

## Topic 1

# The Macromolecule

### 1.1 The Macromolecule

9/9:

- Pat Doyle begins; he will teach the next three lectures.
  - They've broken the class up into modules taught alternatingly.
  - Aside: Alfredo has taught this course 10 times; Doyle never has (he's replacing Greg Rutledge this year).
- Announcements.
  - Slides and homework 1 have been posted.
  - Slides should be posted before lecture, but may not be posted much before.
- Lecture outline.
  - Connectivity: Thermodynamic limit, architecture, and molecular weight.
  - Configurations: Structural, chemical, stereo, and geometrical isomerism.
  - Conformations: Rotational isomeric states.
- **Connectivity:** The joining of small parts (monomers) into larger molecules (polymers).
- **Degree of polymerization:** The number of repeat units in a polymer. *Denoted by  $N$ .*
  - Derivable from the molecular weight(s).
- Example: Polyethylene.
  - In this course, vinyl examples will be our workhorses, but we will “riff off of them” to other polymer types.
  - The **repeat unit** here is  $\text{CH}_2\text{CH}_2$ , consistent with the IUPAC nomenclature of polyethylene.
  - Ethylene is also the monomer.
  - The end groups do look different, but the **thermodynamic limit** addresses them.
- **Repeat unit:** A part of a polymer whose repetition would produce the complete polymer chain (except for the end groups) by linking the repeat units together successively along a chain.
- **Thermodynamic limit:** The finding that as  $N \rightarrow \infty$ , the end group chemistry matters less. *Also known as polymer limit.*
  - The thermodynamic limit is also sometimes discussed in the context of statistical mechanics, where collective behavior also matters more than individual or picoscale.

- **Glass transition temperature:** The temperature at which a substance will go from brittle to kind of rubbery. *Denoted by  $T_g$ .*
- **Flory-Fox correlation:** The simple model that the  $T_g$  of a polymer asymptotically approaches a limit  $T_g(M \rightarrow \infty)$  for higher and higher molecular weights at some empirically derived rate  $A$ . *Given by*

$$T_g(M_n) := T_g(M \rightarrow \infty) - \frac{A}{M_n}$$

- Alkane series often obey this simple  $1/x$  relation.
- Another example of thermodynamic limits: Regardless of polymer structure, a power law defines polymer viscosity.

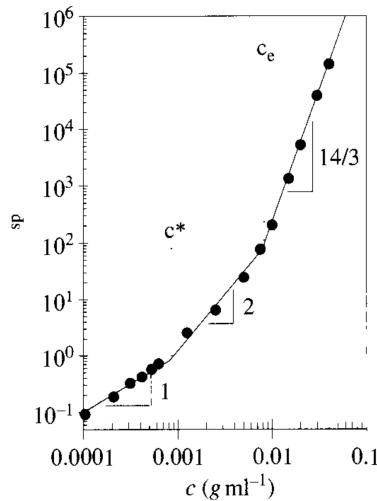


Figure 1.1: Polymer viscosity scales universally by power laws.

- Namely, polymer viscosity increases up to a critical concentration  $c^*$  at a slope of 1, then to an entanglement concentration  $c_e$  at a slope of 2, and then at a slope of  $14/3$  past that.
- Thus, there are three universal scaling regimes.
- A log-log plot is used to show power-law scalings, like in high school trigonometry!
- Aside: Power laws are present everywhere once you get big enough, down to the volume of our lungs relative to our bodies in bigger and bigger animals.
- This class isn't super stringent on nomenclature, but it's good to know terms for when we read papers (Table 1.1).
  - Alfredo will talk about block copolymers a good bit!
- Polymer architectures.
  - Linear polymers.
    - Polyrotaxanes and other supramolecular assemblies can have interesting properties. Example: Catenated DNA!
    - Cross-linked systems (nice gelation).
    - Branched polymers can have a single monomer, or multiple as in graft (Table 1.1).
    - Dendritic polymers have different generations with regular branching for very dense structures.
    - There are a few more classes, as well.

| Copolymer type | Arrangement of monomeric units                              | Representation   | Connective       | Example  |
|----------------|---|--|------------------|--|
| unspecified    | unknown or unspecified                                      | (A- <i>co</i> -B)  | - <i>co</i> -    | poly[styrene- <i>co</i> -(methyl methacrylate)]                            |
| statistical    | obeys known statistical laws                                | (A- <i>stat</i> -B- <i>stat</i> -C)  | - <i>stat</i> -  | poly(styrene- <i>stat</i> -acrylonitrile- <i>stat</i> -butadiene)          |
| random         | obeys Bernoullian statistics                                | (A- <i>ran</i> -B)   | - <i>ran</i> -   | poly[ethene- <i>ran</i> -(vinyl acetate)]                                  |
| alternating    | alternating   | (AB) <sub>n</sub>  | - <i>alt</i> -   | poly[(ethylene glycol) <sup>a</sup> - <i>alt</i> -(terephthalic acid)]     |
| periodic       | periodic with respect to at least three monomeric units     | (ABC) <sub>n</sub><br>(ABB) <sub>n</sub><br>(AABB) <sub>n</sub><br>(ABAC) <sub>n</sub> | - <i>per</i> -   | poly[formaldehyde- <i>per</i> -(ethene oxide)- <i>per</i> -(ethene oxide)] |
| block          | linear arrangement of blocks                                | -AAAAA-BBBBB-  | - <i>block</i> - | polystyrene- <i>block</i> -polybutadiene                                   |
| graft          | polymeric side chain different from main chain <sup>b</sup> | -AAAAAAAAAA-<br> <br>B<br>B<br>B<br>B<br>B<br>   | - <i>graft</i> - | polybutadiene- <i>graft</i> -polystyrene                                   |

<sup>a</sup> ethane-1,2-diol, <sup>b</sup> main chain (backbone) is specified first in the name.

Table 1.1: IUPAC nomenclature of copolymers.

- We'll now discuss some nomenclature on molecular weight.
- Aside: Other than nature, synthetic chemists cannot make dispersity 1 polymers; “polymer chemists aren't gods, despite some thinking they are.”
- ***i*-mer:** A segment of a polymer with degree of polymeriation *i*.
- ***M<sub>i</sub>*:** The molecular weight of the *i*-mer. *Given by*

$$M_i := iM_0$$

- ***M<sub>0</sub>*:** The molecular weight of the repeat unit in a polymer chain.
- ***n<sub>i</sub>*:** The number of *i*-mers.
- **Number fraction** (of an *i*-mer): The probability of picking an *i*-mer out of solution when picking a chain. *Denoted by *x<sub>i</sub>*. Given by*

$$x_i := \frac{n_i}{\sum_i n_i}$$

- **Weight fraction** (of an *i*-mer): The probability that a repeat unit picked out of solution belongs to an *i*-mer. *Also known as mass fraction. Denoted by *w<sub>i</sub>*. Given by*

$$w_i := \frac{n_i M_i}{\sum_i n_i M_i} = \frac{n_i (iM_0)}{\sum_i n_i (iM_0)} = \frac{i n_i}{\sum_i i n_i}$$

- Note that *i n<sub>i</sub>* is the total number of monomers in the *i*-mer, and  $\sum_i i n_i$  is the total number of monomers in solution.
- **Number-average molecular weight:** The arithmetic mean of the molecular masses of the individual macromolecules. *Denoted by *M<sub>n</sub>*. Given by*

$$M_n := \sum_i x_i M_i = M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i}$$

- **Weight average molecular weight:** A measurement of molecular weight that gives more contribution to higher-weight molecules. *Denoted by  $M_w$ . Given by*

$$M_w := \sum_i w_i M_i = M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i}$$

- Both  $M_n$  and  $M_w$  look like moments of a distribution (i.e., first and second moment).
  - We could generalize even more, but we don't need to.
  - However, to figure out if we have a tight or wide distribution, we often look at ratios of our moments. This leads to the following definition.
- **Dispersity:** A measure of the breadth of the distribution of fragment molecular weights in a polymer sample. *Also known as polydispersity index, PDI. Denoted by  $D$ . Given by*

$$D := \frac{M_w}{M_n} = \frac{\text{second moment}}{\text{first moment}}$$

- In Lodge and Hiemenz (2020), they also derive the **variance**. You don't need to worry about the math, though.
- **Variance:** Another measure of the breadth of the distribution of fragment molecular weights. *Denoted by  $\sigma^2$ . Given by*

$$\sigma^2 := M_n^2[D - 1]$$

- **Schulz-Zimm distribution:** An idealized mathematical model for polymer molecular weight distribution.
- With these definitions, we can now do homework problem number 1!
- Experimental techniques to measure molecular weight.
  - Size exclusion chromatography.
  - Osmotic pressure.
  - End group analysis.
  - Light scattering techniques.
    - More sensitive to higher moments.
- We now move onto polymer configurations.

- **Configurations:** The way things are connected or bonded together.
  - Physicists and chemists have many competing definitions of “configurations,” but the one above is what we'll use in this class. Essentially, think of it as a synonym for constitutional isomerism.
  - Under this definition, you have to *break bonds* to create a new configuration.
  - We are *not* yet talking about rotamers (what we'll call **conformations**). As you make your polymers longer and longer, the conformational space you can explore gets bigger.
- There are 3 main types of structural isomers (i.e., configurations): **Positional, stereo, and geometric** isomers.
- **Positional** (isomers): Changing connectivity.
- **Stereoisomers:** Related to chiral centers.
- **Geometric** (isomers): Related to double bonds.

- More on positional isomers.

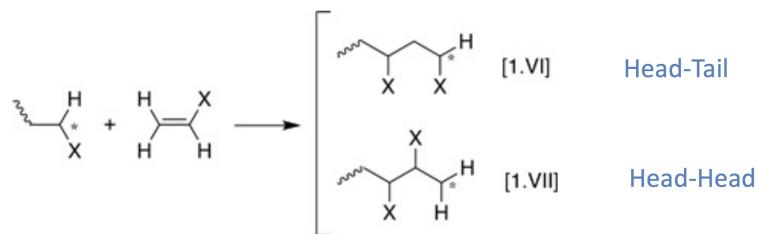


Figure 1.2: Head-head and head-tail monomer addition.

- **Head-head** vs. **head-tail** bonding in vinyl monomers.
- Head-tail is more common, and differences can change the  $T_g$  substantially.
- **Head-head** (orientation): Monomer addition wherein the substituted carbon attaches to the growing chain end. *Also known as head-to-head*.
- **Head-tail** (orientation): Monomer addition wherein the unsubstituted carbon attaches to the growing chain end. *Also known as head-to-tail*.
- More on stereoisomers.
- Doyle reviews **chirality**, **rectus** vs. **sinister**, and the **Cahn-Ingold-Prelog nomenclature**.
- **Pseudochiral** (center): A chiral center where two of the substituents are identical *except* for chirality.
  - In this case, CIP nomenclature gives priority to the branch with more R chiral centers.
- Chiral centers in polymers give rise to **tacticity**.

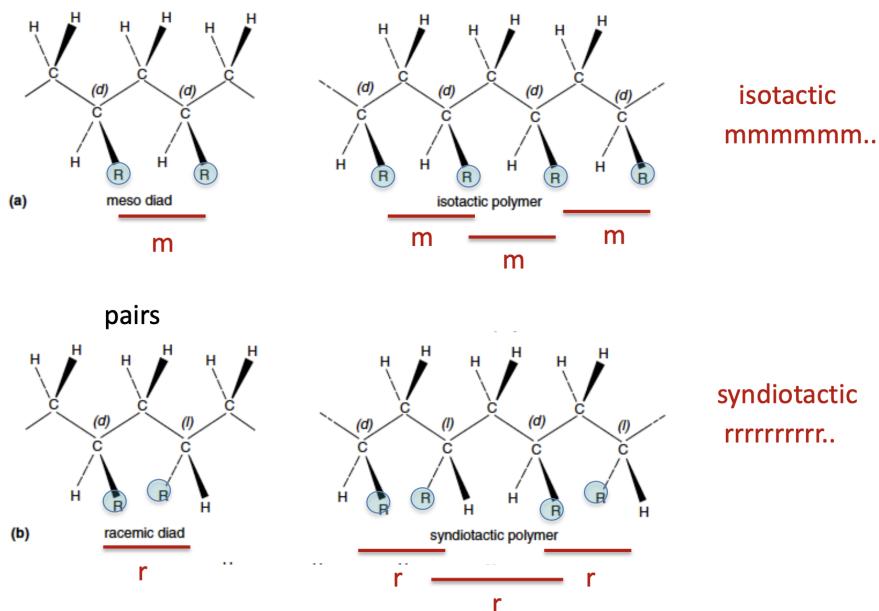


Figure 1.3: Tacticity.

- There are **meso diads** and **racemic diads**; which ones you have determine if the polymer is **isotactic**, **syndiotactic**, or **atactic**.

- **Meso** (diad): Two adjacent chiral centers with a local plane of symmetry halfway between them.
- **Racemic** (diad): Two adjacent chiral centers *without* a local plane of symmetry halfway between them.
- **Isotactic** (polymer): A polymer containing only meso diads.
- **Syndiotactic** (polymer): A polymer containing only racemic diads.
- **Atactic** (polymer): A polymer containing both meso and racemic diads.
- Example: Atactic polystyrene tends to be more amorphous than syndiotactic or isotactic polymers, which can be semicrystalline.
  - Nobel prize (1963) to Ziegler and Natta for a catalyst generating isotactic polystyrene (PS-it).
    - Note that the initial Ziegler-Natta catalysts weren't metallocenes! The introduction of these types only came later.
  - Syndiotactic polystyrene (PS-st) came later in 1986 and had superior properties.
    - PS-st crystallizes an order of magnitude faster than PS-it; has half the entanglement molecular weight; and is commonly used today in auto parts, electronics, and medical equipment.
- Tacticity is often measured by certain splittings (or their absence) in  $^1\text{H}$  NMR.
  - Isotactic polymers put the geminal methylene protons into distinct chemical environments; syndiotactic polymers do not. Atactic polymers will have a mix of both, and the mix can be quantified with integration.
  - $^{13}\text{C}$  NMR can be used, too.
- More on geometric isomers.
  - Example: Polybutadiene can be formed *trans* or *cis*, as guided by a catalyst.
  - Natural rubber is *cis*-1,4-polyisoprene. Other types of tree sap can give *trans*-1,4-polyisoprene.
- We now move onto polymer conformations.
- **Conformations:** The spacial arrangements possible (or "probable," taking energy into account) for a polymer.
  - No bonds are *broken* here, just rotated.
- Reviews **Newman projections**.
  - **Staggered** configuration is defined as  $0^\circ$ .
  - **Eclipsed** configuration then starts at  $60^\circ$ .
  - There are energy penalties to being in different conformations.
    - As one example, eclipsed is higher energy than staggered due to sterics.
    - Generally sinusoidal relation in a plot of potential energy  $V$  against dihedral angle  $\theta$ .
    - The energy difference between rotamers is approximately  $3k_{\text{B}}T$ , which is not huge but big enough that the system will spend most of its time in the valleys. Each "valley" is a **conformer**.
    - So then since probability is proportional to  $e^{-V/k_{\text{B}}T}$ , the probability that a molecule will be staggered is greater than that it will be eclipsed.
  - In molecules longer than ethane, we break degeneracy of the valleys.
  - The rapid growth of conformers: Ethane has 3 conformers. Propane has  $3^2$ . Butane has  $3^3$ . Decane has  $3^{10}$ . Polyethylene with  $N = 10^5$  already has on the order of  $10^{47\,000}$  possible conformers, a huge conformational space.

- This is because each bond has 3 valleys!
- Many of the models we'll develop are ways of enumerating these conformations in relation to some higher-order measurement of the polymer, such as the **n-band difference**.
- Polymers are indeed often moderately sized coils rather than fully stretched out rods.
- Example: 166 kbp DNA (approximately 684 **Kuhn steps**, discussed next lecture) can be videotaped moving around, and it never fully elongates.
- Stretched out polymers shrink back over some characteristic time.
- Polymers with high degrees of polymerization result in many possible conformations without breaking bonds — this is what we'll discuss in the next two lectures!
- A good conversions to keep in mind:  $2.5 \text{ kJ/mol} \approx 1k_B T$ .
- Today is probably the most jampacked bits and pieces day; other lectures will be more focused, but this is important background.

## 1.2 Conformation: Ideal Chains

9/11:

- Lecture outline.
  - Conformation (degrees of freedom).
  - Ideal chain models.
  - Entropic elasticity.
- Many material properties we care about are correlated with the size of the polymer.
- This size is measured by a vector **R** that goes from one end of the polymer to the other.

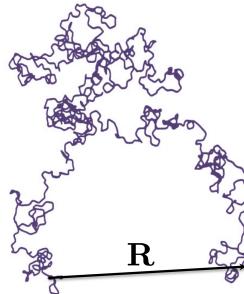


Figure 1.4: End-to-end polymer vector.

- We define **R** as the sum of all constituent bond vectors **l** (end-to-end of each chemical bond along the backbone). Symbolically,

$$\mathbf{R} := \sum_{i=1}^n \mathbf{l}_i$$

- Note that **R** has length  $|\mathbf{R}| = R$ .
- Today, we will look at several models that can be used to calculate the expected length of this vector,  $\langle R \rangle$ .

- Freely Jointed Chain (FJC) model.

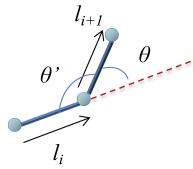


Figure 1.5: A joint in a polymer chain.

- In this model, there are no restrictions on how adjacent bonds rotate relative to each other. Rather, this is just a random walk. In effect, this means that there are no energy barriers and no excluded volume.
  - It follows that  $\langle R \rangle = 0$ .
  - However, while  $\langle R \rangle = 0$ , we have

$$\begin{aligned} \langle R^2 \rangle &= \left\langle \sum_{i=1}^n \mathbf{l}_i \cdot \sum_{j=1}^n \mathbf{l}_j \right\rangle \\ &= \sum_{i=1}^n \sum_{j=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= \sum_{i=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=1}^n \sum_{j=1, j \neq i}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= nl^2 + 0 \end{aligned}$$

- The second term goes to zero as  $n \rightarrow \infty$  because there is no correlation among segments (i.e., they are randomly oriented).
- This gives us the following important scaling law.

$$\langle R^2 \rangle^{1/2} \propto n^{1/2}$$

- This means that scaling is consistent with the polymer taking a “coil-like” conformation.
- This combined with the fact that the polymer’s fully stretched length is  $nl$  gives us the following expression for the number of backbone bonds in a polymer.

$$\frac{(\text{fully stretched length})^2}{\langle R^2 \rangle} = n$$

- Note that Lodge and Hiemenz (2020) uses  $\theta$  for the *complement* of bond angle, as in Figure 1.5. Other texts may use a different convention.
- Now, let’s refine the FJC by accounting for nearest neighbor correlations.
- First, we’ll look at a polymer with only two segments (i.e.,  $n = 2$ )
  - Suppose every joint is *fixed* at complementary angle  $\theta$ , but there is no energy penalty to rotate in  $\phi$ .
  - From Figure 1.5, trigonometry tells us that

$$\mathbf{l}_i \cdot \mathbf{l}_{i+1} = l^2 \cos \theta$$

- Thus, under the conditions of this model,

$$\begin{aligned}\langle R^2 \rangle &= 2l^2 + \sum_{i=1}^2 \sum_{\substack{j=1 \\ j \neq i}}^2 \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= 2l^2 + 2 \langle l^2 \cos \theta \rangle \\ &= nl^2(1 + \cos \theta)\end{aligned}$$

- The important takeaway is that with this chemical realism, the chain is bigger than in the previous model!

■ It is also noteworthy that the  $nl^2$  scaling relation is retained.

- This is a precursor to the freely rotating chain, where we can rotate in  $\phi$  but not in  $\theta$ .

- Let's now look at the full Freely Rotating Chain (FRC) model.

- As we elongate the chain, there is a slow decay of “memory of correlation” since  $\phi$  rotates freely. Eventually (see Lodge and Hiemenz (2020, pp. 239–40) for the derivation), we asymptote to

$$\langle R^2 \rangle = nl^2 \underbrace{\left( \frac{1 + \cos \theta}{1 - \cos \theta} \right)}_{C_n}$$

where  $C_n$  may be an empirically derived **characteristic ratio**.

- Model 3: Symmetric hindered rotations.

- Recall from last class that certain rotational conformations have lower energies than others.
- As such, we can give a Boltzman weighting to the energetic valleys.
- Thus, we reevaluate our hindered rotations with a Boltzmann weighting and the following expression crashes out of the math.

$$\langle R^2 \rangle = nl^2 \underbrace{\left( \frac{1 + \cos \theta}{1 - \cos \theta} \right) \left( \frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)}_{C_\infty}$$

■ Note that it's still just  $nl^2$  times a constant!

- The **characteristic ratio**  $C_\infty$  can be calculated for models or obtained from experiments. The following rearranged definition is also important.

$$C_\infty := \frac{\langle R^2 \rangle_0}{nl^2}$$

- Alert: Be aware of sign changes due to different conventions for  $\theta$  and  $\phi$  in different texts!

- There are tables of characteristic ratios in both Lodge and Hiemenz (2020) and Rubinstein and Colby (2003).

| Polymer                          | Structure  | $C_\infty$ |
|----------------------------------|--|------------|
| 1,4-Polyisoprene (PI)            | $-(\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3))-$    | 4.7        |
| 1,4-Polybutadiene (PB)           | $-(\text{CH}_2\text{CH}=\text{CHCH}_2)-$               | 5.5        |
| Polypropylene (PP)               | $-(\text{CH}_2\text{CH}_2(\text{CH}_3))-$              | 6.0        |
| Poly(ethylene oxide) (PEO)       | $-(\text{CH}_2\text{CH}_2\text{O})-$                   | 6.7        |
| Poly(dimethyl siloxane) (PDMS)   | $-(\text{OSi}(\text{CH}_3)_2)-$                        | 6.8        |
| Polyethylene (PE)                | $-(\text{CH}_2\text{CH}_2)-$                           | 7.4        |
| Poly(methyl methacrylate) (PMMA) | $-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOCH}_3))-$ | 8.2        |
| Atactic polystyrene (PS)         | $-(\text{CH}_2\text{CHC}_6\text{H}_5)-$                | 9.5        |

Table 1.2:  $C_\infty$  values for common polymers at 413 K.

- $C_\infty$  gets bigger with bigger side chains.
- Typical range is 5-10; can go up to 20 or higher, though.
- Example: What is the size of a polyethylene molecule at 413 K and having molecular weight  $10^4$  g/mol?
  - Approach: We want to find  $\langle R^2 \rangle$  and take its square root; that will be our answer.
  - We can look up that the length  $l$  of a typical C–C bond is 0.154 nm.
  - Based on the molecular weight and the known weight of the ethylene ( $\text{CH}_2\text{CH}_2$ ) repeat unit,

$$N = \frac{10^4 \text{ g/mol}}{28 \text{ g/mol}} \approx 357.1$$

- Because there are two carbon-carbon bonds per repeat unit,  $n = 2N$ .
- Thus,

$$\begin{aligned} \langle R \rangle &= \langle R^2 \rangle^{1/2} \\ &= [nl^2 C_\infty]^{1/2} \\ &= [(2 \cdot 357.1)(0.154 \text{ nm})^2(7.4)]^{1/2} \\ \langle R \rangle &\approx 11 \text{ nm} \end{aligned}$$

- Let's compare the answer in the above example to the straight chain estimation.

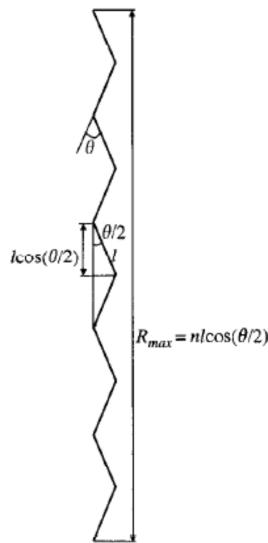


Figure 1.6: Straight chain estimation of a polyolefin.

- In this case,

$$R_{\max} = nl \cos(\theta/2)$$

- We can look up that for a typical C–C bond,  $\theta = 180^\circ - 109.5^\circ = 70.5^\circ$ .
- Thus,

$$\begin{aligned} R_{\max} &= nl \cos(\theta/2) \\ &= (2 \cdot 357.1)(0.154 \text{ nm}) \cos(70.5/2) \\ R_{\max} &\approx 90 \text{ nm} \end{aligned}$$

- This calculation is a bit tedious, so Kuhn refined the coarse grained FJC model to be computationally simpler.
- Model 4: Kuhn's Equivalent Chain.

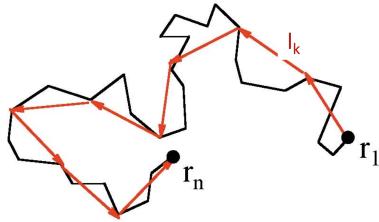


Figure 1.7: Kuhn steps.

- Building off of models 3 and 1, let's postulate the existence of an FJC along our polymer. This FJC will have  $N$  steps of length  $l_k$ , where  $l_k$  is a Kuhn step.
- This gives us two variables to define. We thus need two equations by which to define them.

- Equation 1: By the universal scaling law,

$$Nl_k^2 = \langle R^2 \rangle = C_\infty nl^2$$

- Equation 2: If the total length of the chain is  $R_{\max}$ , and the chain is being broken up into  $N$  Kuhn steps each of length  $l_k$ , then

$$R_{\max} = Nl_k$$

- By solving this system of equations, we can then define  $N$  and  $l_k$  purely in terms of previously derived variables.

- **Kuhn step:** A subsegment of a polymer chain with length defined as follows. *Denoted by  $l_k$ . Given by*

$$l_k := \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty nl^2}{R_{\max}}$$

- **Number of Kuhn steps:** The number of Kuhn steps in a polymer chain. *Denoted by  $N$ . Given by*

$$N := \frac{R_{\max}}{l_k} = \frac{R_{\max}^2}{C_\infty nl^2}$$

- Example: In the case of a fully elongated carbon-carbon chain (Figure 1.6), the number of Kuhn steps is

$$l_k = \frac{C_\infty nl^2}{R_{\max}} = \frac{C_\infty nl^2}{nl \cos(\theta/2)} = \frac{C_\infty l}{\cos(\theta/2)}$$

- Note that the symbols  $R_{\max}$  and  $L$  will be used interchangeably for the straight-chain length of a polymer.
- $R_{\max}$  largely depends on the chemistry of the polymer (e.g., specific atoms' bond angles).
- We'll now look at some models for "stiff" chains, such as dsDNA or microtubules.
  - These tend to have even higher  $C_\infty$  values.
  - Note that twists in the chain are *much* bigger than individual nucleobases.
  - Molecular simulations of 75 bp dsDNA shows barely any bending. Indeed, there is a high correlation between end vectors even though they are very far away.

- A model for very stiff polymers: The Worm-Like Chain (WLC).

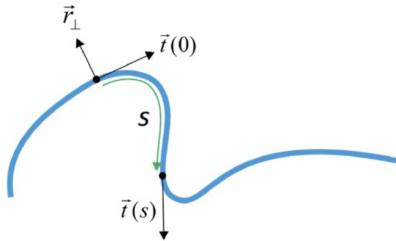


Figure 1.8: Worm-like chain.

- Represent a segment as an infinitesimal elastic rod.
- This rod has a contour you can be some point  $s$  along, where  $s \in [0, L]$ .
- The direction of the rod is defined by a tangent vector  $\mathbf{t}(s)$ .
- We also give the rod some bending energy  $U_b$ , related to how the tangent changes as we go along  $s$ . But physically, this is just curvature squared. To get the right units, we throw in a bending stiffness parameter  $\kappa_b$ , which incorporates some chemical / molecular details. Throw in a  $1/2$  from mechanics definitions, and we get

$$U_b = \frac{1}{2} \kappa_b \int_0^L \left( \frac{\partial \mathbf{t}}{\partial s} \right)^2 ds$$

- An implication of this is that correlation decays exponentially per

$$\langle \mathbf{t}(0) \cdot \mathbf{t}(s) \rangle = e^{-sk_B T/\kappa_b}$$

- I.e., you use memory of how oriented you are in one part of the chain when you get farther away from that point.
- Since  $\kappa_b/k_B T$  has units of length by dimensional analysis, we can define it to be the **persistence length**.
- From this tangent correlation function, we can calculate many interesting properties — including the mean squared end-to-end distance!

$$\langle R^2 \rangle = 2aL \left[ 1 - \frac{a}{L} \left( 1 - e^{-L/a} \right) \right]$$

- The calculation is complicated, so Dolye skips it.
- This equation reveals some interesting polymer behavior in two limits: That of *long* and *short* stiff polymers.
  - When the polymer gets long,  $a/L \rightarrow 0$  and  $\langle R^2 \rangle \rightarrow 2aL$ .
  - When the polymer gets short,  $a/L \rightarrow \infty$  and  $\langle R^2 \rangle \rightarrow L^2$ .
    - This makes intuitive sense as if it's short, it should be roughly straight and have end-to-end distance approximately equal to its length!
    - Note that in real life, there *are* polymers where the persistence length is longer than the length of the polymer! These behave like rigid rods.
- Lastly, it follows from definition of Kuhn steps that

$$2aL = \langle R^2 \rangle = Nl_k^2 = \frac{R_{\max}}{l_k} \cdot l_k^2 = Ll_k$$

- Thus, the Kuhn length is twice the persistence length! Symbolically,

$$2a = l_k$$

- **Persistence length:** A characteristic length over which a stiff polymer loses memory of its orientation along other parts of the chain. *Denoted by  $a$ . Given by*

$$a := \frac{\kappa_b}{k_B T}$$

- In conclusion, two biggest models to remember: Kuhn model (rigid steps) and WLC (continuum approximation with persistence length for semi-rigid chains).
- Example: Actin has a persistence length of  $10\text{ }\mu\text{m}$ ; since most cells are smaller than this, actin is functionally a rigid rod within a cellular context.
- Example: Measuring persistence length of dsDNA.
  - Adsorb DNA onto a surface that loosely binds it, so that it can still move around but won't fall off.
  - Then look at thousands of strands next to each other and calculate tangent lengths!
  - Reference: Kundukad et al. (2014).
- Example: Bottlebrush polymers in cartilage.
  - These have highly charged side chains, but fewer with age.
  - This causes more bending.
  - We can observe this with atomic force microscopy.
- Example: As you increase the concentration of salt in solution, you shrink the **Debye length** and also the persistence length.
  - This modifies the effect of charges on dsDNA.
- Example: Actin cytoskeleton filaments.
  - Made out of polymerized protein subunits.
  - A very thin polymer, biologically speaking.
  - Very long persistence length, as mentioned earlier.
  - As cells move, they push actin against the cell membrane to distort it! This works because actin is a very rigid rod, so rigid that it can overcome the membrane pressure.
- Example: Conjugated polymers.
  - They calculated the persistence length using DFT, and then measured it experimentally.
  - Some of their polymers are stiffer than dsDNA!
  - Rotation around one particular engineered bond is used to estimate persistence length.
- **Flexible** (polymer): A polymer for which chain length is much greater than persistence length.
- **Semi-flexible** (polymer): A polymer for which chain length is approximately equal to persistence length.
- **Rod-like** (polymer): A polymer for which chain length is much shorter than persistence length.
- Summary of ideal chains.
  - All chains show a similar, universal scaling relation that  $R \approx N^{1/2}$ .
  - For ideal chains, local interactions set the rigidity length scale and excluded volume is not significant.
  - This approximation is ok for dilute solutions at **theta conditions** and polymer **melts**.

- **Theta condition:** When you've essentially turned off excluded volume for the chain.
- **Polymer melt:** A condition in which the polymer is essentially in a solution of itself.
- Nomenclature for polymer solution regimes.



Figure 1.9: The volume occupied by polymers.

- **Hard volume** (of a polymer): The volume occupied by the chain, where each repeat unit is considered to occupy a sphere with radius equal to the bond length and the polymer is the sum of these “beads” touching each other. *Also known as occupied volume. Denoted by  $v$ . Given by*

$$v \propto nl^3$$

- The volume of each bead is thus on the order of the bond length.
- **Pervaded volume** (of a polymer): The sphere encapsulating the volume in which the polymer chain is *expected* to move around. *Denoted by  $V$ ,  $V_p$ . Given by*

$$V \propto \langle \mathbf{R}^2 \rangle^{3/2} \propto n^{3/2} l^3$$

- From this, we can see that

$$\frac{v}{V} \propto n^{-1/2}$$

- It follows that the pervaded volume is mostly empty as  $n$  becomes large.
- **Critical concentration:** The concentration at which all polymers in solution can “see” each other. *Also known as coil overlap concentration. Denoted by  $c^*$ .*

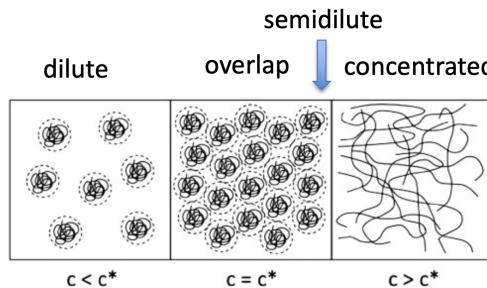


Figure 1.10: Concentration regimes.

- In dilute solutions, polymers will all be coiled up within their own pervaded volume and will not interact.
- When they reach the critical concentration, all of the pervaded volumes are essentially touching each other.
- Past the critical concentration, we get entanglement and no longer see individual polymer coils in their own pervaded volume.

- This is the same  $c^*$  as in Figure 1.1!
- Unifying implication: These concentrations are related to pervaded volume, which is related to expected size.
- Next time.
  - Adding in excluded volume, which will wrap up our discussion on chains.
  - Then Alfredo on thermodynamics of interactions.

### 1.3 Conformation: Real Chains

9/16:

- Announcements.
  - PSet 1 due Thursday. We can do 1-2 right now; 3-4 will be possible after today.
  - Reach out if we have questions!
- Lecture outline.
  - Ideal chains.
    - Gaussian chains.
    - Entropic elasticity.
  - Real chains.
    - Excluded volume.
    - Solvent quality.
    - Expansion factor  $\alpha$ .
- Review from last lecture.
  - Our workhorse model for polymer chain length is Kuhn's equivalent chain, which is in turn based on the FJC random walk.
  - This is a coarse-grained model because atoms don't matter, and we're neglecting to consider excluded volume and energy.
- Aside: Another measure of polymer size worth being aware of is the Radius of Gyration.

- The radius of gyration  $R_g$  is defined as the 2nd moment of the monomers relative to their center of mass  $\mathbf{R}_{\text{cm}}$ .

$$R_g^2 = \frac{1}{N} \sum_{i=1}^N (\mathbf{R}_i - \mathbf{R}_{\text{cm}})^2$$

- Since the center of mass is defined as

$$\mathbf{R}_{\text{cm}} = \frac{1}{N} \sum_{j=1}^N \mathbf{R}_j$$

we can do some algebra to learn that

$$\langle R_g^2 \rangle = \frac{1}{6} \langle R^2 \rangle$$

- Covered in the lecture reading.
- Question: How many monomers before Kuhn steps have statistical meaning?
  - About 100 before you converge to a Gaussian distribution.

- We'll derive the “easy force response of a freely jointed chain.”
- Before we relate Kuhn's equivalent chain (a 3D model) to polymer size, let's look at the 1D analog: The full probability distribution of a 1D random walk.

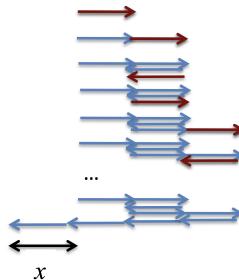


Figure 1.11: Progression of a 1D random walk over time.

- In 1D, you can either go in the positive or negative direction by a distance  $b$ .
- Imagine you keep doing this for  $n$  steps, after which we'll say you've gone a distance  $x$  from your starting point.
- If  $n_1$  is the number of steps right and  $n_2$  is the number of steps left, then

$$x = b(n_1 - n_2)$$

- Let's now analyze this problem statistically.
- From the perspective of statistics, the 1D random walk is equivalent to the coin flipping problem. Specifically, the total number  $\Omega$  of ways (microstates) in which you can move a distance  $x$  is

$$\Omega = \frac{n!}{n_1!n_2!} = \binom{n}{n_1} = \binom{n}{n_2}$$

- $\Omega$  is then a binomial, and as such is maximized when  $n_1$  is close to  $n_2$ . But when  $n_1 \approx n_2$ ,  $x = b(n_1 - n_2)$  is small.
- The overall implication is that you are most likely to end up back where you started!
- Aside: Why is  $\Omega$  a binomial?
  - Binomials mathematically originate from “ $n$  choose  $k$ ” counting of unordered *combinations*. For example, if you have 4 objects A, B, C, and D, there are  $\binom{4}{2} = \frac{4!}{(4-2)!2!} = 6$  ways you can choose two of them: AB, AC, AD, BC, BD, and CD. Note that choosing AB is the same as choosing BA, i.e., order does not matter. This situation is related to a binomial because the “first” time we choose an object out of ABCD, we have 4 options. Suppose we choose B. Then when we go back to choose a second object, we have 3 remaining choices: ACD. Thus, there are  $4 \cdot 3 = 12 = \frac{4!}{(4-2)!}$  paths to two objects (aka *permutations*). But choosing A then B is the same as choosing B then A when it comes to combinations, so we have overcounted by exactly the number of ways there are to arrange 2 objects, which is  $2!$ . Thus, we must divide by  $2!$  again to get  $\frac{4!}{(4-2)!2!} = 6$ .

- This established, where in the context of the 1D random walk are we “choosing” objects, and what objects are we choosing?
- Suppose we are taking  $n = 4$  steps, and we want to identify the total number  $\Omega$  of ways we can move a distance  $x = 0$ . By solving the system of equations  $4 = n_1 + n_2$  and  $0 = b(n_1 - n_2)$ , we can learn that  $n_1 = n_2 = 2$ . This means that we must take  $n_1 = 2$  steps to the right, and  $n_2 = 2$  steps to the left in order to end up back at zero. But when do we take these steps? Diagramming this out, there are four timeslots at which we can take a step (\_\_\_\_\_), and two of those must eventually be filled by steps to the right R. The

first time we *choose* a timeslot, we have 4 options: R\_\_\_\_, \_R\_\_\_, \_\_R\_, and \_\_\_R. Then the second time we choose, we have three remaining options; moreover, if we fill (for example) the first and then the second timeslot, that's equivalent to filling the second and then the first! This is how we relate the 1D random walk to “ $n$  choose  $k$ ” probability.

- Now that we know the number of ways we can move a distance  $x$ , we can calculate the probability  $P(x)$  of moving a distance  $x$  by dividing by the total number of possible paths (which is just  $\Omega_{\text{tot}} = 2^n$ ).

$$P(x) = \frac{\Omega}{\Omega_{\text{tot}}} = \frac{n!}{n_1! n_2! 2^n}$$

- Moreover, because  $\Omega$  is a *binomial*,  $P(x)$  is a *binomial distribution*.
- **Stirling’s approximation** allows us to expand the factorials for large  $n$ , and subsequently prove that the above binomial distribution converges to the following Gaussian distribution.

$$P(x, n) = \left( \frac{1}{2\pi nb^2} \right)^{1/2} \exp\left( \frac{-x^2}{2nb^2} \right)$$

- This allows us to then get back to the following familiar expression.

$$\langle x^2 \rangle = nb^2$$

- From this 1D model, we can generalize to the Gaussian distribution of an end-to-end vector in 3D.

$$P(\mathbf{R}, N) = \left( \frac{3}{2\pi Nb^2} \right)^{3/2} \exp\left( -\frac{3R^2}{2Nb^2} \right)$$

- Note the units of reciprocal volume, as we’d expect for a spatial probability.
- Using spherical coordinates gets us to a familiar expression again, as follows.

$$\langle R^2 \rangle = \int_0^\infty R^2 P(\mathbf{R}, N) 4\pi R^2 dR = Nb^2$$

- Note that  $R^2$  appears twice. The first time, it is because  $R^2$  is what we’re taking the expected value of over all space. The second time, it is because an easy way to take the integral of a radial probability distribution is in spherical coordinates.
- $P(\mathbf{R}, N)$  is radial because the random walk does not have a particular direction in mind in 3D space; you are equally likely to end up  $x$  units from the origin in the  $+x$  direction, as you are in the  $-x$  direction,  $-z$  direction, or any other direction you can imagine.

- This concludes our discussion of Gaussian chains.
- We’ll now discuss entropic elasticity.

- Recall from thermodynamics that

$$F = U - TS$$

- $F$  is free energy;
- $U$  is internal potential energy;
- $T$  is temperature;
- $S$  is entropy.
- For an FJC,  $U = 0$  (by definition) and  $S$  is the only thing we have to consider.
- Recall from Boltzmann that

$$S = k_B \ln[\Omega(\mathbf{R}, N)]$$

- The generalization of our above definition of probability is the following.

$$P(\mathbf{R}, N) = \frac{\Omega(\mathbf{R}, N)}{\int_{\mathbb{R}^3} \Omega(\mathbf{R}, N) d\mathbf{R}}$$

- We'll denote the denominator by  $\Omega_N$  going forward, representing the fact that it is a function of  $N$  and not  $\mathbf{R}$ .
- Then substituting and bashing out the math, we get

$$\begin{aligned} S(\mathbf{R}, N) &= k_B \ln[P(\mathbf{R}, N)] + k_B \ln(\Omega_N) \\ &= -\frac{3k_B R^2}{2Nb^2} + k_B \ln\left(\frac{3}{2\pi Nb^2}\right)^{3/2} + k_B \ln(\Omega_N) \\ &= -\frac{3k_B R^2}{2Nb^2} + S_N \end{aligned}$$

- We will call the second two terms  $S_N$  because they're less interesting, and they only depend on  $N$  (not  $\mathbf{R}$ ).
- By substituting the above back into  $F = U - TS$ , it follows that our entropic free energy for the FJC is

$$F = \frac{3k_B T R^2}{2Nb^2} + S_N$$

- In this context, we can think of  $S_N$  as an additive normalization constant.
- With this result, we can determine how to minimize  $F$  relative to  $R$ .
- Minimizing  $F$  relative to  $R$  is a goal because the radius at which the free energy is minimal will be the radius of polymer coils in solution (everything wants to minimize energy).

- Using this (FJC) model, we can calculate an entropic spring force  $\mathbf{F}(\mathbf{R}, N)$ .
    - We know that
- $$\mathbf{F}(\mathbf{R}, N) = \frac{\partial F}{\partial \mathbf{R}} = \frac{\partial F}{\partial R} \hat{\mathbf{R}} + \frac{\partial F}{\partial \theta} \hat{\theta} + \frac{\partial F}{\partial \phi} \hat{\phi} = \frac{3k_B T}{Nb^2} \hat{\mathbf{R}}$$
- It follows that at a molecular level, a polymer constitutes a linear Hookean spring ( $F = kx$ ), where the whole prefactor to  $\hat{\mathbf{R}}$  is our spring constant  $k$ .
  - Rearranging, we can express the above equation with a relative extension.
- $$\mathbf{F}(\mathbf{R}, N) = \frac{3k_B T}{b} \left( \frac{\hat{\mathbf{R}}}{Nb} \right)$$
- $Nb$  is the length of the fully extended freely jointed chain, and  $\hat{\mathbf{R}}$  is a partial extension. Thus, their the fraction is a **relative extension**.
  - It has been experimentally shown that up to about 30% extension, these force laws hold!<sup>[1]</sup>
  - We'll now begin discussing **real chains**.
    - Up to now, we've been discussing **ideal chains**, which occur at Theta conditions and in melts.
    - Real chains.
      - Local chemistry is coarse-grained out by Kuhn lengths.
      - Non-local elements are related by excluded volume. Essentially, monomers may have some interaction (favorable or unfavorable) when they float near each other in solution.
    - In ideal chains...
      - There are only local effects;
      - Ideal is synonymous with either theta conditions or melts.
    - To ground our mathematical/physical analysis, we will approximate monomers in a polymer as an ideal “gas” of monomers in a volume  $R$  (Figure 1.13a).

<sup>1</sup>Thus, Kuhn steps are like a higher level of theory to rationalize an experimentally observed result!

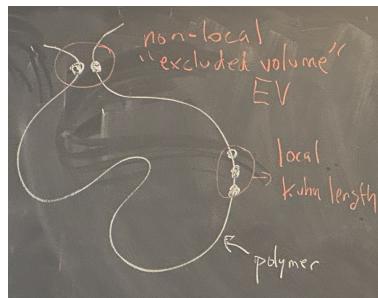


Figure 1.12: Local and non-local interactions in a polymer.

(a) Gas in a volume  $R$ . (b) Excluded volume. (c) Distance between monomers.

Figure 1.13: Monomer gas model of a polymer's excluded volume.

– For nonlocal interactions, we will consider “hard sphere” monomers.

- In particular, for two hard-sphere monomers with center-to-center distance  $\delta$ , Figure 1.13b tells us that excluded volume  $V_{\text{ex}} = v$  is

$$V_{\text{ex}} = \frac{4}{3}\pi\delta^3$$

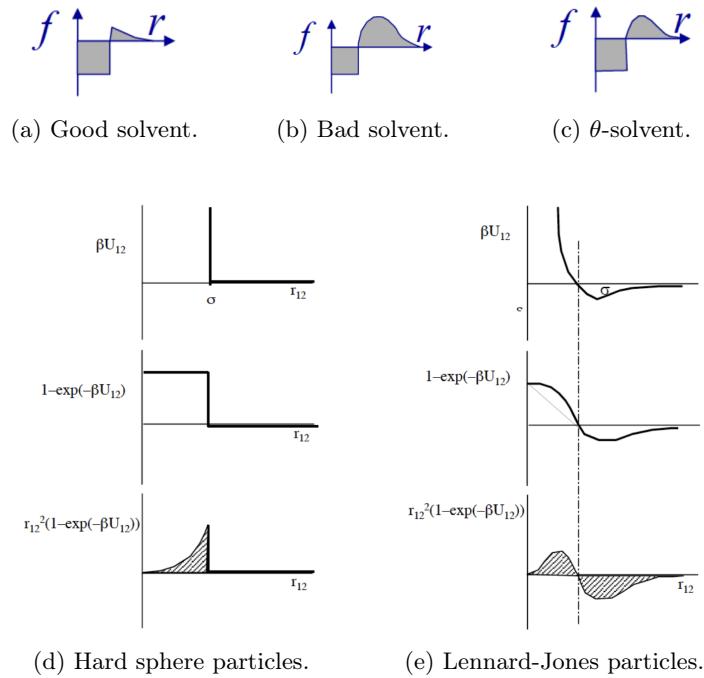
– Let’s generalize: The Boltzmann weighting for the probability of finding two monomers at a distance  $r$  from each other is

$$f(r) = \exp\left(-\frac{U(r)}{k_B T}\right) - 1$$

- $f(r)$  is called the **Mayer- $f$  function**.
- It is equal to zero when there is no interaction (i.e.,  $U = 0$ ) because when  $U = 0$ , all  $r$  are equally probable.
- It follows through some math — see Rubinstein and Colby (2003) — that the excluded volume is equal to

$$V_{\text{ex}} = -4\pi \int_0^\infty r^2 f(r) dr$$

- Notice that we’re in polar coordinates.
- What is going on here?? Why is excluded volume related to the probability of finding monomers near each other?
- Note that  $U(r)$  (which is the monomer interaction) also incorporates the solvent since the energy is not that of two bare monomers, but those monomers with a medium between them (e.g., two styrene monomers in a sea of toluene).
- The excluded volume is a way of quantifying interactions.
- The Mayer- $f$  function can be visualized through plots and integrals.
  - Depending on  $U$ , we have three possibilities.

Figure 1.14: Visualizing the Mayer- $f$  function.

- In a good solvent, the coils unwind and the volume expands. Repulsion dominates (Figure 1.14a).
- In a bad solvent, the coils bunch up. Attraction dominates (Figure 1.14b).
- In a  $\theta$ -solvent, repulsion balances attraction (Figure 1.14c).
  - We can also plot out precursors to and variants of the Mayer- $f$  function for specific potentials of interest.
    - Thus, we can see that in the hard-sphere potential (Figure 1.14d), there is only a repulsive contribution and thus no  $\theta$ -temperature or  $\theta$ -solvent.
    - In contrast, for the Lennard-Jones potential (Figure 1.14e), there are both repulsive and attractive contributions. Thus, there *will* be a  $\theta$ -temperature in each  $\theta$ -solvent.
- In a theta solvent,  $V_{\text{ex}}(T) = 0$ .
  - The temperature  $T$  at which  $V_{\text{ex}} = 0$  is called the **Boyle temperature**; it is the temperature at which excluded volume is zero. Basically, you always have excluded volume, but if that excluded volume is balanced by a bit of attraction, you can have something that looks ideal.
  - PSet 1, Q5 explores the relation between  $V_{\text{ex}}$  and  $T$  more explicitly!
- The heart of polymer physics is Flory mean-field approximations.

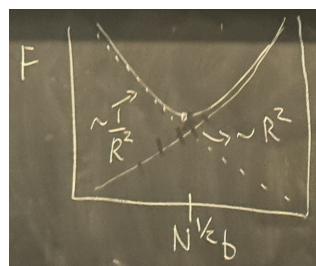


Figure 1.15: A post-facto compression penalty.

- In a  $\theta$ -solvent,  $F = -TS$  (because  $U = 0$ ).
- As we derived above, for this situation, the entropic free energy  $F_{\text{ent}}$  is

$$F_{\text{ent}} = \frac{3k_{\text{B}}T}{2} \frac{R^2}{Nb^2}$$

and

$$\frac{\partial F}{\partial R} = \frac{3k_{\text{B}}TR}{Nb^2}$$

- At equilibrium,  $\partial F/\partial R = 0$ . It follows that

$$\begin{aligned} \frac{3k_{\text{B}}TR}{Nb^2} &= 0 \\ R &= 0 \end{aligned}$$

- But this is inconsistent with the finding that  $\langle R^2 \rangle = Nb^2$ .
- We will address this with a post facto compression penalty. Indeed, if we set

$$F_{\text{ent}} = \frac{3k_{\text{B}}T}{2} \left( \frac{R^2}{Nb^2} + \frac{Nb^2}{R^2} \right)$$

then  $\partial F/\partial R = 0$  implies

$$\begin{aligned} R &= N^{1/2}b \\ R^2 &= Nb^2 \end{aligned}$$

- The nice thing about this compression penalty is that the graph of  $1/R^2 + R^2$  forms a nice energy well, dictated by the rates at which one or the other increases. See Figure 1.15.

- Now analogously to a **Virial expansion** (from thermodynamics), we are going to do another expansion.

$$\frac{F_{\text{int}}}{V k_{\text{B}} T} = \frac{1}{2!} v c^2 + \frac{1}{3!} w c^3 + \dots$$

- This takes the perspective that we disregard monomer connectivity, and evaluate the enthalpic interaction energy  $F_{\text{int}}$  as if it was a gas of monomers in a spherical container of radius  $R$ .
- $c = N/R^3$  is the concentration of the monomers, and  $V \propto R^3$ .
- We are throwing out prefactors like  $4/3$  and  $\pi$ .
- This gives us a term for binary interactions, ternary interactions, etc.

- In a good solvent,  $R > Nb^2$  because the polymer swells due to  $V_{\text{ex}}$ .

- Free energy is then

$$F = \frac{3k_{\text{B}}TR^2}{2Nb^2} + \frac{1}{2} V_{\text{ex}} \frac{N^2}{R^3} k_{\text{B}} T$$

- Then  $\partial F/\partial R = 0$  implies

$$\begin{aligned} 0 &= \frac{k_{\text{B}}TR}{Nb^2} - \frac{3V_{\text{ex}}N^2k_{\text{B}}T}{2R^4} \\ R^5 &= \frac{1}{2}N^3b^2V_{\text{ex}} \\ R &\approx b^{2/5}V_{\text{ex}}^{1/5}N^{3/5} \end{aligned}$$

- Taking everything into account with renormalized group theory yields something pretty close!
- This stands in contrast to the ideal  $R \approx N^{1/2}b$ .

- In a bad solvent, enthalpic interactions matter more than entropic interactions because the polymer is compressed into a globule regardless.

– Thus, we have to balance the first two terms in  $F_{\text{int}}$  to determine the scaling.

$$\begin{aligned} 0 &= \frac{\partial F_{\text{int}}}{\partial R} \\ &= \frac{\partial}{\partial R} \left\{ k_{\text{B}} T R^3 \left[ \frac{1}{2} v \left( \frac{N}{R^3} \right)^2 + \frac{1}{6} w \left( \frac{N}{R^3} \right)^3 \right] \right\} \\ &= k_{\text{B}} T \frac{\partial}{\partial R} \left( \frac{v N^2}{2 R^3} + \frac{w N^3}{6 R^6} \right) \\ 0 &= -\frac{3vN^2}{2R^4} - \frac{wN^3}{R^7} \\ R^3 &= -\frac{2wN}{3v} \\ R &\propto \left( \frac{w}{-v} \right)^{1/3} N^{1/3} \end{aligned}$$

- Combining the enthalpic and entropic terms, the full Flory free energy has many terms that all balance; you play with the ingredients to see what fits.

$$\frac{F}{k_{\text{B}} T} = \frac{V_{\text{ex}} N^2}{2 R^3} + \frac{w N^3}{6 R^6} + \frac{3 R^2}{2 N b^2} + \frac{3 N b^2}{2 R^2}$$

- The chain or polymer must be long enough for excluded volume to factor in.
  - In  $F_{\text{ev}} \geq k_{\text{B}} T$ , we have a good solvent.
  - We then do some more math and get

$$z = \frac{V_{\text{ex}} N^{1/2}}{b^3} < 1$$

- There is additional material in the slides.
  - Importantly, as you go away from  $\theta$ -conditions, you still have an  $N^{1/2}$  relation.
  - $1 - \theta/T$  is related to the homework; it's a perturbation of a Taylor series.
- The **expansion factor**  $\alpha$  is just the ratio of the real volume to the ideal.

## 1.4 Chapter 1: Introduction to Chain Molecules

*From Lodge and Hiemenz (2020).*

- 9/14:
- Begins with the uses and history of polymers.
  - **Macromolecule:** A large or long molecule.
  - **Polymer:** A macromolecule made by repeating one (or a few) chemical units many times.
    - All polymers are macromolecules, but not all macromolecules are polymers.
  - Lodge and Hiemenz (2020) will often write molecular weights without the unit “g/mol,” but we should write them with this unit.
  - Some types of polymerization involve only the joining of monomers; others involve this joining, but with the elimination of a small molecule byproduct (like H<sub>2</sub>O or HCl).

- Figure 1.6's derivation uses the **law of cosines** from high school trigonometry.
- Polyolefin size: Based on typical C–C bond angles and lengths...
  - The straight-chain length is approximately  $N \cdot 0.25 \text{ nm}$ ;
  - The actual end-to-end distance is approximately  $N^{1/2} \cdot 0.25 \text{ nm}$ .
- **Oligomer:** A molecule made of repeat units but for which  $N < 10$ .
- Note that *polymers* typically have  $M \geq 1000 \text{ g/mol}$ , but this cutoff is arbitrary (and probably on the low side).
- Polymer architectures.
- **Branched** (polymer): A linear molecule with additional polymeric chains issuing from its (linear) backbone.
- **Short-chain branch:** A small substituent (such as a methyl or phenyl group) on the repeat unit.
  - These are generally not considered branches.
- Branching can occur *by design, adventitiously, or through grafting*.
  - By design, we may introduce polyfunctional junctions into the formulation.
  - Adventitiously, “an atom [may be] abstracted from the original linear molecule, with chain growth occurring from the resulting active site” (Lodge & Hiemenz, 2020, p. 7).
    - This commonly happens with polyethylene!
- **Graft to** (polymerization): Pre-formed but still reactive polymer chains can be added to sites along an existing backbone.
- **Graft from** (polymerization): Multiple initiation sites along a chain can be exposed to monomer.
- Note: **Graft through** polymerization is not covered.
- For simple branching (no loops), a molecule with  $v$  branches has  $v + 2$  chain ends.
- **Comb** (polymer): A polymer in which a series of relatively uniform branches emanate from along the length of a common backbone.
- **Star** (polymer): A polymer in which all branches radiate from a central junction.
- **Cross-linked** (polymer): A polymer with such extensive branching that the macroscopic object may be considered to consist of essentially one molecule.
  - These polymers are given cohesiveness by covalent bonds instead of intermolecular forces, and thus have very different properties from non-cross-linked polymers.
- **Hyperbranched** (polymer): A polymer that is highly branched, but in which the components remain as discrete entities.
- **Dendrimer:** A class of hyperbranched polymers that are tree-like, in that they have completely regular structures formed by successive condensation of branched monomers.
  - Start with a  $B_3$  junction (generation 0), condense on three  $AB'_2$  monomers and deprotect (generation 1), condense on six  $AB'_2$  monomers and deprotect (generation 2), etc.
  - At generation 6 or 7, the surface of the molecule becomes so congested that adding further complete generations is impossible.
- **Cycle** (polymer): A polymer in which the two chain ends react to close the loop. *Also known as ring.*

- **Homopolymer:** A polymer with only a single kind of repeat unit.
  - Note that polymers made with two different monomers can still be homopolymers. For example, a polyester condensed from diacid and diol *monomers* still only has one kind of *repeat unit*.
- **Copolymer:** A polymer with two kinds of repeat units.
- **Terpolymer:** A polymer with three kinds of repeat units.
- **Multicomponent** (polymer): A polymer with four or more kinds of repeat units.
- **Random** (copolymer): A copolymer in which the A-B sequence is governed strictly by chance, subject only to the relative abundances of repeat units.
- **Statistical** (copolymer): A copolymer in which monomer addition at a growing chain end may depend on the preceding monomer(s), according to a statistical law.<sup>[2]</sup>
- **Alternating** (copolymer): A copolymer containing a regular pattern of alternating repeat units.
- **Block** (copolymer): A copolymer containing long, uninterrupted sequences of each monomer.
- ***n*-block** (copolymer): A block copolymer containing *n* uninterrupted sequences of each monomer.
  - For small *n*, the terms **diblock**, **triblock**, and **tetrablock** are commonly used.
  - If a triblock copolymer consists of a sequence of monomer A, followed by monomer B, followed by monomer A, we may call it an **ABA triblock copolymer**.

9/16:

- In addition to classifying polymers by architecture, we can classify them by the reactions used to make them.
- **Addition and condensation** polymerization are the most common, but there are more.
- **Addition** (polymerization): A polymerization for which the following three statements apply. *Also known as chain-growth. Defined by*
  1. The repeat unit in the polymer and monomer have the same composition (although bonding is different in each).
  2. The polymerization proceeds through a **chain reaction** mechanism, with either free radicals or ionic groups responsible for propagating the chain reaction.
  3. The product molecules *often* have an all C–C backbone, with pendant substituent groups.
- **Condensation** (polymerization): A polymerization for which the following three statements apply. *Also known as step-growth. Defined by*
  1. The polymer repeat unit arises from the reaction of two different functional groups, which *usually* originate on different monomers. In this case, the repeat unit is different from either monomer. In addition, small molecules are *often* eliminated during the condensation reaction.
  2. Mechanistically, the reactions occur in steps; in other words, the formation of the linkage functional group between two small molecules is not essentially different from that between one of these growing polymers and a monomer.
  3. The product molecules have the functional groups formed by the condensation reactins interspersed regularly along the backbone of the polymer molecule.
- Properties of condensation polymerizations.
  - Either two difunctional monomers with different functional groups, or one difunctional monomer with a functional group of each kind.

<sup>2</sup>The copolymers we make with CCs are all statistical, since addition is governed by probability-based reactivity ratios.

- Beware the creation of loops!
  - Very sensitive to impurities.
    - Example: Trace methanol in a polyester condensation could cap some carbonyl derivatives as methyl esters, preventing them from reacting further.
    - Functionality greater than 2 can introduce branching.
    - Introduction of reagents with varying functionalities in carefully controlled amounts affords control over polymer size and geometry.
  - The physics in this text apply equally well to organic and inorganic (e.g., PDMS) polymers.
  - Biopolymers are briefly introduced.
  - Polymer nomenclature.
  - IUPAC recommendation.
    - Polymers formed from a single monomer.
      - Take the IUPAC name of the monomer, enclose it in parentheses, and add the prefix “poly”.
      - Example: poly(1-chloroethylene) for PVC.
      - Polymers need not be synthesized from the monomer named. For example, poly(1-hydroxyethylene) is synthesized from the hydrolysis of poly(1-acetoxyethylene).
    - Polymers formed from multiple monomers.
      - Apply the preceding rules to the repeat unit.
      - Example: poly(hexamethylene adipamide) is nylon-6,6.
    - Commercially important cross-linked polymers.
      - Typically go without names, or at best, by specifying the monomers that go into it.
      - Example: “Phenol-formaldehyde resin” for bakelite.
  - Notes on common names.
    - Many polymers have a common/outdated chemical name, a trade name, and/or an acronym.
    - Examples: polyethylene glycol, Teflon, PVC.
  - On positional isomerism.
    - Head-to-head addition is more common (1) at higher temperatures and (2) with halogenated monomers.
    - Head-to-tail is dominant because of (1) resonance stabilization at the head position and (2) steric exposure of the tail.
    - Polymer cleavage can provide information about head-head vs. head-tail polymerization: Since diols are cleavable by periodate, poly(vinyl alcohol) can have its weight measured, be subject to cleavage conditions, and have the resultant fragments' weight remeasured to calculate the average frequency of diols.
  - Stereoisomerism reviewed.
  - On geometric isomerism.
    - Not only can you have *cis*- or *trans*-backbones, but isoprene (for example) can polymerize through either — or both! — of its double bonds.

- **Mass concentration** (of an  $i$ -mer): The number of grams per mole of  $i$ -mer per unit volume. *Denoted by  $c_i$ . Given by*

$$c_i := \frac{n_i M_i}{V}$$

- $M_n$  and  $M_w$  are by far the most important and most common measurements of polymer average weight, but there are also others such as the  **$z$ -average molecular weight**.

- **$z$ -average molecular weight**: The third moment of the weight distribution. *Denoted by  $M_z$ . Given by*

$$M_z := M_0 \frac{\sum_i i^3 n_i}{\sum_i i^2 n_i}$$

- **Monodisperse** (sample): A polymer sample for which  $D = 1$ .
- **Narrow** (distribution): A polymer weight distribution for which  $D < 1.5$ .
- **Broad** (distribution): A polymer weight distribution for which  $D > 2$ .
- Lodge and Hiemenz (2020) derive the variance expression given in class.
- **Mean** (of a distribution  $i$ ): The numerical average of the distribution. *Denoted by  $\langle i \rangle$ . Given by*

$$\langle i \rangle := \frac{\sum_i i n_i}{\sum_i n_i} = \sum_i i x_i \quad \langle i \rangle := \int_0^\infty i P(i) di$$

- **Normalized** (distribution): A discrete distribution  $x_i$  or continuous distribution  $P(i)$  satisfying the following respective criterion. *Constraints*

$$\sum_i x_i = 1 \quad \int_0^\infty P(i) di = 1$$

- **$k$ -th moment** (of a normalized distribution): The number defined as follows. *Denoted by  $\mu_k$ . Given by*

$$\mu_k := \sum_i x_i i^k \quad \mu_k := \int_0^\infty i^k P(i) di$$

- The mean is therefore the first moment of a distribution!
- $M_w$  and  $M_z$  are proportional to the ratios of the 2nd to the 1st moment and the 3rd to the 2nd moment, respectively.
- **$k$ -th moment about the mean** (of a normalized distribution): The number defined as follows. *Denoted by  $v_k$ . Given by*

$$v_k := \sum_i x_i (i - \langle i \rangle)^k$$

- It follows that the variance is the second moment about the mean.
- **Schulz-Zimm distribution**: A one-parameter mathematical model for polymer weight distributions, where varying the one parameter affords reasonable descriptions for typical narrow or moderately broad samples. *Given by*

$$P(M_i) := \frac{z^{z+1}}{\Gamma(z+1)} \frac{M_i^{z-1}}{M_n^z} e^{-zM_i/M_n}$$

- $\Gamma$  denotes the **gamma function**, a popular extension of the factorial function.
- Lodge and Hiemenz (2020) extend their discussion of this distribution quite a bit and graph some examples of it. One such graph is included in the lecture 2 slides.

- Measurement of molecular weight.
- **Size exclusion chromatography:** A method of measuring polymer molecular weight that can provide information about the full distribution of weights. *Also known as SEC.*
  - Benefits.
    - The dominant method today; almost all polymer chemistry laboratories have SEC capabilities.
    - Automated analysis of a few milligrams of sample in a good solvent can be achieved in half an hour.
  - Limitations.
    - Poor resolution.
    - Reliance on standards.
- **Matrix-assisted laser desorption/ionization mass spectrometry:** A method of measuring polymer molecular weight that can provide information about the full distribution of weights. *Also known as MALDI.*
  - Benefits.
    - High resolution.
  - Limitations.
    - Relatively new and still being expanded in scope.
    - Resolution is diminished as  $M$  increases.
    - Sensitivity is diminished as  $M$  increases: Higher MW polymers are just harder to get into the gas phase.
      - Sensitivity is also a heretofore unknown function of molecular weight, so extracting  $M_n$  and  $M_w$  quantitatively is unreliable.
      - Microscopic differences in drops and their structure add further uncertainty.
    - Works better for more polar polymers (PE is almost impossible).
    - More highly charged species confound data.
  - Section 1.8.3 covers the basics of how MALDI works.
    - “A great deal remains to be learned about both the desorption and ionization processes, and standard practice is to follow particular recipes (matrix and salt) that have been found to be successful for a given polymer” (Lodge & Hiemenz, 2020, p. 35).
- If SEC and MALDI can be done reliably, accurately, and conveniently, then there is little need for any other technique.
- **Colligative** (property): A property of a solution that depends on the *the number* of solute particles alone, with no consideration of their nature.
- Some techniques provide information on *only*  $M_n$  by measuring colligative properties.
  - Osmotic pressure (most common), freezing point depression, boiling point elevation, light scattering, end group analysis, etc.
  - Osmotic pressure is based on equilibrium thermodynamics, and thus affords absolute measurements *without* calibration!
  - End group analysis relies on the fact that if a molecule only has two ends, counting the number of ends is equivalent to counting the number of molecules.
    - Common techniques: Acid-base titration (acidic or basic end groups), NMR (esp.  $^1\text{H}$  qNMR).
- Some techniques provide information on *only*  $M_w$ .

- Light scattering is also based on equilibrium thermodynamics (so absolute and no calibration needed).
- Misc. techniques: Sedimentation, gel electrophoresis, and intrinsic viscosity.
- End group analysis principles.
  1. “The chemical structure of the end group must be sufficiently different from that of the repeat unit for the chosen analytical technique to resolve the two clearly” (Lodge & Hiemenz, 2020, p. 32).
  2. “There must be a well-defined number of end groups per polymer, at least on average. For a linear polymer, there will be two and only two end groups per molecule, which may or may not be distinct from each other. For branched polymers, the relation of the number of end groups to the number of polymers is ambiguous, unless the total number of branching points is also known” (Lodge & Hiemenz, 2020, p. 32).
  3. “The technique is limited to relatively low molecular weights, as the end groups become more and more dilute as  $N$  increases... As a general rule end groups present at the 1% level (corresponding to degrees of polymerization of 100 for a single end group, 200 for both end groups) can be reliably determined; those at the 0.1% level cannot” (Lodge & Hiemenz, 2020, pp. 32–33).

## 1.5 Chapter 6: Polymer Conformations

*From Lodge and Hiemenz (2020).*

- **Globule:** A compressed conformation of a polymer similar to a dense ball.
- **Random coil:** A conformation of a polyemter where the monomer subunits are oriented randomly while still being bonded to adjacent units.
- The approximately  $0.7k_B T$  ( $3k_B T$  from class appears to be wrong) energy difference between the trans and either gauche state implies that the gauche states will be about  $e^{-0.7} \approx 0.5$  times as populated as the trans states.
- **Ergodic** (system): A system for which the time average of its states is equivalent to the ensemble average.
  - For example, polymer conformations are ergodic because the end-to-end distance of a polymer averaged over time as it wiggles around is the same as its end-to-end distance averaged over a large collection of structurally identical chains at a given instant in time.
- **Isotropic** (quantity): A quantity that is not biased in any particular direction.
  - For example, the polymer end-to-end vector should not orient in any particular direction in the absence of external bias. This is why  $\langle \mathbf{R} \rangle = 0$ , as discussed in class.
- A more rigorous basis for why the cross terms in the FJC expansion of  $\langle R^2 \rangle$  equal zero.
  - For any two vectors  $\mathbf{l}_i, \mathbf{l}_j$ , we have
 
$$\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle = l^2 \langle \cos \theta \rangle$$
 where  $\theta$  is the angle between them when translated through space to be tail-to-tail.
  - Since we are assuming lack of correlation,  $\theta$  is equally likely to be anywhere along its principle branch of  $[0, \pi]$ . Thus,
 
$$\langle \cos \theta \rangle = \int_0^\pi \cos \theta \cdot \frac{d\theta}{\pi - 0} = 0$$
  - This zeroes out the cross term.
- Lodge and Hiemenz (2020, pp. 239–40) explicitly derive the full FRC result for  $\langle R^2 \rangle$ .

- It is an exact, analytical derivation; the only assumptions are that  $n \rightarrow \infty$  (generally justified within measurement error for  $n > 100$ ) and  $\theta \neq 0$  (generally justified because most bonds are not straight from one to the next).
- Lessons from the FRC.
  - $\langle R^2 \rangle$  grows relative to the FJC approximation. This is reasonable because we have less doubling back.
  - We still have  $\langle R^2 \rangle \propto nl^2$ , despite the increase in complexity of the model.
  - When  $\theta \approx 70.5^\circ$  (as for a C–C bond),  $\langle R^2 \rangle \approx 2nl^2$  under this model.
- Flory (1969) derives  $\langle R^2 \rangle$  for the symmetric hindered rotations model.
- Theorem: Under the assumptions that  $n \rightarrow \infty$  and polymer chains can freely pass through themselves,  $\langle R^2 \rangle = Cnl^2$  where  $C$  is a numerical constant that depends only on local constraints and not on  $n$ .
- The principle of Kuhn's equivalent chain follows from this theorem: Memory of orientation is lost at a far enough distance away from the original link, making it so that “for any chain of  $n$  links whose relative orientations are constrained, we can always generate an equivalent chain with a new (bigger) link that is freely jointed, so that the original chain and the new chain have the same [ $\langle R^2 \rangle$ ]” (Lodge & Hiemenz, 2020, p. 241).
- Common backbone bond lengths.

| Bond Type       | C–C  | C=C  | C–O  | C–N  | Si–O |
|-----------------|------|------|------|------|------|
| Bond Length (Å) | 1.53 | 1.34 | 1.43 | 1.47 | 1.6  |

Table 1.3: Common polymer backbone bond lengths.

- For polymers with multiple backbone bonds, add  $n_1 l_1^2 + n_2 l_2^2 + \dots$  for each type of backbone bond.
- Larger  $C_\infty$  implies stiffer chains.
- Characteristic ratio terminology.
  - $C_n$  describes the characteristic ratio for a type of chain with *exactly*  $n$  bonds.
  - $C_\infty$  is  $C_n$ , but specifically in the large  $n$  limit where  $n \rightarrow \infty$ .
- Common monomer parameters ( $C_\infty$ , Kuhn length, monomer volume, etc.) are compiled in a table on Lodge and Hiemenz (2020, p. 243), sourced from Fetters et al. (1994). This significantly extends Table 1.2.
- Although the Kuhn length varies monotonically with  $C_\infty$ , it is not as good a measure of flexibility.
  - Example: The Kuhn length for polystyrene is just a bit longer than for polyisoprene, but polystyrene is much stiffer (as reflected by a  $C_\infty$  more than double polyisoprene's).
  - See Problem 6.4 for more.
- **Monomer volume:** The volume of a single monomer of interest. Denoted by  $v_0$ .
- A good visual for semiflexible, worm-like chains: A garden hose ( $a$  is approximately 1 foot).
- The persistence length is equal to the end-to-end vector onto the direction of the first bond??  $a = \langle \hat{\mathbf{l}}_1 \cdot \mathbf{R} \rangle$ ? See Lodge and Hiemenz (2020, p. 246).
  - It seems that all subsequent results about the WLC differ significantly from our treatment in class.

- Radius of gyration content and derivations of the in-class equation, as well as relation to the textbook's definition of persistence length.
- The distribution of most probable sizes is Gaussian.
  - Derivation of the binomial is *exactly* as I rationalized!
  - Lodge and Hiemenz (2020, pp. 255–56) also derives the 3D Gaussian from the binomial using only first principles.
  - Problem 6.20 shows that the Gaussian is useful for  $N$  as small as 10.
  - It is important to keep in mind that the Gaussian is a continuous approximation for a discrete function; thus, its values can never be *exactly* accurate, and some (e.g., finite probabilities at lengths greater than the contour length) may be meaningless.
  - The pure Gaussian tells us that the most probable *vector* value  $\mathbf{R}$  is 0, but multiplying by  $4\pi R^2$  reveals that the most probable *scalar* value  $R$  is finite.
    - Analogous to normalization of the  $s$  electrons in the hydrogen atom and molecular speeds in the Maxwell-Boltzmann distribution.
- **Dilute** (solution): A solution for which the concentration  $c$  is much less than the critical concentration  $c^*$ .
- A note on excluded volume.
  - Tends to *expand* the coil, because the polymer feels like it has less space available to it.
  - Two cases where excluded volume disappears: Polymer melt and  $\theta$  solvent.
    - Polymer melt: Two monomers still cannot occupy the same space, but there is no benefit to expanding the coil because the adjacent space is *already* surrounded by monomers.
      - Conjectured by Flory long ago, and confirmed by SANS in the 1970s.
    - $\theta$  solvent: A non-very-good solvent that makes monomers prefer to be near each other than far away.

## 1.6 Chapter 7: Thermodynamics of Polymer Mixtures

*From Lodge and Hiemenz (2020).*

- 10/12:
- Lodge and Hiemenz (2020, pp. 310–14) has some additional information on the derivation of the full Flory free energy and its four constituent terms.