6

Polymer Conformations

6.1 Conformations, Bond Rotation, and Polymer Size

The remarkable properties of polymers derive from their size. As pointed out in Chapter 1, it is not the high molecular weight per se that gives polymers mechanical strength, flexibility, elasticity, etc., but rather their large spatial extent. In this chapter, we will learn how to describe the three-dimensional shape of polymers in an average sense, and how the average size of the object in space will depend on molecular weight. We will also explore the equilibrium distribution of sizes.

To gain an appreciation of the possibilities, consider a polyethylene molecule with $M = 280,000$ g/mol (this is a reasonable value for a randomly selected molecule in some commercial grades of polyethylene). As the monomer ($-CH_2-CH_2-$) molecular weight is 28 g/mol, the degree of polymerization, N, is 10,000, and there are 20,000 C—C backbone bonds. Assuming a perfectly linear structure (actually not likely for a commercial polyethylene), the contour length L of this molecule would be roughly $20,000 \times 1.5$ Å $= 30,000$ Å or about 3 μm, because 1.5 Å is approximately the average length of a C—C bond. This is simply huge. If stretched out to its full extent, L would be half the size of a red blood cell, and possibly visible under a high-power optical microscope. Some commercial polymers are 10 times bigger than this one, and some DNA molecules have molecular weights in excess of 10^9 g/mol. However, as we will see, it is very rare indeed for a chain to be so extended, and the contour length is not usually the most useful measure of size. Now consider the opposite extreme, where the same polyethylene molecule collapses into a dense ball or *globule*. The density of bulk polyethylene is about 0.9 g/mL. The volume occupied by this 280,000 g/mol molecule would be $(280,000/0.9)/(6 \times 10^{23})$ mL $= 520,000$ Å^3, and if we assume it is a sphere, the radius would be $((3/4\pi)\text{volume})^{1/3} \approx 50$ Å. The range from 50 Å at the smallest to 3 μm at the largest covers three orders of magnitude; it is a remarkable fact that such a mundane molecule could adopt conformations with sizes varying over that range. If the dense sphere were a tennis ball, the chain contour would be the length of a football field.

Polyethylene, and most carbon chain polymers, is not likely to adopt either of these extreme conformations. The reason is easy to see. Select a C—C bond anywhere along the chain; we can represent the structure as $R'CH_2-CH_2R''$. There is rotation about this bond, with three energetically preferred relative orientations of R' and R'' called *trans* (t), *gauche plus* (g$^+$), and *gauche minus* (g$^-$) (see Figure 6.1a). For the chain of 20,000 bonds, there are three possible conformations for each bond, and therefore $3^{20,000} \approx 10^{10,000}$ possible conformations. This number is effectively infinite. If our molecule were in a high temperature liquid state, and if we assume it takes 1 ps to change one bond conformation, then the molecule would not even approach sampling all possible conformations over the history of the universe. Similarly, it would be highly improbable for it to even visit any given conformation twice. We can now see why the chance of being fully extended, in the all-*trans* state, is unlikely to say the least; the probability is about 1 in $10^{10,000}$. The dense sphere state might be marginally more probable, as there are many sequences of t, g$^+$, and g$^-$ that might produce something close to that, but it is still essentially impossible without the action of some external force. What the polymer does instead is form what is called a *random coil* (Figure 6.2). The different sequences of t, g$^+$, and g$^-$ cause the chain to wander about haphazardly in space, with a typical size intermediate between the dense sphere and the extended chain. With so
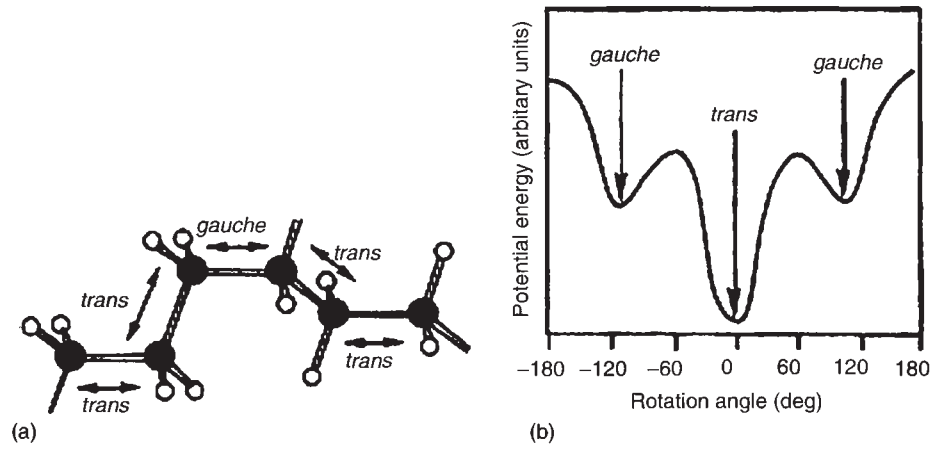
Figure 6.1 Backbone bond conformations for polyethylene. (a) Illustration of *trans* and *gauche* arrangements of the backbone bonds. (b) Schematic plot of the potential energy as a function of rotation angle about a single backbone bond.
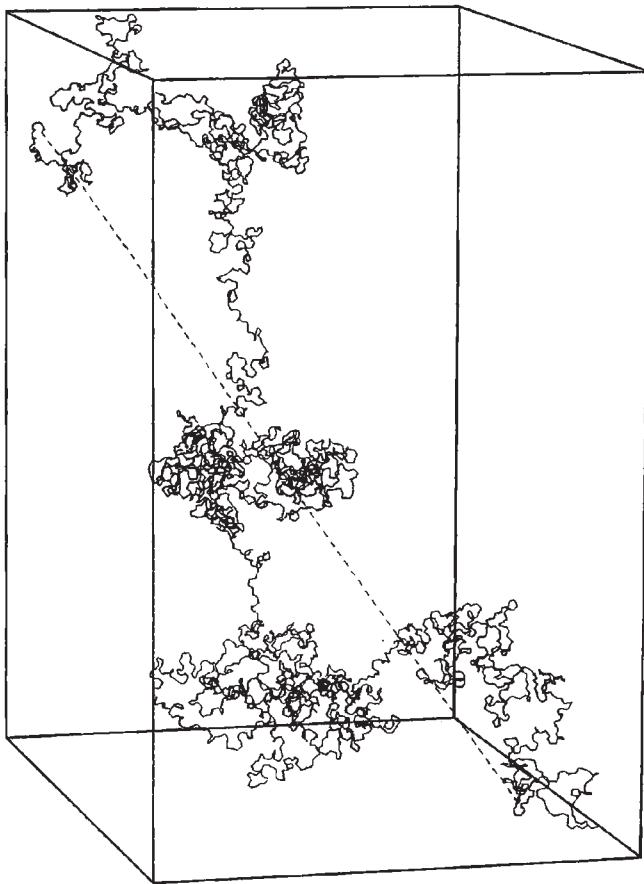

Figure 6.2 Illustration of a random walk in three dimensions. The walk has 4000 steps, and the walk touches each face of the box. (From Lodge, A.S., *An Introduction to Elastomer Molecular Network Theory*, Bannatek Press, Madison, 1999. With permission.)

many possibilities, we obviously cannot predict any instantaneous conformation or size, but we will be able to say a great deal about the average size.

The preceding argument, although fundamentally sound, neglects a very important aspect of chain conformations. The energies of the t, g^+, and g^- states are not equal; for polyethylene t is energetically favorable relative to g^+ or g^- by about $\Delta E = 3$ kJ/mol (or 0.7 kcal/mol). Therefore, at equilibrium, the population of t states will exceed that of g^+ or g^- by the appropriate Boltzmann factor, $\exp(-\Delta E/RT)$, which in this case is about 2 at $T = 500$ K ($RT \approx 4.2$ kJ/mol or 1 kcal/mol). (We have injected some statistical mechanics here. For a large collection or *ensemble* of molecules at equilibrium, the relative populations of any two possible states are given by this Boltzmann factor.) This bias is still not enough to put much of a dent into the vast number of possible conformations, but it does matter when computing the detailed conformational statistics for a given polymer chain. There is a further issue of importance, namely, how high are the energy barriers among the t, g^+, and g^- states? If these are too high, conformational rearrangements will not occur rapidly. Figure 6.1b shows a schematic plot of the potential energy as a function of rotation about the C—C bond in polyethylene. The barrier heights are on the order of 10 kJ/mol (2.5 kcal/mol), which corresponds to about 2.5 times RT, the available thermal energy per mole at 500 K. Thus rotation should be relatively facile for polyethylene. (To put this energy barrier on a chemist's scale, it is comparable to the energy of a weak hydrogen bond.) However, for polymers with larger side-groups or with more complicated backbone structures, these barriers can become substantial. For example, in poly(n-hexyl isocyanate) (—N(C_6H_{13})—C(O)—) the n-hexyl side chain forces the backbone to favor a helical conformation, and the molecule becomes relatively extended.

At this point it might look like a very daunting task to calculate the probable conformation of a given polymer, and it will require some detailed information about bond rotational potentials, etc., for each structure. However, it turns out that we can go a long way without any such knowledge. What we will calculate first is the average distance between the ends of a chain, as a function of the number of steps in a chain. We will show that this is given by a simple formula, and that all the details about chemical structures, bond potentials, etc., can be grouped into a single parameter. We will also consider the distribution of possible values of this end-to-end distance. The average could, in principle, be taken in two different ways. One would be to follow a single chain as it samples many different conformations—a time average. Another would be to look at a large collection of structurally identical chains at a given instant in time—an ensemble average. In this example, these two averages should be the same; when this occurs, we say the system is *ergodic*. In a real polymer sample, a measurement will also average over a distribution of chain lengths or molecular weights; that is a different average, which we will have to reckon with when we consider particular experimental techniques.

6.2 Average End-to-End Distance for Model Chains

In this section, we calculate the root-mean-square (rms) end-to-end distance $\langle h^2 \rangle^{1/2}$ for an imaginary chain, made up of n rigid links, each with length ℓ. The model is sketched in Figure 6.3. At this stage there is no need to worry about whether the link is meant to represent a real C—C bond or not; we will make the correspondence to real polymers later. If we arbitrarily select one end as the starting point, each link can be represented by a vector, $\vec{\ell}_i$, with $i = 1, 2, 3, \ldots n$. The instantaneous end-to-end vector, $\vec{h}$, is simply the sum of the link vectors:

$$\vec{h} = \sum_{i=1}^{n} \vec{\ell}_i \qquad (6.2.1)$$

If we have a chain that wiggles around over time, or if we look at an ensemble of similar chains, there is no reason for $\vec{h}$ to point in any one direction more than any other, and the average $\langle \vec{h} \rangle = 0$; we say the sample is *isotropic*. What we really care about is the average end-to-end *distance*, which
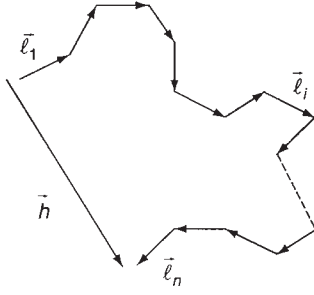
Figure 6.3 Model chain consisting of n links of length ℓ. Each link is represented by a vector, $\vec{\ell}_i$, and the end-to-end vector $\vec{h}$ extends from the start of the first link to the end of the last one.

we can calculate remembering that the length of a vector is obtained by taking the dot product of the vector with itself:

$$\langle h^2 \rangle^{1/2} = \langle \vec{h} \cdot \vec{h} \rangle^{1/2} = \left\langle \sum_{i=1}^{n} \vec{\ell}_i \cdot \sum_{j=1}^{n} \vec{\ell}_j \right\rangle^{1/2} \tag{6.2.2}$$

The double sum can be broken into two parts, remembering also that the summations can be taken outside the average as follows:

$$\langle h^2 \rangle = \left\langle \sum_{i=1}^{n} \vec{\ell}_i \cdot \sum_{j=1}^{n} \vec{\ell}_j \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle$$

$$= \sum_{i=1}^{n} \left\langle \vec{\ell}_i \cdot \vec{\ell}_i \right\rangle + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle$$

$$= n\ell^2 + \sum_{i=1}^{n} \sum_{j \neq i}^{n} \left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle \tag{6.2.3}$$

where the first term, $n\ell^2$, accounts for the "self-terms," i.e., each of the n link vectors dotted into itself, and the second term accounts for the "cross terms," i.e., each link vector dotted into the $n-1$ other link vectors.

We now develop explicit results for $\langle h^2 \rangle^{1/2}$, with three different rules for how the orientation of a given link, $\vec{\ell}_i$, is constrained by the orientation of its predecessor, $\vec{\ell}_{i-1}$.

Case 6.2.1 The Freely Jointed Chain

In this simplest possible case, the orientation of link i is unaffected by link $i-1$, and is equally likely to point in any direction. It can even lie on top of link $i-1$ by pointing in the opposite direction. (Remember we are dealing with imaginary links, not real chemical bonds, so this is permissible.) Mathematically we represent this approximation using the relation

$$\vec{\ell}_i \cdot \vec{\ell}_{i-1} = \ell^2 \cos \theta \tag{6.2.4}$$

where θ is the angle between $\vec{\ell}_i$ and $\vec{\ell}_{i-1}$. For the freely jointed chain, θ ranges freely from $0°$ to $180°$. Thus on average

$$\left\langle \vec{\ell}_i \cdot \vec{\ell}_{i-1} \right\rangle = \ell^2 \langle \cos \theta \rangle = 0 \tag{6.2.5}$$

When the orientations of two links are *uncorrelated*, then $\langle \cos \theta \rangle = 0$, because $\cos \theta$ ranges from -1 to $+1$, with $+$ or $-$ values equally probable. If we consider the relative orientations of any two different links along the freely jointed chain, they must all be uncorrelated, so that

$$\left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle = 0 \tag{6.2.6}$$

whenever $i \neq j$. In other words if the orientation of a given link is unaffected by its nearest neighbor, it must also be unaffected by more distant neighbors. From Equation 6.2.3 we now obtain the simple but tremendously important result

$$\langle h^2 \rangle = n\ell^2 \quad \text{or} \quad \langle h^2 \rangle^{1/2} = \sqrt{n}\ell \tag{6.2.7}$$

because all the cross terms vanish. This is the classic result for the so-called *random walk* (or *random flight*): the root-mean-square excursion is given by the step length times the square root of the number of steps. We will invoke this result repeatedly in subsequent chapters.

At this point you may be thinking "Fine, but even if the link is not a C—C bond, a real polymer chain cannot reverse its direction 180° at a joint, so how can this result be relevant?" Good question. Be patient for a bit.

Case 6.2.2 The Freely Rotating Chain

Now we make the model a bit more realistic. We will constrain the angle between adjacent links to be a fixed value, θ, but still allow free rotation of the link around the cone defined by θ (see Figure 6.4). What happens? Now, $\vec{\ell}_i \cdot \vec{\ell}_{i-1} = \ell^2 \cos \theta$ does not average to zero because θ is fixed. For simplicity, we will define $\alpha = \cos \theta$ just to avoid writing $\cos \theta$ over and over. Returning to Equation 6.2.3, what we need to calculate is the double sum over all possible $\langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle$, i.e., the cross terms as well as the self-terms. We now know $\langle \vec{\ell}_i \cdot \vec{\ell}_j \rangle = \ell^2 \alpha$ when $|i - j| = 1$, but what about $|i - j| = 2, 3$, etc.? This is a little sneaky: $\vec{\ell}_i$ has a component parallel to $\vec{\ell}_{i-1}$, with length $\ell\alpha$, but it also has a component perpendicular to $\vec{\ell}_{i-1}$ (with length $\ell \sin \theta$). However, because of the free rotation, over time the perpendicular part will average to zero (see Figure 6.4). So from the point of view of bond $\vec{\ell}_{i-2}$, *on average* $\vec{\ell}_i$ looks just like a bond of length $\ell\alpha$ pointing in the same direction as $\vec{\ell}_{i-1}$, and thus $\langle \vec{\ell}_{i-2} \cdot \vec{\ell}_i \rangle = \ell^2 \alpha^2$. The same argument can be extended to any pair of bonds i, j:

$$\left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle = \ell^2 \alpha^{|i-j|} \tag{6.2.8}$$

Now we define a new summation index $k = |i-j|$ and write

$$\sum_{i=1}^{n} \sum_{j \neq i}^{n} \left\langle \vec{\ell}_i \cdot \vec{\ell}_j \right\rangle = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \ell^2 \alpha^{|i-j|}$$

$$2 \sum_{k=1}^{n-1} \ell^2 \alpha^k (n - k) = 2n\ell^2 \sum_{k=1}^{n-1} \alpha^k - 2\ell^2 \sum_{k=1}^{n-1} k\alpha^k \tag{6.2.9}$$

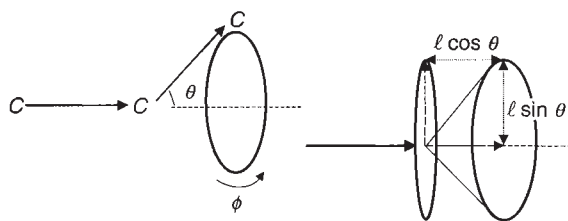**Figure 6.4** Definition of the angles θ and ϕ for the freely rotating and hindered rotation chains; the correspondence to a polyethylene molecule is suggested by the locations of the carbons.

The factor of 2 comes about because there are two ways to get each value of k (one with $i > j$ and one with $i < j$). The term $(n - k)$ arises because there are $n - 1$ nearest neighbors ($k = 1$), $n - 2$ next nearest neighbors ($k = 2$), etc. Note also that careful attention has to be paid to the limits of the sums.

The relevant summations have algebraic answers that are derived in the Appendix, namely:

$$\sum_{k=1}^{n-1} \alpha^k = \alpha \frac{1 - \alpha^{n-1}}{1 - \alpha} \approx \frac{\alpha}{1 - \alpha} \tag{6.2.10a}$$

for $n \to \infty$, assuming $|\alpha| < 1$ (i.e., $\theta \neq 90°$), and

$$\sum_{k=1}^{n-1} k\alpha^k = \alpha \frac{1 - \alpha^n}{(1 - \alpha)^2} \approx \frac{\alpha}{(1 - \alpha)^2} \tag{6.2.10b}$$

where again we let $n \to \infty$ to reach the last expression. Now we insert Equation 6.2.10a and Equation 6.2.10b into Equation 6.2.9, and we recall Equation 6.2.3 to obtain

$$
\begin{aligned}
\langle h^2 \rangle &= n\ell^2 + 2n\ell^2 \left(\frac{\alpha}{1 - \alpha} \right) - 2\ell^2 \frac{\alpha}{(1 - \alpha)^2} \\
&= n\ell^2 \left\{ \frac{1 + \alpha}{1 - \alpha} - \frac{2}{n} \cdot \frac{\alpha}{(1 - \alpha)^2} \right\} \approx n\ell^2 \left\{ \frac{1 + \alpha}{1 - \alpha} \right\} \\
&= n\ell^2 \left\{ \frac{1 + \cos\theta}{1 - \cos\theta} \right\}
\end{aligned}
\tag{6.2.11}
$$

where again we assume n is large in the penultimate step. (We also reinserted $\cos\theta$ for α.) We can learn three important things from this result.

1. $\langle h^2 \rangle$ is *larger* than the freely jointed chain result if $\theta < 90°$ ($\cos\theta > 0$). This is very reasonable; if each link has some preference for heading in the same direction as the previous link, the chain will double back on itself less often. As an example, for C–C single bonds, θ is close to 70.5° (the complement to the tetrahedral angle) and for this value $\langle h^2 \rangle \approx 2n\ell^2$.
2. $\langle h^2 \rangle$ is still *proportional* to $n\ell^2$; the proportionality factor is just a number that depends on the details of the local constraints placed on link orientation. In particular, therefore, $\langle h^2 \rangle^{1/2}$ is still proportional to $\sqrt{n}$.
3. The previous statement applies strictly only in the large n limit, i.e., when the term proportional to $1/n$ in Equation 6.2.11 is negligible and when α^{n-1} vanishes. This is a commonly encountered caveat in polymer science: we can derive relatively simple expressions, but they will often be valid only in the large n limit. The answer to "How large is large enough?" will depend on the particular property, but when the correction is proportional to $1/n$, as it is in Equation 6.2.11, it will drop to the order of 1% when $n \approx 100$, which is not a particularly large number of backbone bonds.

Case 6.2.3   Hindered Rotation Chain

In a real polyethylene chain, the rotation about the cone is not free; there are three preferred conformations (t, g^+, g^-) as discussed in Section 6.1. Furthermore, all values of the rotation angle ϕ are possible to some extent (see Figure 6.1b). The derivation of $\langle h^2 \rangle$ is more complicated for this case, as you might expect, but it is similar in spirit to that for the freely rotating chain; it may be found in Flory's second book [1]. The large n result is

$$\langle h^2 \rangle = n\ell^2 \left\{ \frac{1 + \cos\theta}{1 - \cos\theta} \right\} \left\{ \frac{1 + \langle \cos\phi \rangle}{1 - \langle \cos\phi \rangle} \right\} \tag{6.2.12}$$

where $\langle \cos \phi \rangle$ is the average of $\cos \phi$ over the appropriate potential energy curve (Figure 6.1b). However, the important message is that $\langle h^2 \rangle$ is still proportional to $n\ell^2$; all that has changed is a numerical prefactor that depends on specific local constraints. This point, in fact, can be stated as a theorem:

If we take the limit $n \to \infty$, and if we consider "phantom" chains that can double back on themselves, then $\langle h^2 \rangle = Cn\ell^2$, where C is a numerical constant that depends only on local constraints and not on n.

The physical content of this theorem can be summarized as follows. If we have a chain of links with any degree of conformational freedom, no matter how limited that freedom may be, and if we track the conformation over enough links, the orientation of the last link will have lost all memory of the orientation of the first. At this point we could replace that entire subset of links with one new link, and it would be freely jointed with respect to the next set and the previous set. In other words, for any chain of n links whose relative orientations are constrained, we can always generate an equivalent chain with a new (bigger) link that is freely jointed, so that the original chain and the new chain have the same $\langle h^2 \rangle$. We will illustrate this concept in the next section.

The issue of how large n needs to be for this theorem to be useful was mentioned before; n of a hundred or so is usually more than adequate. The fact that real polymers occupy real volume means that polymer chains cannot double back on themselves, or have two or more links at the same point in space. This so-called "excluded volume" problem is actually very serious, and makes an exact solution for $\langle h^2 \rangle$ of a real polymer much more complicated. However, it turns out that there are two practical situations in which we can make this problem essentially go away; one is in a molten polymer, and the other is in a particular kind of solvent, called a theta solvent. Under these circumstances, a polymer is said to exhibit "unperturbed" dimensions. Thus this theorem is of tremendous practical importance. Further discussion of the excluded volume effect will be deferred to Section 6.8, and then it will be revisited in more detail in Chapter 7.7.

6.3 Characteristic Ratio and Statistical Segment Length

We can define a quantity C_n, called the *characteristic ratio*, which for any polymer structure describes the effect of local constraints on the chain dimensions:

$$C_n \equiv \frac{\langle h^2 \rangle_0}{n\ell^2} \tag{6.3.1}$$

In this equation, $\langle h^2 \rangle_0$ is the actual mean-square end-to-end distance of the polymer chain, and the subscript 0 reminds us that we are referring to unperturbed dimensions. In Equation 6.3.1, n denotes the number of chemical bonds along the polymer backbone, and ℓ is the actual length of a backbone bond, e.g., 1.5 Å for C—C. (For polymers containing different kinds of backbone bonds, such as polyisoprene or poly(ethylene oxide), it is appropriate simply to add $n_1\ell_1^2 + n_2\ell_2^2 + \cdots$ where n_i and ℓ_i are the number and length of bonds of type i, respectively.) C_n is a measure of chain flexibility: the larger the value of C_n, the more the local constraints have caused the chain to extend in one direction. As defined in Equation 6.3.1, C_n depends on n, but it approaches a constant value at large n; this is often denoted C_∞. For the freely rotating chain, C_∞ is $(1 + \cos \theta)/(1 - \cos \theta)$ from Equation 6.2.11. The dependence of C_n on n is shown in Figure 6.5 for several theoretical chains. The values of C_∞ for several common polymers are listed in Table 6.1. For polymers that have primarily C—C or C—O single bonds along the backbone, C_∞ ranges from about 4 to about 12. Using these values, or those provided in reference books, it is straightforward to estimate $\langle h^2 \rangle_0$ for any polymer of known structure and molecular weight.

Although calculating $\langle h^2 \rangle_0$ for a given polymer is thus a solved problem, this approach using C_∞ is not always the most convenient. For example, it requires remembering particular bond lengths
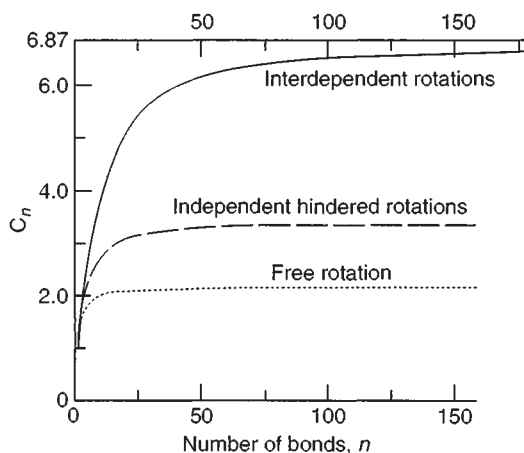
Figure 6.5 Characteristic ratio as a function of the number of bonds for three model chains. The dotted curve represents the freely rotating chain with $\theta = 68°$. The long dashed curve corresponds to a particular hindered rotation chain with the preferred values of ϕ 120° apart, but in which values of ϕ for neighboring bonds are independent. The smooth curve applies to an interdependence among values of ϕ on neighboring bonds. (Reproduced from Flory, P.J., *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York, 1969. With permission.)

and the number of bonds per repeat unit. A more popular approach was suggested in the previous section. We could rewrite Equation 6.3.1 in the following way:

$$\langle h^2 \rangle_0 = C_\infty n\ell^2 = n\ell_{eff}^2 = Nb^2 \tag{6.3.2}$$

where $\ell_{eff} = \ell\sqrt{C_\infty}$ is a new effective bond length with the following meaning: the real chain with local constraints has an end-to-end distance, which is the same as that of a freely jointed chain with the same number of links n, but with a different (larger) step length ℓ_{eff}. Continuing in this vein, we can replace the number of bonds, n, with the number of monomers or repeat units, N, and subsume the proportionality factor between n and N into a new effective step length, b. The quantity b, defined by Equation 6.3.2, is called the *statistical segment length*. The calculation of $\langle h^2 \rangle_0$ through

Table 6.1 Representative Values of the Characteristic Ratio, Statistical Segment Length, and Persistence Length for Various Flexible Polymers, Calculated from the Experimental Quantities, $\langle h^2 \rangle_0/M$ (Å^2 mol/g), via Equation 6.3.2 and Equation 6.4.5b

Polymer	C_∞	b (Å)	ℓ_p (Å)	$\langle h^2 \rangle_0/M$ (Å^2 mol/g)	T (°C)
Poly(ethylene oxide)	5.6	6.0	4.1	0.80_5	140
1,4-Polybutadiene	5.3	6.9	4.0	0.87_6	140
1,4-Polyisoprene	4.8	6.5	3.5	0.62_5	140
Poly(dimethylsiloxane)	6.6	5.8	5.3	0.45_7	140
Polyethylene	7.4	5.9	5.7	1.2_5	140
Polypropylene	5.9	5.3	4.6	0.67	140
Polyisobutylene	6.7	5.6	5.2	0.57	140
Poly(methyl methacrylate)	9.0	6.5	6.9	0.42_5	140
Poly(vinyl acetate)	8.9	6.5	6.8	0.49	25
Polystyrene	9.5	6.7	7.3	0.43_4	140

The experimental chain dimensions were obtained by small-angle neutron scattering, as compiled in Fetters, L.J., Lohse, D.J., Witten, T.A., and Zirkel, A., *Macromolecules*, 27, 4639, 1994. The uncertainties in $\langle h^2 \rangle_0$ and M are typically a few percent. The temperature of the measurement is indicated, because the distribution of chain conformations depends on temperature.

N and b treats the real chain as though it were a freely jointed chain with N links of length b. This proves to be a useful computational scheme, but it is important to realize that b has no simple correspondence with the physical chain; it is not a measure of the real size of a real monomer. Furthermore, it contains no new information beyond that embodied in C_∞. Values of b are also given in Table 6.1. Note that although b varies monotonically with C_∞, it is not as simple a measure of flexibility. For example, b for polystyrene (6.7 Å) and polyisoprene (6.5 Å) differ by only a few percent, whereas polyisoprene is considered to be a relatively flexible polymer, and polystyrene a relatively stiff one. The resolution of this apparent paradox is left to Problem 6.2. Values of C_∞ and b may be determined experimentally in various ways, but the most direct route is by scattering measurements of the chain dimensions; this method will be described in detail in Chapter 8.

The approach taken above, and indeed for the remainder of the book, is that C_∞ or b are structure-specific parameters that we can look up as needed; the dependence of $\langle h^2 \rangle_0$ on molecular weight is universal and therefore more important to understand. However, it is of considerable interest to ask whether the techniques of computational statistical mechanics can be used to calculate C_∞ from first principles, i.e., from knowledge of bond angles, rotational potentials, etc. A highly successful scheme for doing so, called the rotational isomeric state approach, was developed by Flory [1]. It is beyond the scope of this book to describe it, but it is worth mentioning that even today it is not a trivial matter to execute such calculations, and that controversy exists about the correct values of C_∞ for some relatively simple chemical structures. These controversies are also not easily resolved by experiment; combined uncertainties in measured molecular weights and chain dimensions often exceed 10%.

Example 6.1

It is an interesting fact that bulk polyethylene has a positive coefficient of thermal expansion (about 2.5×10^{-4} per °C at room temperature), whereas the individual chain dimensions have a negative coefficient (d $\ln \langle h^2 \rangle_0/dT = -1.2 \times 10^{-3} \deg^{-1}$). In other words, when a piece of polyethylene is heated, the volume increases while the individual chain dimensions shrink. How does this come about?

Solution

Thermal expansion corresponds to a decrease in the density of the material, which reflects primarily an increase in the average distance *between* molecules; the radii of the individual atoms and the bond lengths also tend to increase, but to a much smaller extent. In contrast, the reduction in $\langle h^2 \rangle_0$ is primarily of intramolecular origin. From Equation 6.3.1, we can see that as n is independent of T and ℓ, if anything, increases with T, then there must be a decrease in the characteristic ratio, C_∞. The origin of this effect can be seen from Figure 6.1. As temperature increases, the Boltzmann factors that dictate the relative equilibrium populations of *trans* and *gauche* conformations change, and the *gauche* states become relatively more populated. As the *trans* conformations favor larger $\langle h^2 \rangle_0$, the net result is a reduction in C_∞. Note that this simple relation between C_∞ and the relative populations of *trans* and *gauche* states does not necessarily extend to more complicated backbone structures. For example, d $\ln \langle h^2 \rangle_0/dT$ is positive for 100% *cis*-1,4-polybutadiene, but negative for the all-*trans* versions (see Problem 6.5). This observation is not easy to anticipate based on the molecular structure.

6.4 Semiflexible Chains and the Persistence Length

For many macromolecules, the backbone does not consist of a string of single bonds with facile rotations, but rather some combination of bonds that tend to make the backbone continue in one direction. Such chains are called semiflexible, and examples (see Figure 6.6) include polymers with mostly aromatic rings along the backbone, such as poly(p-phenylene); polymers with large

Poly(p-phenylene)   Poly(p-phenylene terephthalamide)

Poly(n-hexyl isocyanate)   Poly(γ-benzyl-L-glutamate)
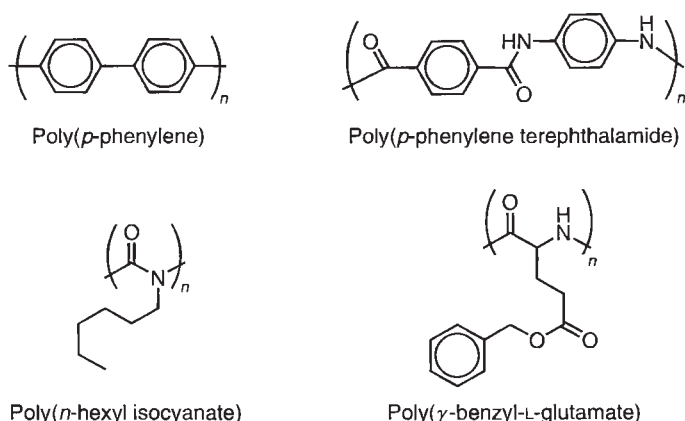
Figure 6.6 Examples of polymer structures that are semiflexible or stiff chains.

side-groups that for steric reasons induce the backbone to adopt a helical conformation, such as poly(n-hexyl isocyanate) and poly(γ-benzyl-L-glutamate); biopolymers such as DNA and collagen that involve intertwined double or triple helices. Short versions of these molecules are essentially "rigid rods," but very long versions will wander about enough to be random coils. The description of chain dimensions in terms of either C_∞ or b turns out not to be as useful for this class of macromolecules. Therefore it is desirable to have a method to calculate the dimensions of such molecules, and particularly to understand the crossover from rod-like to coil-like behavior. Such a scheme is provided by the so-called *worm-like chain* of Kratky and Porod [2]; the fundamental concept is that of the *persistence length*, ℓ_p, which is a measure of how far along the backbone one has to go before the orientation changes appreciably. A garden hose provides a good everyday analogy to a semiflexible polymer, with a persistence length on the order of 1 ft. A 2 in. section of hose is relatively stiff or rigid, whereas the full 50 ft hose can be wrapped around and tangled with itself many times like a random coil. We will first define ℓ_p for flexible chains and see how it is simply related to C_∞. Then we will develop in terms of ℓ_p an expression for $\langle h^2 \rangle$ that can be used to describe flexible, semiflexible, and rigid chains.

The persistence length represents the tendency of the chain to continue to point in a particular direction as one moves along the backbone. It can be calculated by taking the projection of the end-to-end vector on the direction of the first bond ($\vec{\ell}_1/\ell$ is a unit vector in the direction of $\vec{\ell}_1$):

$$\ell_p \equiv \left\langle \frac{1}{\ell} \vec{\ell}_1 \cdot \vec{h} \right\rangle = \left\langle \frac{1}{\ell} \vec{\ell}_1 \cdot \sum_{i=1}^{n} \vec{\ell}_i \right\rangle$$

$$= \frac{1}{\ell} \left\{ \left\langle \vec{\ell}_1 \cdot \vec{\ell}_1 \right\rangle + \left\langle \vec{\ell}_1 \cdot \vec{\ell}_2 \right\rangle + \ldots + \left\langle \vec{\ell}_1 \cdot \vec{\ell}_n \right\rangle \right\}$$

(6.4.1)

For the freely jointed chain, as discussed above, all the terms in the expansion in Equation 6.4.1 are zero except the first, and thus $\ell_p = \ell$. For chains with more and more conformational constraints that encourage the backbone to straighten out, more and more terms in the expansion will contribute positively, and ℓ_p increases. In the limit that every bond points in the same direction the persistence length tends to infinity. When $\ell_p > L$, where $L = n\ell$ is the contour length of the chain, such a molecule is called a rigid rod.

6.4.1 Persistence Length of Flexible Chains

We now seek a relation between ℓ_p and C_∞ for long, flexible chains. We can rewrite Equation 6.4.1 as

$$\ell_p = \frac{1}{\ell} \sum_{j=1}^{n} \left\langle \vec{\ell}_1 \cdot \vec{\ell}_j \right\rangle = \frac{1}{\ell} \sum_{j=x}^{n} \left\langle \vec{\ell}_x \cdot \vec{\ell}_j \right\rangle \tag{6.4.2}$$

where x is any arbitrary bond in the chain. We can make this substitution because for a flexible chain, only a few terms j with small $|j - x|$ will contribute. Now we change the limits of the sum over j to extend over the complete chain; in other words we look in both directions from bond x. This amounts to a double counting, so we multiply ℓ_p by 2:

$$2\ell_p = \frac{1}{\ell} \sum_{j=1}^{n} \left\langle \vec{\ell}_x \cdot \vec{\ell}_j \right\rangle + \ell \tag{6.4.3}$$

Where did the extra ℓ on the right hand side of Equation 6.4.3 come from? Well, the double counting was not quite complete; there were two terms with $|x - j| = 1$, two with $|x - j| = 2$, etc., but only one with $x = j$. We need this contribution of ℓ in order to obtain $2\ell_p$, and therefore the missing "self" term is appended to Equation 6.4.3.

In order to remove the arbitrary choice of bond x, we sum over all possible choices of x, and assume that we get the same answer for each x; this approximation neglects the effects of chain ends, so it is valid only in the limit of large n.

$$\ell_p = \frac{1}{2n\ell} \sum_{j=1}^{n} \sum_{x=1}^{n} \left\langle \vec{\ell}_x \cdot \vec{\ell}_j \right\rangle + \frac{\ell}{2} \tag{6.4.4}$$

Here we divided by n in front of the double sum because we added n identical terms through the sum over x. All of these manipulations finally pay off: we recognize this double sum as exactly $\langle h^2 \rangle$ from Equation 6.2.2, and hence

$$\ell_p = \frac{1}{2n\ell} \langle h^2 \rangle + \frac{\ell}{2} = \frac{1}{2n\ell} C_\infty n\ell^2 + \frac{\ell}{2} = (C_\infty + 1)\frac{\ell}{2} \tag{6.4.5a}$$

In some derivations of this relation, the joint limit $n \to \infty$ and $\ell \to 0$ is taken (see following section). In this case, the extra ℓ on the right hand side of Equation 6.4.3 would vanish, and Equation 6.4.5a would become

$$\ell_p = \frac{1}{2n\ell} \langle h^2 \rangle = \frac{1}{2n\ell} C_\infty n\ell^2 = C_\infty \frac{\ell}{2} \tag{6.4.5b}$$

The difference between Equation 6.4.5a and Equation 6.4.5b is not particularly important, especially for stiffer chains where $C_\infty \gg 1$; we will use the latter form below, because it is simpler.

A related quantity in common use is the *Kuhn length* [3], ℓ_k, which is defined as twice the persistence length:

$$\ell_k \equiv 2\ell_p = C_\infty \ell \tag{6.4.6}$$

We thus have three different, but fully equivalent expressions for the mean-square unperturbed end-to-end distance of a flexible chain:

$$\langle h^2 \rangle_0 = C_\infty n\ell^2 = Nb^2 = L\ell_k \tag{6.4.7}$$

All three are useful and frequently employed, so they are worth remembering. Estimates of the persistence lengths of flexible polymers are also listed in Table 6.1.

Returning to Equation 6.4.1, we can actually extract a very appealing physical meaning for ℓ_p and ℓ_k. The terms in the expansion become progressively smaller as the average orientation of bond i becomes less correlated with that of the first bond. In fact, when bond i is on average perpendicular to the first bond (i.e., is uncorrelated), $\langle \vec{\ell}_1 \cdot \vec{\ell}_j \rangle \approx 0$. All higher-order terms will also vanish. Thus the persistence length measures how far we have to travel along the chain before it will, on average, bend 90°. Similarly, the Kuhn length tells us how far we have to go along the chain contour before it will, on average, reverse direction completely. Equation 6.4.6 also provides a simple interpretation for C_∞: it is the number of backbone bonds needed for the chain to easily bend 180°.

6.4.2 Worm-Like Chains

So far, all that the persistence length has given us is a new way to express $\langle h^2 \rangle_0$ for flexible chains. To obtain a useful result for semiflexible and stiff chains, we will return to the freely rotating chain of Section 6.2 and transform it into a continuous worm-like chain. This we do by taking a special limit alluded to earlier; we will let the number of bonds, n, go to infinity, but the length of each bond, ℓ, will go to zero, while maintaining the contour length $L = n\ell$ constant. We begin by relating ℓ_p to $\alpha = \cos \theta$ of the freely rotating chain, starting from Equation 6.4.1:

$$
\begin{aligned}
\ell_p &= \frac{1}{\ell} \left\{ \langle \vec{\ell}_1 \cdot \vec{\ell}_1 \rangle + \langle \vec{\ell}_1 \cdot \vec{\ell}_2 \rangle + \cdots + \langle \vec{\ell}_1 \cdot \vec{\ell}_n \rangle \right\} \\
&= \frac{1}{\ell} \left\{ \ell^2 + \ell^2 \alpha + \ell^2 \alpha^2 + \cdots + \ell^2 \alpha^{n-1} \right\} \\
&= \ell \{ 1 + \alpha + \alpha^2 + \cdots + \alpha^{n-1} \} = \ell \left(\frac{1 - \alpha^n}{1 - \alpha} \right) = \frac{\ell}{1 - \alpha}
\end{aligned}
\tag{6.4.8}
$$

The last transformation utilized the summation results in Equation 6.2.10a, and the large n limit. Thus we can write

$$
\alpha = 1 - \frac{\ell}{\ell_p} \approx \exp(-\ell/\ell_p) \quad \text{for} \quad \ell \to 0
\tag{6.4.9}
$$

where we invoke the series expansion (see the Appendix):

$$
e^x = 1 + x + \frac{x^2}{2!} + \cdots
$$

Now we recall Equation 6.2.11 for the freely rotating chain, but retaining the term in α^n:

$$
\begin{aligned}
\langle h^2 \rangle &= n\ell^2 \frac{1 + \alpha}{1 - \alpha} - 2\ell^2 \alpha \frac{(1 - \alpha^n)}{(1 - \alpha)^2} \\
&= n\ell^2 \left(\frac{2 - \ell/\ell_p}{\ell/\ell_p} \right) - 2\ell^2 (1 - \ell/\ell_p) \left(\frac{1 - \exp[-L/\ell_p]}{(\ell/\ell_p)^2} \right) \\
&= L\ell_p (2 - \ell/\ell_p) - 2\ell_p^2 (1 - \ell/\ell_p)(1 - \exp[-L/\ell_p])
\end{aligned}
\tag{6.4.10}
$$

and thus

$$
\langle h^2 \rangle = 2\ell_p L - 2\ell_p^2 (1 - \exp[-L/\ell_p]) \quad \text{as} \quad \ell \to 0
\tag{6.4.11}
$$

This expression is the result for the worm-like chain obtained by Kratky and Porod [2]. (Note that we took $(n - 1)\ell \approx n\ell = L$ in Equation 6.4.10.) It is left as an exercise (Problem 6.6) to show that in the coil limit ($L \gg \ell_p$) this expression reverts to Equation 6.4.7 and that in the rod limit ($L \ll \ell_p$), $\langle h^2 \rangle = L^2$, as it should. Examples of experimental persistence lengths for semiflexible polymers are given in Table 6.2.

Table 6.2 Representative Values of Persistence Lengths for Semiflexible Polymers. Note That Values May Depend Either Weakly or Strongly on the Choice of Solvent[a]

Polymer	Solvent	ℓ_p (Å)
Hydroxypropyl cellulose	Dimethylacetamide	65
Poly(p-phenylene)[b]	Toluene	130
Poly(p-phenylene terephthalamide)	Methane sulfonic acid[c]	100
	96% Sulfuric acid	180
Poly(n-hexyl isocyanate)	Hexane[d]	420
	Dichloromethane	210
DNA (double helix)	0.2 M NaCl	600
Xanthan (double helix)	0.1 M NaCl	1200
Poly(γ-benzyl-L-glutamate)	Dimethylformamide	1500
Schizophyllan	Water	2000

[a]Data are summarized in Sato, T. and Teramoto, A., *Adv. Polym. Sci.*, 126, 85, 1996, except for [b]Vanhee, S., Rulkens, R., Lehmann, U., Rosenauer, C., Schulze, M., Koehler, W., and Wegner, G., *Macromolecules*, 29, 5136, 1996; [c]Chu, S.G., Venkatraman, S., Berry, G.C., and Einaga, Y., *Macromolecules*, 14, 939, 1981; and [d]Murakami, H., Norisuye, T., and Fujita, H., *Macromolecules*, 13, 345, 1980.

Figure 6.7 shows a plot of a dimensionless form of Equation 6.4.11, obtained by dividing through by ℓ_p^2 and plotting against L/ℓ_p. This independent variable is the number of persistence lengths in the chain, i.e., an effective degree of polymerization. The curve illustrates the smooth crossover from the rod-like behavior at small L/ℓ_p, with $\langle h^2 \rangle_0 \sim M^2$, to the coil-like behavior at large L/ℓ_p, with $\langle h^2 \rangle_0 \sim M$. Thus the worm-like chain model is able to describe both flexible and semiflexible chains with one expression. The double logarithmic format of Figure 6.7 is often employed in polymer science, when both the independent variable (such as M) and the dependent
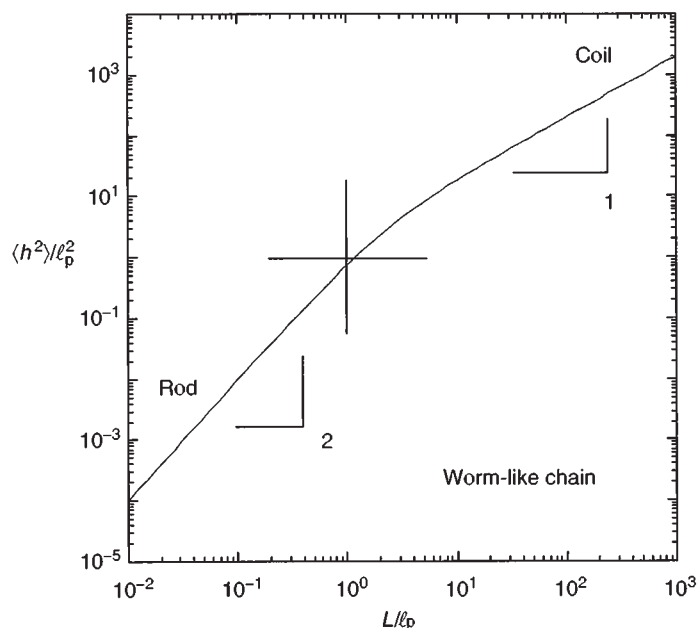

Figure 6.7 The mean-square end-to-end distance, normalized by the squared persistence length, as a function of the number of persistence lengths per chain (given by the ratio of contour and persistence lengths), according to the Kratky–Porod worm-like chain. The asymptotic slopes of 2 (rod limit) and 1 (coil limit) are also shown, as is the location of a chain with length equal to one persistence length.

variable can range over several orders of magnitude. If the functional relation is a power law, then in this format the plot will be a straight line and the slope gives the power law exponent.

6.5 Radius of Gyration

So far we have considered chain dimensions solely in terms of the average end-to-end distance. However, there are two severe limitations to this approach. First, the end-to-end distance is generally very difficult to measure experimentally. Second, for many interesting polymer structures (e.g., stars, rings, combs, dendrimers, etc.) it cannot even be defined unambiguously. The end-to-end distance assigns particular significance to the first and last monomers, but all monomers are of importance. A useful way to incorporate this fact is to calculate the average distance of all monomers from the center of mass. We denote the instantaneous vector from the center of mass to monomer i as $\vec{s}_i$, as shown in Figure 6.8. The center of mass at any instant in time for any polymer structure is the point in space such that

$$\sum_{i=1}^{N} m_i \vec{s}_i = 0 \tag{6.5.1}$$

where m_i is the mass of monomer i. Note that the center of mass does not need to be actually on the chain (in fact, it is unlikely to be). The root-mean-square, mass-weighted average distance of monomers from the center of mass is called the *radius of gyration*, R_g, or $\langle s^2 \rangle^{1/2}$, and is determined by

$$R_g = \langle s^2 \rangle^{1/2} \equiv \left\{ \frac{\sum_{i=1}^{N} m_i \langle s_i^2 \rangle}{\sum_{i=1}^{N} m_i} \right\}^{1/2} = \left\{ \frac{1}{N} \sum_{i=1}^{N} \langle s_i^2 \rangle \right\}^{1/2} \tag{6.5.2}$$

Here, just as with the end-to-end vector, it is useful to take $\langle s_i^2 \rangle = \langle \vec{s}_i \cdot \vec{s}_i \rangle$ in order to obtain an average distance rather than an average vector (which would zero by isotropy). In the second transformation we have assumed equal masses, i.e., a homopolymer, and $m_i = m$ cancels out. (Note that the summations run up to N, the number of monomers, and not n, the number of backbone bonds.) It is worth mentioning that the term radius of gyration is unfortunate, in that it invites confusion with the radius of gyration in mechanics; the latter refers to the mass-weighted, root-mean-square distance from an axis of rotation, not from a single point. However, the term radius of gyration in reference to Equation 6.5.2 appears to be firmly entrenched in polymer
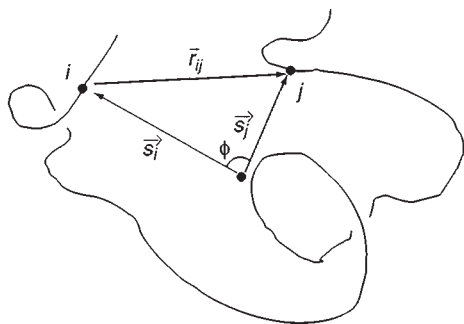

Figure 6.8 Illustration of the vectors from the center of mass to monomers i and j, $\vec{s}_i$ and $\vec{s}_j$, respectively, and the vector from monomer i to monomer j, $\vec{r}_{ij}$.

science. A more correct description will emerge in Section 6.7, namely that $\langle s^2 \rangle$ is the "second moment of the monomer distribution about the center of mass," but this terminology is rather unwieldy for daily use.

It is clear that R_g can be defined for any polymer structure, and thus avoids the second objection to $\langle h^2 \rangle$ listed above. It can be measured directly by light scattering techniques, as will be described in Chapter 8, and indirectly through various solution dynamics properties, as explained in Chapter 9, thereby avoiding the first objection. However, we went to some trouble to calculate $\langle h^2 \rangle_0$ for various chains, and to establish the utility of C_∞, b, and ℓ_p. Is that all out the window? No, it is not. We will now show that R_g is, in fact, very simply related to $\langle h^2 \rangle_0$ for an unperturbed linear chain, namely

$$R_g^2 = \frac{\langle h^2 \rangle_0}{6} = \frac{Nb^2}{6} = \frac{\ell_p L}{3} \tag{6.5.3}$$

Consider the dot product of the vectors from the center of mass to any two monomers i and j. By the law of cosines

$$\vec{s}_i \cdot \vec{s}_j = |\vec{s}_i||\vec{s}_j| \cos \phi = \frac{1}{2} \left[s_i^2 + s_j^2 - r_{ij}^2 \right] \tag{6.5.4}$$

where ϕ is the angle between $\vec{s}_i$ and $\vec{s}_j$, and r_{ij}^2 is the square distance between monomers i and j (see Figure 6.8). Now we take the average of each term in Equation 6.5.4, and then double sum over i and j:

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \vec{s}_i \cdot \vec{s}_j \right\rangle = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle s_i^2 \right\rangle + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle s_j^2 \right\rangle - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle r_{ij}^2 \right\rangle = 0 \tag{6.5.5}$$

This expression equals zero because

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle \vec{s}_i \cdot \vec{s}_j \right\rangle = \left\langle \sum_{i=1}^{N} \vec{s}_i \cdot \sum_{j=1}^{N} \vec{s}_j \right\rangle = \langle 0 \cdot 0 \rangle = 0 \tag{6.5.6}$$

from Equation 6.5.1 (assuming all masses are equal). Returning to the second part of Equation 6.5.5, and utilizing Equation 6.5.2, we obtain

$$\frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle s_i^2 \right\rangle = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle s_j^2 \right\rangle = \frac{N^2}{2} R_g^2 \tag{6.5.7}$$

which can be rearranged to

$$R_g^2 = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left\langle r_{ij}^2 \right\rangle \tag{6.5.8}$$

This equation turns out to be a useful alternative definition of R_g. It expresses R_g in terms of the average distances between all pairs of monomers in the molecule; the location of the center of mass is not needed. Furthermore, Equation 6.5.8 is valid for any structure; it need not be a linear chain, and it need not have unperturbed dimensions.

Now we can derive the specific result Equation 6.5.3 for the freely jointed chain by realizing that

$$\left\langle r_{ij}^2 \right\rangle = |i - j| b^2 \tag{6.5.9}$$

or, in other words, $\langle r_{ij}^2 \rangle$ represents the end-to-end mean-square distance between any pair of monomers i and j separated by $k = |i - j|$ links. We can thus write

$$R_g^2 = \frac{b^2}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} |i - j| = \frac{b^2}{2N^2} \sum_{k=1}^{N-1} 2k(N - k) \qquad (6.5.10)$$

which comes from the fact that there are $2(N-1)$ terms where $|i - j| = 1$; $2(N - 2)$ terms where $|i - j| = 2$; $2(N - 3)$ terms where $|i - j| = 3$; etc. (If this seems mysterious, draw an $N \times N$ matrix, where the rows are numbers $i = 1 \ldots N$ and the columns are $j = 1 \ldots N$. For each matrix element, enter $|i - j|$. There will be N 0's along the main diagonal, $N - 1$ 1's immediately adjacent to [and on both sides of] the main diagonal, $N-2$ 2's in the next place over, etc.). Therefore

$$R_g^2 = \frac{b^2}{N^2} \left\{ N \sum_{k=1}^{N-1} k - \sum_{k=1}^{N-1} k^2 \right\} = \frac{b^2}{N^2} \left\{ \frac{N^2(N - 1)}{2} - \frac{N(N - 1)(2N - 1)}{6} \right\}$$

$$= \frac{b^2}{N^2} \left\{ \frac{3N^2(N - 1) - (N - 1)(2N^2 - N)}{6} \right\} \qquad (6.5.11)$$

$$= \frac{Nb^2}{6} - \frac{b^2}{6N} \approx \frac{Nb^2}{6}$$

where once again the last formula applies in the high N limit.

Example 6.2

A useful rule of thumb for polymers is that R_g is about 100 Å when $M = 10^5$ g/mol. This number can be used to estimate R_g for any other M by recalling the proportionality of R_g to $M^{1/2}$. Use the data in Table 6.1 to assess the reliability of this rule of thumb.

Solution

We can take the values for $\langle h^2 \rangle_0 / M$ directly from the fifth column and multiply each one by 10^5. The largest will be 125,000 Å^2 for polyethylene, and the smallest will be 42,500 Å^2 for poly(methyl methacrylate). Then we need to divide by 6 and take the square root to obtain R_g:

For polyethylene, $R_g = (125,000/6)^{1/2} = 144$ Å

For poly(methyl methacrylate), $R_g = (42,500/6)^{1/2} = 84$ Å

All of the other polymers in Table 6.1 will give values between these two. We may conclude that the rule of thumb is reliable to at least one significant figure, and is better than that for many polymers.

Example 6.3

Use the experimental data for R_g for polystyrenes dissolved in cyclohexane in Figure 6.9 to estimate C_∞, ℓ_p, and b. Note that these data are for remarkably large molecular weights.

Solution

The straight line fit to the data gives $R_g = 0.25 \, M^{0.51}$. To make things convenient, we can choose $N = 10^5$, for which $M = 104 \times 10^5 = 1.04 \times 10^7$ g/mol. From the fitting equation we obtain $R_g = 948$ Å. The number of backbone bonds $n = 2 \times 10^5$, and we use a more precise estimate of the bond length of 1.53 Å. From Equation 6.3.2 and Equation 6.5.3, then

$$C_\infty = \frac{\langle h^2 \rangle_0}{n\ell^2} = \frac{6 \times (948)^2}{2 \times 10^5 (1.53)^2} = 11.5$$
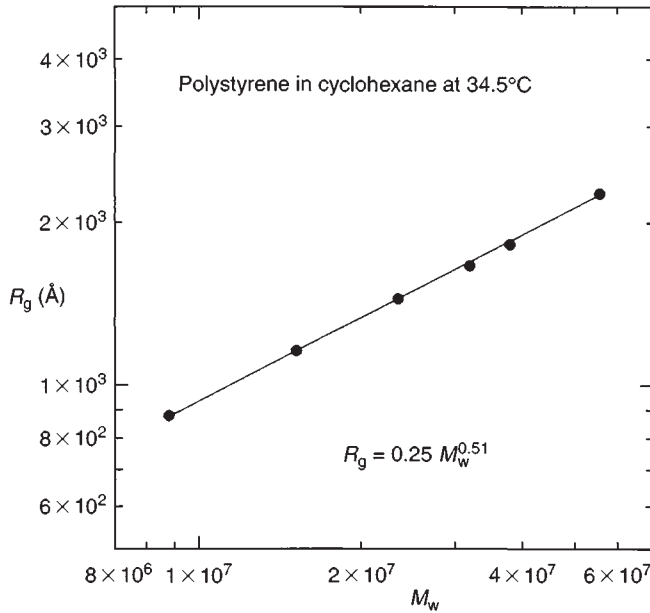
Figure 6.9 Radius of gyration for very high molecular weight polystyrene in cyclohexane at the theta temperature. (Data from Miyake, Y., Einaga, Y., and Fujita, M., *Macromolecules*, 11, 1180, 1978.)

Also from Equation 6.3.2 and Equation 6.5.3,

$$b = \frac{\sqrt{6}}{\sqrt{N}} R_g = \frac{\sqrt{6}}{\sqrt{1 \times 10^5}} \times 948 = 7.3 \ \text{Å}$$

Finally, from Equation 6.4.5b we have

$$\ell_p = C_\infty \frac{\ell}{2} = 11.5 \times \frac{1.53}{2} = 8.8 \ \text{Å}$$

These values are systematically larger than those given in Table 6.1. Part of this difference may be attributed to experimental uncertainty, but most of the difference stems from the fact that the polystyrene data in Table 6.1 were obtained from molten polystyrenes, whereas the data in Figure 6.9 are for dilute solutions. Although the chain dimensions in a dilute theta solution and in the bulk both increase as $M^{1/2}$, the prefactor (e.g., C_∞) can be slightly different. In fact, the dimensions of a given polymer may differ by as much as 10% between two different theta solvents.

The worm-like chain of Section 6.4.2 also has an expression for R_g^2, which is

$$R_g^2 = \frac{1}{3}\ell_p L - \ell_p^2 + \frac{2\ell_p^4}{L^2}(\exp[-L/\ell_p] - 1) + \frac{2\ell_p^3}{L} \tag{6.5.12}$$

This result can be derived from the expression for $\langle h^2 \rangle$, Equation 6.4.11, by way of the relation 6.5.8 and a transformation of sums to integrals; this is left as Problem 6.8. An example of the application of the worm-like chain model is shown in Figure 6.10. The material is poly(n-hexyl isocyanate) (see Figure 6.6) dissolved in hexane and the coil dimensions were measured by light scattering (see Chapter 8). The smooth curve corresponds to Equation 6.5.12 with a persistence length of 42 nm, and the contour length determined as L (nm) $= M$ (g/mol)/715 (g/mol/nm). The factor of 715 therefore reflects the molar mass per nanometer of contour length. The correspondence between the data and the model is extremely good, except for the two very highest M samples.
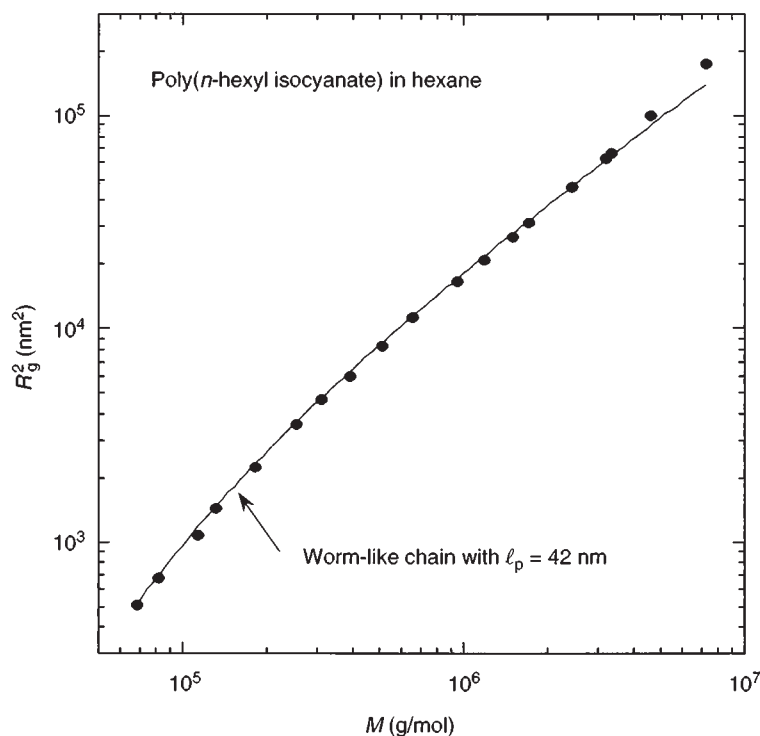
Figure 6.10 Radius of gyration versus molecular weight for poly(*n*-hexyl isocyanate) in hexane. The curve corresponds to the worm-like chain model with a persistence length of 42 nm. (Data from Murakami, H., Norisuye, T., and Fujita, H., *Macromolecules*, 13, 345, 1980.)

This deviation may be attributed to the onset of excluded volume effects, whereby the coil conformations are larger than anticipated by the freely jointed chain (Gaussian) limit.

6.6 Spheres, Rods, and Coils

We have derived results for $\langle h^2 \rangle_0$ for coils, rods, and everything in between. The conformation is assumed to be determined by the steric constraints induced by connecting the monomers chemically. But we could also think about the molecule more abstractly, as a series of freely jointed effective subunits. Now suppose we have the ability to "dial in" a through-space interaction between these subunits, an interaction that might be either attractive or repulsive. The former could arise naturally through dispersion forces, for example; all molecules attract one another in this way, and if we put our chain in a vacuum, those forces might dominate. If the attractive interaction were sufficiently strong, the chain could collapse into a dense, roughly spherical ball or globule. Repulsion could arise if each subunit bore a charge of the same sign, a so-called polyelectrolyte. This is commonly encountered in biological macromolecules, DNA for example. If the repulsive interaction were sufficiently strong, the chain could extend out to be a rod. It is instructive to think of the globule, coil, and rod as the three archetypical possible conformations of a macromolecule, and for many systems coil ↔ globule and coil ↔ rod transitions are experimentally accessible. For example, proteins in their native state are often globular, but upon denaturing the attractive interactions that cause them to fold are released, and the molecule becomes more coil-like. Similarly, a synthetic, neutral polymer dispersed in a bad solvent will collapse into a globule when it precipitates out of solution. A relatively short DNA double helix is

reasonably rod-like ($\ell_p \approx 600$ Å), but if the double helix is denatured or "melted," the two separated strands can become coils. A poly(carboxylic acid) such as poly(methacrylic acid) in water will have a different density of charges along the chain as the pH is varied. At high pH, virtually every monomer will bear a negative charge and although the chain will not straighten out into a completely rigid, all-*trans*-backbone chain, it will show a size that scales almost linearly with M rather than as $\sqrt{M}$. In short, polymers can adopt conformations varying from dense spheres through flexible coils to rigid rods.

The scaling of the size with molecular weight is quite different in each case. We can encompass the various possibilities by writing a proportionality between the size and the degree of polymerization:

$$R_g \sim N^\nu \tag{6.6.1}$$

For the globule or dense object, $\nu = 1/3$. The volume occupied by the molecule is proportional to N and thus the radius goes as $(\text{volume})^{1/3}$. For the unperturbed coil $\nu = 1/2$, as we have seen. However, we will find out in Chapter 7 that in a good solvent $\nu \approx 3/5$ due to the excluded volume effect. For a rod, clearly $\nu = 1$. Equation 6.6.1 is an example of a scaling relation; it expresses the most important aspect of chain dimensions, namely how the size varies with the degree of polymerization, but provides no numerical prefactors. The value of the exponent is universal, in the sense that any particular value of ν (1/3, 1/2, 3/5, or 1) will apply to all molecules in the same class.

As illustrated at the very beginning of this chapter, the size of these various structures (globule, coil, and rod) would be very different for a given polymer. Then we considered a polyethylene molecule, which in the liquid state will always be a coil. Now consider a representative DNA from bacteriophage T2. It has a contour length of 60 μm or almost 0.1 mm. As a coil, it should have $R_g = (L_k/6)^{1/2} \approx 1$ μm or 10,000 Å. With $M \approx 10^8$ and assuming a density of 1 g/mL, it would form a dense sphere with a radius of 340 Å. It is an amazing fact that the bacteriophage actually packages the DNA molecule to almost this extent. As shown in Figure 6.11, upon experiencing an osmotic shock the bacteriophage releases the DNA, which had been tightly wound up inside its head. The mechanism by which the DNA is packed so tightly remains incompletely understood. It is particularly remarkable, given that DNA carries negative charges all along its contour, which should create a strong repulsion between two portions of helix. This example also underscores another important point about chain dimensions: they can be very sensitive to the environment of the molecule, and not only to the intramolecular bonding constraints.

6.7 Distributions for End-to-End Distance and Segment Density

So far in this chapter we have only considered the *average* size and conformation of a polymer. Now we will figure out how to describe the *distribution* of sizes or conformations for a particular chain. We seek an expression for the probability $P(N, \vec{h})\, d\vec{h}$ that a random walk of N steps of length b will have an end-to-end vector, $\vec{h}$, lying between $\vec{h}$ and $\vec{h} + d\vec{h}$, as illustrated in Figure 6.12a. In other words, if the start of the chain defines the origin, we want the probability that the other end falls in an infinitesimal box with coordinates between x and $x + dx$, y and $y + dy$, and z and $z + dz$. From such a function, we will be able to obtain related functions for the probability $P(N, h)\, dh$ that the same walk has an end-to-end distance, $h = |\vec{h}|$, lying between h and $h + dh$, and the probability $\rho(N, r)\, dr$ that a monomer will be found between a distance r and $r + dr$ from the center of mass. It turns out that all of these distributions are approximately Gaussian functions, just like the familiar normal distribution for error analysis. In particular, the answer for $P(N, \vec{h})$ is

$$P(N, \vec{h}) = \left[\frac{3}{2\pi N b^2}\right]^{3/2} \exp\left[-\frac{3|h|^2}{2N b^2}\right] \tag{6.7.1}$$
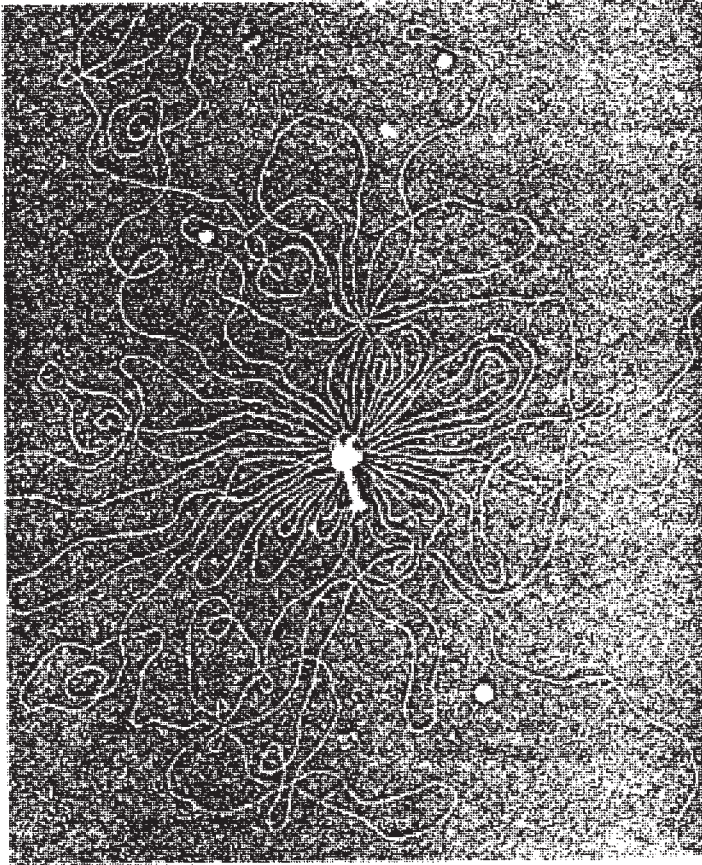
a result that we will now derive.

Figure 6.11 The DNA within a single T2 bacteriophage is released by "osmotic shock." (Reproduced from Kleinschmidt, A.K., et al., *Biochim. Biophys. Acta*, 61, 857, 1962. With permission.)

6.7.1 Distribution of the End-to-End Vector

We begin with a one-dimensional random walk with N steps of length b. In other words, at each step we go a distance b in either the $+x$ or the $-x$ direction, with the probability of $+$ or $-$ each
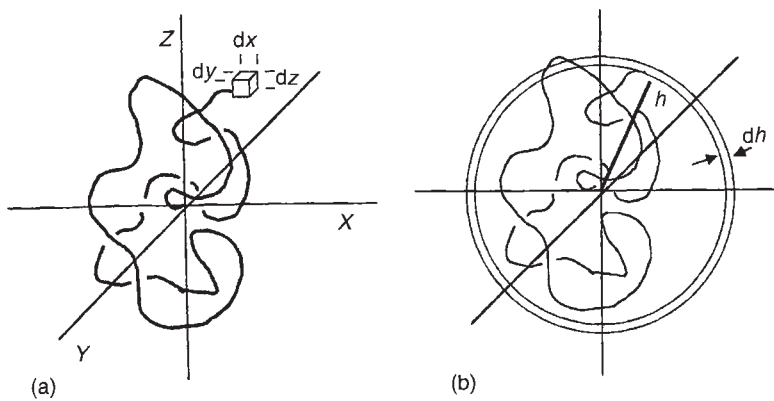

Figure 6.12 A flexible coil with one end at the origin and the other in (a) a volume element $dx\,dy\,dz$ and (b) a spherical shell of volume $4\pi h^2\,dh$.

being 1/2. At the end of the N steps, let p be the total number of $+$ steps and q be the total number of $-$ steps. Clearly $N = p + q$ and the net distance traveled will be $x = b(p - q)$. The probability of any given outcome for this kind of process is given by the binomial theorem:

$$P(N, x) = \left(\frac{1}{2}\right)^p \left(\frac{1}{2}\right)^q \frac{N!}{p!q!} \tag{6.7.2}$$

This expression arises as follows. The probability of a sequence of events that are independent is equal to the product of the probabilities of each event; this gives the factors of $(1/2)^p$ and $(1/2)^q$. However, this would underestimate what we want, namely a net displacement of x. This is because $(1/2)^p(1/2)^q$ assumes we have all $p+$ steps in succession, followed by $q-$ steps, whereas in fact the order of the individual steps does not matter, only the total p and q. There are N possible choices for the first step, then $N - 1$ for the next and so on, which increases the total probability by a factor of $N!$. This, however, now overestimates the answer, because all of the $p+$ steps are indistinguishable, as are all of the $q-$ steps. There are $p!$ possible permutations of the $+$ steps, all of which would give the same answer, and similarly $q!$ permutations of the $-$ steps; both of these factors are counted in $N!$, so we have to divide by them out. Thus we arrive at Equation 6.7.2.

Now we make the simple substitutions

$$p = \frac{1}{2}\left(N + \frac{x}{b}\right), \quad q = \frac{1}{2}\left(N - \frac{x}{b}\right) \tag{6.7.3}$$

to obtain

$$P(N, x) = \left(\frac{1}{2}\right)^N N! \frac{2!}{\left(N + \frac{x}{b}\right)!} \frac{2!}{\left(N - \frac{x}{b}\right)!} \tag{6.7.4}$$

The expression is simplified by means of Stirling's large N approximation, namely

$$\ln N! \approx N \ln N - N \tag{6.7.5}$$

which gets rid of the nasty factorials. (It is worth noting that Stirling's approximation is excellent when N is on the order of Avogadro's number, but it is not quantitatively accurate for $N \approx 100$; nevertheless these errors largely cancel in deriving the Gaussian distribution.) Utilizing this, Equation 6.7.4 can be expanded:

$$\ln P(N, x) = -\frac{1}{2}\left(N + \frac{x}{b}\right)\ln\left(1 + \frac{x}{bN}\right) - \frac{1}{2}\left(1 - \frac{x}{bN}\right)\ln\left(1 - \frac{x}{bN}\right) \tag{6.7.6}$$

after some algebra. Now we recall the expansion of $\ln(1 + x)$ when $x \ll 1$, namely

$$\ln(1 + x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \cdots \tag{6.7.7}$$

and realize that $(x/bN) \to 0$ as N gets very big. Thus $\ln(1 + x) \approx x$ applies

$$\ln P(N, x) = -\frac{1}{2}\left(N + \frac{x}{b}\right)\left(\frac{x}{Nb}\right) - \frac{1}{2}\left(N - \frac{x}{b}\right)\left(\frac{x}{Nb}\right)$$
$$= \frac{-x^2}{2Nb^2} \tag{6.7.8}$$

or

$$P(N, x) \sim \exp\left[\frac{-x^2}{2Nb^2}\right] \tag{6.7.9}$$

We insert a proportional sign here to allow for the appropriate normalization (see below). Now to convert to a three-dimensional N-step random walk, we take $N/3$ steps along x, $N/3$ along y, and $N/3$ along z, and recognize that the probabilities along the three directions are independent.

Therefore

$$P(N,\vec{h}) = P\left(\frac{N}{3},x\right)P\left(\frac{N}{3},y\right)P\left(\frac{N}{3},z\right) \sim \exp\left[\frac{-3|h|^2}{2Nb^2}\right]$$ (6.7.10)

where we have inserted $|h|^2 = x^2 + y^2 + z^2$. The final step is the normalization, which accounts for the fact that if we look over all space for the end of our walk, we must find it exactly once. This is expressed by

$$\int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} \int\limits_{-\infty}^{\infty} P(N,\vec{h})\, dx,dy,dz = 1$$ (6.7.11)

You can find in a table of integrals that

$$\int\limits_{-\infty}^{\infty} \exp\left(-kx^2\right) dx = \sqrt{\frac{\pi}{k}}$$

and thus from the triple integral of Equation 6.7.11 we find that the result is $[3/2\pi Nb^2]^{-3/2}$. Therefore we need to multiply our exponential factor by $[3/2\pi Nb^2]^{3/2}$ to satisfy Equation 6.7.11 and arrive at the result given in Equation 6.7.1.

This Gaussian distribution function for $\vec{h}$ is plotted against $|\vec{h}|$ in Figure 6.13a. Although it is a distribution function for a vector quantity, it only depends on the length of h; this is a natural consequence of assuming that x, y, and z steps are equally probable. It is peaked at the origin, which means that the single most probable outcome is $\vec{h} = 0$, i.e., the walk returns to the origin. However, because of the prefactor, the probability of this particular outcome shrinks as $N^{-3/2}$, even though it is more likely than any other single outcome. Finally, this expression for $P(N,\vec{h})$ was obtained by assuming large N (no surprise here). How large does N have to be for the Gaussian function to be useful? It turns out that even for $N \approx 10$, the real distribution for a random walk looks reasonably Gaussian. Already for very small N it is symmetric and peaked at the origin, but it
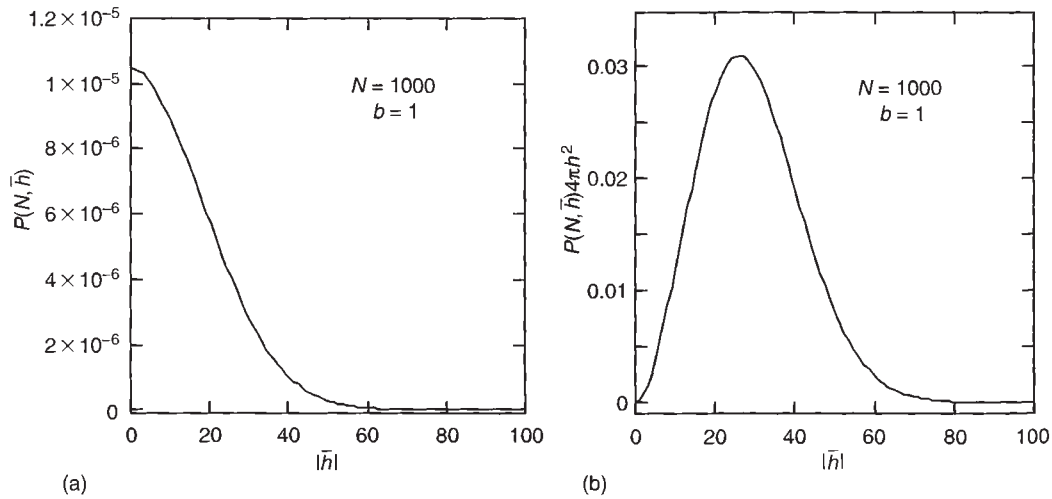

Figure 6.13 Gaussian probability distributions for a chain of N steps of length b, plotted as (a) the probability of an end-to-end vector $\vec{h}$ versus $|\vec{h}|$ and (b) the probability of an end-to-end distance h.

will be "bumpy" because b has a discrete value. As N gets larger, the fact that b is discrete becomes less and less important, although the fact that we are representing a discrete function by a continuous one never goes away for finite N. Indeed, we can assert that even though the Gaussian distribution may provide numerical answers that are very accurate, it can never be exactly correct for a real chain. That is because a real chain has a finite contour length that $|\vec{h}|$ can never exceed, whereas Equation 6.7.1 provides a finite probability for any value of $|\vec{h}|$ all the way out to infinity.

6.7.2 Distribution of the End-to-End Distance

We now turn to obtaining $P(N, h)$ for the distance h. The transformation is illustrated in Figure 6.12b. We consider a spherical shell at a distance h from the origin. It has a surface area $4\pi h^2$ and a thickness dh, so its volume is $4\pi h^2\, dh$. Any walk whose end-to-end vector $\vec{h}$ lies in this shell will have the same length h, so the answer we seek is just

$$P(N, h)\, dh = 4\pi h^2 P(N, \vec{h})\, dh$$

$$= 4\pi h^2 \left[\frac{3}{2\pi N b^2}\right]^{3/2} \exp\left[\frac{-3\left|\vec{h}\right|^2}{2N b^2}\right] dh \tag{6.7.12}$$

This function is already normalized correctly. It should satisfy the one-dimensional integral

$$\int_0^\infty P(N, h)\, dh = 1 \tag{6.7.13}$$

and you can show that it does, armed with the knowledge that

$$\int_0^\infty x^2 \exp(-k x^2)\, dx = \frac{1}{4k}\sqrt{\frac{\pi}{k}}$$

Note that the normalization integral goes from 0 to ∞, as h cannot be negative.

This distribution function is plotted in Figure 6.13b and is rather different from $P(N, \vec{h})$. In particular, it vanishes at the origin and has a peak at a finite value of h before decaying to zero as $N \to \infty$. The fact that it vanishes at the origin is due to multiplying the exponential decay by h^2. There is thus a big difference between finding the most probable *vector* position (which is the origin) and finding the most probable *distance* (the position of the peak in $P(N, h)$, see Problem 6.10). You have probably encountered this contrast before, for example, in the radial distribution function for the s electrons of a hydrogen-like atom, or for the Maxwell distribution of molecular velocities in a gas. In the former, the most probable position of the electron is at the nucleus, but the most probable distance is a finite quantity, the Bohr radius. In the latter, the most probable velocity in the gas is zero, but the most probable speed is finite.

As a simple application of this distribution function, we can ask what is the mean square value of h?

$$\langle h^2 \rangle = \int_0^\infty h^2 P(N, h)\, dh$$

$$\tag{6.7.14}$$

$$= \int_0^\infty h^2 4\pi h^2 \left[\frac{3}{2\pi N b^2}\right]^{3/2} \exp\left[\frac{-3\left|\vec{h}\right|^2}{2N b^2}\right] dh$$

where now we need to know

$$\int_0^\infty x^4 \exp(-kx^2)\, dx = \frac{3}{8k^2}\sqrt{\frac{\pi}{k}}$$

Applying this in Equation 6.7.14 we obtain

$$\langle h^2 \rangle = 4\pi \left[\frac{3}{2\pi Nb^2}\right]^{3/2} \frac{3}{8}\left(\frac{3}{2Nb^2}\right)^{-2}\sqrt{\pi}\left(\frac{2Nb^2}{3}\right)^{1/2} = Nb^2 \qquad (6.7.15)$$

as expected. The quantity $\langle h^2 \rangle$ is also called the *second moment* of the distribution $P(N, h)$. (You may recall the discussion of moments in the context of molecular weights in Chapter 1.7.)

6.7.3 Distribution about the Center of Mass

The last thing we consider in this section is the related distribution $\rho(N, r)\, dr$, the probability that a monomer is between r and $r + dr$ from the center of mass. It turns out that there is no simple analytical expression for this distribution, even for a Gaussian chain [4], but the resulting distribution is well approximated by a Gaussian:

$$\rho(N, r) = N4\pi r^2 \left[\frac{3}{2\pi\langle s^2 \rangle}\right]^{3/2} \exp\left[\frac{-3r^2}{2\langle s^2 \rangle}\right] \qquad (6.7.16)$$

where we use the second moment $\langle s^2 \rangle = Nb^2/6$ explicitly in the expression (compare Equation 6.7.1, where Nb^2 could have been replaced by $\langle h^2 \rangle$). One important point is the factor of N in front. This is simply a new normalization so that

$$\int_0^\infty \rho(N, r)\, dr = N \qquad (6.7.17)$$

which reflects the fact that when we look for monomers over all space, we must find all N of them.

The segment density distribution can also be used for a solid object, where there is no need to identify N separate subunits. In such a case $\rho(r)$ can be used to find $R_g = \langle s^2 \rangle^{1/2}$, from

$$\langle s^2 \rangle = \frac{\int_0^\infty r^2\rho(r)\, dr}{\int_0^\infty \rho(r)\, dr} = \frac{\int_0^\infty 4\pi r^4\rho(\vec{r})\, dr}{\int_0^\infty 4\pi r^2\rho(\vec{r})\, dr} \qquad (6.7.18)$$

The integral in the denominator provides the necessary normalization. As an example, consider a solid sphere with radius R_0 and uniform density ρ_0. The distribution function for $\rho(\vec{r})$ is just a constant, ρ_0, for $0 \leq r \leq R_0$, and 0 for $r > R_0$. (Note that this simple function is $\rho(\vec{r})$, not $\rho(r)$ because the latter must increase as r^2 for $r \leq R_0$; there are more monomers near the surface of the sphere than at the center.) Substituting $\rho(\vec{r})$ into Equation 6.7.18 we obtain

$$\langle s^2 \rangle = \frac{\int_0^{R_0} \rho_0 4\pi r^4\, dr}{\int_0^{R_0} \rho_0 4\pi r^2\, dr} = \frac{R_0^5/5}{R_0^3/3} = \frac{3}{5}R_0^2 \qquad (6.7.19)$$

Thus for a solid sphere

Table 6.3 Formulae for the Radii of Gyration for Various Shapes

Structure	R_g^2	Parameters
Gaussian coil	$\dfrac{Nb^2}{6}$	Degree of polymerization N
Gaussian star	$\dfrac{3f - 2}{f} \dfrac{N_{arm}b^2}{6}$	Statistical segment length b Arm degree of polymerization N_{arm} Number of arms f
Gaussian ring	$\dfrac{Nb^2}{12}$	Statistical segment length b Degree of polymerization N
Solid sphere	$\dfrac{3}{5}R^2$	Statistical segment length b Sphere radius R
Solid ellipsoid	$\dfrac{1}{5}\left(R_1^2 + R_2^2 + R_3^2\right)$	Ellipsoid principal radii R_1, R_2, R_3
Thin rod	$\dfrac{1}{12}L^2$	Rod length L
Cylinder	$\dfrac{1}{12}L^2 + \dfrac{1}{2}r^2$	Cylinder radius r, length L
Thin disk	$\dfrac{1}{2}r^2$	Disk radius r

$$R_g = \sqrt{\frac{3}{5}}R_0 \tag{6.7.20}$$

This result serves to emphasize an important point that R_g reflects an *average* of the monomer distribution and not the *total spatial extent* of the object. There are always monomers further than R_g from the center of mass as well as monomers closer than R_g to the center of mass. Expressions for R_g for other shapes are listed in Table 6.3.

6.8 Self-Avoiding Chains: A First Look

We mentioned at the end of Section 6.2 that there is a further important issue in chain conformations, that of excluded volume. The simple fact is that a real polymer occupies real space and no two monomers in the chain can share the same location concurrently. This means that the statistics of the conformation are no longer those of a random walk, but rather a *self-avoiding walk*. This difference might appear subtle, which it is, but the consequences are profound.

Most importantly, we can no longer write down an analytical expression for any of the desired distribution functions such as $P(N, h)$. Nor can we calculate in any simple yet rigorous way the dependence of R_g on N. The mathematical reason for this difficulty is the way the problem becomes more complicated as N increases. In the case of the random walk, the orientation of any link or step is dictated by random chance and its position in space is determined only by where the previous link is. For the self-avoiding walk, in contrast, we would need to ask where every previous link is in order to establish whether a particular orientation would be allowed for the link in question. It would not be allowed if it intersected any previous link. Consequently, the calculation becomes more and more complicated as N increases. Some very sophisticated mathematics has been employed on this problem, but we will not discuss this at all. We can draw an important qualitative conclusion, however: the excluded volume effect will tend to make the average coil size *larger*, as the chain seeks conformations without self-intersections. From the most sophisticated analysis, $R_g \sim N^{0.589}$ instead of $N^{1/2}$; in other words the exponent ν from Equation 6.6.1 is 0.589 (although most people use 0.6 as a reasonable approximation).

As also mentioned in Section 6.2, there are two experimental situations in which this complication goes away, and $\nu = 0.5$ again. One case is a molten polymer. Here a chain still cannot have two monomers occupying the same place, but there is no benefit to expanding the coil. The reason is that space is full of monomers, and a monomer on one chain cannot tell if its immediate neighbor in space belongs to a different chain, or is attached by many bonds to the same chain. Consequently, it does not gain anything by expanding beyond the Gaussian distribution. The second case is for a chain dissolved in a particular kind of solvent called a theta solvent. A theta solvent is actually a not-very-good solvent, in the sense that for energetic reasons monomers would much prefer to be next to other monomers than next to solvent molecules. This has a tendency to shrink the chain, and a theta solvent refers to a particular solvent at a particular temperature where the expansion due to the self-avoiding nature of the chain is exactly canceled by shrinking due to unfavorable polymer–solvent interactions. We will explore this in more detail in the next chapter, where we consider the thermodynamics of polymer solutions.

6.9 Chapter Summary

In this chapter, we have examined the spatial extent of polymer chains as a function of molecular weight and chemical structure. The principal results are the following:

1. A single chain can adopt an almost infinite number of possible conformations; we must settle for describing the average size.
2. For any chain with some degree of conformational freedom the average size will grow as the square root of the degree of polymerization: this is the classic result for a random walk. Furthermore, the distribution of chain sizes is approximately Gaussian.
3. The prefactor that relates size to molecular weight is a measure of local flexibility; three interchangeable schemes for quantifying the prefactors are the characteristic ratio, the statistical segment length, and the persistence length.
4. Chemical structures for which the chain orientation can reverse direction in about 20 backbone bonds or less are called "flexible"; much stiffer polymers are termed "semiflexible." This latter class is best considered through the worm-like chain model using the persistence length as the key measure of local flexibility.
5. The radius of gyration is the most commonly employed measure of size; it can be defined for any chemical structure and it is directly measurable.
6. Because of excluded volume, real chains dissolved in a good solvent are not random walks, but self-avoiding walks. The corresponding size grows with a slightly larger power of molecular weight. In theta solvents or in the melt, the excluded volume effect is canceled out and the random walk result applies.

Problems

1. Experimental chain dimensions for poly(ethylene terephthalate) (PET) at 275°C are given by $\langle h^2 \rangle_0 / M \approx 0.90 \text{ Å}^2 \text{ mol/g}$. Calculate C_∞, the statistical segment length, and the persistence length for this polymer. Based on these numbers, is PET a flexible polymer, or not? What would you expect based on the molecular structure?
2. Resolve the paradox noted in Section 6.3: polystyrene is considered to be relatively stiff, and polyisoprene relatively flexible, yet their statistical segment lengths are almost identical.
3. For freely jointed copolymers with n_A steps of length ℓ_A and n_B steps of length ℓ_B find $\langle h^2 \rangle$ (large n limit) for strictly alternating, random, and diblock architectures. Are the answers the same or different? Why?