

Chapter 2

Molecular Conformations

2.1 Introduction

Polymers can exist in various *conformations* and various *configurations*. Two polymers which differ only by rotations about single bonds are said to be two different conformations of that polymer. A schematic view of two polymer conformations is shown in Fig. 2.1. Two polymers which have the same chemical composition but can only be made identical (*e.g.*, superposable) by breaking and reforming bonds are said to be two configurations of that polymer. Two examples in Fig. 2.2 are polymers that contain asymmetric carbon atoms or that contain double bonds. Asymmetric carbon atoms can exist in *d* or *l* states while double bonds can exist in *cis* or *trans* states. No manner of rotations about single bonds can turn polymers in different configuration states into superposable polymers.

The above definitions of *conformation* and *configuration* are standard, but they have not always been rigorously followed in the literature. For example, Paul Flory, who won a Nobel prize for studies of polymer conformations, used configuration in his writings when he meant conformation. Fortunately a writer's meaning is usually obvious from context. It is recommended that you strive to use the correct terminology as defined above. These notes strive to follow that convention.

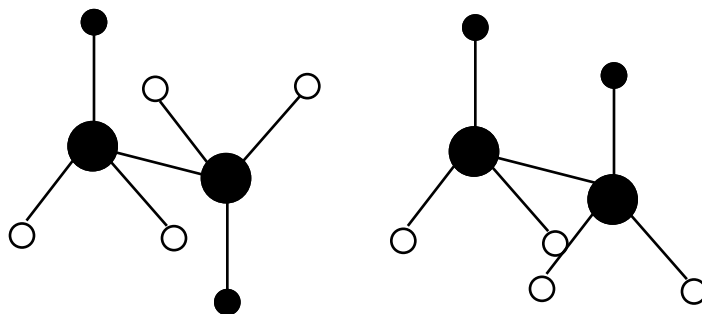


Figure 2.1: Two molecules with different conformations. These two molecules can be made identical with a rotation of 180° about the central single bond.

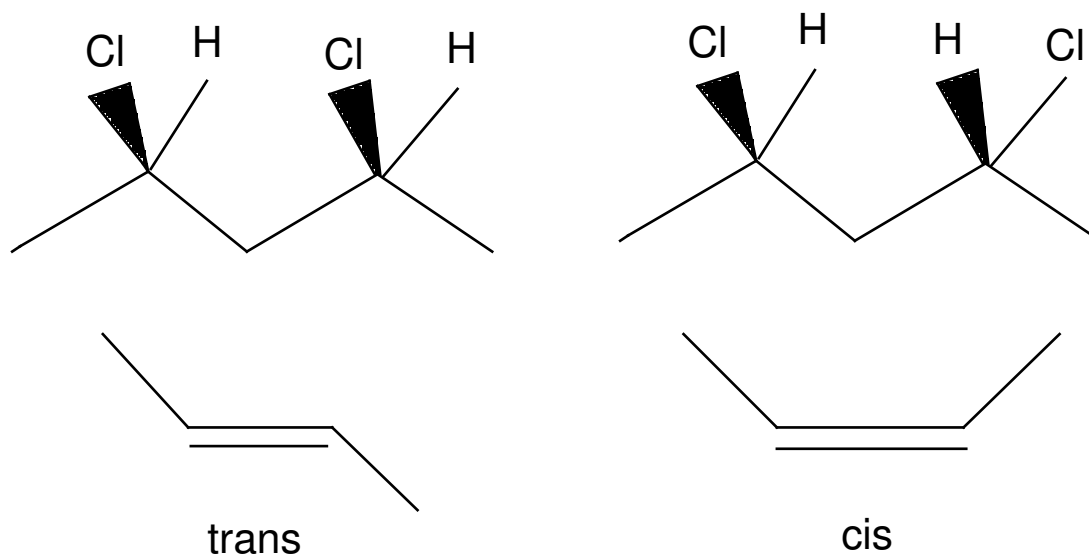


Figure 2.2: Two distinct configurations of polymers can exist at asymmetric carbon atoms (top) and across double bonds (bottom).

To understand polymers, we must understand the shape or the form that polymers have in solution as well as in solid state. We will therefore spend some time studying the conformations of isolated polymer chains. An isolated polymer chain is clearly a good model for a gas phase or a dilute solution polymer. It turns out that the description of an isolated polymer chain is also a good description for polymer chains in concentrated solutions, or even in the solid state.

The first thing to realize about polymers is that they are usually very long and are best described as resembling a *random coil*. In a collection of polymers (gas phase, solution, or solid state), the various individual polymer molecules will assume many possible conformations. Each conformation will be a different variation on a random coil. The different conformations arise by thermal energy and the relatively low barrier to rotations about single bonds. The shapes of the possible conformations have a direct bearing on the physical properties of the polymer. Some properties that can be influenced included solution viscosity, solution light scattering, and mechanical properties. For example, rigid rod polymers generally assume more extended conformations than polymers with more flexible backbones. These more extended shapes give rigid rod polymers very different properties. To be specific, rigid rod polymers are generally stiffer and have a higher glass-transition temperature.

Figure 2.3 shows an extended chain polymer and a random coil polymer. The extended chain picture is the way we might choose to draw a polymer structure. The random coil picture, however, is a more realistic view of the shape of real polymer molecules. In this chapter we will discuss various theoretical methods for characterizing the shape of random coil polymers. The major results will be predictions of the end-to-end distance for linear polymers. The ideas that enter into the analysis give insight about the shape of polymers. As discussed in the Introduction chapter (chapter 1),

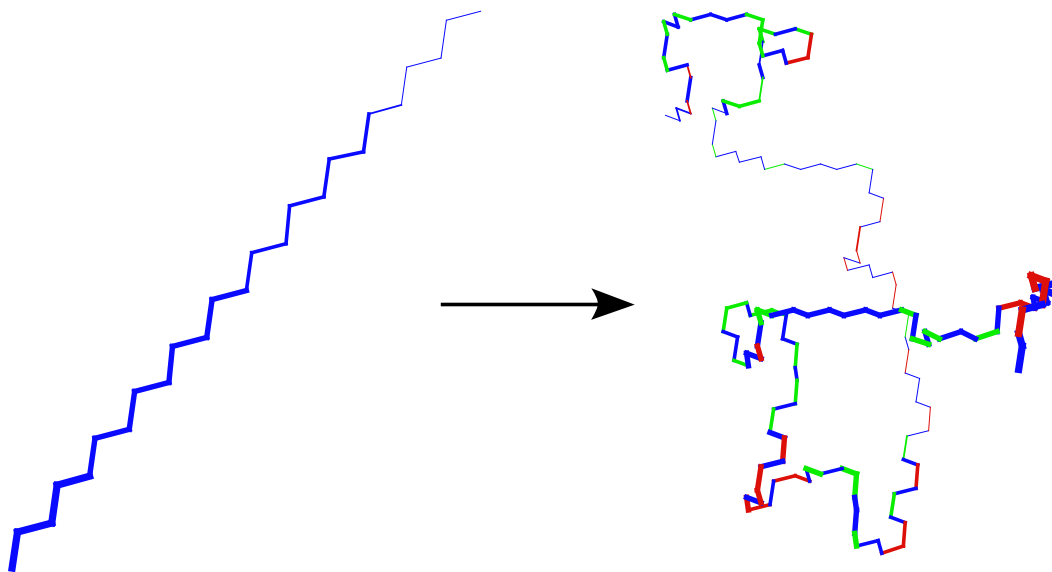


Figure 2.3: Extended chain polymer on the left. A more realistic picture of a polymer as a random coil on the right. The colors indicate rotation angle about each bond. Blue is for trans bonds while red and green are for gauche bonds.

this type of polymer characterization is theoretical characterization.

2.2 Nomenclature

We will restrict ourselves to linear polymers and we will consider all their possible conformations. To describe any given conformation we must first define a nomenclature or coordinate system. We begin with a polymer having n bonds. These n bonds connect $n + 1$ backbone atoms. We can thus define any conformation by giving the $3(n + 1)$ Cartesian coordinates of the $n + 1$ atoms along the polymer backbone. This nomenclature works but is normally more cumbersome than desired and we thus make some simplifications.

We begin with the bond length (l). In many polymers the bonds in the polymer backbone are all identical and therefore have a constant bond length. For example, in PE the bonds are all carbon-carbon bonds and they are all typically about 1.53\AA long. For simplicity we will restrict ourselves to polymers with constant bond lengths. A generalization to non-constant bond lengths can be made later if necessary. With constant bond lengths, we can consider a polymer conformation as a 3D random walk of n steps where each step has length l . Instead of listing absolute coordinates of each atom in the backbone, we choose to describe a polymer by listing the *relative* directions of each step in the random walk.

Directions in space are most conveniently described using polar angles. Figure 2.4 shows an arbitrary direction in space emanating from the origin of a coordinate system. The angle with respect to the z axis is called the polar angle and is usually denoted by θ . The angle that the

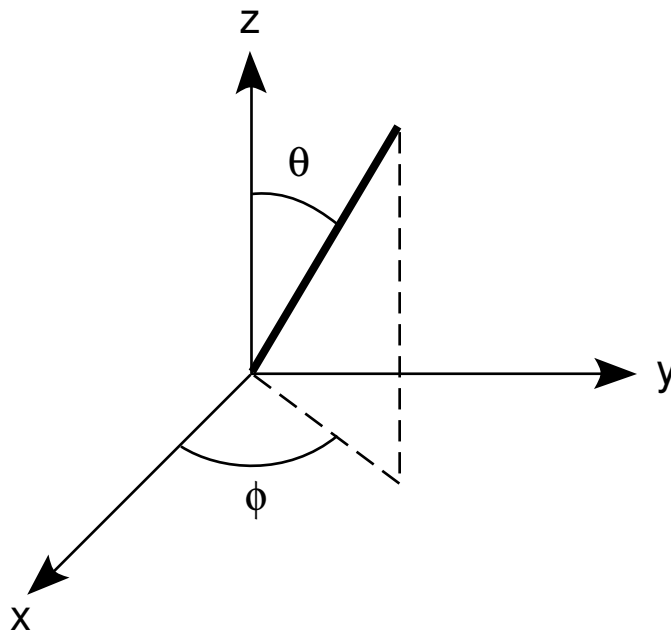


Figure 2.4: Definitions of the polar angle θ and the azimuthal angle ϕ for any vector in a right-handed coordinate system.

projection of the direction onto the x - y plane makes with any consistently chosen reference point in that plane is called the azimuthal angle and is usually denoted by ϕ . All possible directions in space can be spanned by choosing θ from 0 to π and ϕ from 0 to 2π . In other words, any direction from the origin can be defined by a unique pair of θ and ϕ .

We will represent a polymer as a 3D random walk of n steps where n is the number of bonds (note that n is not necessarily the same as the degree of polymerization or the number of repeat units; some repeat units have more than one bond and for n we count all of these bonds). In the random walk, each step can be described by polar and azimuthal angles, θ and ϕ , where those angles are given with respect to an axis system centered on the atom at the start of that bond. For n bonds, each bond will have its own angles, θ_i and ϕ_i , and the complete chain will be described with the 3 original coordinates for the first atom and the $2n$ angles for the steps of the random walk. We thus require $2n + 3$ variables to specify a conformation of a polymer with constant bond length.

Normally we will not be concerned with the absolute location in space of the polymer chain. If we do everything relative to the location of the first bond, then we do not need to know the 3 original coordinates nor the 2 polar angles of the first bond. Subtracting these five variables, we can define an arbitrary polymer conformation with $2n - 2$ or $2(n - 1)$ variables. The $2(n - 1)$ variables are the polar and azimuthal angles for each bond except the first bond. If we ever generalize to different l 's for each bond, we must add to these $2(n - 1)$ variables, n new variables which specify the length of each bond.

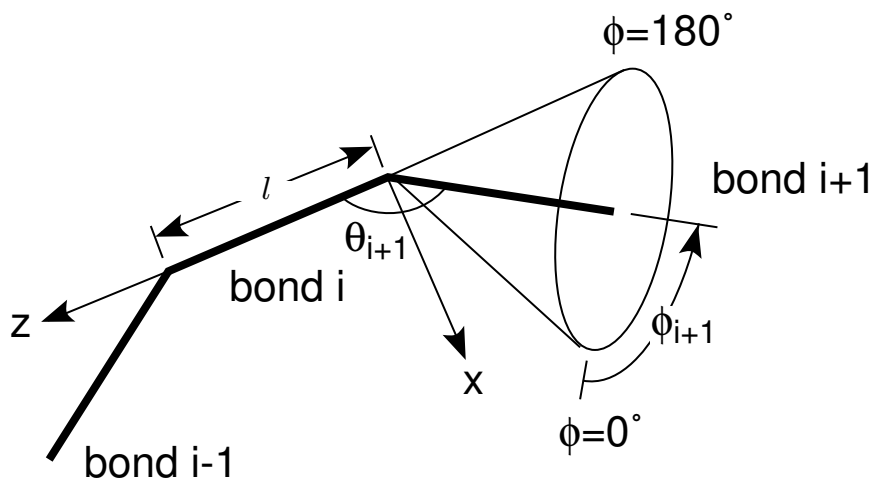


Figure 2.5: Definition of polar and azimuthal angles for bond i . With the illustrated selection of x , y , and z axes, the polar angle is the bond angle for bond $i + 1$ and the azimuthal angle is the dihedral angle for bond $i + 1$.

It is convenient to choose a coordinate system that lends physical interpretations to the polar and azimuthal angles of each bond in the polymer chain. As illustrated in Fig. 2.5, we consider the central bond as bond i and take the z axis to point back along bond i . With this choice for the z axis, the polar angle for bond $i + 1$ is just the bond angle between bond i and bond $i + 1$ (see Fig. 2.5). From now on, we will refer to the polar angle as the bond angle. The possible orientations for bond $i + 1$ when the bond angle is θ_{i+1} sweep out the cone illustrated in Fig. 2.5. The azimuthal angle (ϕ) for bond $i + 1$ is the counter-clockwise angle around that cone from some suitably selected reference point. We choose the x axis to define the reference point such that the azimuthal angle for bond $i + 1$ is 180° when bond i is a *trans* bond. This choice is arbitrary, but is consistent with the bulk of the modern literature (note: Flory choose $\phi = 0$ to correspond to *trans* bonds which makes his results shifted by 180° from these notes). Another term for such an azimuthal angle is the *dihedral* angle for bond $i + 1$ — a term that we will adopt throughout these notes. Finally, the y axis is chosen to be perpendicular to the x and z axes and directed to make the x - y - z coordinates a right-handed coordinate system.

2.3 Property Calculation

The goal of theoretical characterization of polymers is to be able to predict certain properties of those polymers. When a polymer exists in a single conformation, the task is simple — we merely calculate the property for that conformation. Random coil polymers, however, can exist in many different conformations. An observed macroscopic property of an ensemble of polymer chains will be an average value of that property over the range of polymer conformations. We denote the average value of any property over an ensemble of random coil polymer chains as $\langle Property \rangle$.

The way to find $\langle Property \rangle$ is to examine a large number of polymer chains by considering a large number of random walks. For the simplest models (models of short chains) we will be able to examine all possible random walks. When we can consider all possible random walks we can assign to each random walk a probability which equals the probability that that conformation will be selected when one polymer is selected from an ensemble of random coils. Assuming we can calculate some polymer property (*e.g.*, size, stiffness, etc.) for each specific conformation, we can average them to get the average of that property for the bulk polymer sample. The average property is defined by

$$\langle Property \rangle = \sum_i Property(conf\ i) \times Probability(conf\ i) \quad (2.1)$$

where $Property(conf\ i)$ is the value of the property calculated for conformation i and $Probability(conf\ i)$ is the probability of that conformation occurring.

For small molecules you can often do the above averaging process exactly. In other words you can enumerate all possible conformations, find the probability and property of each conformation, and then find the average property by averaging the results. Some small molecules have only one conformation and the task is relatively simple — the average property is equal to the property of the single conformation. Other molecules have only a few conformations and the task is still relatively simple. For a non chemistry example, consider the roll of a single dice and consider the property of the number of pips showing on each role. A die has six faces which represent six possible conformations of the die after each roll. When counting pips, the $Property(conf\ i) = i$. Assuming the die is a fair die (*i.e.*, not loaded) the probability of each conformation is the same and equal to $1/6$ (thus $Probability(conf\ i) = 1/6$). The property of the number of pips therefore has the exact average value of

$$\langle pips \rangle = \sum_i^6 i \times \frac{1}{6} = \frac{1}{6} + \frac{2}{6} + \frac{3}{6} + \frac{4}{6} + \frac{5}{6} + \frac{6}{6} = 3.5 \quad (2.2)$$

For polymer calculations there will usually be too many conformations to make the above exact calculation procedure possible. Instead we will select conformations at random and use a Monte Carlo procedure to get the average property. By the Monte Carlo procedure, if the probability of selecting a particular conformation at random is proportional to the actual probability of conformation i (selection probability $\propto Probability(conf\ i)$), then the average property for a polymer sample can be approximated by

$$\langle Property \rangle \approx \frac{1}{N} \sum Property(sample\ i) \quad (2.3)$$

where N is the number of randomly generated polymer chains. The larger N , the more accurate will be the calculated average property.

We can illustrate the Monte Carlo method with the dice problem. A Monte Carlo solution to the dice problem would be to roll a die many times, total the pips, and divide by the number of

rolls. If the die was rolled sufficiently many times and if the die was fair (*i.e.*, symmetric and not loaded), the Monte Carlo solution would be very close to the exact answer of 3.5. After a few rolls, the answer might differ from 3.5. After many rolls, however, the answer would be very unlikely to show much deviation from 3.5.

The success of the Monte Carlo procedure is dependent on one's ability to select polymer conformations with realistic probabilities that accurately reflect the true distribution of conformations. This problem is easily solved in the dice problem by rolling a die. Unfortunately for polymer problems we cannot physically select real polymers. Instead we have to generate conformations mathematically or in a computer. The problem we must solve is the development of rules or algorithms for realistically generating conformations. We will approach this problem in a series of steps. We will begin with the simplest possible rules. At each subsequent step we will add more realism to the procedure used to generate the random conformations. The final results can be used to accurately predict many polymer properties.

2.4 Freely-Jointed Chain

In a freely-jointed chain all $2(n - 1)$ angular variables are allowed to assume any values with equal probability. In other words the direction of any bond is equally likely to occur in any of the possible directions of space — the joints at each bond thus move freely to allow all these possible orientations.

Let's begin with one particular property — the polymer size. Size can be characterized by calculating the end-to-end distance, r , or the radius of gyration, s . As an average property, these properties are usually calculated as a root mean squared end-to-end distance (or a root mean squared radius of gyration). End-to-end distance is the distance from the beginning of the chain to the end of the chain (see Fig. 2.6). The root mean squared end-to-end distance is the square root of the average of the squared end-to-end distances:

$$\text{rms } r = \sqrt{\langle r^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^N r_i^2} \quad (2.4)$$

where N is the total number of possible conformations and r_i is the end-to-end distance for conformation i . The radius of gyration is the average of the distances of each of the atoms in the polymer chain to the center of mass of the polymer. The root mean squared radius of gyration is the square root of the average of the squared radius of gyration:

$$\text{rms } s = \sqrt{\langle s^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^N s_i^2} \quad (2.5)$$

where s_i is the radius of gyration for conformation i .

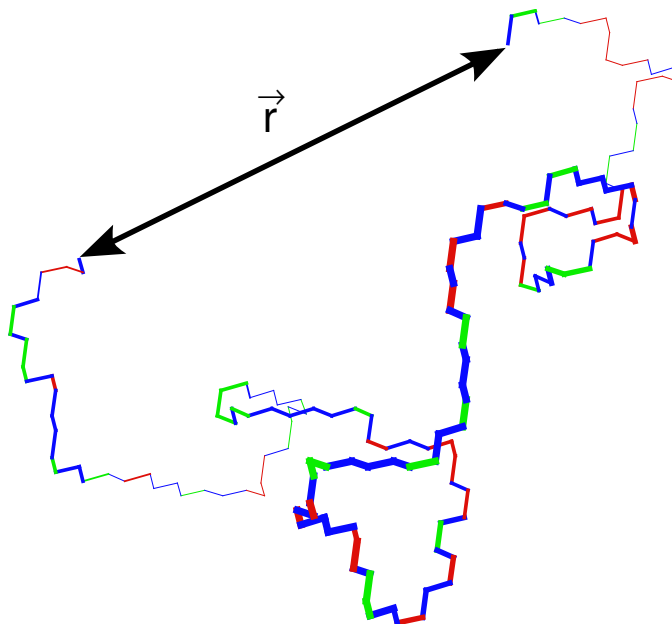


Figure 2.6: The length of a vector (\vec{r}) from the first atom to the last atom on a linear polymer chain is the end-to-end distance for that polymer conformation. This figure shows the end-to-end vector.

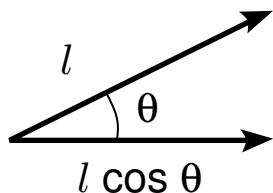


Figure 2.7: The projection of a bond of length l onto the z axis is $l_z = l \cos \theta$ where θ is the angle between the bond and the z axis.

2.4.1 Freely-Jointed Chain Analysis

We begin our analysis of the freely-jointed chain by analyzing a single direction in space — we will analyze the z axis direction. For any of the bonds in the chain (or steps in the random walk), the bond length along the z axis is $l_z = l \cos \theta$ (see Fig. 2.7) where θ is the angle between the bond direction and the z -axis direction. θ is also the polar angle in the coordinate system defined in Fig. 2.5 in which the z axis is along the previous bond. The average value of l_z is found by integrating over all possible bond projections or all possible bond directions:

$$\langle l_z \rangle = \int_{-l}^l l_z p(l_z) dl_z = \int \int l \cos \theta p(\theta, \phi) dS \quad (2.6)$$

where $p(\theta, \phi)$ is the probability that any given bond has directional angles of θ and ϕ . The integration is over the surface of a sphere centered on the origin and dS is the differential of surface area.

For a freely-jointed chain all angles are all equally likely and therefore $p(\theta, \phi)$ must be a constant;

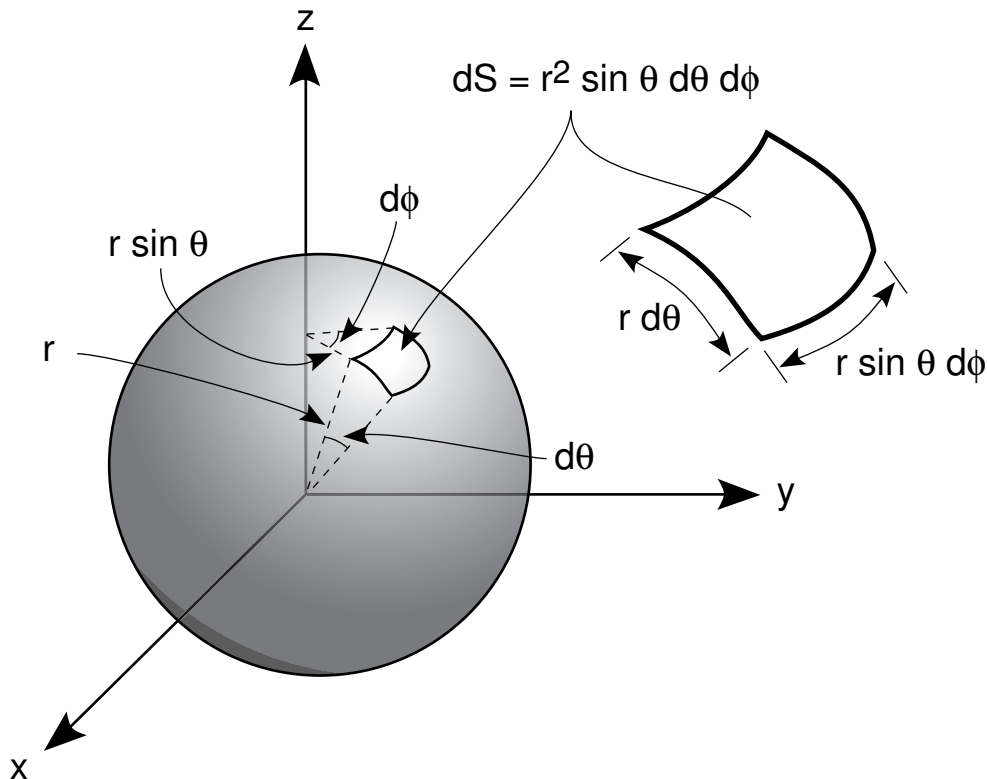


Figure 2.8: The differential of surface integration for polar coordinates is the area of the surface element on the right side of the figure which is a top view of the left side. For small angles this area is $dS = r^2 \sin \theta d\theta d\phi$.

we call it k . To find k , we integrate over the surface of sphere, which represents all possible directions in space, and note that the integral over $p(\theta, \phi)$, which is a probability distribution function, must be 1. Because dS for surface integration over a sphere is $r^2 \sin \theta d\theta d\phi$ (see Fig. 2.8) we can integrate over the unit sphere ($r = 1$) to get:

$$1 = k \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta = 4\pi k \quad (2.7)$$

or

$$k = p(\theta, \phi) = \frac{1}{4\pi} \quad (2.8)$$

We can now insert $p(\theta, \phi)$ into the expression for $\langle l_z \rangle$ and integrate. The result is

$$\langle l_z \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{l \cos \theta \sin \theta}{4\pi} = \frac{l}{2} \int_0^\pi \cos \theta \sin \theta d\theta = 0 \quad (2.9)$$

This result could have been anticipated. When random walk steps in all directions are equally likely, we are equally likely to jump in the positive direction as in the negative directions. These equally likely jumps cancel out to give zero average jump size.

A simple average step size is not useful and we therefore instead consider the average *squared* step length. It is for this reason that we constantly work with root-mean-squared end-to-end

distances in our discussion of polymer size. Squaring each step length makes all step size positive and we are guaranteed to get a nonzero result. With the known $p(\theta, \phi)$ function, we can easily calculate the mean squared jump size:

$$\langle l_z^2 \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{l^2 \cos^2 \theta \sin \theta}{4\pi} = \frac{l^2}{2} \int_0^\pi \cos^2 \theta \sin \theta d\theta \quad (2.10)$$

$$= \frac{l^2}{2} \left[-\frac{1}{3} \cos^2 \theta \right]_0^\pi = \frac{l^2}{3} \quad (2.11)$$

The root mean squared distance per step is:

$$\sqrt{\langle l_z^2 \rangle} = \frac{l}{\sqrt{3}} \quad (2.12)$$

The above result gives as an average jump size per step, but we are concerned with the total z axis root-mean-squared end-to-end distance. The solution to this problem is approached by considering a set of typical jump directions. For a chain of n bonds, some of the bonds will point in the positive z direction and some will point in the negative z direction. If n is large, the root mean squared length of all positive jumps will be the same as that of all negative jumps and each will be equal to the average of all jumps. We let n_+ be the total number of jumps in the positive direction and n_- be the total number of jumps in the negative direction. Then the root-mean-squared distance traveled in the z direction, denoted by z , is

$$z = (n_+ - n_-) \sqrt{\langle l_z^2 \rangle} = (n_+ - n_-) \frac{l}{\sqrt{3}} \quad (2.13)$$

To solve for z we must determine $(n_+ - n_-)$. The factor $(n_+ - n_-)$ is like the result of a coin toss experiment. Each step is considered a coin toss, if z increases on the step the coin toss result is heads, if z decreases, the coin toss result is tails. In the coin toss results, the expected result is to have equal numbers of heads and tails. If a large number of coin tosses are made the distribution of $(n_+ - n_-)$ will be a Gaussian function centered at zero (mean of zero). We can thus represent the factor $(n_+ - n_-)$, or more usefully the distance in the z direction, with the following Gaussian distribution function:

$$W(z)dz = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{z^2}{2\sigma^2}} dz = \frac{\beta}{\sqrt{\pi}} e^{-\beta^2 z^2} dz \quad (2.14)$$

where σ is the standard deviation in z -direction distance and the term β is defined in terms of standard deviation by

$$\beta = \frac{1}{\sqrt{2\sigma^2}} \quad (2.15)$$

The freely-jointed chain problem is solved if we can find the standard deviation in z -direction distance. For a *single* step the variance, or the standard deviation squared, follows simply from the formula for variance:

$$\sigma_1^2 = \langle l_z^2 \rangle - \langle l_z \rangle^2 = \langle l_z^2 \rangle \quad (2.16)$$

Statistical analysis tells us that for n steps, the standard deviation in z is n times the standard deviation for a single step or

$$\sigma^2 = n\sigma_1^2 = n\langle l_z^2 \rangle \quad (2.17)$$

Substituting the above result for $\langle l_z^2 \rangle$ gives

$$\beta = \frac{1}{\sqrt{2n\langle l_z^2 \rangle}} = \sqrt{\frac{3}{2nl^2}} \quad (2.18)$$

An alternate route to finding β is to find the variance by integration (*i.e.*, find the average value of z^2 and subtract the square of the average value of z , which we know to be zero). The result is

$$\frac{\langle z^2 \rangle}{n} = \langle l_z^2 \rangle = \frac{\lambda^2}{3} = \frac{1}{n} \int_{-\infty}^{\infty} z^2 W(z) dz = \frac{1}{2n\beta^2} \quad (2.19)$$

Solving for β again gives

$$\beta = \sqrt{\frac{3}{2nl^2}} \quad (2.20)$$

The expression for β together with the Gaussian distribution function give the distribution function for chain length in one direction. Now we need to solve the three-dimensional problem. Because the chain is freely jointed, the three axes are independent of each other. From probability theory, the probability that a given polymer chain jumps distances of x , y , and z in each of the three Cartesian directions is the product of the probabilities for each of the axes considered separately. The probability that a chain has an end-to-end distance characterized by a vector (x, y, z) is thus

$$W(x, y, z) dx dy dz = W(x)W(y)W(z) dx dy dz \quad (2.21)$$

Because the analysis for $W(z)dz$ given above applies equally well to the x and y directions, we have

$$W(x, y, z) dx dy dz = \left(\frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 r^2} dx dy dz \quad (2.22)$$

where $r^2 = x^2 + y^2 + z^2$ is the square of the distance from the origin to the end of the chain at (x, y, z) .

As stated above, $W(x, y, z) dx dy dz$ gives the probability that a chain's end-to-end vector is characterized by a vector (x, y, z) . In other words, it is the probability that a chain that begins at the origin ends in a box center at the point (x, y, z) or size $dx dy dz$ (see Fig. 2.9). One dimension of $W(x, y, z) dx dy dz$ is plotted in Fig. 2.9. The function is a Gaussian distribution function centered at the origin or centered about the mean value of zero.

The function $W(x, y, z) dx dy dz$ solves the freely-jointed chain problem, but it is not in the most useful form. We are normally not concerned with absolute end of the chain (*i.e.*, location (x, y, z)), but rather with the end-to-end distance r . To find this result we sum up all possible (x, y, z) coordinates that give the same r value. In other words, we integrate over the volume element V

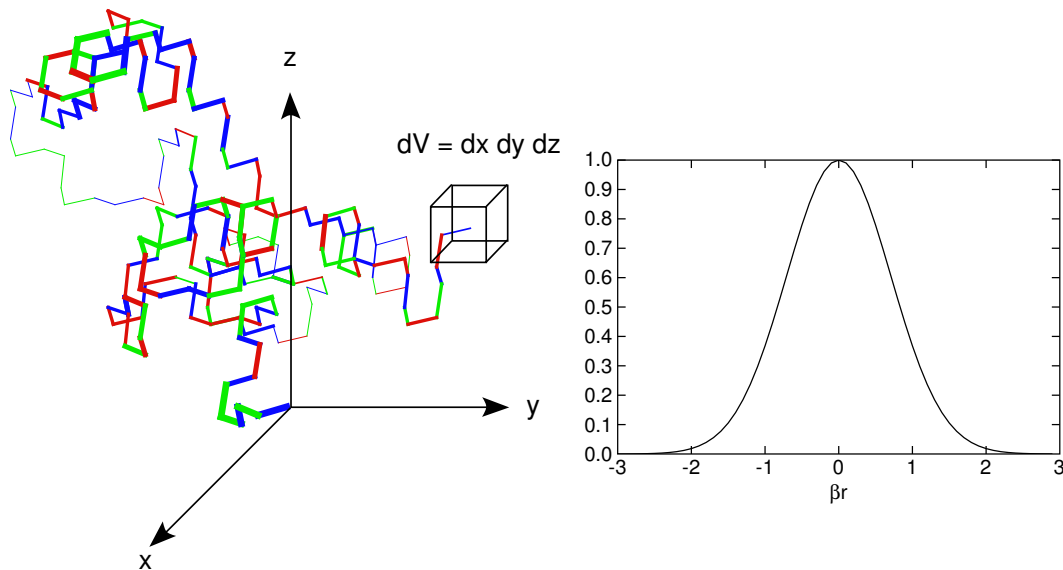


Figure 2.9: The left side shows a chain that starts at the origin and ends in a box centered a (x, y, z) . The right side is a one-dimensional plot of $W(x, y, z)dx dy dz$.

of width dr where $\sqrt{x^2 + y^2 + z^2}$ is between r and $r + dr$. The volume element of constant r is a spherical shell as shown in Fig. 2.10. Integrating over this volume element yields a probability distribution in terms of the end-to-end distance r :

$$W(r)dr = \int_V W(x, y, z)dx dy dz = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 4\pi r^2 e^{-\beta^2 r^2} dr \quad (2.23)$$

This type of distribution function is called a *radial* distribution function.

Figure 2.11 schematically plots the end-to-end distance distribution function, $W(r)dr$. We can characterize the distribution function by finding some key points. The function $W(r)dr$ always increases to some maximum and then decrease towards zero. The peak value is found by finding where the derivative of $W(r)dr$ is zero. The maximum value, r_{max} , occurs at

$$r_{max} = \frac{1}{\beta} = l\sqrt{\frac{2n}{3}} = 0.82l\sqrt{n} \quad (2.24)$$

The average value of r , $\langle r \rangle$, is found by integrating $W(r)dr$:

$$\langle r \rangle = \int_0^\infty rW(r)dr = \frac{2}{\beta\sqrt{\pi}} = l\sqrt{\frac{8n}{3\pi}} = 0.92l\sqrt{n} \quad (2.25)$$

Likewise, the mean-squared value of r , $\langle r^2 \rangle$, is

$$\langle r^2 \rangle = \int_0^\infty r^2W(r)dr = \frac{3}{2\beta^2} = l^2n \quad (2.26)$$

and the root mean squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (2.27)$$

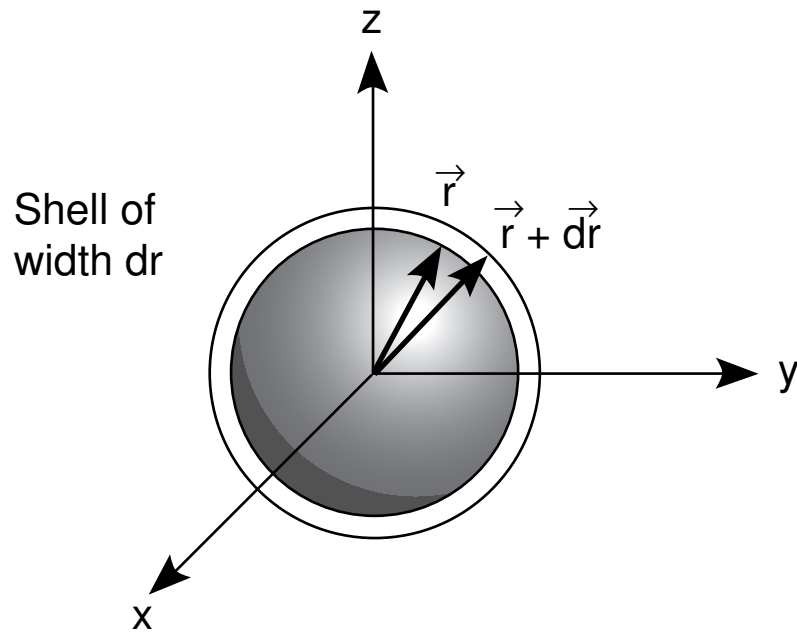


Figure 2.10: Cross section of a spherical shell between radii of r and $r + dr$.

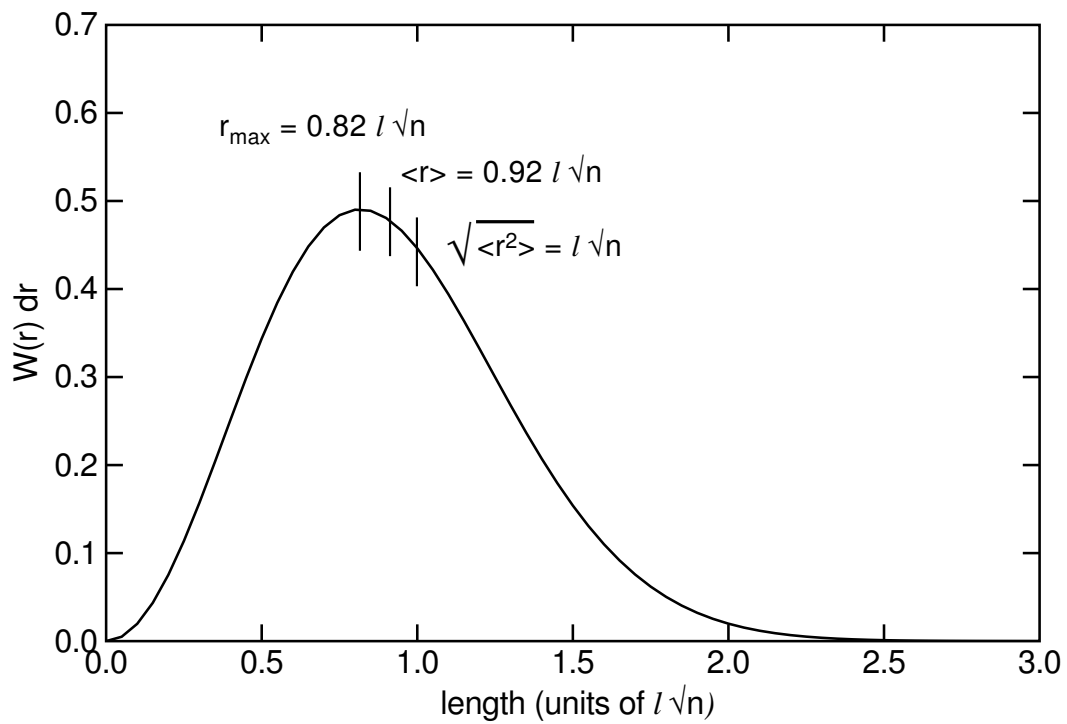


Figure 2.11: A typical plot of $W(r)dr$. The key values r_{\max} , average r or $\langle r \rangle$, and root-mean-squared r are indicated on the figure.

The above key values are indicated in Fig. 2.11. For constant l and n , they always rank in the order $r_{max} < \langle r \rangle < \langle r^2 \rangle$.

The variance in the end-to-end distance can be found from the mean and mean-squared end-to-end distances:

$$\sigma^2 = \langle r^2 \rangle - \langle r \rangle^2 = \frac{3}{2\beta^2} - \frac{4}{\beta^2\pi} = \frac{0.23}{\beta^2} = 0.15nl^2 \quad (2.28)$$

From this results, the coefficient of variation (standard deviation divided by the mean) is

$$CV = \frac{\sigma}{\langle r \rangle} = 42\% \quad (2.29)$$

This result can be characterized as a fairly large coefficient of variation.

2.4.2 Comment on Freely-Jointed Chain

We only used two facts in deriving $W(r)$. First we assumed that the chain can be simulated by a random walk. Second, we assumed there are enough steps to make the random walk a Gaussian distribution. To find the Gaussian curve we therefore only had to find the mean (mean = 0) and the standard deviation ($\sigma = \sqrt{n\langle l_z^2 \rangle}$). The final result predicts that the root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (2.30)$$

In other words the root mean squared end-to-end distance is proportional to the square root of the number of bonds and linear in the bond length.

The linear dependence on bond length is a trivial result. It is merely a scaling parameter. Thus if we double all bond lengths we double the end-to-end distance. It can also be thought of as a consequence of units. If we solve the problem in inches and then in millimeters, we should get answers that differ only by the units conversion factor for inches to millimeters of 25.4. This expected result will only occur if the end-to-end distance is linear in bond length.

The dependence of root-mean-squared end-to-end distance on the square root of the number of bonds is a profound, or at least a non-trivial, result. Let's consider the origins of the square root dependence on bond length. Our analysis is one of a completely random three dimensional random walk. The square root of n dependence comes from the expression for the standard deviation of the walk which contains \sqrt{n} . If we repeated the analysis for one- or two-dimensional random walks we would find the same result. The root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (2.31)$$

in any dimension. We thus conclude that the square root of n dependence is a property of the random walk nature of polymers and unrelated to geometrical effects. Only polymer features that alter the random walk nature of the chain can alter the square root dependence on n .

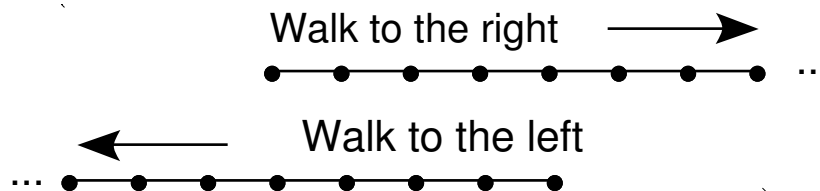


Figure 2.12: The only two possible one-dimensional, self-avoiding random walks.

To anticipate a future result that does alter the random walk nature of polymers, we consider self-avoiding random walks. In self-avoiding random walks, the path cannot revisit any spot that was previously visited. Because no two atoms in a polymer chain can occupy the same space, a self-avoiding random walk is a better model for a polymer chain than the completely random walk discussed previously. A self-avoiding random walk, however, is not a completely random walk because some steps may be influenced by previous steps. In other words, some steps may be biased away from moving in a given direction because doing so would revisit a previous part of the random walk.

The exact analysis of two- and three-dimensional self-avoiding random walks is not possible. One-dimensional, self-avoiding random walks, however, are trivial to analyze. As shown in Fig. 2.12 there are only two possible one-dimensional, self-avoiding random walks. A one-dimensional random walk must begin with one step to the left or to the right. If the first step is to the left, the next step must also be to the left because a step to the right would revisit the starting location. Continuing on, the chain that starts to the left must make all steps to the left. The other possible chain is the one that starts with its first step to the right. This chain can only continue with repeated steps to the right. There are thus only two possible chains. One makes all n steps to the left and its length is nl . The other makes all n steps to the right and its length is also nl . Averaging over all possible chain conformations, the root-mean-squared end-to-end distance for a one-dimensional, self-avoiding random walk is

$$\sqrt{\langle r^2 \rangle} = nl \quad (2.32)$$

In contrast to the completely random walk, this result is now linear in n . Because of scaling requirements it remains *linear* in l .

In two- and three-dimensional random walks, the effect of imposing self avoiding characteristics will be less dramatic. A one-dimensional, self-avoiding, random walk is hardly random. All steps (except the first one) are determined by the requirement of being self avoiding and not by random chance. Two- and three-dimensional, self-avoiding random walks will not be restricted as much. Some steps will be influenced by self-avoiding requirements, but most will have other options than can be reached by random chance. Without proof, we state that the end-to-end distance for two- and three-dimensional random walks will be proportional to n to some power between 0.5 and 1.0. The two extremes are completely random walks (power equal to 0.5) and self-avoiding random

walks in which every step is determined by the self-avoiding requirement (power of 1.0). The former extreme is the random walk result from above; the later extreme is the one-dimensional, self-avoiding random walk result.

We now return to the random walk analysis and its assumption that the polymer chains are long enough such that a Gaussian distribution function accurately represents the results. How big do the chains have to be to be large enough? The Gaussian distribution was applied to the factor $(n_+ - n_-)$. For large chains with random n_+ and n_- jumps, we require $|n_+ - n_-| \ll n$. $W(r)dr$ is accurate as long as this inequality is true. $W(r)dr$, however, is supposed to work for all values of r which includes r near $r_{max} = nl$. The maximum value of r can only occur when all jumps are in the same direction which means either $n_+ = n$ and $n_- = 0$ or $n_- = n$ and $n_+ = 0$. In each of these cases $|n_+ - n_-| = n$ and the requirement that $|n_+ - n_-|$ be much less than n is violated. In other words, as r gets large, the chain becomes less Gaussian and $W(r)dr$ becomes increasing inaccurate.

To assess the accuracy of $W(r)dr$, some researchers have constructed more detailed analyses that account for deviations from Gaussian behavior at large r . One published result is

$$W(r)dr = (\text{Const})4\pi r^2 \exp \left\{ -\beta^2 r^2 \left[1 + \frac{3}{10} \left(\frac{r}{r_{max}} \right)^2 + \dots \right] \right\} dr \quad (2.33)$$

The first term within the square brackets is 1 which is the previous result for a Gaussian distribution. The rest of the terms within the square brackets are correction terms that are small for small r and become more significant for large r . Only the first and largest correction term is given. Let's consider a chain of n bonds and say that the uncorrected $W(r)dr$ is adequate as long as the correction term is less than 0.01 (or less than 1%). $W(r)dr$ will then be good for a chain that is up to f times larger than the root-mean-squared end-to-end distance (*i.e.*, good for $r \leq f\sqrt{\langle r^2 \rangle}$) as long as

$$\frac{3}{10} \left(\frac{f\sqrt{\langle r^2 \rangle}}{r_{max}} \right)^2 = \frac{3f^2}{10n} < 0.01 \quad \text{or} \quad f = \sqrt{\frac{n}{30}} \quad (2.34)$$

For example consider a chain of $n = 100$ bonds (a fairly short polymer chain). Solving this equation for f results in $f = 1.83$. Therefore the first correction term in $W(r)dr$ is less than 1% for $0 < r < 1.83l\sqrt{n} = 18.3l$. When $18.3l < r < nl = r_{max} = 100l$ the first correction term is greater than 1%.

We can relate the range of small correction terms to the standard deviation in root mean squared end-to-end distance. The upper limit in r for small corrections is $fl\sqrt{n}$ where $l\sqrt{n}$ is the root mean squared end-to-end distance. From above, the standard deviation in end-to-end distance is $0.15l\sqrt{n}$. Therefore the upper limit in r for small corrections is

$$\frac{fl\sqrt{n} - l\sqrt{n}}{0.15l\sqrt{n}} = \frac{\sqrt{\frac{n}{30}} - 1}{0.15} \quad (2.35)$$

standard deviations above the mean. For the above example with $n = 100$ bonds, this equation shows the $W(r)dr$ is accurate as long as r is less than 5.50 standard deviations above the mean. In

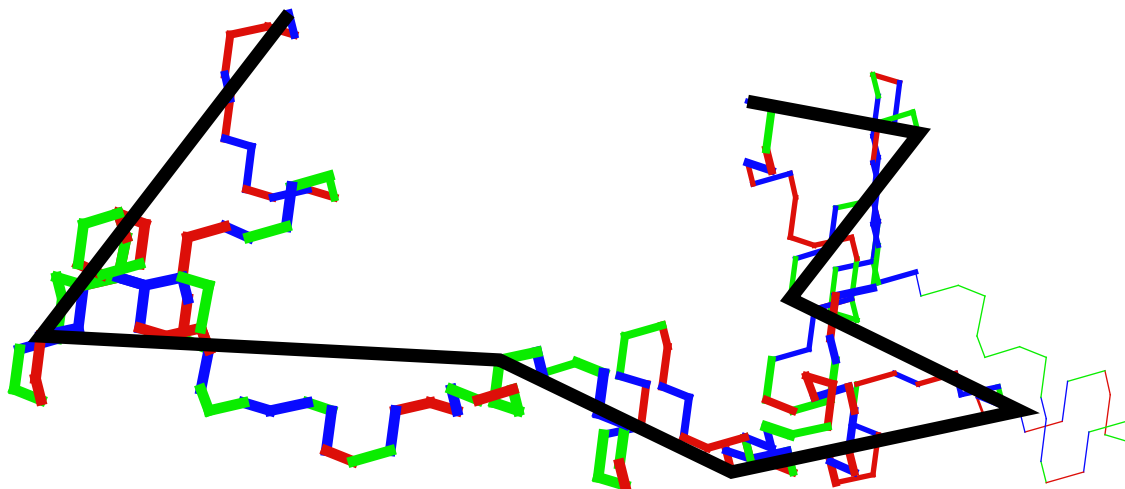


Figure 2.13: The thin lines are a real polymer chain of n bonds. The thick lines are the superposed equivalent freely-jointed chain of $n' = n/m$ bonds.

a normal distribution very few chains will be more than 5.50 standard deviations above the mean. Thus even for a relatively short 100 bond chain, the correction factor is insignificant. We conclude that the correction factors are insignificant for most real polymer chains.

2.5 Equivalent Freely Jointed Chain

Real polymers are not freely jointed; the bond directions θ and ϕ are not free but are restricted by local environment to be biased towards specific values. The major restrictions are caused by nearby bonds. In other words, the conformation of any bond is correlated with the conformations of nearby bonds. As the distance between any two bonds increases, the correlation decreases with the conformations of distant bonds eventually becoming uncorrelated. Say that it takes m bonds for the correlation to drop to zero and then construct from an n bond chain an n' bond chain with $n' = n/m$. Let the average length of each new bond be l' which will be proportional to l (or $l' = kl$). We call the new chain of n' bonds of average length l' the equivalent freely-jointed chain for the original n bond chain. An example equivalent freely-jointed chain is shown in Fig. 2.13.

Because the bond conformations are uncorrelated over long distances, the random walk steps in this new chain are freely-jointed. Using the freely-jointed chain result the root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l' \sqrt{n'} = l \sqrt{Cn} \quad (2.36)$$

where

$$C = \frac{k}{\sqrt{m}} \quad (2.37)$$

By using the equivalent freely-jointed chain, we have shown that the end-to-end distance of a realistic chain is proportional to $l\sqrt{n}$. The proportionality constant is \sqrt{C} . C is normally greater

than one and therefore \sqrt{C} is sometimes called the expansion factor and sometimes denoted as α . It tells how much the real chain is expanded relative to a freely jointed chain. The square of the expansion factor, or C , is known as the characteristic ratio. It is defined by

$$C = \frac{\langle r^2 \rangle}{nl^2} \quad (2.38)$$

In the freely-jointed chain, $C = 1$. In real polymers the characteristic ratio is a function of n or the number of bonds and is usually greater than 1. It is customary to write the bond-dependent characteristic ratio as C_n . In relatively ideal polymers C_n approaches a limiting constant value for large n . The value of C_n at large n for such polymers characterizes the random coil nature of that polymer. Low values of C_n correspond to tightly coiled polymers and high values of C_n correspond to polymers that are loosely coiled or extended.

In real polymers, self-avoiding requirements or excluded volume effects, to be described later, cause C_n to increase without bound as n increases without bound. A scaling law derived by deGennes states that for large n , C_n increases in proportion to $n^{0.2}$. Thus we have

$$C_n = \frac{\langle r^2 \rangle}{nl^2} \propto n^{0.2} \quad (2.39)$$

or

$$\sqrt{\langle r^2 \rangle} \propto ln^{0.6} \quad (2.40)$$

This result agrees with the previous discussion of self-avoiding random walks which claimed that the power-law dependence on n for a real chain is between 0.5 (for a completely random chain) and 1.0 (for a chain with all steps controlled by self-avoiding requirements).

Our discussion on the equivalent freely-jointed chain shows that any real polymer can be reduced to any expression for end-to-end distance that is proportional to $l\sqrt{n}$ (provided we ignore, for the moment, excluded volume effects). The thing that distinguishes one polymer from another is the characteristic ratio C . We thus embark on a series of models whose main purpose is to use theoretical arguments for calculating the characteristic ratio.

2.6 Vector Analysis of Polymer Conformations

We will find it useful to develop an alternate approach to the analysis of end-to-end distance in polymers. The new analysis will be based on vectors and analytical geometry. We associate with each bond a vector. Let the vectors \vec{u}_1 to \vec{u}_n be the vectors along the n bonds. Then a vector from one end of the chain to the other is simply the sum of these vectors:

$$\vec{r} = \sum_{i=1}^n \vec{u}_i \quad (2.41)$$

The mean squared end-to-end distance is

$$\langle r^2 \rangle = \langle \vec{r} \cdot \vec{r} \rangle = \left\langle \sum_{i=1}^n \vec{u}_i \cdot \sum_{j=1}^n \vec{u}_j \right\rangle \quad (2.42)$$

Expanding this expression for a polymer chain with a constant bond length, l , results in

$$\langle r^2 \rangle = \sum_{i=1}^n \vec{u}_i \cdot \vec{u}_i + 2 \sum_{i < j} \langle \vec{u}_i \cdot \vec{u}_j \rangle \quad (2.43)$$

where the sum over $i < j$ means all combinations of i and j such that i is less than j . The factor of 2 in front of the sum includes, by symmetry, the terms when i is greater than j . The dot product of a vector with itself is simply the square of the length of the vector. Thus we can write

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i < j} \langle \cos \theta'_{ij} \rangle \quad (2.44)$$

where θ'_{ij} is the angle between the vectors along bond j and along bond i . If vector j is equal to $i + 1$ (*i.e.*, the bond next to bond i) then θ'_{ij} is the supplement of the bond angle between bonds i and $i + 1$.

For the freely-jointed chain, the bond directions are uncorrelated and $\langle \cos \theta'_{ij} \rangle$ is zero which yields $\sqrt{\langle r^2 \rangle} = l\sqrt{n}$ as before. This result was obtained with less work than the previous analysis. The previous analysis, however gave a full distribution function (a Gaussian distribution) while this one only gives the root-mean-squared end-to-end distance. For more complicated models, we will need to evaluate the term $\langle \cos \theta'_{ij} \rangle$.

We can use a vector analysis to investigate the relation between end-to-end distance and radius of gyration - s . In vector notation, we can write an expression for s^2 in which \vec{r}_i is the location of the i^{th} atom along the polymer chain and \vec{z} is the location of the center of mass:

$$s^2 = \frac{1}{n} \sum_i (\vec{r}_i - \vec{z}) \cdot (\vec{r}_i - \vec{z}) \quad (2.45)$$

Expanding this sum results in

$$ns^2 = \sum_i r_i^2 + nz^2 - 2\vec{z} \cdot \sum_i \vec{r}_i \quad (2.46)$$

where r_i is the distance from the origin to atom i and z is the distance from the origin to the center of mass. The definition of the center of mass is

$$\vec{z} = \frac{1}{n} \sum_i \vec{r}_i \quad \text{or} \quad \sum_i \vec{r}_i = n\vec{z} \quad (2.47)$$

Substituting this expression in to the above results gives

$$ns^2 = \sum_i r_i^2 - nz^2 = \sum_i r_i^2 - n(\vec{z} \cdot \vec{z}) = \sum_i r_i^2 - \frac{1}{n} \sum_i \sum_j \vec{r}_i \cdot \vec{r}_j \quad (2.48)$$

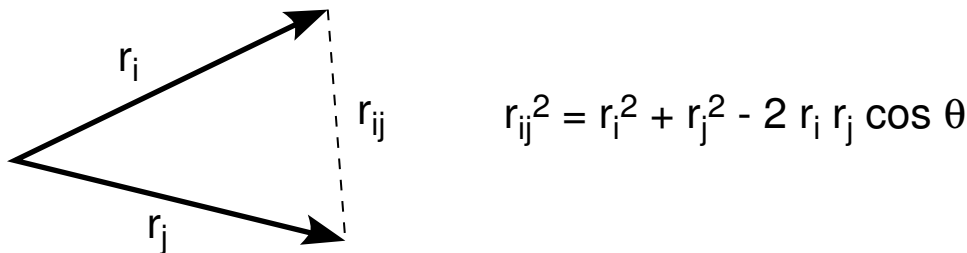


Figure 2.14: A triangle framed by vectors \vec{r}_i and \vec{r}_j . The vector \vec{r}_{ij} connects the two ends of vectors \vec{r}_i and \vec{r}_j .

To evaluate the vector dot product $\vec{r}_i \cdot \vec{r}_j$, consider the triangle in Fig. 2.14. By the cosine law the length of the vector \vec{r}_{ij} connecting the ends of vectors \vec{r}_i and \vec{r}_j is

$$r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos \theta = r_i^2 + r_j^2 - 2\vec{r}_i \cdot \vec{r}_j \quad (2.49)$$

Solving for $\vec{r}_i \cdot \vec{r}_j$ gives

$$\vec{r}_i \cdot \vec{r}_j = \frac{r_i^2 + r_j^2 - r_{ij}^2}{2} \quad (2.50)$$

The expression for the radius of gyration then simplifies to:

$$s^2 = \frac{1}{2n^2} \sum_j \sum_i r_{ij}^2 = \frac{1}{n^2} \sum_j \sum_{i < j} r_{ij}^2 \quad (2.51)$$

In this step we made use of symmetry ($r_{ij} = r_{ji}$) and the fact that $r_{ii} = 0$.

Because the vectors \vec{r}_i are the coordinates of the atoms in the polymer chain, the distance r_{ij} is the end-to-end distance for a sub-polymer chain of $j - i$ bonds. By the discussion in the section on the equivalent freely-jointed chain, we can write this distance as

$$r_{ij}^2 = C(j - i)l^2 \quad (2.52)$$

We do not know the value of C but it is the characteristic ratio for the polymer under consideration and may depend on $j - i$ (especially for small $j - i$). Ignoring the $j - i$ dependence of C , inserting this result, and reordering the summation over i yields:

$$s^2 = \frac{Cl^2}{n^2} \sum_{j=1}^n \sum_{i=1}^{j-1} i = \frac{Cl^2}{n^2} \sum_{j=1}^n \frac{j(j-1)}{2} \approx \frac{Cl^2}{2n^2} \sum_{j=1}^n j^2 = \frac{Cl^2}{2n^2} \frac{n(n+1)(2n+1)}{6} \quad (2.53)$$

For large polymer chains (large n) this result simplifies to

$$\sqrt{\langle s^2 \rangle} = \sqrt{\frac{Cnl^2}{6}} = \sqrt{\frac{\langle r^2 \rangle}{6}} \quad (2.54)$$

We conclude that whenever $\langle r^2 \rangle = Cnl^2$ for a polymer, that the radius of gyration is directly proportional to (and smaller than) the end-to-end distance. This result holds for large molecules

when C_n is independent of n . An important corollary to this result is that everything we learn while studying the end-to-end distance also applies to the radius of gyration. The reverse is also true. Any analysis or experiments that give us information about the radius of gyration also give us information about the end-to-end distance.

The approximations used to relate radius of gyration to end-to-end distance can be understood using a matrix representation. Using the equivalent freely-jointed chain approximation, the radius of gyration squared is the sum of all terms above the diagonal of the following matrix:

$$\begin{pmatrix} 0 & Cl^2 & 2Cl^2 & 3Cl^2 & 4Cl^2 & \dots \\ - & 0 & Cl^2 & 2Cl^2 & 3Cl^2 & \dots \\ - & - & 0 & Cl^2 & 2Cl^2 & \dots \\ - & - & - & 0 & Cl^2 & \dots \\ - & - & - & - & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (2.55)$$

The terms near the diagonal are random walk, long-chain approximations for short chains and may be inaccurate. If the matrix is large, however, there will be many more terms far from the diagonal than close to the diagonal. For large matrices, the inaccuracies in the terms close to the diagonal will have only a negligible effect on the sum of all terms. Thus the relation between $\langle s^2 \rangle$ and $\langle r^2 \rangle$ derived above will be accurate. In order for the derived relation, rewritten here as

$$\frac{\langle r^2 \rangle}{\langle s^2 \rangle} = 6 \quad (2.56)$$

to be accurate, the chain must be slightly larger than is required for $\langle r^2 \rangle$ to be equal to Cnl^2 . The relation will be inaccurate for short chains or for chains that are not random walk coils (*e.g.*, extended chain polymers).

2.7 Freely-Rotating Chain

Commonly the bond angles in polymers are fixed or narrowly fixed to constant values. For example, in polyethylene the bonds angles are all close to 112° . It takes much more energy to distort bond angles than it does to induce rotations about single bonds. We therefore consider a random walk where all bond angles, θ_i , are constant and equal to one value θ . The more easily moved dihedral or rotational angles are considered to all be equally likely. Thus there is free rotation about each bond and hence we call this model the “freely-rotating chain” model. The conformation of a given chain is reduced to specifying the dihedral angles for $n - 1$ bonds (all bonds except the first bond).

To analyze the freely-rotating chain we use the vector approach outlined in the previous section. By taking successive projections of one bond onto another, we can show (See Flory book) that $\langle \cos \theta'_{ij} \rangle = \cos^m \theta'$ where $m = |j - i|$ where $\theta' = \pi - \theta$ is the supplement of the fixed bond angle.

The resulting vector analysis becomes

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i < j} \cos^{j-i} \theta' \quad (2.57)$$

This expression can be imagined as the sum of all the terms in the matrix of size $n \times n$ in which the element at row i and column j is $\cos^{|j-i|} \theta'$:

$$l^2 \times \begin{pmatrix} 1 & \cos \theta' & \cos^2 \theta' & \cos^3 \theta' & \dots & \cos^{n-1} \theta' \\ \cos \theta' & 1 & \cos \theta' & \cos^2 \theta' & \dots & \cos^{n-2} \theta' \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cos^{n-1} \theta' & \cos^{n-2} \theta' & \dots & \cos^2 \theta' & \cos \theta' & 1 \end{pmatrix} \quad (2.58)$$

The n diagonal terms sum to n which give the first term (nl^2) in the $\langle r^2 \rangle$ expression. Writing out the required terms for the summation term by inspection of this matrix gives

$$\langle r^2 \rangle = nl^2 + 2l^2 [(n-1) \cos \theta' + (n-2) \cos^2 \theta' + \dots + (n-(n-1)) \cos^{n-1} \theta'] \quad (2.59)$$

which can be written as

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} (n-i) \cos^i \theta' \quad (2.60)$$

We rewrite this summation in simpler terms by letting $x = \cos \theta'$:

$$\langle r^2 \rangle = nl^2 + 2l^2 (nS_1 - xS_2) \quad (2.61)$$

where

$$S_1 = \sum_{i=1}^{n-1} x^i \quad \text{and} \quad S_2 = \sum_{i=1}^{n-1} ix^{i-1} \quad (2.62)$$

The terms S_1 and S_2 can be evaluated in closed form for all values of n . For polymer problems, we are normally concerned with large n for which these sums converge to constant values and we can treat the two sums as infinite series. The infinite geometric series S_1 has the well known result

$$S_1 \approx \sum_{i=1}^{\infty} x^i = x (1 + x + x^2 + x^3 + \dots) = \frac{x}{1-x} \quad (2.63)$$

For S_2 , we use a trick by noticing that

$$S_2 = \frac{d}{dx} \sum_{i=1}^{n-1} x^i = \frac{dS_1}{dx} \quad (2.64)$$

For large n we thus have

$$S_2 \approx \frac{d \left(\frac{x}{1-x} \right)}{dx} = \frac{1}{(1-x)^2} \quad (2.65)$$

Substituting S_1 and S_2 into the expression for $\langle r^2 \rangle$ gives

$$\langle r^2 \rangle = nl^2 + 2l^2 \left[\frac{nx}{1-x} - \frac{x}{(1-x)^2} \right] \quad (2.66)$$

For large n , the second term in the brackets quickly becomes negligible and we have

$$\langle r^2 \rangle = nl^2 + \frac{2nl^2x}{1-x} = nl^2 \frac{1+x}{1-x} \quad (2.67)$$

Finally we substitute for x and note that $\cos \theta = -\cos \theta'$ (where θ is the bond angle and $\theta' = \pi - \theta$ is the supplement of the bond angle). We get

$$\langle r^2 \rangle = nl^2 \frac{1 - \cos \theta}{1 + \cos \theta} \quad (2.68)$$

The root-mean-squared end-to-end distance for large, freely-rotation chains is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \sqrt{\frac{1 - \cos \theta}{1 + \cos \theta}} \quad (2.69)$$

The characteristic ratio is

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \frac{1 - \cos \theta}{1 + \cos \theta} \quad (2.70)$$

Note that the characteristic ratio is independent of n . This independence is a consequence of our assumption of large n . It is possible to evaluate S_1 and S_2 for any value of n and get an exact result. The exact result gives a C_n that depends on n but rapidly converges to the above result for large n .

For an example we consider polyethylene. All carbon bonds are in approximately tetrahedral geometries. We can thus approximate all bond angles by the tetrahedral angle of $\theta = 109.47^\circ$ or $\cos \theta = -1/3$ (note: it is easier to remember the tetrahedral angle as the $\cos^{-1}(-1/3)$ than it is to remember it as 109.47°). For a freely-rotating polyethylene chain

$$\sqrt{\langle r^2 \rangle} = l\sqrt{2n} \quad (2.71)$$

and the characteristic ratio is $C_n = 2$. Real polyethylene is not totally symmetric and thus the C—C—C bonds deviate slightly from 109.47° to 112° . The C—C—H and H—C—H bonds shrink slightly to compensate. This slight increase in bond angle increases the characteristic ratio by 10% to $C_n = 2.20$.

2.8 Hindered Rotating Chain

The dihedral angle is clearly not free to assume all possible values. Instead the angle is restricted by steric interactions. Consider the potential energy for rotation about the central C—C bond in butane ($\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$) shown in Fig. 2.15. The rotations about the central C—C bond

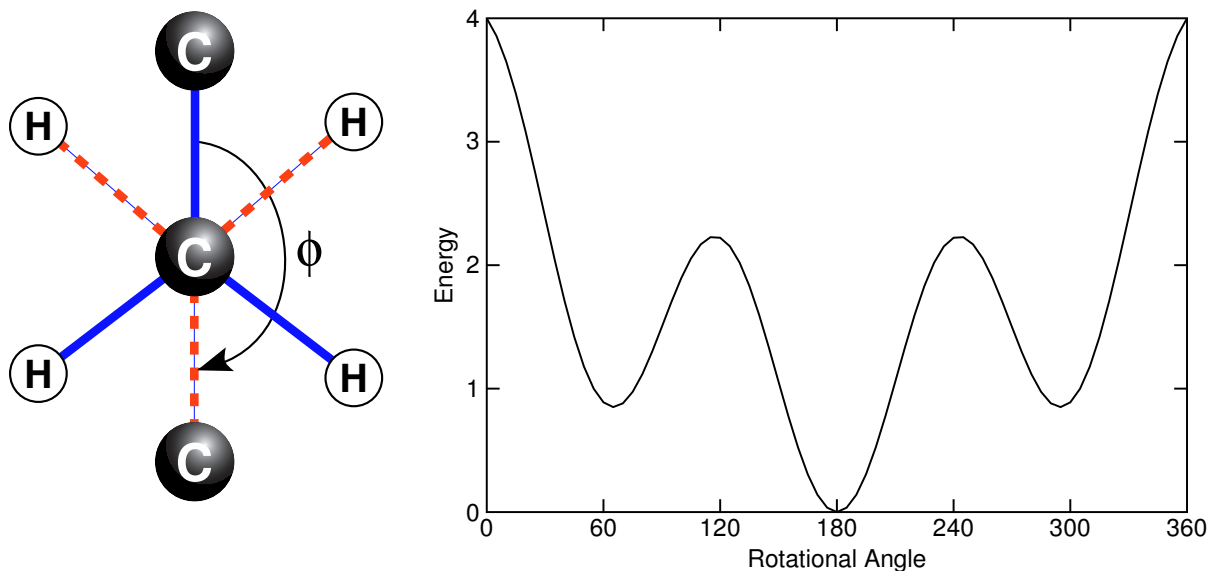


Figure 2.15: Left side is an end view of the central C—C bond in butane. The right side plots to potential energy as a function of angle with $\phi = 180^\circ$ defined as the *trans* position illustrated on the left side.

in butane are a reasonable model for the C—C rotations in polyethylene. A preferred analogy would be higher molecular weight alkanes. Those experiments and their analysis have been done, but with more effort and less accuracy than available for butane.

The *trans* state illustrated on the left side of Fig. 2.15 is the lowest energy state. It is lowest because the two CH_3 groups, which are larger than the H atoms, are as far apart as possible. As rotations occur the groups appended to each of the central C atoms come into closer proximity and the steric energy increases. There are local maxima at $\phi = \pm 120^\circ$. These maxima occur when the CH_3 groups are aligned with H atoms on the other carbon atom. There are local minima when $\phi = \pm 60^\circ$. These minima occur when all the groups are staggered (as in the left of Fig. 2.15) but the CH_3 groups are adjacent to each other rather than opposite each other as in the *trans* state. These local minima are called the *gauche+* and *gauche-* states. Finally there is a local maximum at $\phi = 0^\circ$, which occurs when the two CH_3 groups on either end of the butane chain are aligned and as close together as possible.

When rotations are hindered by potential energy functions such as those shown in Fig. 2.15, it is clear that the rotations will not be free. All rotational angles are perhaps possible, but the dihedral angles will have a preference for the low energy states. For butane, most bonds will be at or near the *trans* state ($\phi = 180^\circ$) or at or near the local *gauche* minima ($\phi = \pm 60^\circ$). Thermal energy will allow the angles to deviate from these states and to overcome the barriers to transitions from one state to another. The populations of all rotational angles, however, will not be equal. We thus replace the freely-rotating chain with a more realistic hindered-rotating chain model.

End-to-end distance for a hindered-rotation chain is more difficult to find than the freely-

rotating chain model. We omit the details and give the results. The final equation is found using the vector analysis and averaging the dot products $\vec{u}_i \cdot \vec{u}_j$, while accounting for unequal populations of the possible rotational angles. The result is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \sqrt{\frac{1 - \cos \theta}{1 + \cos \theta}} \sqrt{\frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle}} \quad (2.72)$$

where $\langle \cos \phi \rangle$ is the average value of the rotational angle. The characteristic ratio is

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \frac{1 - \cos \theta}{1 + \cos \theta} \frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} \quad (2.73)$$

Note that if this hindered-rotation chain becomes freely-rotating chain then $\langle \cos \phi \rangle = 0$ and the results reduce to the freely-rotating chain results.

For a detailed example, let's consider polyethylene with $l = 1.53\text{\AA}$, $n = 5000$ bonds, and $\theta = 112^\circ$. The simplest model, the freely-jointed chain model, gives

$$\sqrt{\langle r^2 \rangle} (\text{freely jointed}) = 108\text{\AA} \quad (2.74)$$

and a characteristic ratio of 1. The next most realistic model, the freely-rotating chain model, gives

$$\sqrt{\langle r^2 \rangle} (\text{freely rotating}) = 108\sqrt{2.20}\text{\AA} = 160\text{\AA} \quad (2.75)$$

and a characteristic ratio of 2.20. For the hindered-rotation chain model we need to know $\langle \cos \phi \rangle$. We thus need some new information. For example, we will say that experiments show that 60% of the bonds have $\phi = 180^\circ$ (*trans*) and 20% each have ϕ 's of $+60^\circ$ or -60° (*gauche+* or *gauche-*). Then the average dihedral angle gives

$$\langle \cos \phi \rangle = -0.6 + 0.2 \times (0.5) + 0.2 \times (0.5) = -0.4 \quad (2.76)$$

The end-to-end distance for the hindered-rotation chain is

$$\sqrt{\langle r^2 \rangle} (\text{hindered rotation}) = 108\sqrt{2.20}\sqrt{2.33}\text{\AA} = 245\text{\AA} \quad (2.77)$$

and the characteristic ratio is $C_n = 5.13$. We can compare this result to the experimental result for polyethylene which is 6 to 7 (depending on temperature). The hindered rotating chain gives a result that is close to the correct results, but is still too low. In the next section we consider improvements on the hindered rotating chain model.

2.9 More Realistic Analysis

We can list two general factors that influence the end-to-end distance, but are not included in the hindered rotation chain model — short range interactions and long range interactions. The next step in our analysis is to include some, or preferable all, of these effects.

We consider short-range interactions as interactions with neighboring bonds that affect the relative probabilities of the dihedral angle. When we include short range interactions we cannot take a simple average of $\cos \phi$ as in the hindered rotation model. We need to account for the effect of neighboring bonds. In its simplest implementation we might assume that the conformation of one bond depends on relative energies that are influenced by the conformation of the previous bond. Each step of the random walk then requires an adjustment of the jump-direction probabilities according to the conformation of the previous bond. Some probability analysts call such models Markov chains instead of random walks. After we develop a model that does a good job of accounting for short-range interactions, we will have a good model for polymer conformations that are unperturbed by the long-range interactions described below. We will call the polymers generated by this modified random walk or Markov chain process “unperturbed polymer conformations.” The end-to-end distance of these chains will be called the unperturbed end-to-end distance and will be denoted with a subscript zero — $\langle r^2 \rangle_0$.

Long-range interactions are all interactions that are not short-range interactions. To be more specific, long-range interactions are interactions between atoms or molecular units that are not covalently bonded to each other. Defined this way, long range interactions include interactions between two parts of the polymer that are separated by many bonds or between the polymer and solvent molecules. We discuss three types of long-range interactions.

The first important perturbation to random walks is that while random walks can cross their own path, a polymer conformation cannot — random walks used to simulate polymer chains should be self-avoiding random walks. This new feature is called the effect of *excluded volume*. The elements of the chain exclude other elements from their occupied volume. If included in the analysis, excluded volume will perturb the end-to-end distance and cause it to increase. Besides increasing the end-to-end distance, excluded volume will cause the root-mean-squared end-to-end distance to no longer be proportional to \sqrt{n} . When excluded volume effects are significant, we can assume that $\langle r^2 \rangle$ is proportional to some power of n such as p (where $p > 0.5$):

$$\langle r^2 \rangle \propto n^p l^2 \quad (2.78)$$

According to deGennes, $p = 1.2$ and therefore the characteristic ratio increases as $n^{0.2}$:

$$C_n = \frac{\langle r^2 \rangle}{nl^2} \propto n^{0.2} \quad (2.79)$$

A second long-range interaction is interactions between the polymer and the solvent. A solvent can cause the unperturbed end-to-end distance to increase or decrease. A good solvent will cause it to increase. In effect the polymer will prefer interactions with the solvent over interactions with itself and therefore will expand to maximize polymer-solvent interactions. A poor solvent will cause the unperturbed end-to-end distance to contract. The polymer wants to avoid the solvent and thus will contract on itself to avoid polymer-solvent interactions. In the extreme case, a poor solvent will

cause the polymer to completely contract and precipitate out of solution. This extreme example of a poor solvent is better characterized as a non-solvent.

The last types of long-range interactions are specific interactions. By specific interactions we mean identifiable interactions between remote parts of the chains. Two examples are hydrogen bonding and ionic interactions.

After considering both short-range and long-range interactions we are led to split the problem of theoretical polymer characterization into two parts. The first part is the study of the unperturbed end-to-end distance. We plan to modify the hindered rotation chain model to correctly account for short-range interactions and thereby calculate the correct unperturbed end-to-end distance. After solving this problem we will consider what influence the long-range interactions (including excluded volume effects) have on the results. Let's define α to be the factor by which the linear dimension expands ($\alpha > 1$) or contracts ($\alpha < 1$) due to long-range interactions:

$$\sqrt{\langle r^2 \rangle} = \alpha \sqrt{\langle r^2 \rangle_0} \quad (2.80)$$

The solution to the long-range interaction problem is to find α .

2.10 Theta (Θ) Temperature

We also need to consider temperature effects. Temperature can affect all types of interactions. It can affect short-range interactions by influencing the relative probabilities of the various dihedral angles. Rotations about single bonds are influenced by the presence of thermal energy and thus higher temperature will make it more likely to find conformations in higher-energy rotational angles. Temperature affects long-range interactions mainly through polymer-solvent interactions. In general increasing the temperature improves solvent quality and lowering it decreases solvent quality.

As discussed in the previous section, we will first attempt to solve the short-range interaction problem. The first problem we encounter is how do we know when we have the right answer? Real polymers have long-range interactions and short-range interactions. Thus real polymers have a mean-squared end-to-end distance of $\langle r^2 \rangle$ and not $\langle r^2 \rangle_0$. If we compare our theoretical analysis to experimental results we will normally find disagreement, regardless of whether the analysis to find $\langle r^2 \rangle_0$ was correct or not. Fortunately there is an experimental solution to this problem called the theta (Θ) temperature. For any given polymer-solvent pair, there is a specific temperature, called the Θ temperature, for which the true end-to-end distance is equal to the unperturbed end-to-end distance. Thus experiments at the Θ temperature can be used to measure $\langle r^2 \rangle_0$ which can be compared to experimental predictions.

The concept of Θ temperature can be understood by considering the effect of temperature on polymer-solvent interactions. In general the polymer-solvent interactions for a given polymer-

solvent pair is an increasing function of temperature. As the polymer-solvent interaction increases the solvent becomes a better solvent. Thus increasing temperature leads to a better solvent and to a higher α ; decreasing temperature leads to a poorer solvent and a lower α . For a given polymer-solvent pair, there will be some temperature for which $\alpha = 1$. That temperature is called the theta (Θ) temperature. At the Θ temperature $\langle r^2 \rangle = \langle r^2 \rangle_0$ and experiments at the Θ temperature can be used to measure $\langle r^2 \rangle_0$.

Besides measuring $\langle r^2 \rangle_0$, the Θ temperature has other useful properties. At the Θ temperature, some physical properties (*e.g.*, osmotic pressure) obey ideal laws up to high concentrations. Thus simple theories for analysis of a physical property that do not account for long-range interactions will still work well at the Θ temperature. There is an analogy between the Θ temperature and the Boyle point of a gas. The Boyle point is the temperature where the repulsion between gas molecules due to excluded volume is exactly compensated by their mutual attraction. At the Boyle point, the ideal gas laws are obeyed to very high pressures. Note that conformity to ideal laws is one way of determining the Θ temperature. The temperature can be varied until the measurements obey ideal laws. That temperature is the Θ temperature.

Despite the advantages of the Θ temperature, we note that working in theta solvents is often impractical. To get α down to one, you need a solvent that is sufficiently poor. The solvent may become so poor the precipitation becomes imminent. It is often better to work in a good solvent and correct the results to the unperturbed results. For measurements of physical properties, this correction involves correcting ideal laws for large molecules or long-range interactions.

2.11 Rotational Isomeric State Model

The rotational isomeric state model will be our solution to the problem of accounting for short-range interactions and some long range interactions (*e.g.*, the effect of excluded volume). In general, any polymer conformation is defined by a set of bond lengths, l_i , bond angles, θ_i , and dihedral angles, ϕ_i . In the rotational isomeric state model, we assume that the polymer is restricted to certain types of conformations or to certain isomeric states. Bond lengths are likely to vary only $\pm 3\%$ and thus as before we consider them to be fixed at l . Likewise, bond angles are likely to vary only ± 5 degrees and we consider them to be fixed at θ . The dihedral angles are not allowed to assume any possible angle, but instead are assumed to be restricted to a small number of discrete values. The possible discrete dihedral angles define the set of rotational isomeric states for each bond.

We will illustrate with polyethylene. These ideas will be extended to other polymers later. Due to symmetry of polyethylene there are three possible rotational isomeric states (see Fig. 2.16). The *trans* state ($\phi = +180^\circ$), the *gauche+* state ($\phi = +60^\circ$) and the *gauche-* state ($\phi = -60^\circ$). In the rotational isomeric state model, each bond of polyethylene is assumed to be in one of these three states. No other values of ϕ are allowed. In reality, thermal fluctuations about the minima in

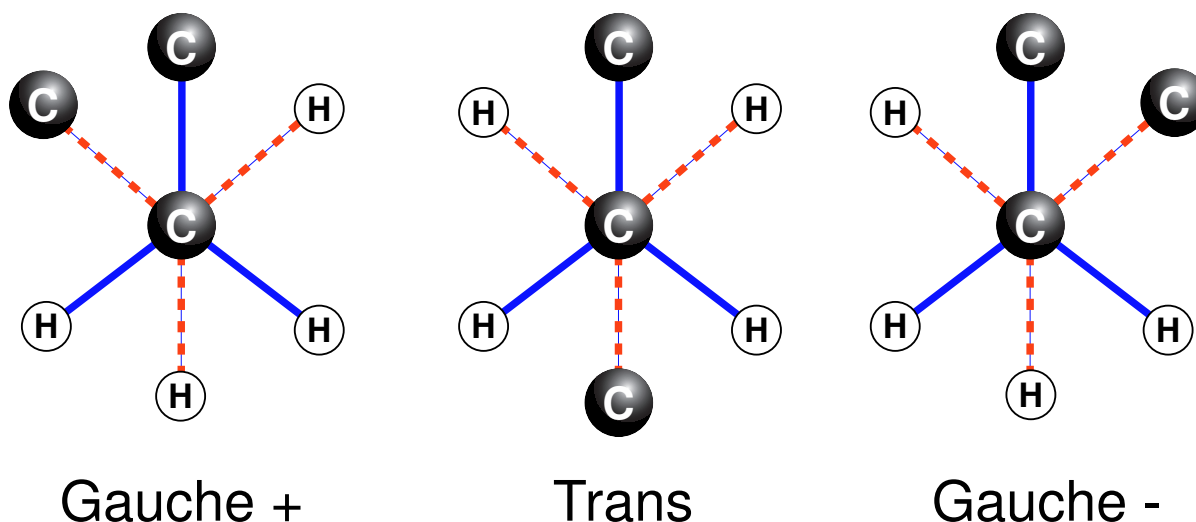


Figure 2.16: The three rotational isomeric states in polyethylene. The dihedral angle, ϕ , is defined as the angle between to white circles.

potential energy will lead to a distribution in ϕ 's around these three local minima. The rotational isomeric state model asserts that we can realistically simulate a polymer chain by ignoring variations in ϕ around the local minima.

In our random walk analysis of the rotational isomeric state, the probability of any bond existing in one of the rotational state i characterized by angle ϕ_i , is given by a Boltzman factor:

$$P(\phi_i) = \frac{e^{-E(\phi_i)/RT}}{Z} \quad (2.81)$$

where Z is a normalizing factor or the sum of the Boltzman energy factors for all possible angles:

$$Z = \sum_{i=1}^3 e^{-E(\phi_i)/RT} \quad (2.82)$$

where $E(\phi_i)$ is the energy associated with the state at dihedral angle ϕ_i and the sum is over the three possible states in Fig. 2.16 (Note: this equation can easily be generalized to more than three rotational isomeric states) Because of short-range interactions discussed above, this probability factor is expected to be affected by neighboring bonds. The simplest model is to assume that the energy, $E(\phi_i)$, is affected by the bond conformation of the previous bond. This important nearest-neighbor interaction is ignored in the hindered rotation chain model. Its inclusion in the rotational isomeric state model is the major advance in realism in this new model.

To account for nearest neighbor interactions, we must consider all bond pairs and all possible conditional probabilities of the form $P(\phi_i|\phi_{i-1})$, which gives the conditional probability that bond i has angle ϕ_i given that the previous bond or bond $i - 1$ has angle ϕ_{i-1} . By analogy with the previous probability factor

$$P(\phi_i|\phi_{i-1}) = \frac{e^{-E(\phi_{i-1}\phi_i)/RT}}{Z(\phi_{i-1})} \quad (2.83)$$

where $Z(\phi_{i-1})$ is a normalizing factor or the sum of the Boltzman energy factors for all angles ϕ_i given that ϕ_{i-1} is fixed:

$$Z = \sum_{j=1}^3 e^{-E(\phi_{i-1}\phi_j)/RT} \quad (2.84)$$

In these equations, $E(\phi_{i-1}\phi_i)$ is the energy associated with two consecutive bonds with dihedral angles ϕ_{i-1} and ϕ_i . In this section we are restricting ourselves to three rotational states of *trans* (t), *gauche+* (g^+), and *gauche-* (g^-). The energy factors we care about are $E(tt)$, $E(tg^+)$, $E(tg^-)$, etc.. The conditional probabilities we are concerned with can conveniently be tabulated in a matrix called the weighting factor matrix. For polyethylene (or for any three-state polymer) we write can write a weighting factor matrix as

$$U = \begin{pmatrix} P(t|t) & P(g^+|t) & P(g^-|t) \\ P(t|g^+) & P(g^+|g^+) & P(g^-|g^+) \\ P(t|g^-) & P(g^+|g^-) & P(g^-|g^-) \end{pmatrix} \quad (2.85)$$

For example, the matrix element $P(t|g^+)$ gives the probability that the next bond is *trans* given that the previous bond was *gauche+*.

Let's begin with the first row and arbitrarily assign the tt state to the ground state. Thus we assume $E(tt) = 0$. The tg^+ and tg^- bond pairs will each be higher in energy than the tt bond pair. In polyethylene, the excess energy associated with the two possible *gauche* bonds will be the same. We let that excess energy be E_g or the extra energy associated with a *gauche* bond. We further define

$$\sigma = e^{-E_g/RT} \quad (2.86)$$

and we can quickly derive $Z(t) = 1 + 2\sigma$ and

$$P(t|t) = \frac{1}{1+2\sigma} \quad P(g^+|t) = \frac{\sigma}{1+2\sigma} \quad P(g^-|t) = \frac{\sigma}{1+2\sigma} \quad (2.87)$$

$Z(t)$ appears in the denominator of each probability as a normalizing factor.

For the second row, we might just consider the energy associated with all the *gauche* bonds and assume $E(g^+t) = E_g$ and $E(g^+g^+) = E(g^+g^-) = 2E_g$. The probabilities would become

$$P(t|g^+) = \frac{\sigma}{\sigma+2\sigma^2} \quad P(g^+|g^+) = \frac{\sigma^2}{\sigma+2\sigma^2} \quad P(g^-|g^+) = \frac{\sigma^2}{\sigma+2\sigma^2} \quad (2.88)$$

This simple analysis ignores an important short-range interaction that occurs when two consecutive bonds are g^+g^- or g^-g^+ . Figure 2.17 illustrates a g^+g^- conformation. Two parts of the polymer chain separated by four bonds are in close proximity which causes a large steric interaction. This interaction is known as the *pentane* effect and causes the energy of g^+g^- or g^-g^+ conformations to be much higher than that g^+g^+ or g^-g^- conformations. If we let E_p be the energy of the pentane effect interaction then $E(g^-g^+) = 2E_g + E_p$ whereas $E(g^+g^+) = 2E_g$. Defining

$$\omega = e^{-E_p/RT} \quad (2.89)$$

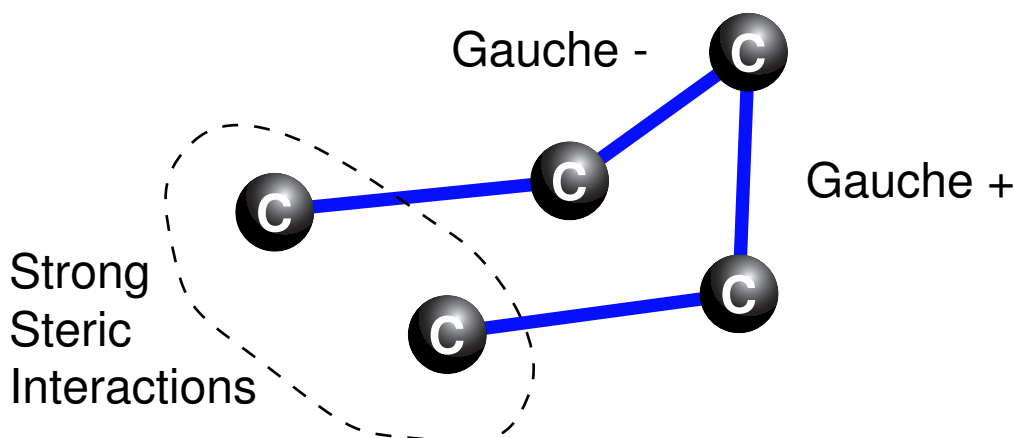


Figure 2.17: The steric interactions caused by the pentane effect when two consecutive bonds are $g^+|g^-$ or $g^-|g^+$.

we derive the conditional probabilities for the second row of U to be

$$P(t|g^+) = \frac{\sigma}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{1}{1 + \sigma + \sigma\omega} \quad (2.90)$$

$$P(g^+|g^+) = \frac{\sigma^2}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{\sigma}{1 + \sigma + \sigma\omega} \quad (2.91)$$

$$P(g^-|g^+) = \frac{\sigma^2\omega}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{\sigma\omega}{1 + \sigma + \sigma\omega} \quad (2.92)$$

Analyzing the third row similarly to the second row and collecting all probabilities in the matrix we arrive at

$$U = \begin{pmatrix} \frac{1}{1+2\sigma} & \frac{\sigma}{1+2\sigma} & \frac{\sigma}{1+2\sigma} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} \end{pmatrix} \quad (2.93)$$

It usually suffices to work with relative probabilities rather than absolute probabilities. By convention we normalize each row to the first element in that row. For a simple polymer like polyethylene, we write the weighting matrix of relative probabilities as

$$U = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix} \quad (2.94)$$

By theory and experiment, the energy terms for polyethylene are well known. The best results give $E_g = 2100$ J and $E_p = 8400$ J. At 300°C these lead to weighting factors of

$$\sigma = e^{-2100\text{J}/RT} = 0.43 \quad \text{and} \quad \omega = e^{-8400\text{J}/RT} = 0.081 \quad (2.95)$$

Thus gauche bonds are only about 46% as likely as trans bonds ($2\sigma/(1 + 2\sigma)$) and $g^+|g^-$ conformations are only about 2.4% as likely ($\sigma\omega/(1 + \sigma + \sigma\omega)$).

We next consider how to use the rotational isomeric state model to predict polymer properties. Imagine a polymer chain of n bonds. A polymer conformation of this chain is determined by setting the states of each bond; each bond can be t , g^+ , or g^- . We can ignore the first two bonds and thus we need to set the states of the terminal $n - 2$ bonds. The first bond can be ignored because it only serves to locate the start of the polymer in space. The second bond direction is determined by the rotational state of bond 1, but this state only serves to locate the initial direction of the random walk. The remaining $n - 2$ bonds need to be determined.

There are two possible solutions to the rotational isomeric state model. Because each bond has a small number of discrete states, the total number of polymer conformations is finite. For a polymer with n bonds of which each bond can be in one of three states, the total number of polymer conformations is 3^{n-2} . One possible approach is to enumerate all possible conformations and calculate properties using the exact process discussed earlier in this chapter. This exact solution can be done for small n , but soon becomes impractical for large n 's typical of real polymers. When n is large the total number of conformations is too large to enumerate, even on the fastest supercomputer.

For large polymers, a preferred approach is to use the Monte Carlo method. We generate a large number of chains using a random walk or Markov chain process. For each bond the probabilities of the next bond being in a given state are determined by the weighting matrix like the one given above and by the state of the previous bond. For each chain we can calculate a property of interest (*e.g.*, end-to-end distance, radius of gyration, *etc.*). The average value of that property after generating sufficiently many chains will be our Monte Carlo solution to the problem.

The above Monte Carlo random walk process requires a computer. The computer program Lattice™ discussed in class is an example of a program that can do Monte Carlo simulations using the rotational isomeric state model. Programs like Lattice™ are, in effect, computer experiments. You set polymer properties by selecting weighting factors, excluded volume, temperature, *etc.*. Then you run the program and calculate the end-to-end distance or the radius of gyration. These computer experimental results can be compared to real experimental results. If the two results agree, you have evidence that the rotational isomeric state is a valid model for polymers. Furthermore the physical concepts of the rotational isomeric state model give you insight about the polymer molecules and the factors that control conformations.

The following pseudo computer code is the program logic, or flow chart, of the main part of any program that does Monte Carlo solutions using the rotational isomeric state model. This flow chart assumes a three rotational isomeric states, but it could easily be generalized to handle any number of states.

```
let v = (1,0,0) or the first bond is t
for bond=2 to number of bonds-1
```

```

let q=Uv be a vector giving the probabilities for t, g+, and g-
pick a random number between 0 and q1+q2+q3
if (random number is between 0 and q1) then
    next bond is t and v = (1,0,0)
else if (random number is between q1 and q2) then
    next bond is g+ and v = (0,1,0)
else if (random number between q2 and q3) then
    next bond is g- and v = (0,0,1)
end if

if desired, check for excluded volume effects
    if jump to occupied site, try another site, reject the entire
        chain, or reject several previous bonds
    if all sites occupied start new chain
end if

next bond

Now have set of n-2 bond conformations which completely define the chain
Calculate properties (e.g. end-to-end distance, radius of gyration, etc.)
Start over with another chain and continue until results converge

```

The key part of this loop is calculating the properties of each generated chain. You can calculate any property that can be reliably calculated for a given polymer conformation. The simplest and most reliable properties are size properties. The program Lattice™ calculates the following properties:

1. Last r (end-to-end distance of current chain)
2. rms r
3. $\langle r \rangle$
4. rms s
5. $\frac{r^2}{nl^2}$ — the characteristic ratio (equal to C_n)
6. $\frac{r^2}{s^2}$ — how close is it to 6?
7. % trans
8. Number of rejected steps
9. Relative entropy

In addition to the above calculations, Lattice™ can also plot many results. It can plot each generated polymer in a three-dimensional view. These stick figures give a feel for typical polymer conformations. It can plot the distribution of end-to-end distances and compare them to the radial Gaussian function calculated for in the freely-jointed chain analysis.

There is one important aspect of Lattice™ and many rotational isomeric state solutions that requires discussion. As implied by its name, Lattice™ generates chains on a tetrahedral lattice. This requires all bonds angles to be the tetrahedral bond angle of 109.47° . Because it is a regular lattice, it also requires all bonds lengths to be the same. This type of simulation is reasonably accurate for polyethylene and for many other carbon-backbone polymers. Lattice simulations, however, cannot give you information about the effect of bond angle (*e.g.*, 112° in real polyethylene *vs.* the 109.47° in a tetrahedral lattice) and cannot simulate polymers with different bond lengths. The advantage of lattice simulations is that they are fast. They can do most of the work with integer arithmetic which is much faster in computers. The use of a lattice makes it possible to do meaningful simulations in personal computers such as Macintoshes. An off-lattice calculation on a Macintosh would be limited to much more rudimentary work and to much shorter chains.

We can simulate many polymers using the rotational isomeric state model. Some interesting polymers are:

1. Polyethylene (see above)
2. Polytetrafluoroethylene (PTFE)
3. Copolymers
4. Polyoxymethylene (POM) (Delrin, Celcon, *etc.*)
5. Polypropylene (PP) — a vinyl polymer

Some results from these types of polymers are discussed in the Lattice™ manual and will be covered in class.

Problems

2-1. The radial distribution function for the freely-jointed chain model was shown in class to be

$$W(r)dr = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 4\pi r^2 e^{-\beta^2 r^2} dr \quad (2.96)$$

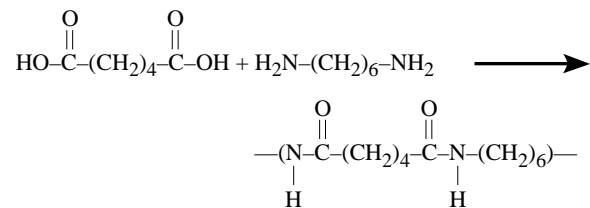
where

$$\beta = \sqrt{\frac{3}{2nl^2}} \quad (2.97)$$

Because the form of the radial distribution function even for non-freely-jointed chains is similar to the freely-jointed chain result (except with a different value for β) it is worth studying this function.

- a. Show that the maximum in $W(r)dr$ occurs at $r = \frac{1}{\beta}$
 - b. Show that the mean value of r is $\langle r \rangle = \frac{2}{\beta\sqrt{\pi}}$.
 - c. Show that the average value of r^2 is $\langle r^2 \rangle = \frac{3}{2\beta^2}$
 - d. What is the standard deviation in r ?
 - e. Express the answers to *a* through *d* in terms of number of bonds (n) and bond length (l).
- 2-2. Pretend that linear polyethylene (PE or $-(\text{CH}_2-\text{CH}_2)_n-$) can be modeled as a freely-jointed chain in which each bond is 1.53\AA long. Using the results from problem 2-1, evaluate the following quantities:
- a. How many bonds are in a 500,000 g/mole PE polymer chain?
 - b. What is the maximum length of the chain?
 - c. What is the most likely end to end distance?
 - d. What is the mean end-to-end distance
 - e. What is the root mean squared end-to-end distance?
 - f. What is the standard deviation in r ?
 - g. Plot the radial distribution function for this polymer chain and indicate on your plot the answers to *c*, *d*, and *e*.
- 2-3. Polymer *A* contains x freely jointed segments each of length l_a and polymer *B* contains y freely jointed segments each of length l_b . One end of *A* is connected to one end of *B* to form a two block, block copolymer.
- a. What is the root-mean-squared end-to-end distance of this block copolymer?
 - b. If segments of *A* are randomly interspersed with segments of *B* and the segments are still freely jointed, what would be the root-mean-squared end-to-end distance of the random copolymer?
- 2-4. How do each of the following affect the radius of gyration?
- a. Decreasing the molecular weight.
 - b. Decreasing the polymer-solvent interaction.
 - c. Adding the effects of excluded volume.
 - d. Reducing the hindrance to rotations about bonds.

2-5. Many polymers have more than one type of bond the different types of bonds may have more the one value for bond length. One example is Nylon 66 whose repeat unit structure is



This polymer has $N-CH_2$ bonds, N -carbonyl bonds, carbonyl- CH_2 bonds, and CH_2-CH_2 bonds. Explain, in general terms, how you would use the rotational isomeric state model to calculate the characteristic ratio of Nylon 66.