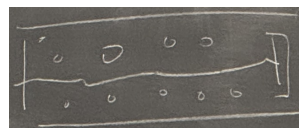
- Ultimately, this quantity will simplify our lives when we want to calculate swelling of charged gels.
- **Bjerrum length:** The distance  $r$  at which  $U_{\text{elec}} = k_B T$ . Denoted by  $r_B, \ell_B$ . Given by

$$\ell_B = \frac{|q_+ q_-|}{4\pi\epsilon k_B T}$$

- Example: The  $\ell_B$  of water is about  $7 \text{ \AA}$ . This means that two charges in water that are closer than  $7 \text{ \AA}$  have a stronger interaction than  $k_B T$ . If they’re farther apart, their interaction is less (so thermal noise will easily destroy that interaction).
- **Degree of ionization:** The number of charged groups per polymer divided by the number of monomers per polymer. Denoted by  $f$ .
- We can now calculate the swelling of a charged gel. Assume the gel is electroneutral.
- In many ways, we will see that our gel is analogous to a piston.



(a) Contracted piston.



(b) Expanded piston.

Figure 4.9: Piston-like view of a charged gel.

- The push out is the “gas” of ions pushing against the boundaries of the gel.
  - We don’t have to worry about electrostatics because we’re assuming charge neutrality.
  - Pressure on the boundary of the gel is maintained by the electrostatic force we derived above, which arises if charges flow out.
- The pull in is the entropic spring force of the chains in the network.
- What we want to answer is, “how much will a chain stretch against the effect of the interactions of charged particles in the system?”
- Let’s calculate the free energy of the system.
  - We have a solvent, a polymer, and the free energy of the gas that wants to expand. So

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{elastic}} + \Delta G_{\text{ideal gas of counterions}}$$

- Flory-Huggins treated  $\Delta G_{\text{mix}}$  and Flory-Rehner treated  $\Delta G_{\text{elastic}}$ , but what about the last term? In this case, recall from thermodynamics that the reversible work done by expanding an ideal gas isothermally (constant  $T$ ) is given by

$$\begin{aligned}\Delta G &= \int_{V_0}^V P \, dV \\ &= \int_{V_0}^V \frac{N_{\text{counterions}} k_B T}{V} \, dV \\ \frac{\Delta G}{k_B T} &= N_{\text{counterions}} \ln \frac{V}{V_0}\end{aligned}$$

- This form is analogous to the “new term” from last time!
  - Last time, this term was irrelevant. It’s not irrelevant now, though, because it is multiplied by the total number of counterions in the gel!
- So if we bash out the math, we get analogously to last time that

$$\left(\chi - \frac{1}{2}\right) \phi_2^2 = -\frac{\rho \hat{V}_1}{M_x} \left(\phi_2^{1/3} - \frac{\phi_2}{2} - \frac{f N_x \phi_2}{2}\right)$$

- Is  $N_x = N_{\text{counterions}}$ ?? Do we need to know anything else about this derivation?
  - Major physical implication of this equation:  $\chi$  can be bigger than 1/2.
    - Essentially, we can dissolve gels that wouldn’t otherwise want to dissolve in a given solvent *because* of the force of ions pushing out.
    - This makes sense as the ion pressure should “push outward,” creating more room for solvent.
  - The rightmost term will, in fact, be a dominant term for a charged gel.
- Consider the piston with a semipermeable membrane that does not allow the “gas” molecules to pass through.
  - Let the cylinder have base area  $A$  and height  $H$ .
  - The pressure from the gas is

$$P_{\text{gas}} = \frac{N_{\text{counterions}} k_B T}{V} = \frac{f n N k_B T}{V}$$

- $f$  is the degree of ionization,  $n$  is the number of chains, and  $N$  is the degree of polymerization of each chain.



- On the other hand, recall from Lecture 1.3 that the elastic force  $F$  generated by a single polymer chain is

$$F \propto \frac{k_{\text{B}}TH}{Nb^2}$$

- $b$  is a Kuhn length.
- Thus since  $V = AH$ , the pressure (force/area) for all  $n$  chains is

$$P_{\text{elastic}} = \frac{nF}{A} = \frac{nk_{\text{B}}TH}{Nb^2A} = \frac{nk_{\text{B}}TH^2}{Nb^2V}$$

- Then

$$\begin{aligned} P_{\text{gas}} &= P_{\text{elastic}} \\ \frac{fnNk_{\text{B}}T}{V} &= \frac{nk_{\text{B}}TH^2}{Nb^2V} \\ fN^2 &= \frac{H^2}{b^2} \\ H &\propto Nb f^{1/2} \end{aligned}$$

- Takeaway: This **counterion pressure** is huge.
- What resources can I read about all of this?? It doesn't appear to be in any of our textbooks, and internet resources appear to often be too in depth.
- Announcements.
  - Office hours time tomorrow and Friday.
  - PSet 4 deadline extended to Sunday night.