

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 CH_2CH_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.

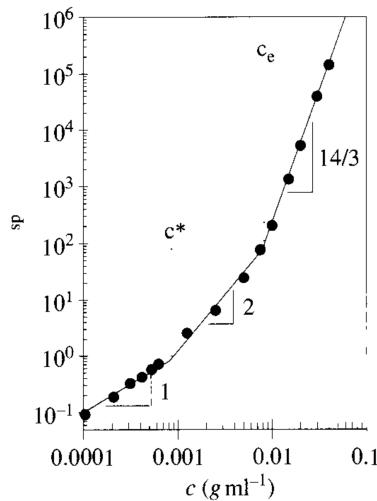


Figure 1.1: Polymer viscosity scales universally by power laws.

- 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) _n	- <i>alt</i> -	poly[(ethylene glycol) ^a - <i>alt</i> -(terephthalic acid)]
periodic	periodic with respect to at least three monomeric units	(ABC) _n (ABB) _n (AABB) _n (ABAC) _n	- <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 ^b	-AAAAAAAAAA- B B B B B 	- <i>graft</i> -	polybutadiene- <i>graft</i> -polystyrene

^a ethane-1,2-diol, ^b 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_i*:** The molecular weight of the *i*-mer. *Given by*

$$M_i := i M_0$$

- ***M₀*:** The molecular weight of the repeat unit in a polymer chain.
- ***n_i*:** 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_i*. 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 weight fraction. Denoted by *w_i*. Given by*

$$w_i := \frac{n_i M_i}{\sum_i n_i M_i} = \frac{n_i (i M_0)}{\sum_i n_i (i M_0)} = \frac{i n_i}{\sum_i i n_i}$$

- Note that *i n_i* 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_n*. 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 σ^2 . Given by*

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

- **Schultz-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.

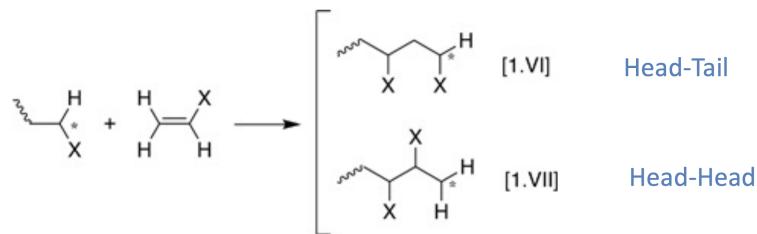


Figure 1.2: Head-head and head-tail monomer addition.

- **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**.

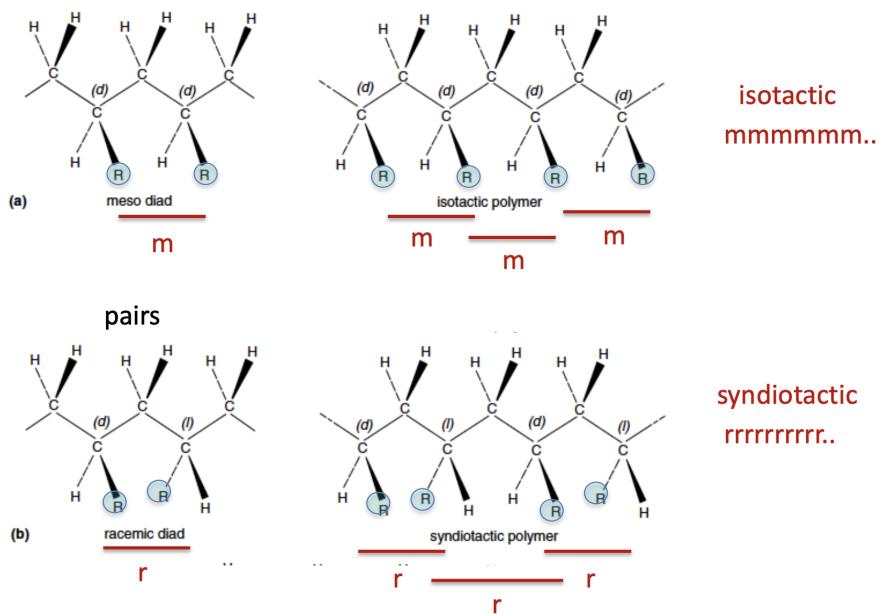


Figure 1.3: Tacticity.

- 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 ^1H 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}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° .
 - **Eclipsed** configuration then starts at 60° .
 - 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 θ .
 - 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^{47000} 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.

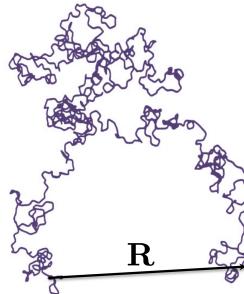


Figure 1.4: End-to-end polymer vector.

- 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.

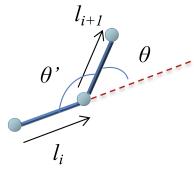


Figure 1.5: A joint in a polymer chain.

- 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 θ 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 θ , but there is no energy penalty to rotate in ϕ .
 - 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 ϕ but not in θ .

- 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 ϕ 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_∞ 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 θ and ϕ in different texts!

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

Polymer	Structure	C_∞
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)	$-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOC}_2\text{H}_5))-$	8.2
Atactic polystyrene (PS)	$-(\text{CH}_2\text{CHC}_6\text{H}_5)-$	9.5

Table 1.2: C_∞ values for common polymers at 413 K.

- C_∞ 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 (CH_2CH_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.

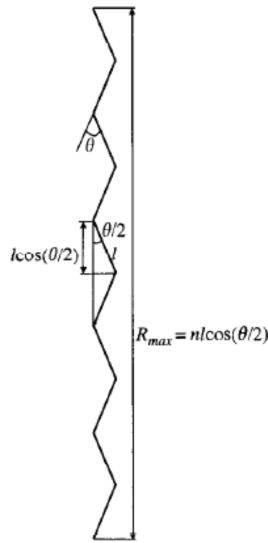


Figure 1.6: Straight chain estimation of a polyolefin.

- 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.

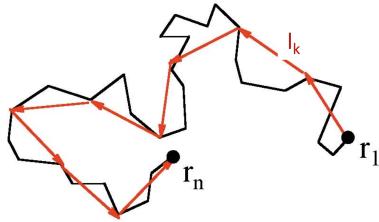


Figure 1.7: Kuhn steps.

- 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,

$$Nl_k^2 = \langle R^2 \rangle = C_\infty n l^2$$

- 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*

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

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

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

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

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

- 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_∞ 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).

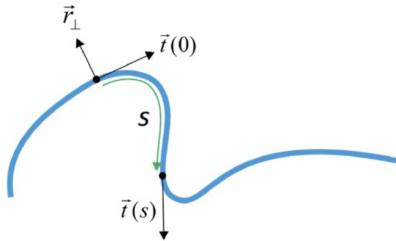


Figure 1.8: Worm-like chain.

- 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 κ_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,

$$2a = L$$

- **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 1000s 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.

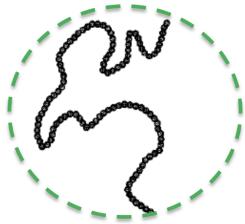


Figure 1.9: The volume occupied by polymers.

- **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. *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 . 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. *Denoted by c^* .*

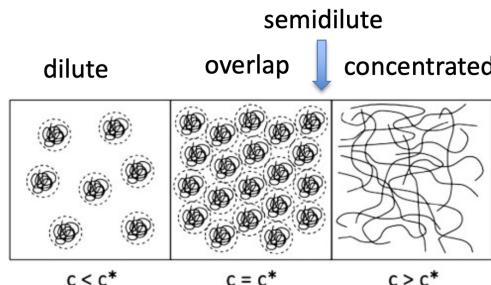


Figure 1.10: Concentration regimes.

- 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.