Rudiments of Polymer Physics

Justin Bois

California Institute of Technology

Student of Niles Pierce and Zhen-Gang Wang

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1 Introduction

A polymer is a chain of several polyatomic units called monomers bonded together. Given the diversity of possible monomeric units and ways in which they can be bound together, there is a myriad of naturally occurring polymers with enormous diversity in their properties. For example, proteins, glass, rubber, DNA, plastics, and chewing gum all consist of polymers. Given their ubiquity and importance in so many systems, attempts to model polymers have aggressively proceeded from many different fronts of attack. This brief summary serves to introduce the reader to some of the basic models used to describe polymers in solution. This document is very much a work in progress, and for the time being contains only the simplest descriptions of single-molecule models for non-branched polymers.

The reader is assumed to have a reasonable math background (including some knowledge of probability and statistics and partial differential equations) and have some knowledge of elementary statistical mechanics.

The development follows primarily from [1, 2, 3, 4], and many results are shown without direct references at this early stage in the development of the document.

2 Discrete models

A polymer in solution may look like a long string of spaghetti in a bowl, like a stiff rod, or somewhere in between. Whatever its stiffness or configuration, it is constantly bombarded by random collisions with the solvent molecules, thereby continuously changing its configuration. For the time being, we will not investigate the dynamics of polymer diffusion, but rather look at static, time-averaged properties of polymers by employing a number of different models. Note that those presented are just the simplest, most instructive models, and there are many other representations for polymeric chains.

2.1 The freely jointed chain

One of the simplest models for a polymer is the *freely jointed chain*, or FJC. In the FJC model, a polymer is approximated as a series of N straight
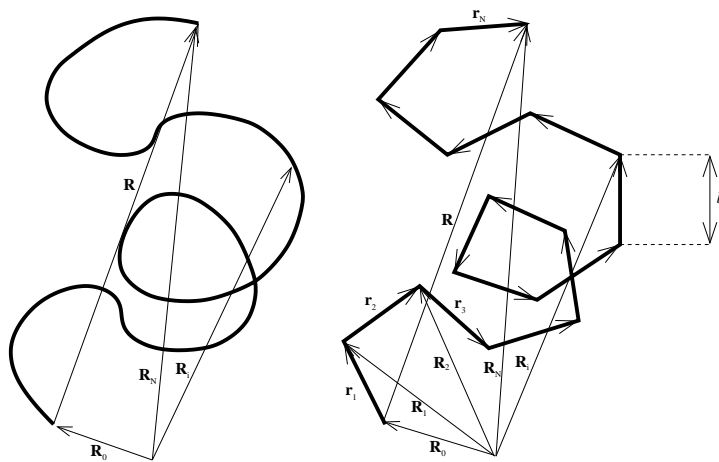
Figure 2.1: A drawing of a polymer and its representation as a FJC. Note that $\mathbf{r}_i = \mathbf{R}_i - \mathbf{R}_{i-1}$ and that $\mathbf{R} = \mathbf{R}_N - \mathbf{R}_0 = \sum_{i=1}^{N} \mathbf{r}_i$. The $\mathbf{R}_i$'s are not important for the present discussion, but become important as we move from discrete to continuous models in section 3.

segments of a given length, b, as depicted in figure 2.1. The orientation of each segment of the FJC is independent of all others. The segment length, b, is called the *Kuhn statistical length* and describes the stiffness of the chain. If the Kuhn length is large, the chain tends to be stiff. Smaller Kuhn lengths are characteristic of more flexible chains. * In such a way, the parameter b describes the nature of short-range self-interactions of the polymer. In other words, if the orientation of a given small piece of the polymer is strongly correlated to the small piece immediately before it, b will be large, but if the orientation of the small piece of the polymer is unrelated to that of the piece immediately before it, b will be small. So the Kuhn statistical length describes the minimum length between two points on a polymer that are essentially uncorrelated.

Since the orientation of each successive statistical segment vector (henceforth referred to as simply "segment" for brevity), $\mathbf{r}_i$, is completely independent of all others, our model is without long-range self-interactions. This

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*It should be noted that, strictly speaking, this is not precisely a measure of the chain stiffness, since a Gaussian chain has no stiffness. The Kuhn statistical length is formally only a measure of chain stiffness for the Kratky-Porod wormlike chain. [5]

means that the chain can bend back and lay over itself. While this is physically unrealistic, the FJC model is still extremely useful and often produces reasonable results in describing experimentally observed phenomena (*e.g.* in [6]).

Naturally, we would like the models we develop to provide all relevant thermodynamic information. Therefore, we would ultimately like to be able to compute partition functions for polymer conformations. Rather than compute partition functions based on probability distributions for all possible conformations, it is more convenient to use a probability distribution for the end-to-end vector of the chain, $\mathbf{R}$ [†] , or the radius of gyration, R_g (the average distance of the polymer from its center of mass). These quantities may be measured experimentally by light scattering experiments or by novel more recently developed single molecule experiments (*e.g.* [6]). This is analogous to using few-particle reduced distribution functions in other areas of statistical mechanics. [2] Therefore, we fill focus much of the discussion on characterizing the end-to-end vector, $\mathbf{R}$, which is easier to handle than R_g.

Let $\mathbf{\Phi}(\mathbf{R}, N)$ be the probability distribution function for $\mathbf{R}$ given that we have a chain of N segments. Since the orientation of each segment is independent of all others, $\mathbf{\Phi}(\mathbf{R}, N)$ will approach a Gaussian distribution for large N by the central limit theorem. Therefore, we need only to consider the first and second moments to completely describe the distribution.

The first moment is easily calculated as

$$\langle \mathbf{R} \rangle = \left\langle \sum_{i=1}^{N} \mathbf{r}_i \right\rangle = \sum_{i=1}^{N} \langle \mathbf{r}_i \rangle = \mathbf{0} \tag{2.1}$$

since $\langle \mathbf{r}_i \rangle = \mathbf{0} \ \forall \ i$ because the orientation of each vector is randomly distributed. The second moment is also easily calculated:

$$\mathbf{R}^2 \equiv \mathbf{R} \cdot \mathbf{R} \ = \ \left(\sum_{i=1}^{N} \mathbf{r}_i \right)^2 = \sum_{i=1}^{N} \mathbf{r}_i^2 + 2 \sum_{i=1}^{N} \sum_{j=1}^{N-i} \mathbf{r}_i \cdot \mathbf{r}_{i+j}. \tag{2.2}$$

$$\Rightarrow \langle \mathbf{R}^2 \rangle \ = \ \sum_{i=1}^{N} \langle \mathbf{r}_i^2 \rangle + 2 \sum_{i=1}^{N} \sum_{j=1}^{N-i} \langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle = N \langle \mathbf{r}_i^2 \rangle = N b^2 \tag{2.3}$$

[†]Here, $\mathbf{R}$ is defined to be the end-to-end vector. In section 3, when we begin looking at continuous models, $\mathbf{R}$ is a continuous representation of the vectors $\mathbf{R}_i$ in figure 2.1.

because $\langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle = 0 \ \forall \ m \neq n$ since they are uncorrelated. Given the second moment, we arrive at the formal definition for the Kuhn statistical length:

$$b \equiv \lim_{L \to \infty} \frac{\langle \mathbf{R}^2 \rangle}{L} \tag{2.4}$$

where L is the total path length of the chain, equal to Nb in this case. Taking the limit in equation (2.4) is then trivial for the FJC. The second moment is often used as a characteristic length of the chain. We have determined, then, that for a FJC,

$$\bar{R} \equiv \sqrt{\langle \mathbf{R}^2 \rangle} = b\sqrt{N}. \tag{2.5}$$

Given both moments, $\mathbf{\Phi}(\mathbf{R}, N)$ is a Gaussian distribution with zero mean and a variance of

$$\sigma^2 = \langle \mathbf{R}^2 \rangle - \langle \mathbf{R} \rangle^2 = Nb^2. \tag{2.6}$$

Thus,

$$\mathbf{\Phi}(\mathbf{R}, N) = \left(\frac{3}{2\pi Nb^2} \right)^{\frac{3}{2}} \exp \left(-\frac{3\mathbf{R}^2}{2Nb^2} \right). \tag{2.7}$$

Using $\mathbf{\Phi}(\mathbf{R}, N)$, we can obtain interesting insights on thermodynamic properties. Following the development of [3], we assume that all conformations with a given end-to-end distance are of equal energy. Then, we can obtain the entropy of the chain by equation (2.7) using the standard method and absorbing all constants into the reference entropy.

$$\begin{aligned} S(\mathbf{R}, N) & \propto & k \ln(\mathbf{\Phi}(\mathbf{R}, N)) \\ \Rightarrow S & = & S_0 - \frac{3k\mathbf{R}^2}{2Nb^2} \end{aligned} \tag{2.8}$$

The free energy is then

$$F = E - TS = F_0 + \frac{3kT\mathbf{R}^2}{2Nb^2} \tag{2.9}$$

We see that the free energy is related quadratically to the end-to-end vector, as if the chain is an "entropic spring".

An exact solution for the FJC is derived in section 5 of [1]. As seen in figure 2.2, our approximate Gaussian distribution works well, even for $N \sim 4$. The most important shortcoming is that the Gaussian distribution gives a finite probability that the chain is longer than its path length. However, for most purposes, the Gaussian approximation works very well.
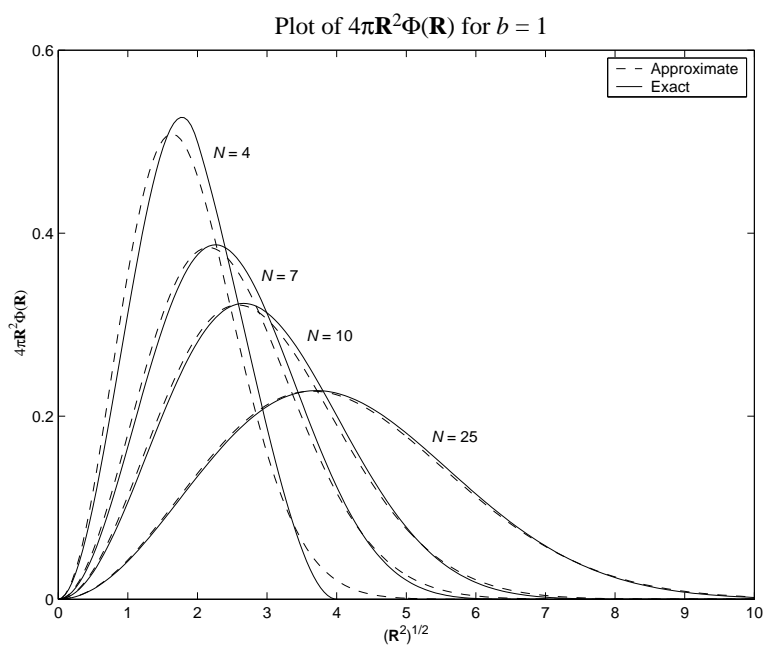
Figure 2.2: A plot of the exact and approximate solutions for a FJC. The approximation of large N appears to be reasonable even when N is below 10.
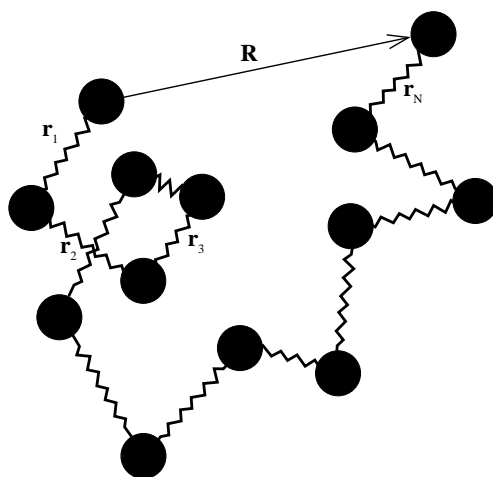
Figure 2.3: A drawing of a Gaussian chain. Although they are not shown, the vectors $\mathbf{R}_i$ are defined analogously as in the FJC model. When the spring constant is appropriately chosen for the harmonic oscillators (see equation (2.10)), the distribution function for $\mathbf{R}$ is identical to that of a FJC.

2.2 The Gaussian chain

A common model used to describe polymers is a *Gaussian chain*, depicted in figure 2.3. A Gaussian chain is modeled as a collection of beads connected by springs functioning as harmonic oscillators. We define the potential the spring exerts of two successive beads as

$$U_0\left(\mathbf{r}_i\right) = \frac{3}{2b^2}kT\mathbf{r}_i^2 \tag{2.10}$$

where $\mathbf{r}_i$ is the vector between them, T is the temperature, and k is Boltzmann's constant. Notice that the spring constant is similar to that expressed in the "entropic spring" description of the free energy of the FJC. With such a definition for the potential of a harmonic oscillator, the average displacement of the two beads is b, as we will see shortly, which correlates to the length of the segments of a FJC.

For the Gaussian chain, our approach to finding the distribution function for the end-to-end vector will be different than in the example of a FJC. We start by finding the distribution function for a single segment, $\psi\left(\mathbf{r}_i\right)$. The

probability will be Boltzmann weighted, so we have

$$\psi\left(\mathbf{r}_i\right) \propto \exp\left(-\frac{U_0}{kT}\right) = \exp\left(-\frac{3\mathbf{r}_i^2}{2b^2}\right). \tag{2.11}$$

Now we just have to normalize it, defining c as the normalization constant and $r_i \equiv |\mathbf{r}_i|$ and utilizing a Gaussian integral.

$$
\begin{aligned}
\int d\mathbf{r}_i\,\psi\left(\mathbf{r}_i\right) &= c\int_0^{2\pi} d\phi \int_0^{\pi} d\theta\,\sin\theta \int_0^{\infty} dr_i\,r_i^2 \exp\left(-\frac{3r_i^2}{2b^2}\right) \\
&= 4\pi c \int_0^{\infty} dr_i\,r_i^2 \exp\left(-\frac{3r_i^2}{2b^2}\right) = c\left(\frac{2\pi b^2}{3}\right)^{\frac{3}{2}} = 1 \\
\Rightarrow c &= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \\
\Rightarrow \psi\left(\mathbf{r}_i\right) &= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\mathbf{r}_i^2}{2b^2}\right). \tag{2.12}
\end{aligned}
$$

This is a Gaussian distribution with $\langle \mathbf{r}_i^2 \rangle = b^2$, thus verifying our claim of an average bond length of b.

Since each segment is unrelated to the others, we can now write the *conformational distribution function*, $\mathbf{\Psi}\left(\{\mathbf{r}_i\}, L\right)$, which describes all possible spacial orientations of the $\mathbf{r}_i$'s for a chain of total path length L.

$$\mathbf{\Psi}\left(\{\mathbf{r}_i\}, L\right) = \prod_{i=1}^{N} \psi\left(\mathbf{r}_i\right) = \left(\frac{3}{2\pi b^2}\right)^{\frac{3N}{2}} \exp\left(-\frac{3}{2b^2}\sum_{i=1}^{N}\mathbf{r}_i^2\right). \tag{2.13}$$

Now that we have the conformational distribution function, we can get the end-to-end distribution function by

$$\mathbf{\Phi}\left(\mathbf{R}, N\right) = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \cdots \int d\mathbf{r}_N\,\delta\left(\mathbf{R} - \sum_{i=1}^{N}\mathbf{r}_i\right)\mathbf{\Psi}\left(\{\mathbf{r}_i\}, L\right), \tag{2.14}$$

where the delta function serves to enforce that the end-to-end vector is given by the sum of the segments. The calculation of the integral is lengthy and is omitted here, but the result is

$$\mathbf{\Phi}(\mathbf{R}, N) = \left(\frac{3}{2\pi N b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3\mathbf{R}^2}{2N b^2}\right). \tag{2.15}$$

The chain is thusly called a Gaussian chain because the bond lengths and the end-to-end vector are Gaussian distributed. It should be noted that this model is by no means an adequate description of the local properties of the chain, but gives the same end-to-end vector distribution function as the FJC. For many applications, especially when the continuous analogs of the models are used, the Gaussian chain is the easiest to deal with mathematically and is therefore often used in place of the FJC (as we will do in section 3.1).

We note now that since each segment of the Gaussian chain is independent of the others, a chain of length N may be constructed by stringing two chains of length N_1 and N_2 together with $N_1 + N_2 = N$. Noting this, we can trivially find the distribution function of the vector connecting any two arbitrary segments m and n in a Gaussian chain.

$$\mathbf{\Phi}\left(\mathbf{R}_n - \mathbf{R}_m, n - m\right) = \left(\frac{3}{2\pi b^2 \left|n - m\right|}\right)^{\frac{3}{2}} \exp\left(-\frac{3\left(\mathbf{R}_n - \mathbf{R}_m\right)^2}{2b^2 \left|n - m\right|}\right). \quad (2.16)$$

And similarly,

$$\left\langle \left(\mathbf{R}_n - \mathbf{R}_m\right)^2 \right\rangle = \left|n - m\right| b^2. \quad (2.17)$$

Now we will calculate the *mean square radius of gyration*, R_g^2, which is the mean square distance between all the segments in the chain. Physically, this is the average distance of the chain from the center of mass, $\mathbf{R}_G$. Thus,

we can compute R_g^2 following the development in [4].

$$\mathbf{R}_G = \frac{1}{N}\sum_{m=1}^{N}\mathbf{R}_m \tag{2.18}$$

$$\Rightarrow R_g^2 = \frac{1}{N}\sum_{i=1}^{N}\left\langle(\mathbf{R}_i-\mathbf{R}_G)^2\right\rangle$$

$$= \frac{1}{N}\sum_{i=1}^{N}\left\langle\left(\mathbf{R}_i-\frac{1}{N}\sum_{m=1}^{N}\mathbf{R}_m\right)^2\right\rangle$$

$$= \frac{1}{N}\sum_{i=1}^{N}\left\langle\mathbf{R}_i^2-\frac{2\mathbf{R}_i}{N}\cdot\sum_{m=1}^{N}\mathbf{R}_m+\frac{1}{N^2}\sum_{m=1}^{N}\sum_{j=1}^{N}\mathbf{R}_m\cdot\mathbf{R}_j\right\rangle$$

$$= \left\langle\frac{1}{N}\sum_{i=1}^{N}\mathbf{R}_i^2-\frac{1}{N^2}\sum_{i=1}^{N}\sum_{m=1}^{N}\mathbf{R}_i\cdot\mathbf{R}_m\right\rangle$$

$$= \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{m=1}^{N}\left\langle(\mathbf{R}_i-\mathbf{R}_m)^2\right\rangle. \tag{2.19}$$

Using equation (2.17), we can complete the calculation.

$$R_g^2 = \frac{1}{2N^2}\sum_{m=1}^{N}\sum_{n=1}^{N}|n-m|\,b^2\approx\frac{b^2}{2N^2}\int_0^N dn\int_0^N dm\,|n-m|$$

$$= \frac{b^2}{N^2}\int_0^N dn\int_0^n dm\,(n-m)=\frac{N}{6b^2}=\frac{\langle\mathbf{R}^2\rangle}{6}. \tag{2.20}$$

Approximating the sum as an integral gives a closed-form solution and is reasonable for large N. Figure 2.4 shows a comparison of the exact (given by the sum) and the approximate closed-form mean square radius of gyration.

2.3   The freely rotating chain

Another reasonable model to describe chains absent of long-range self-interactions is the *freely rotating chain*. A drawing of a freely rotating chain is shown in figure 2.5. The angle θ is fixed for each segment, but each segment can freely
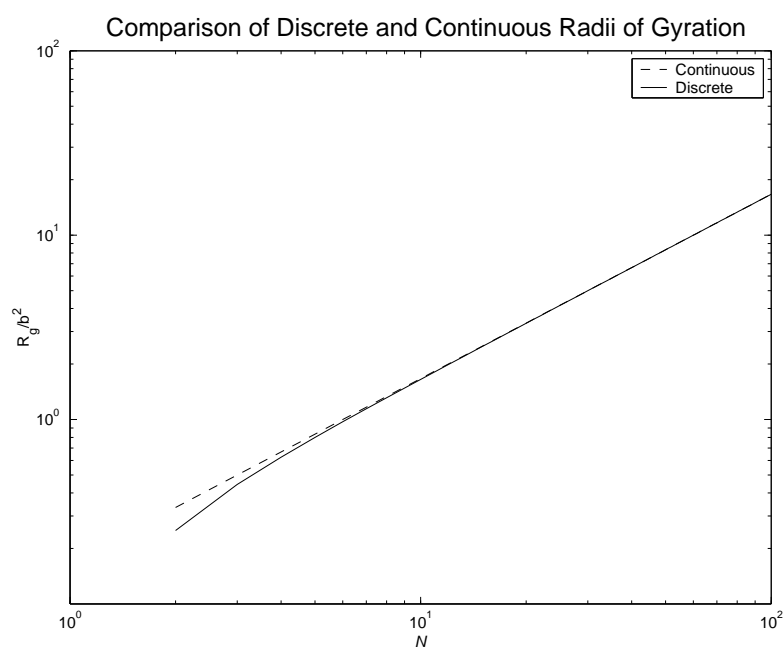
Figure 2.4: A comparison of the approximate and exact mean square radii of gyration for a Gaussian chain. The approximation is reasonable even for $N \sim 10$ and below.
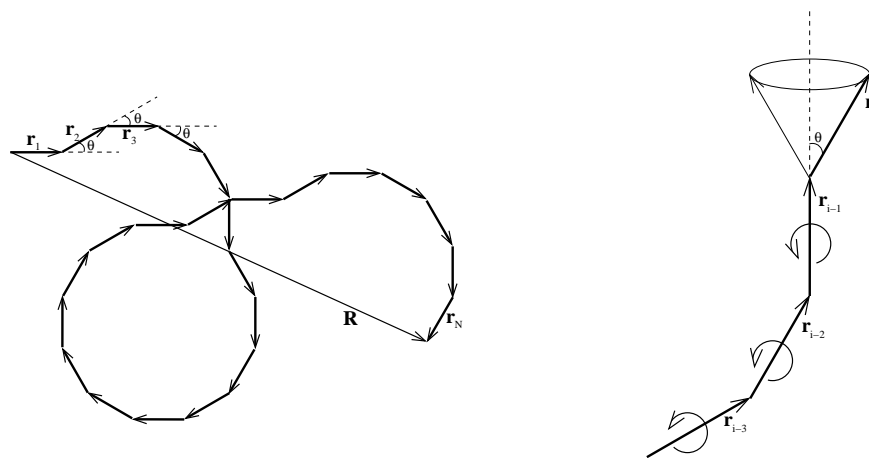
Figure 2.5: At *left*, a 2-D representation of a freely rotating chain. As before, although they are not shown, the vectors $\mathbf{R}_i$ are defined analogously as in the FJC model in figure 2.1 and the lengths of each $\mathbf{r}_i$ is again b. Note that full rotation is permissible about each bond in the ϕ direction, as shown at *right*. Note also that each successive segment is not independent of those previous to it. In such a way, the chain can exhibit stiffness for small N.

rotate in the ϕ direction. The distribution function for the end-to-end vector, $\mathbf{R}$, is difficult to obtain for the discrete case (we will examine a continuous limit of this chain, called a Kratky-Porod wormlike chain, in a subsequent section), so we will only compute $\bar{R}^2 = \langle \mathbf{R}^2 \rangle$ here. This alone is enlightening because it provides interesting insights into the limiting cases of this model and the nature of the inherent stiffness.

Since equation (2.2) is general, it also holds for the freely rotating chain. A recursion relation is needed to calculate $\langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle$. The relationship is derived by successively projecting each segment vector, $\mathbf{r}_i$, onto the unit vector along the direction of the subsequent one, $\mathbf{r}_{i+1}$. Thus,

$$\mathbf{r}_i = \frac{(\mathbf{r}_i \cdot \mathbf{r}_{i+1}) \, \mathbf{r}_{i+1}}{|\mathbf{r}_{i+1}|^2} = \frac{(\mathbf{r}_i \cdot \mathbf{r}_{i+1}) \, (\mathbf{r}_{i+1} \cdot \mathbf{r}_{i+2}) \cdots (\mathbf{r}_{i+j-2} \cdot \mathbf{r}_{i+j-1})}{(b^2)^{j-1}} \, \mathbf{r}_{i+j-1}. \quad (2.21)$$

So, we have $\mathbf{r}_i$ in terms of dot products of successive segments. We know from elementary vector geometry that the dot product of the successive segments is

$$\langle \mathbf{r}_i \cdot \mathbf{r}_{i-1} \rangle = b^2 \cos \theta. \quad (2.22)$$

The vector $\mathbf{r}_i$ is then given by

$$\mathbf{r}_i = \frac{(b^2)^{j-1} (\cos\theta)^{j-1}}{(b^2)^{j-1}} \mathbf{r}_{i+j-1} = (\cos\theta)^{j-1} \mathbf{r}_{i+j-1}. \tag{2.23}$$

Now we can calculate the relevant quantity:

$$\langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle = (\cos\theta)^{j-1} \langle \mathbf{r}_{i+j-1} \cdot \mathbf{r}_{i+j} \rangle = b^2 (\cos\theta)^j. \tag{2.24}$$

Given that $\langle \mathbf{r}_i^2 \rangle = b^2$, we have

$$\begin{aligned}
\langle \mathbf{R}^2 \rangle &= \sum_{i=1}^{N} \langle \mathbf{r}_i^2 \rangle + 2 \sum_{i=1}^{N} \sum_{j=1}^{N-i} \langle \mathbf{r}_i \cdot \mathbf{r}_{i+j} \rangle \\
&= b^2 \left(N + 2 \sum_{i=1}^{N} \left[\sum_{j=1}^{N-i} (\cos\theta)^j \right] \right). \tag{2.25}
\end{aligned}$$

The sum in square brackets is itself a geometric series in $\cos\theta$ with

$$\sum_{j=1}^{N-i} (\cos\theta)^j = \frac{\cos\theta \left(1 - (\cos\theta)^{N-i} \right)}{1 - \cos\theta}. \tag{2.26}$$

Now we have

$$\begin{aligned}
\sum_{i=1}^{N} \sum_{i=1}^{N-i} (\cos\theta)^j &= \sum_{i=1}^{N} \frac{\cos\theta \left(1 - (\cos\theta)^{N-i} \right)}{1 - \cos\theta} \\
&= \frac{\cos\theta}{1 - \cos\theta} \sum_{i=1}^{N} 1 - (\cos\theta)^{N-i} \\
&= \frac{\cos\theta}{1 - \cos\theta} \left(N - \sum_{i=1}^{N} (\cos\theta)^{N-i} \right) \\
&= \frac{\cos\theta}{1 - \cos\theta} \left(N - (\cos\theta)^N \sum_{i=1}^{N} (\sec\theta)^i \right). \tag{2.27}
\end{aligned}$$

The summation is a geometric series in $\sec\theta$. Using this fact and some

algebraic manipulations, we obtain

$$\sum_{i=1}^{N}\sum_{i=1}^{N-i}(\cos\theta)^{j} = \frac{\cos\theta}{1-\cos\theta}\left(N-(\cos\theta)^{N}\frac{\sec\theta\left(1-(\sec\theta)^{N}\right)}{1-\sec\theta}\right)$$

$$= \frac{N\cos\theta}{1-\cos\theta}\left(1-\frac{1-(\cos\theta)^{N}}{N\left(1-\cos\theta\right)}\right). \qquad (2.28)$$

Substitution of equation (2.28) into (2.25) yields the final result of

$$\langle\mathbf{R}^{2}\rangle = Nb^{2}\left(1+\frac{2\cos\theta}{1-\cos\theta}\left(1-\frac{1-(\cos\theta)^{N}}{N\left(1-\cos\theta\right)}\right)\right)$$

$$= Nb^{2}\left(\frac{1+\cos\theta}{1-\cos\theta}-\frac{2\cos\theta}{N}\frac{1-(\cos\theta)^{N}}{\left(1-\cos\theta\right)^{2}}\right). \qquad (2.29)$$

Clearly, if N is large, the second term vanishes and we get

$$\bar{R}\equiv\sqrt{\langle\mathbf{R}^{2}\rangle}=b\sqrt{N\left(\frac{1+\cos\theta}{1-\cos\theta}\right)}, \qquad (2.30)$$

which shows that, as in the case of the FJC and Gaussian chains, the end-to-end distance scales as $\sqrt{N}$. However if the second term is non-zero, the chain is said to have "stiffness."

To characterize how stiff the chain is, we wish to find some relationship describing the "memory" of the chain. Suppose the first segment of the chain points in the direction $\mathbf{u}_0$. We now ask, how does the end-to-end vector of the chain, $\mathbf{R}$, correlate with the original orientation, $\mathbf{u}_0$? If $\mathbf{R}$ is on average along the same direction as the original orientation, the chain is very stiff. If not, it is more flexible. Thus, it is natural to calculate

$$\langle\mathbf{R}\cdot\mathbf{u}_{0}\rangle = \left\langle\mathbf{R}\cdot\frac{\mathbf{r}_{1}}{|\mathbf{r}_{1}|}\right\rangle=\frac{1}{b}\left\langle\mathbf{r}_{1}\cdot\sum_{i=1}^{N}\mathbf{r}_{i}\right\rangle=\frac{1}{b}\sum_{i=1}^{N}\langle\mathbf{r}_{1}\cdot\mathbf{r}_{i}\rangle=\frac{1}{b}\sum_{i=1}^{N}b^{2}\left(\cos\theta\right)^{i-1}$$

$$= b\sum_{i=1}^{N}\left(\cos\theta\right)^{i-1}=b\frac{1-(\cos\theta)^{N}}{1-\cos\theta}. \qquad (2.31)$$

We used the results from equations (2.24) and (2.26) to arrive at this result.

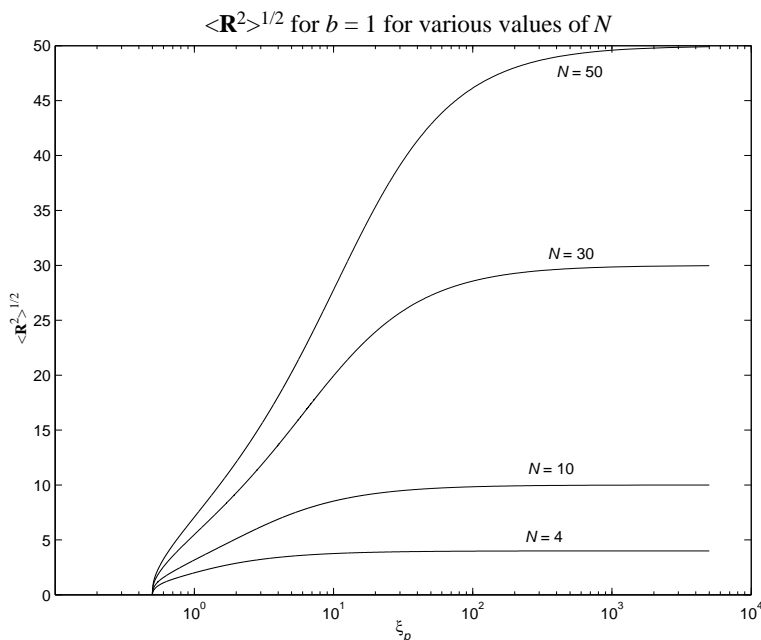$\langle\mathbf{R}^2\rangle^{1/2}$ for $b = 1$ for various values of N

Figure 2.6: A plot of $\bar{R} \equiv \sqrt{\langle\mathbf{R}^2\rangle}$ vs. ξ_p for a freely rotating chain. Note that $\bar{R}$ goes to zero as ξ_p goes to zero. The appearance to the contrary in the plot is an artifact of the logarithmic scaling.

In the limit of a long chain (large $L = Nb$),

$$\lim_{L\to\infty} \langle\mathbf{R}\cdot\mathbf{u}_0\rangle \equiv \frac{1}{2\lambda} \equiv \xi_p = \frac{b}{1 - \cos\theta}, \tag{2.32}$$

where ξ_p is called the *persistence length* of the chain. This describes the stiffness in the chain in that it describes how long the orientation of the chain *persists* through its length. Clearly, the smaller θ is, the stiffer the chain will be. A θ of zero corresponds to a completely rigid rod. Figure 2.6 shows how $\bar{R} \equiv \sqrt{\langle\mathbf{R}^2\rangle}$ varies with ξ_p for a freely rotating chain.

3   Continuous models

The models proposed thus far present a polymer chain as a set of discrete segments that have some relationship to each other. Based on the nature of

these relationships, we can construct a continuous model of the polymer that describes the same characteristics as the discrete model.

3.1   The continuous Gaussian chain

In the discrete FJC, the segment length and the Kuhn statistical lengths were one and the same. When we take a continuous limit, though, we naturally want the limit as the segment length goes to zero. Therefore, we need to draw a distinction between the segment length and the Kuhn statistical length, which, as stated before, is a representation of the stiffness of the chain. [*] Therefore, we define the segment length to be Δs, where s denotes path length, and retain the same notation for the Kuhn statistical length, still calling it b. Thus, b^2 becomes $b\Delta s$ in our current development.

Next, we note that the total path length of a chain is $L = N\Delta s$. This, of course, must be preserved as we take the continuous limit.

The necessary limits to take to get the continuous description are now obvious. We take $\Delta s \to 0$, $N \to \infty$, and $N\Delta s \to L$. We define this limit as the *functional integral* limit ($\lim_{FI}$), since it defines a functional integral as a limit of the discrete chain. Since we will be integrating over the conformational distribution function, given by equation (2.13), we seek

$$
\begin{aligned}
\lim_{FI} d\{\mathbf{r}_i\}\ \mathbf{\Psi}\left(\{\mathbf{r}_i\}, L\right) &= \lim_{FI} d\{\mathbf{R}_i\}\ \mathbf{\Psi}\left(\{\mathbf{R}_i\}, L\right) \\
&= \lim_{FI} \left(\prod_{i=0}^{N} d\mathbf{R}_i\right)\ \mathbf{\Psi}\left(\{\mathbf{R}_i\}, L\right) \qquad (3.1)
\end{aligned}
$$

since the $\mathbf{R}_i$'s are themselves simple functions of the $\mathbf{r}_i$'s.

For this analysis, we will follow the treatment of [2]. At first, we only

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[*]See footnote on page 2. The same comments apply to the persistence length. [5]

consider the exponential.

$$
\begin{aligned}
\lim_{FI} \exp\left(-\frac{3}{2b\Delta s}\sum_{i=1}^{N}\mathbf{r}_i^2\right) &= \lim_{FI} \exp\left(-\frac{3}{2b}\sum_{i=1}^{N}\left(\frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{\Delta s}\right)^2 \Delta s\right) \\
&= \lim_{FI} \exp\left(-\frac{3}{2b}\sum_{i=1}^{N}\left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 \Delta s\right) \\
&= \exp\left(-\frac{3}{2b}\int_{0}^{L} ds \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2\right). \quad (3.2)
\end{aligned}
$$

Here, $\mathbf{R} = \mathbf{R}(s)$ is the continuous representation of the discrete case vectors $\mathbf{R}_i$ as a function of s and *not* the end-to-end vector of the chain. The lower bound on the integral was obtained by defining the arbitrary reference point for $\mathbf{R}$ to be the starting point of the chain.

Now we will take $\lim_{FI}$ of the differential.

$$
\lim_{FI}\prod_{i=0}^{N} d\mathbf{R}_i = \mathcal{D}\mathbf{R}. \quad (3.3)
$$

This denotes that the functional integral is defined as a limit of the iterated integrals for the discrete chain.

Finally, we'll take the limit for the normalization constant.

$$
\lim_{FI}\left(\frac{3}{2\pi b\Delta s}\right)^{\frac{3N}{2}} = (\infty)^{\infty}. \quad (3.4)
$$

This appears to be a problem. However, the normalization is necessary to ensure that the probability that the chain will be in some conformation is unity. Since it is just a normalization constant, it does not create any problems when using the conformational distribution function. An easy way to deal with it is to define the normalization constant as $\mathcal{N}$ with the definition $\delta \mathbf{R} \equiv \mathcal{N}\,\mathcal{D}\mathbf{R}$ such that

$$
\begin{aligned}
\int_{\mathbf{R}(0)=\mathbf{0}} \mathcal{D}\mathbf{R}\,\Psi(\mathbf{R}, L) &= \int_{\mathbf{R}(0)=\mathbf{0}} \mathcal{D}\mathbf{R}\,\mathcal{N}\exp\left(-\frac{3}{2b}\int_{0}^{L} ds \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2\right) \\
&\equiv \int_{\mathbf{R}(0)=\mathbf{0}} \delta\mathbf{R}\,\exp\left(-\frac{3}{2b}\int_{0}^{L} ds \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2\right) = 1. (3.5)
\end{aligned}
$$

Thus, we have arrived at a continuous conformational distribution function for a Gaussian chain. We found

$$\lim_{FI} d\left(\{\mathbf{r}_i\}\right) \Psi\left(\{\mathbf{r}\}, L\right) = \mathcal{D}\mathbf{R}\ \Psi\left(\mathbf{R}, L\right) = \delta\mathbf{R}\ \exp\left(-\frac{3}{2b} \int\limits_0^L ds\ \left(\frac{\partial\mathbf{R}}{\partial s}\right)^2\right) \quad (3.6)$$

where $\mathbf{R}$ is a function of path length, s.

It should be noted that $\Psi\left(\mathbf{R}, L\right)$ may also be represented in terms of the unit tangent vector, $\mathbf{u}$. We recall from differential geometry that

$$\mathbf{u} = \frac{\partial\mathbf{R}}{\partial s}. \quad (3.7)$$

Taking Ψ as a function of u and finding $\mathcal{D}\mathbf{u}$ from the $d\mathbf{u}_i$'s in a manner similar to equation (3.3), we get

$$\mathcal{D}\mathbf{u}\ \Psi\left(\mathbf{u}, L\right) = \delta\mathbf{u}\ \exp\left(-\frac{3}{2b} \int\limits_0^L ds\ \mathbf{u}^2\right). \quad (3.8)$$

3.2 The continuous freely rotating chain (Kratky-Porod wormlike chain)

To build a continuous analog to the freely rotating chain, we need to define a limit analogous to $\lim_{FI}$ for the Gaussian chain. Naturally, we want to retain similar limits as in $\lim_{FI}$, so we put $b \to 0$, $N \to \infty$, and $Nb \to L$. We still need to deal with θ. In the limit of $b \to 0$, the angle θ will go to zero, so we impose $\theta \to 0$. Finally, we impose our definition of the persistence length given by equation (2.32). We will denote this limit $\lim_{worm}$, since it is the limit to get a *Kratky-Porod wormlike chain.*

Because we did not derive an expression for the conformational distribution function for the freely rotating chain, we will only compute the continuous analogs for the end-to-end vector $\langle\mathbf{R}^2\rangle$ and for $\langle\mathbf{R}\cdot\mathbf{u}_0\rangle$.

In the calculation of $\langle\mathbf{R}^2\rangle$, Recall equation (2.29), repeated here for convenience in reference:

$$\langle\mathbf{R}^2\rangle = Nb^2 \left(\frac{1+\cos\theta}{1-\cos\theta} - \frac{2\cos\theta}{N}\frac{1-(\cos\theta)^N}{(1-\cos\theta)^2}\right).$$

We first note that

$$
\begin{aligned}
(\cos\theta)^N &= \exp\left(N\ln\left(\cos\theta\right)\right) \\
&= \exp\left(N\left(\cos\theta - 1 - \frac{(\cos\theta - 1)^2}{2} + \cdots\right)\right) \\
&= \exp\left(Nb\left(\frac{(\cos\theta - 1)}{b} - \frac{(\cos\theta - 1)^2}{2b} + \cdots\right)\right) \quad (3.9)
\end{aligned}
$$

since the Taylor expansion for the natural logarithm function is given by

$$
\ln x = \sum_{k=1}^{\infty} (-1)^{k+1} \frac{(x-1)^k}{k}. \tag{3.10}
$$

To take $\lim_{worm}$ of this expression, we first apply equation (2.32), then put $\theta \to 0$, and finally put $Nb \to L$ to get

$$
\lim_{worm} (\cos\theta)^N = \exp\left(-2\lambda L\right). \tag{3.11}
$$

With equation (3.11) in hand, we can evaluate the limit.

$$
\begin{aligned}
\lim_{worm} \langle \mathbf{R}^2 \rangle &= \lim_{worm} Nb\frac{b}{1 - \cos\theta}\left(1 + \cos\theta\right) - \left(\frac{b}{1 - \cos\theta}\right)^2 \cos\theta \left(1 - (\cos\theta)^N\right) \\
&= \frac{L}{\lambda} - \frac{1 - \exp\left(-2\lambda L\right)}{2\lambda^2}. \tag{3.12}
\end{aligned}
$$

Recalling equation (2.31) and (3.11), we can easily calculate the continuous analog for $\langle \mathbf{R} \cdot \mathbf{u}_0 \rangle$ as

$$
\lim_{worm} \langle \mathbf{R} \cdot \mathbf{u}_0 \rangle = \lim_{worm} \frac{b}{1 - \cos\theta}\left(1 - (\cos\theta)^N\right) = \frac{1 - \exp\left(-2\lambda L\right)}{2\lambda}. \tag{3.13}
$$

Using equations (3.12) and (3.13) and the definitions in of equations (2.4) and (2.32), we can calculate

$$
b = \lim_{L \to \infty} \frac{\langle \mathbf{R}^2 \rangle}{L} = \frac{1}{\lambda} \tag{3.14}
$$

and

$$
\xi_p = \lim_{L \to \infty} \langle \mathbf{R} \cdot \mathbf{u}_0 \rangle = \frac{1}{2\lambda}. \tag{3.15}
$$

Therefore,

$$b = 2\xi_p, \tag{3.16}$$

which is in general true. [5]

We can now look at important limiting cases. When the chain is much longer than its persistence length ($\lambda L \gg 1$), the efects of the stiffness on the end-to-end vector become negligible. Conversely, when the chain is short compared to its persistence length ($\lambda L \ll 1$), the chain is very stiff. We take the appropriate limits recalling equations (3.12) and (3.13), employing l'Hôpital's rule when necessary.

$$\lim_{\lambda L \to \infty} \left\langle \mathbf{R}^2 \right\rangle = \lim_{\lambda L \to \infty} \frac{L}{\lambda} - \frac{L^2}{2\left(\lambda L\right)^2}\left(1 - \exp\left(-2\lambda L\right)\right) = \frac{L}{\lambda} \tag{3.17}$$

$$\lim_{\lambda L \to \infty} \left\langle \mathbf{R} \cdot \mathbf{u}_0 \right\rangle = \frac{1}{2\lambda} \tag{3.18}$$

$$
\begin{aligned}
\lim_{\lambda L \to 0} \left\langle \mathbf{R}^2 \right\rangle &= \lim_{\lambda L \to 0} \frac{2\lambda L - 1 + \exp\left(-2\lambda L\right)}{2\lambda^2} \\
&= \lim_{\lambda L \to 0} \frac{2L^2\left(\lambda L\right) - L^2 + L^2\exp\left(-2\lambda L\right)}{2\left(\lambda L\right)^2} \\
&= \lim_{\lambda L \to 0} \frac{2L^2 - 2L^2\exp\left(-2\lambda L\right)}{4\lambda L} \\
&= \lim_{\lambda L \to 0} \frac{4L^2\exp\left(-2\lambda L\right)}{4} = L^2
\end{aligned} \tag{3.19}
$$

$$
\begin{aligned}
\lim_{\lambda L \to 0} \left\langle \mathbf{R} \cdot \mathbf{u}_0 \right\rangle &= \lim_{\lambda L \to 0} L\frac{1 - \exp\left(-2\lambda L\right)}{2\lambda L} \\
&= \lim_{\lambda L \to 0} L\frac{2\exp\left(-2\lambda L\right)}{2} = L
\end{aligned} \tag{3.20}
$$

Equations (3.17) and (3.18) give the *random coil, (random flight)* limit and equations (3.19) and (3.20) give the *stiff rod* limit.

We will return to the Kratky-Porod wormlike chain (WLC) in section 3.4.2.

3.3   The Green function

In section 3.1 we found the conformational distribution function for a Gaussian chain, as given by equation (3.6). This signifies the probability distribution function for the polymer *over all conformational space.* Although we did not explicitly find them, these distributions exist for other models. This distribution provides more information than we need or want to (or can) deal with. Therefore, it is wise to find a reduced distribution function to describe the system, since this is often all we need to extract thermodynamic information from experiments.[2] A good choice (and one we've been dealing with in most of our developments) is to use the end-to-end vector distribution function. We will define a conditional probability that fixes the end to end vector such that the chain begins at $\mathbf{R}'$ and ends at $\mathbf{R}$ with total path length L. We call this the *Green function* (the rationale behind this name will become clear later) and denote it as $\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right)$.

Given its definition, the Green function can be obtained by taking the appropriate integral over the conformational distribution function.

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) = \int_{\mathbf{R}(0)=\mathbf{R}'}^{\mathbf{R}(L)=\mathbf{R}} \delta\mathbf{R}\,\boldsymbol{\Psi}\left(\mathbf{R}, L\right). \tag{3.21}$$

Given the Green function, the conformational partition function for a given end to end vector $\left(\mathbf{R} - \mathbf{R}'\right)$ for a chain of total length L is given by

$$Z\left(\mathbf{R}, \mathbf{R}'|L\right) = \int d\mathbf{R}\,d\mathbf{R}'\,\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right). \tag{3.22}$$

In a manner similar to that on page 8, we can piece together two (and three and four and . . .) chains. This is represented in the property of the Green function given by

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) = \int d\mathbf{R}''\,\mathbf{G}\left(\mathbf{R}, \mathbf{R}''|L - l\right)\mathbf{G}\left(\mathbf{R}'', \mathbf{R}'|l\right)\ \text{for } l < L. \tag{3.23}$$

An alternate (and equivalent) definition of the Green function is to define its start at the origin, i.e. $\mathbf{R}' = \mathbf{0}$. Thus, its end-to-end vector is $\mathbf{R} - \mathbf{R}' = \mathbf{R}$. Then the Green function is denoted simply by $\mathbf{G}\left(\mathbf{R}|L\right)$.

Often times other information pertaining to the conformation of the chain is important. The Green functions in equations (3.21) and (3.23) are valid for flexible chains. For chains with stiffness, the orientation, or unit tangent vector, $\mathbf{u}$, of the chain is also important. In such a case, we can still define $\mathbf{G}$ from the conformational distribution function. The trick is to incorporate the end-to-end vector, $\mathbf{R}$ (assuming $\mathbf{R}' = \mathbf{0}$) into the integral. Given that $\mathbf{u}$ is the unit tangent vector for the chain,

$$\mathbf{R} = \int_0^L ds\, \mathbf{u}. \tag{3.24}$$

Recalling equation (3.8), we can define the Green function for a chain with length L, starting at the origin, ending at $\mathbf{R}$, with initial orientation $\mathbf{u}_0$, and final orientation $\mathbf{u}$ as

$$\mathbf{G}\left(\mathbf{R}, \mathbf{u} | \mathbf{u}_0, L\right) = \int_{\mathbf{u}(0)=\mathbf{u}_0}^{\mathbf{u}(L)=\mathbf{u}} \delta\mathbf{u}\, \delta\left(\mathbf{R} - \int_0^L ds\, \mathbf{u}\right) \Psi\left(\mathbf{u}, L\right). \tag{3.25}$$

3.3.1   The Green function for a Gaussian chain in an external field

Equation (3.6) gives the conformational distribution function for the Gaussian chain. If we were to place the chain in an external field (defined per unit length of the chain), $U_e\left(\mathbf{R}\right)$, the contribution of the field to the conformational distribution function is Boltzmann weighted. Thus, we get

$$\Psi\left(\mathbf{R}, L\right) \propto \exp\left(-\frac{3}{2b}\int_0^L ds\, \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 - \frac{1}{kT}\int_0^L ds\, U_e\left(\mathbf{R}\right)\right). \tag{3.26}$$

For the case of the Gaussian chain represented by equation (3.26), we get

$$
\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) = \int\limits_{\mathbf{R}(0)=\mathbf{R}'}^{\mathbf{R}(L)=\mathbf{R}} \delta\mathbf{R}\,\mathbf{\Psi}\left(\mathbf{R}, L\right)
$$

$$
= \int\limits_{\mathbf{R}(0)=\mathbf{R}'}^{\mathbf{R}(L)=\mathbf{R}} \delta\mathbf{R}\, \exp\left(-\frac{3}{2b}\int\limits_0^L ds\, \left(\frac{\partial\mathbf{R}}{\partial s}\right)^2 - \frac{1}{kT}\int\limits_0^L ds\, U_e\left(\mathbf{R}\right)\right) \quad (3.27)
$$

$$
= \lim_{FI} \int d\mathbf{R}_0\, \delta\left(\mathbf{R}_0 - \mathbf{R}'\right) \int \left(\prod_{i=1}^N d\mathbf{R}_i\right) \mathcal{N}\delta\left(\mathbf{R}_N - \mathbf{R}\right)
$$

$$
\times \exp\left(-\frac{3}{2b\Delta s}\sum_{i=1}^N \left(\mathbf{R}_i - \mathbf{R}_{i-1}\right)^2 - \frac{\Delta s}{kT}\sum_{i=1}^N U_e\left(\frac{\mathbf{R}_i - \mathbf{R}_{i-1}}{2}\right)\right) (3.28)
$$

Note that the Green function is defined as a functional integral, a limit of an iterated integral. [2]

3.3.2   The Green function for a WLC in an external field

We did not directly arrive at a $\mathbf{\Psi}\left(\mathbf{R}\right)$ for the Kratky-Porod wormlike chain. We will use the result proven in [1, 5] and assert that the WLC may be treated as a differential space curve. We know from elasticity theory that the bending energy for a stiff rod of length L is given by

$$
U = \frac{\epsilon}{2}\int\limits_0^L ds\, \left(\frac{\partial\mathbf{u}}{\partial s}\right)^2, \tag{3.29}
$$

where ϵ is the bending modulus. For a WLC, this bending modulus is given by

$$
\epsilon = \frac{kT}{2\lambda}. \tag{3.30}
$$

The conformational distribution function is just a Boltzmann weighting of this bending energy.

$$
\mathbf{\Psi}\left(\mathbf{u}, L\right) \propto \exp\left(-\frac{1}{4\lambda}\int\limits_0^L ds\, \left(\frac{\partial\mathbf{u}}{\partial s}\right)^2\right). \tag{3.31}
$$

Adding in the Boltzmann weighted energy from the external field, we get

$$\mathbf{\Psi}\left(\mathbf{u}, L\right) \propto \exp\left(-\frac{1}{4\lambda} \int\limits_0^L ds \left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 - \frac{1}{kT} \int\limits_0^L ds\, U_e\left(\mathbf{R}\right)\right). \qquad (3.32)$$

Thus, the Green function is given by taking the appropriate integral over the conformational distribution function per equation (3.25). We must take the functional integral limit as in equation (3.27), but we will not show that explicitly.

$$\mathbf{G}\left(\mathbf{R}, \mathbf{u} \middle| \mathbf{u}_0, L\right) = \int\limits_{\mathbf{u}(0)=\mathbf{u}_0}^{\mathbf{u}(L)=\mathbf{u}} \delta\mathbf{R}\, \delta\left(\mathbf{R} - \int\limits_0^L ds\, \mathbf{u}\right)$$

$$\times \exp\left(-\frac{1}{4\lambda} \int\limits_0^L ds \left(\frac{\partial \mathbf{u}}{\partial s}\right)^2 - \frac{1}{kT} \int\limits_0^L ds\, U_e\left(\mathbf{R}\right)\right). \qquad (3.33)$$

3.4 The Green function as a solution to a partial differential equation

As we saw in the discussions at the beginning of section 3.3, obtaining the Green function for a polymer configuration reveals all of the thermodynamic information for the chain. However, the forms of the Green functions given by equations (3.27) and (3.33) are entirely cumbersome and difficult to use in any practical sense. Therefore, it would be very beneficial to find an alternate, more tractable representation of the Green function.

It turns out that by employing the techniques of Feynman and Hibbs [7], we can derive partial differential equations that describe the Green function. We will derive the PDE for the continuous Gaussian chain following the development of [2] and state the result for the WLC as derived by [5].

3.4.1 The Gaussian chain governing PDE

Assume we have a chain with Green function $\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right)$. Now we increase the chain length from L to $L + \epsilon$ where ϵ is small. Using equation (3.27), we

can write

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) =$$

$$\int\limits_{\mathbf{R}(0)=\mathbf{R}'}^{\mathbf{R}(L+\epsilon)=\mathbf{R}} \delta\mathbf{R} \, \exp\left(-\frac{3}{2b}\int\limits_{0}^{L+\epsilon} ds \left(\frac{\partial\mathbf{R}}{\partial s}\right)^2 - \frac{1}{kT}\int\limits_{0}^{L+\epsilon} ds \, U_e\left(\mathbf{R}\right)\right) \quad (3.34)$$

Using equation (3.23), we can write

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L+\epsilon\right) = \int d\mathbf{R}'' \, \mathbf{G}\left(\mathbf{R}, \mathbf{R}''|\epsilon\right) \mathbf{G}\left(\mathbf{R}'', \mathbf{R}'|L\right). \quad (3.35)$$

Here, we have specified that $\mathbf{R}''$ ends at the point on the chain corresponding to path length L. In doing this, there is a tiny piece of the chain between L and $L + \epsilon$, *i.e.* between $\mathbf{R}''$ and $\mathbf{R}$. The Green's function between these two points will approach a delta function as $\epsilon \to 0$. We can employ the definition of the delta function which describes it as a limit of the Gaussian distribution. Thus, for small ϵ,

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}''|\epsilon\right) \approx \left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \exp\left(-\frac{3\left(\mathbf{R}-\mathbf{R}''\right)^2}{2b\epsilon} - \frac{\epsilon}{kT}U_e\left(\frac{\mathbf{R}+\mathbf{R}''}{2}\right)\right). \quad (3.36)$$

The term with U_e is negligible in the limit of small ϵ, so this is still a valid representation of the delta function.

Substituting equation (3.36) into (3.35) gives

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L+\epsilon\right) = \left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\mathbf{R}'' \, \exp\left(-\frac{3\left(\mathbf{R}-\mathbf{R}''\right)^2}{2b\epsilon} - \frac{\epsilon}{kT}U_e\left(\frac{\mathbf{R}+\mathbf{R}''}{2}\right)\right)$$
$$\times \mathbf{G}\left(\mathbf{R}'', \mathbf{R}'|L\right) \quad (3.37)$$

We make the substitution of $\mathbf{R}'' = \mathbf{R} + \eta$ with $d\mathbf{R}'' = d\eta$. This gives

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L+\epsilon\right) =$$

$$\left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \exp\left(-\frac{3\eta^2}{2b\epsilon} - \frac{\epsilon}{kT}U_e\left(\mathbf{R}+\frac{\eta}{2}\right)\right) \mathbf{G}\left(\mathbf{R}+\eta, \mathbf{R}'|L\right). \quad (3.38)$$

It is now convenient to Taylor expand the respective terms in equation (3.38). We notice that

$$\lim_{\epsilon \to 0^+} \left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \exp\left(-\frac{3\eta^2}{2b\epsilon}\right) = \delta\left(\eta\right). \quad (3.39)$$

The term has an essential singularity as $\epsilon \to 0^+$ because it is a delta function in that limit. Furthermore, for small ϵ, the delta function ensures that only terms with very small η contribute significantly to the integral. Therefore we should Taylor expand the rest of the terms about $\eta = 0$.

$$\frac{1}{kT}\epsilon U_e \left(\mathbf{R} + \frac{\eta}{2}\right) = \frac{1}{kT}\left(\epsilon U_e\left(\mathbf{R}\right) + \frac{\epsilon}{2}\eta \cdot \frac{\partial U_e}{\partial \mathbf{R}}\right) + \mathcal{O}\left(\epsilon\eta\right). \qquad (3.40)$$

We substitute this expansion into the exponential and then expand the exponential to get

$$\exp\left(-\frac{\epsilon U_e}{kT}\left(\mathbf{R} + \frac{\eta}{2}\right)\right) = 1 - \frac{1}{kT}\epsilon U_e\left(\mathbf{R}\right) + \mathcal{O}\left(\epsilon\eta\right) \qquad (3.41)$$

Now we Taylor expand the two Green functions

$$\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L+\epsilon\right) = \mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) + \epsilon\frac{\partial}{\partial L}\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) + \mathcal{O}\left(\epsilon^2\right) \qquad (3.42)$$

and

$$\begin{aligned}
\mathbf{G}\left(\mathbf{R} + \eta, \mathbf{R}'|L\right) &= \mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) + \eta \cdot \frac{\partial}{\partial \mathbf{R}}\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) \\
&+ \frac{1}{2}\eta\eta : \frac{\partial^2}{\partial R^2}\mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) + \mathcal{O}\left(\eta^3, \eta^4\right).
\end{aligned} \qquad (3.43)$$

Here, $:$ denotes the dyadic product. Since after expansion all Green functions are of the same form, we will define $\mathbf{G} \equiv \mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right)$ for brevity. We can now put it all together to get

$$\begin{aligned}
\mathbf{G} + \epsilon\frac{\partial \mathbf{G}}{\partial L} + \mathcal{O}\left(\epsilon^2\right) &= \left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \exp\left(-\frac{3\eta^2}{2b\epsilon}\right)\left(1 - \frac{1}{kT}\epsilon U_e\left(\mathbf{R}\right) + \mathcal{O}\left(\epsilon\eta\right)\right) \\
&\times \left(\mathbf{G} + \eta \cdot \frac{\partial}{\partial \mathbf{R}}\mathbf{G} + \frac{1}{2}\eta\eta : \frac{\partial^2}{\partial R^2}\mathbf{G} + \mathcal{O}\left(\eta^3, \eta^4\right)\right)
\end{aligned} \qquad (3.44)$$

Before we multiply the sums together, we should note that $\mathbf{G}$ is not a function of η. We note further that all the integrals with respect to η are Gaussian integrals of the form

$$\left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \eta^n \exp\left(-\frac{3\eta^2}{2b\epsilon}\right), \, n \text{ integer}, \qquad (3.45)$$

which is a standard Gaussian integral. These integrals are zero for all odd powers of n. The integrals for $n = 0, 2, 4$ are

$$\left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \exp\left(-\frac{3\eta^2}{2b\epsilon}\right) = 1 \tag{3.46}$$

$$\left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \eta^2 \exp\left(-\frac{3\eta^2}{2b\epsilon}\right) = \frac{b\epsilon}{3} \tag{3.47}$$

$$\left(\frac{3}{2\pi b\epsilon}\right)^{\frac{3}{2}} \int d\eta \, \eta^4 \exp\left(-\frac{3\eta^2}{2b\epsilon}\right) = \epsilon^2. \tag{3.48}$$

Taking all odd powered Gaussian integrals to be zero, substituting equations (3.46), (3.47), and (3.48) into equation (3.44), and simplifying yields

$$\epsilon \left(\frac{\partial}{\partial L} - \frac{b}{6}\frac{\partial^2}{\partial \mathbf{R}^2} + \frac{U_e}{kT}\right) \mathbf{G} + \mathcal{O}\left(\epsilon^2\right) = 0. \tag{3.49}$$

Diving by ϵ and taking $\epsilon \rightarrow 0$ yields

$$\left(\frac{\partial}{\partial L} - \frac{b}{6}\frac{\partial^2}{\partial \mathbf{R}^2} + \frac{U_e}{kT}\right) \mathbf{G} = 0. \tag{3.50}$$

We must now define the boundary conditions. Harking back to equation (3.36), we put ourselves at the start of the chain. For a very short chain, $G\left(\mathbf{R}, \mathbf{R}'|\epsilon\right)$ approaches a delta function as $\epsilon \rightarrow 0^+$. Thus, our first boundary condition is

$$G\left(\mathbf{R}, \mathbf{R}'|0\right) = \delta\left(\mathbf{R} - \mathbf{R}'\right). \tag{3.51}$$

Next, we note that $L < 0$ is nonsense and $\mathbf{G}$ has a discontinuity across zero. Thus, we have arrived at our final partial differential equation to describe a Gaussian chain in an external field.

$$\left(\frac{\partial}{\partial L} - \frac{b}{6}\frac{\partial^2}{\partial \mathbf{R}^2} + \frac{U_e}{kT}\right) \mathbf{G}\left(\mathbf{R}, \mathbf{R}'|L\right) = \delta\left(\mathbf{R} - \mathbf{R}'\right) \delta\left(L\right) \tag{3.52}$$

The equation is a diffusion-like equation with L being the "time" and $\frac{b}{6}$ being the diffusivity. The external field makes the solution difficult, which is why excluded volume is so difficult to deal with.

3.4.2   The wormlike chain governing PDE

The governing PDE for the wormlike chain is derived using a similar technique. The result, taken from [5], is stated here without proof. This solution sets $\mathbf{R}' \equiv \mathbf{0}$.

$$\left(\frac{\partial}{\partial L} - \lambda\frac{\partial^2}{\partial \mathbf{u}^2} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{R}} + \frac{U_e}{kT}\right) \mathbf{G}\left(\mathbf{R}, \mathbf{u}|\mathbf{u}_0, L\right) =$$
$$\delta\left(\mathbf{u} - \mathbf{u}_0\right)\delta\left(\mathbf{R}\right)\delta\left(L\right) \qquad (3.53)$$

In this equation, we see that the "orientation" is diffusing with a diffusivity proportional to the inverse of the persistence length. Thus, the more stiff the chain is, the more slowly the orientation will diffuse along the chain and the longer a given orientation will persist. Aside from the "time" term (represented by the differential with respect to L), there is also a convection term for the position of the chain.

4   Conclusions

We have seen three discrete and two continuous models used to describe polymers. Even though they are simple in concept, they become complicated quickly while manipulating them. The K-P WLC in an external field is often only solvable numerically. Furthermore, it the stiffness parameter has any nontrivial functionality, the PDE of equation (3.53) has nonconstant coefficients. While using these and other models, one should choose the simplest model possible to achieve the results he desires.

These models are the cornerstone of many studies in polymer physics and will be the starting point as we delve into studies in excluded volume, self-interactions, concentrated polymer solutions, and polymer dynamics.

References

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