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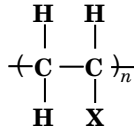
## Models of Polymer Chains

### 1.1 INTRODUCTION

#### 1.1.1 Chain Architecture

A polymer molecule consists of the same repeating units, called monomers, or of different but resembling units. Figure 1.1 shows an example of a vinyl polymer, an industrially important class of polymer. In the repeating unit, X is one of the monofunctional units such as H, CH<sub>3</sub>, Cl, and C<sub>6</sub>H<sub>5</sub> (phenyl). The respective polymers would be called polyethylene, polypropylene, poly(vinyl chloride), and polystyrene. A double bond in a vinyl monomer CH<sub>2</sub>=CHX opens to form a covalent bond to the adjacent monomer. Repeating this polymerization step, a polymer molecule is formed that consists of  $n$  repeating units. We call  $n$  the **degree of polymerization** (DP). Usually,  $n$  is very large. It is not uncommon to find polymers with  $n$  in the range of  $10^4$ – $10^5$ .

In the solid state, polymer molecules pack the space with little voids either in a regular array (crystalline) or at random (amorphous). The molecules are in close contact with other polymer molecules. In solutions, in contrast, each polymer molecule is surrounded by solvent molecules. We will learn in this book about properties of the polymer molecules in this dispersed state. The large  $n$  makes many of the properties common to all polymer molecules but not shared by small molecules. A difference in the chemical structure of the repeating unit plays a secondary role. The difference is usually represented by parameters in the expression of each physical property, as we will see throughout this book.



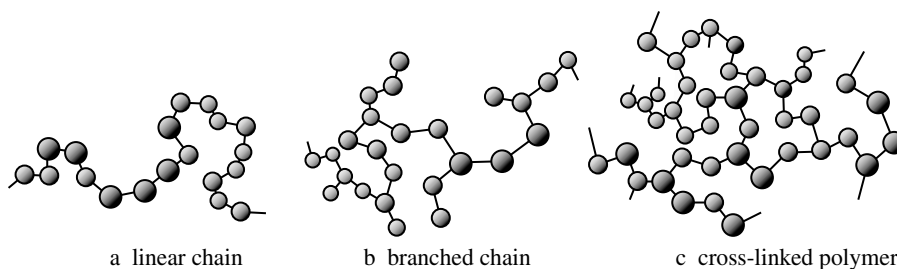
**Figure 1.1.** Vinyl polymer.

Figure 1.2 shows three architectures of a polymer molecule: a **linear chain** (a), a **branched chain** (b), and a **cross-linked polymer** (c). A bead represents a monomer here. A vinyl polymer is a typical linear polymer. A branched chain has branches, long and short. A cross-linked polymer forms a network encompassing the entire system. In fact, there can be just one supermolecule in a container. In the branched chain, in contrast, the branching does not lead to a supermolecule. A cross-linked polymer can only be swollen in a solvent. It cannot be dissolved. We will learn linear chain polymers in detail and about branched polymers to a lesser extent.

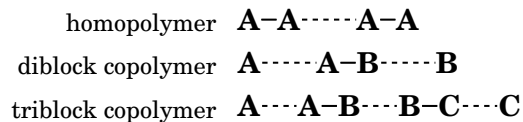
Some polymer molecules consist of more than one kind of monomers. An A–B **copolymer** has two constituent monomers, A and B. When the monomer sequence is random, i.e., the probability of a given monomer to be A does not depend on its neighbor, then the copolymer is called a **random copolymer**. There is a different class of linear copolymers (Fig. 1.3). In an A–B **diblock copolymer**, a whole chain consists of an A block, a B block, and a joint between them. In a triblock copolymer, the chain has three blocks, A, B, and C. The C block can be another A block. A polymer consisting of a single type of monomers is distinguished from the copolymers and is called a **homopolymer**.

### 1.1.2 Models of a Linear Polymer Chain

**1.1.2.1 Models in a Continuous Space** A polymer chain in the solution is changing its shape incessantly. An instantaneous shape of a polymer chain in



**Figure 1.2.** Architecture of polymer chain: a linear chain (a), a branched chain (b), and a cross-linked polymer (c).



**Figure 1.3.** Homopolymer and block copolymers.

solution (Fig. 1.4a) is called a **conformation**. To represent the overall chain conformation, we strip all of the atoms except for those on the backbone (Fig. 1.4b). Then, we remove the atoms and represent the chain by connected bonds (Fig. 1.4c). In linear polyethylene, for instance, the chain is now represented by a link of carbon–carbon bonds only. We can further convert the conformation to a smoothed line of thread (Fig. 1.4d). In the last model, a polymer chain is a geometrical object of a thin flexible thread.

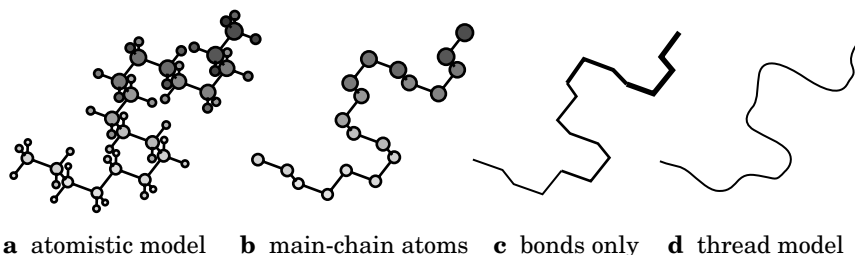
We now pull the two ends of the skeletal linear chain to its full extension (Fig. 1.5). In a vinyl polymer, the chain is in all-*trans* conformation. The distance between the ends is called the **contour length**. The contour length ( $L_c$ ) is proportional to DP or the molecular weight of the polymer. In solution, this fully stretched conformation is highly unlikely. The chain is rather crumpled and takes a conformation of a **random coil**.

Several coarse-grained geometrical models other than the skeletal chain model are being used to predict how various physical quantities depend on the chain length, the polymer concentration, and so forth, and to perform computer simulations. Figure 1.6 illustrates a **bead-stick model** (a), a **bead-spring model** (b), and a **pearl-necklace model** (c).

In the bead-stick model, the chain consists of beads and sticks that connect adjacent beads. Many variations are possible: (1) the bead diameter and the stick thickness can be any nonnegative value, (2) we can restrict the angle between two adjacent sticks or let it free, or (3) we can restrict the torsional angle (dihedral angle) of a stick relative to the second next stick. Table 1.1 compares two typical variations of the model: a **freely jointed chain** and a **freely rotating chain**. When the bond angle is fixed to the tetrahedral angle in the  $sp^3$  orbitals of a carbon atom and the dihedral angle is fixed to the one of the three angles corresponding to *trans*, *gauche* +, and *gauche* –, the model mimics the backbone of an actual linear vinyl polymer. The latter is given a special name, **rotational isometric state model** (RIMS). A more sophisticated model would allow the stick length and the bond

**TABLE 1.1** Bead-Stick Models

Model	Bond Length	Bond Angle	Dihedral Angle
Freely jointed chain	fixed	free	free
Freely rotating chain	fixed	fixed	free



**a** atomistic model   **b** main-chain atoms   **c** bonds only   **d** thread model

**Figure 1.4.** Simplification of chain conformation from an atomistic model (a) to main-chain atoms only (b), and then to bonds on the main chain only (c), and finally to a flexible thread model (d).

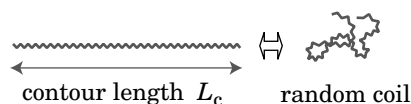
angle to vary according to harmonic potentials and the dihedral angle following its own potential function with local minima at the three angles. In the bead-stick model, we can also regard each bead as representing the center of a monomer unit (consisting of several or more atoms) and the sticks as representing just the connectivity between the beads. Then, the model is a **coarse-grained** version of a more atomistic model. A bead-stick pair is called a **segment**. The segment is the smallest unit of the chain. When the bead diameter is zero, the segment is just a stick.

In the bead-spring model, the whole chain is represented by a series of beads connected by springs. The equilibrium length of each spring is zero. The bead-spring model conveniently describes the motion of different parts of the chain. The segment of this model is a spring and a bead on its end.

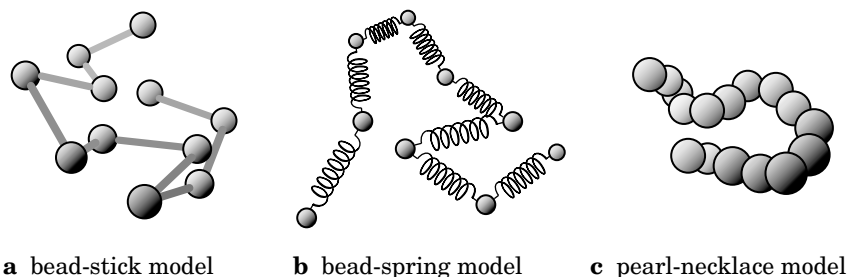
In the pearl-necklace model, the beads (pearls) are always in contact with the two adjacent beads. This model is essentially a bead-stick model with the stick length equal to the bead diameter. The bead always has a positive diameter. As in the bead-stick model, we can restrict the bond angle and the dihedral angle.

There are other models as well. This textbook will use one of the models that allows us to calculate most easily the quantity we need.

**1.1.2.2 Models in a Discrete Space** The models described in the preceding section are in a continuous space. In the bead-stick model, for instance, the bead centers can be anywhere in the three-dimensional space, as long as the arrangement satisfies the requirement of the model. We can construct a linear chain on a discrete



**Figure 1.5.** A random-coil conformation is pulled to its full length  $L_c$ .



**Figure 1.6.** Various models for a linear chain polymer in a continuous space: a bead-stick model (a), a bead-spring model (b), and a pearl-necklace model (c).

space as well. The models on a discrete space are widely used in computer simulations and theories.

The discrete space is called a **lattice**. In the lattice model, a polymer chain consists of monomers sitting on the grids and bonds connecting them. The grid point is called a **site**; Figure 1.7 illustrates a linear polymer chain on a square lattice (a) and a triangular lattice (b), both in two dimensions. The segment consists of a bond and a point on a site. In three dimensions, a cubic lattice is frequently used and also a diamond lattice to a lesser extent. Figure 1.8 shows a chain on the cubic lattice. The diamond (tetrahedral) lattice is constructed from the cubic lattice and the body centers of the cubes, as shown in Figure 1.9. The chain on the diamond lattice is identical to the bead-stick model, with a bond angle fixed to the tetrahedral angle and a dihedral angle at one of the three angles separated by  $120^\circ$ . There are other lattice spaces as well.

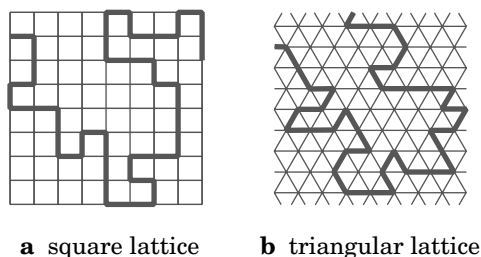
The **lattice coordinate**  $Z$  refers to the number of nearest neighbors for a lattice point. Table 1.2 lists  $Z$  for the four discrete models.

### 1.1.3 Real Chains and Ideal Chains

In any real polymer chain, two monomers cannot occupy the same space. Even a part of a monomer cannot overlap with a part of the other monomer. This effect is called an **excluded volume** and plays a far more important role in polymer solutions than it does in solutions of small molecules. We will examine its ramifications in Section 1.4.

**TABLE 1.2** Coordination Number

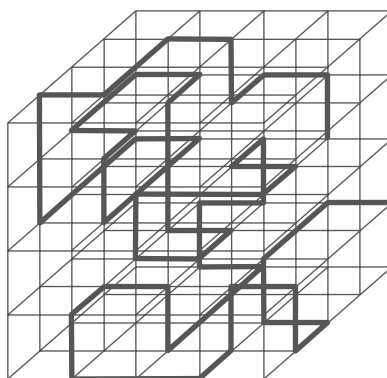
Dimensions	Geometry	$Z$
2	square	4
2	triangular	6
3	cubic	6
3	diamond	4



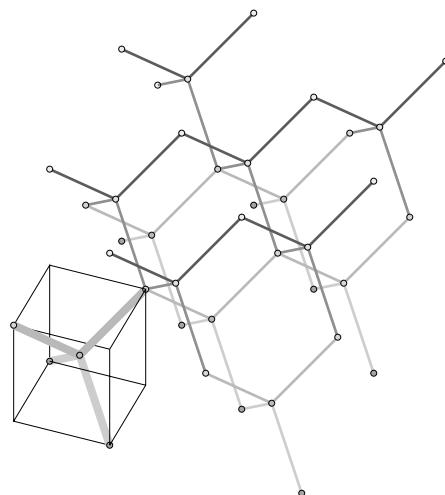
**a** square lattice      **b** triangular lattice

**Figure 1.7.** Linear chains on a square lattice (a) and a triangular lattice (b).

We often idealize the chain to allow overlap of monomers. In the lattice model, two or more monomers of this **ideal chain** can occupy the same site. To distinguish a regular chain with an excluded volume from the ideal chain, we call the regular chain with an excluded volume a **real chain** or an **excluded-volume chain**. Figure 1.10 illustrates the difference between the real chain (right) and the ideal chain (left) for a thread model in two dimensions. The chain conformation is nearly the same, except for a small part where two parts of the chain come close, as indicated by dashed-line circles. Crossing is allowed in the ideal chain but not in the real chain. The ideal chain does not exist in reality, but we use the ideal-chain model extensively because it allows us to solve various problems in polymer solutions in a mathematically rigorous way. We can treat the effect of the excluded effect as a small difference from the ideal chains. More importantly, though, the real chain behaves like an ideal chain in some situations. One situation is concentrated solutions, melts, and glasses. The other situation is a dilute solution in a special solvent called a theta solvent. We



**Figure 1.8.** Linear chain on a cubic lattice.



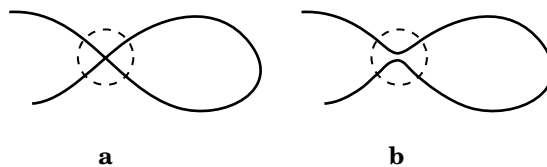
**Figure 1.9.** Diamond lattice.

will learn about the theta solvent in Section 2.3 and the concentrated solution in Chapter 4.

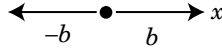
## 1.2 IDEAL CHAINS

### 1.2.1 Random Walk in One Dimension

**1.2.1.1 Random Walk** A linear flexible polymer chain can be modeled as a **random walk**. The concept of the random walk gives a fundamental frame for the conformation of a polymer chain. If visiting the same site is allowed, the trajectory of the random walker is a model for an ideal chain. If not allowed, the trajectory resembles a real chain. In this section, we learn about the ideal chains in three dimensions. To familiarize ourselves with the concept, we first look at an ideal random walker in one dimension.



**Figure 1.10.** Conformations of an ideal chain (a) and a real chain (b) in two dimensions.



**Figure 1.11.** Step motion in one-dimensional random walk.

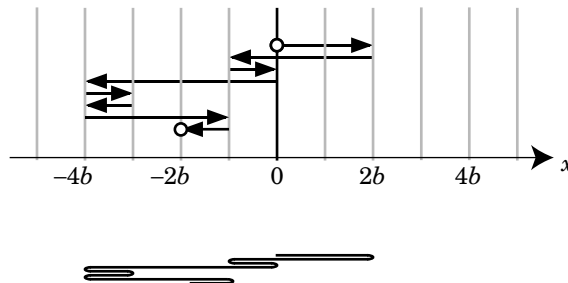
The random walker moves in each step by  $b$  either to the right or to the left, each with a probability of one-half (Fig. 1.11). Each time it decides where to move next independently of its preceding moves. The walker does not have a memory regarding where it has come from. The latter property is called **Markoffian** in stochastic process theory. The walker can come back to the sites previously visited (ideal). The  $N$ -step trajectory of the random walker is a chain of length  $Nb$  folded one-dimensionally, as illustrated in Figure 1.12. The movement of the random walker is specified by a sequence of “+” and “-,” with + being the motion to the right and - being that to the left. In this example the sequence is ++----+-----+----+-+. Thus one arrangement of the chain folding corresponds to an event of having a specific sequence of + and -. Another way to look at this sequence is to relate + to the head and - to the tail in a series of coin tosses.

Suppose there are  $n$  “+” out of a total  $N$  trials ( $n = 0, 1, \dots, N$ ). Then the random walker that started at  $x = 0$  on the  $x$ -axis has reached a final position of  $x = nb + (N - n)(-b) = b(2n - N)$ . How these  $n+$  are arranged is irrelevant to the final position. What matters is how many + there are. If all are +,  $x = Nb$ ; if all are -,  $x = -Nb$ . The probability  $P_n$  to have  $n+$  is given by

$$P_n = 2^{-N} {}_N C_n = 2^{-N} \frac{N!}{n!(N-n)!} \quad (1.1)$$

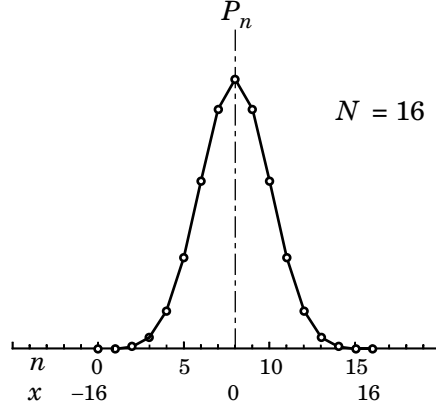
The probability distribution is called a binomial distribution, because  $P_n$  is equal to the  $n$ th term in the expansion of

$$(p + q)^N = \sum_{n=0}^N p^n q^{N-n} {}_N C_n \quad (1.2)$$



**Figure 1.12.** One-dimensional random walk of 16 steps. The trajectory is a folded chain.





**Figure 1.13.** Probability distribution for the number  $n$  of positive moves. The corresponding final position  $x$  is also indicated.

with  $p = q = 1/2$ . Thus we find that  $P_n$  given by Eq. 1.1 is normalized. An example of  $P_n$  is shown in Figure 1.13 for  $N = 16$ . The range of  $n$  is between 0 and  $N$ , which translates into the range of  $x$  between  $-N$  and  $N$ . Only every other integral values of  $x$  can be the final position of the random walker for any  $N$ .

**1.2.1.2 Mean Square Displacement** If we set  $p = q = 1$  in Eq. 1.2, we have the identity

$$2^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!} \quad (1.3)$$

Using the identity, the mean (expectation) of  $n$  is calculated as follows:

$$\langle n \rangle = \sum_{n=0}^N n P_n = 2^{-N} \sum_{n=0}^N \frac{n N!}{n!(N-n)!} = 2^{-N} N \sum_{n=1}^N \frac{(N-1)!}{(n-1)!(N-n)!} = 2^{-N} N 2^{N-1} = N/2 \quad (1.4)$$

On the average, the random walker moves half of the steps to the right. Likewise, the average of  $n^2$  is calculated as

$$\begin{aligned} \langle n^2 \rangle &= \sum_{n=0}^N n^2 P_n = 2^{-N} \sum_{n=0}^N \frac{n^2 N!}{n!(N-n)!} \\ &= 2^{-N} \left[ N(N-1) \sum_{n=2}^N \frac{(N-2)!}{(n-2)!(N-n)!} + N \sum_{n=1}^N \frac{(N-1)!}{(n-1)!(N-n)!} \right] \quad (1.5) \\ &= N(N+1)/4 \end{aligned}$$

Then the variance, the mean square of  $\Delta n \equiv n - \langle n \rangle$ , is

$$\langle \Delta n^2 \rangle = \langle (n - \langle n \rangle)^2 \rangle = \langle n^2 \rangle - \langle n \rangle^2 = N/4 \quad (1.6)$$

Its square root,  $\langle \Delta n^2 \rangle^{1/2}$ , called the standard deviation, is a measure for the broadness of the distribution. Note that both  $\langle n \rangle$  and  $\langle \Delta n^2 \rangle$  increase linearly with  $N$ . Therefore, the relative broadness,  $\langle \Delta n^2 \rangle^{1/2} / \langle n \rangle$ , decreases with increasing  $N$ .

Let us translate these statistical averages of  $n$  into those of  $x$ . Because  $x = b(2n - N)$ , the mean and the variance of  $x$  are

$$\boxed{\langle x \rangle = 0, \quad \langle \Delta x^2 \rangle = \langle x^2 \rangle = Nb^2 \quad \text{1D random walk}} \quad (1.7)$$

where  $\Delta x = x - \langle x \rangle$  is the displacement of the random walker in  $N$  steps. Because  $x = 0$  before the random walk,  $\Delta x = x$ . The average of its square,  $\langle \Delta x^2 \rangle$ , is called the **mean square displacement**.

**1.2.1.3 Step Motion** Now we look at the  $N$ -step process from another perspective. Let  $\Delta x_n$  be the displacement in the  $n$ th step. Then,  $\Delta x_n$  is either  $b$  or  $-b$  with an equal probability. Therefore,  $\langle \Delta x_n \rangle = 0$  and  $\langle \Delta x_n^2 \rangle = b^2$ . Different steps are not correlated. Mathematically, it is described by  $\langle \Delta x_n \Delta x_m \rangle = 0$  if  $n \neq m$ . Combining  $n = m$  and  $n \neq m$ , we write

$$\langle \Delta x_n \Delta x_m \rangle = b^2 \delta_{nm} \quad (1.8)$$

where  $\delta_{nm}$  is the Kronecker's delta ( $\delta_{nm} = 1$  if  $n = m$ ;  $\delta_{nm} = 0$  otherwise). In  $N$  steps, the random walker arrives at  $x$ , starting at  $x = 0$ . The total displacement  $\Delta x = x - 0$  of the  $N$  steps is given as

$$\Delta x = \sum_{n=1}^N \Delta x_n \quad (1.9)$$

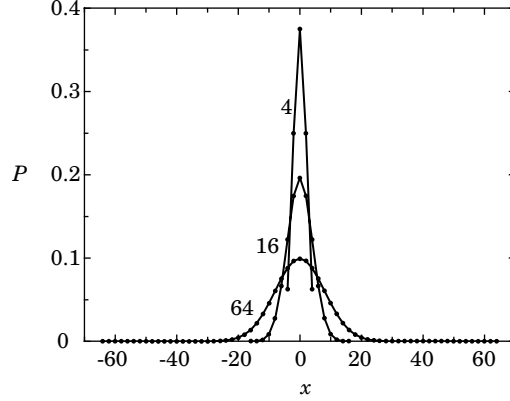
The mean and the variance of  $\Delta x$  are calculated as

$$\langle \Delta x \rangle = \left\langle \sum_{n=1}^N \Delta x_n \right\rangle = \sum_{n=1}^N \langle \Delta x_n \rangle = 0 \quad (1.10)$$

$$\langle \Delta x^2 \rangle = \left\langle \sum_{n=1}^N \Delta x_n \sum_{m=1}^N \Delta x_m \right\rangle = \left\langle \sum_{n,m=1}^N \Delta x_n \Delta x_m \right\rangle = \sum_{n,m=1}^N \langle \Delta x_n \Delta x_m \rangle = \sum_{n=1}^N \langle \Delta x_n^2 \rangle = Nb^2 \quad (1.11)$$

As required, the results are identical to those in Eq. 1.7.

**1.2.1.4 Normal Distribution** Let us see how  $P_n$  or  $P(x)$  changes when  $N$  increases to a large number. Figure 1.14 compares  $P_n$  for  $N = 4, 16, \text{ and } 64$ . As  $N$



**Figure 1.14.** Distribution of the final position  $x$  for 4-, 16-, and 64-step random walks.

increases, the plot approaches a continuously curved line. To predict the large  $N$  asymptote of  $P_n$ , we use Stirling's formula  $\ln N! \cong N(\ln N - 1)$ . Equation 1.1 is rewritten to

$$\begin{aligned} \ln P_n &= -N \ln 2 + N(\ln N - 1) - n(\ln n - 1) - (N - n)[\ln(N - n) - 1] \\ &= -N \ln 2 + N \ln N - n \ln n - (N - n) \ln(N - n) \end{aligned} \quad (1.12)$$

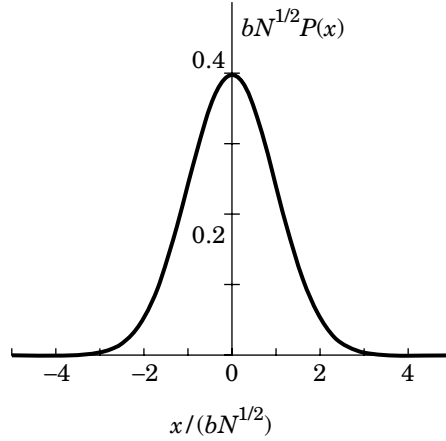
With  $n = (N + x/b)/2$ , this equation is converted to a function of  $x$ :

$$\begin{aligned} \ln P &\cong -N \ln 2 + N \ln N - \frac{1}{2}(N - x/b) \ln[(N - x/b)/2] \\ &\quad - \frac{1}{2}(N + x/b) \ln[(N + x/b)/2] \\ &= N \ln N - \frac{1}{2}(N - x/b) \ln(N - x/b) - \frac{1}{2}(N + x/b) \ln(N + x/b) \\ &= -\frac{1}{2}N \left[ \left(1 - \frac{x}{Nb}\right) \ln \left(1 - \frac{x}{Nb}\right) + \left(1 + \frac{x}{Nb}\right) \ln \left(1 + \frac{x}{Nb}\right) \right] \\ &\cong -\frac{1}{2}N \left(\frac{x}{Nb}\right)^2 = -\frac{x^2}{2Nb^2} \end{aligned} \quad (1.13)$$

where the Taylor expansion was taken up to the second order of  $x/(Nb)$  in the last part, because  $P(x)$  is almost zero except at small  $|x/(Nb)|$ . This equation does not satisfy the normalization condition because we used a crude version of Stirling's formula. Normalization leads Eq. 1.13 to

$$\boxed{P(x) = (2\pi Nb^2)^{-1/2} \exp\left(-\frac{x^2}{2Nb^2}\right)} \quad \text{1D random walk} \quad (1.14)$$

This probability distribution, shown in Figure 1.15, is a **normal distribution** with a zero mean and a variance of  $Nb^2$ . Note that the mean and the variance are the same



**Figure 1.15.** Distribution of the final position  $x$  for a random walk of infinite number of steps.

as those we calculated for its discrete version  $P_n$ . Now  $x$  is continuously distributed. The probability to find the walker between  $x$  and  $x + dx$  is given by  $P(x)dx$ .

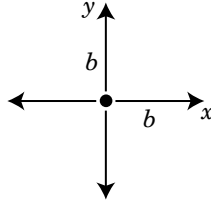
For a large  $N$ , the binomial distribution approaches a normal distribution. This rule applies to other discrete distributions as well and, in general, is called the **law of large numbers** or the **central limit theorem**. When  $N \gg 1$ , the final position  $x$  of the random walker is virtually continuously distributed along  $x$ .

## 1.2.2 Random Walks in Two and Three Dimensions

**1.2.2.1 Square Lattice** We consider a random walk on a square lattice extending in  $x$  and  $y$  directions with a lattice spacing  $b$ , as shown in Figure 1.7a. The random walker at a grid point chooses one of the four directions with an equal probability of  $1/4$  (Fig. 1.16). Each step is independent. Again, the random walker can visit the same site more than once (ideal). The move in one step can be expressed by a displacement  $\Delta \mathbf{r}_1 = [\Delta x_1, \Delta y_1]$ . Similarly to the random walker in one dimension,  $\langle \Delta x_1 \rangle = \langle \Delta y_1 \rangle = 0$  and hence  $\langle \Delta \mathbf{r}_1 \rangle = 0$ . The variances are  $\langle \Delta x_1^2 \rangle = \langle \Delta y_1^2 \rangle = b^2/2$ ; therefore, the mean square displacement is  $\langle \Delta \mathbf{r}_1^2 \rangle = b^2$ . In a total  $N$  steps starting at  $\mathbf{r} = 0$ , the statistics for the final position  $\mathbf{r}$  and the displacement  $\Delta \mathbf{r}$  are:  $\langle x \rangle = \langle \Delta x \rangle = 0$ ,  $\langle y \rangle = \langle \Delta y \rangle = 0$  and hence  $\langle \mathbf{r} \rangle = \langle \Delta \mathbf{r} \rangle = 0$ ;  $\langle x^2 \rangle = \langle \Delta x^2 \rangle = Nb^2/2$ ,  $\langle y^2 \rangle = \langle \Delta y^2 \rangle = Nb^2/2$  and hence  $\langle \mathbf{r}^2 \rangle = \langle \Delta \mathbf{r}^2 \rangle = Nb^2$ .

The  $x$  component of the position after the  $N$ -step random walk on the two-dimensional (2D) square lattice has a zero mean and a variance of  $Nb^2/2$ . When  $N \gg 1$ , the probability density  $P_x(\mathbf{r})$  for the  $x$  component approaches a normal distribution with the same mean and variance. Thus,

$$P_x(\mathbf{r}) = (\pi Nb^2)^{-1/2} \exp[-x^2/(Nb^2)] \quad (1.15)$$



**Figure 1.16.** Step motion in a two-dimensional random walk on a square lattice.

The  $y$ -component  $P_y(\mathbf{r})$  has a similar expression. When the two components are combined, we have the joint probability density  $P(\mathbf{r}) = P_x(\mathbf{r})P_y(\mathbf{r})$  as

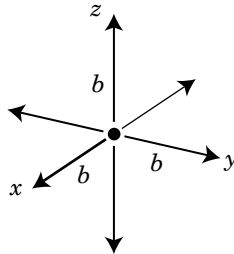
$$P(\mathbf{r}) = (\pi Nb^2)^{-1} \exp\left(-\frac{\mathbf{r}^2}{Nb^2}\right) \quad \text{2D random walk} \quad (1.16)$$

Again, the mean and the variance are held unchanged in the limiting procedure.

**1.2.2.2 Lattice in Three Dimensions** We place the random walker on a cubic lattice with a lattice spacing  $b$  in three dimensions, as shown in Figure 1.8. In each step, the random walker chooses one of the six directions with an equal probability of  $1/6$  (Fig. 1.17). The displacement in one step is expressed by  $\Delta\mathbf{r}_1 = [\Delta x_1, \Delta y_1, \Delta z_1]$ . Statistical properties of  $\Delta\mathbf{r}_1$  and their components are  $\langle\Delta\mathbf{r}_1\rangle = 0$ ,  $\langle\Delta x_1^2\rangle = \langle\Delta y_1^2\rangle = \langle\Delta z_1^2\rangle = b^2/3$ ; therefore,  $\langle\Delta\mathbf{r}_1^2\rangle = b^2$ . In a total  $N$  steps starting at  $\mathbf{r} = 0$ , the statistics for the final position  $\mathbf{r}$  and the displacement  $\Delta\mathbf{r}$  are  $\langle\mathbf{r}\rangle = \langle\Delta\mathbf{r}\rangle = 0$ ;  $\langle\Delta x^2\rangle = \langle\Delta y^2\rangle = \langle\Delta z^2\rangle = Nb^2/3$  and  $\langle\mathbf{r}^2\rangle = \langle\Delta\mathbf{r}^2\rangle = Nb^2$ .

The  $x$  component of the position after the  $N$ -step random walk on the three-dimensional (3D) cubic lattice has a zero mean and a variance of  $Nb^2/3$ . When  $N \gg 1$ , the probability density  $P_x(\mathbf{r})$  for the  $x$  component approaches that of a normal distribution with the same mean and variance. Thus,

$$P_x(\mathbf{r}) = (2\pi Nb^2/3)^{-1/2} \exp[-3x^2/(2Nb^2)] \quad (1.17)$$



**Figure 1.17.** Step motion in a three-dimensional random walk on a cubic lattice.

The other components have a similar expression. When the three components are combined, we have the joint probability density  $P(\mathbf{r}) = P_x(\mathbf{r})P_y(\mathbf{r})P_z(\mathbf{r})$  as

$$P(\mathbf{r}) = (2\pi Nb^2/3)^{-3/2} \exp\left(-\frac{3\mathbf{r}^2}{2Nb^2}\right) \quad \text{3D random walk} \quad (1.18)$$

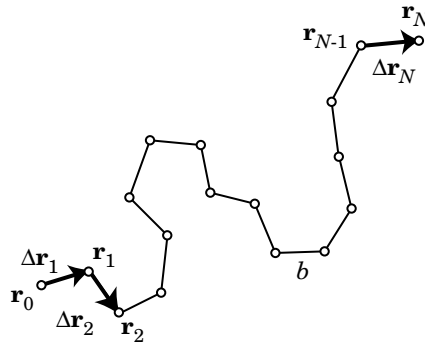
Note that  $P(\mathbf{r})$  depends only on  $|\mathbf{r}|$ ; i.e., the distribution of  $\mathbf{r}$  is isotropic.

The random walk is not limited to rectangular lattices. In the nonrectangular lattices such as a triangular lattice and a diamond lattice with lattice unit  $= b$ , we let the random walker choose one of the  $Z$  nearest-neighbor sites with an equal probability irrespective of its past (Markoffian). Then, the same statistics holds for  $\Delta\mathbf{r}_i$  as the one in the rectangular lattices:

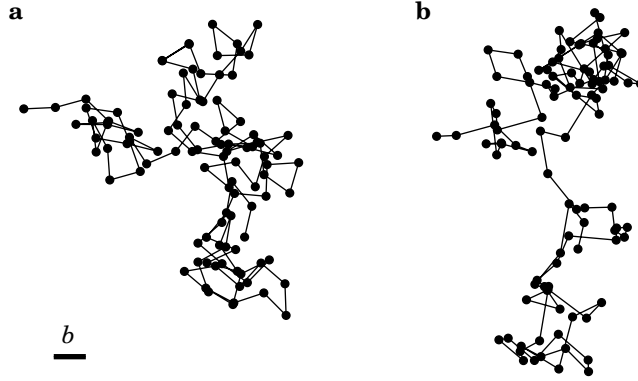
$$\langle \Delta\mathbf{r}_i \rangle = 0, \quad \langle \Delta\mathbf{r}_i \cdot \Delta\mathbf{r}_j \rangle = b^2 \delta_{ij} \quad (1.19)$$

In a total  $N$  steps,  $\langle \Delta\mathbf{r} \rangle = 0$  and  $\langle \Delta\mathbf{r}^2 \rangle = Nb^2$ . Then, for  $N \gg 1$ , the probability density for  $\mathbf{r}$  is given by the same equations (Eqs. 1.16 and 1.18 for the 2D and 3D lattices, respectively). The type of the lattice is irrelevant. When  $N$  is not sufficiently large, however,  $P(\mathbf{r})$  is different from lattice to lattice, reflecting its detailed structure. Note that  $b$  is the lattice unit, not its projection onto the  $x$ ,  $y$ , or  $z$  axis.

**1.2.2.3 Continuous Space** The random walks are not limited to those on a lattice. Here, we consider a random walker who jumps by a fixed distance  $b$ . The trajectory is shown in Figure 1.18 for a two-dimensional version of the continuous-space random walk. Starting at  $\mathbf{r}_0$ , the walker moves by  $\Delta\mathbf{r}_1, \Delta\mathbf{r}_2, \dots, \Delta\mathbf{r}_N$  to arrive at  $\mathbf{r}_N$  in a total  $N$  steps. When the direction is random in three dimensions, the trajectory represents a freely jointed chain (Table 1.1). Like a random walk on the lattice, the  $i$ th jump  $\Delta\mathbf{r}_i$  is not correlated with the  $j$ th jump  $\Delta\mathbf{r}_j$  if  $i \neq j$ . As long as  $\Delta\mathbf{r}_i$  satisfies Eq. 1.19, the displacement in a total  $N$  steps has the same statistical



**Figure 1.18.** Trajectory of a two-dimensional random walk of  $N$  steps with a fixed step displacement length  $b$ .



**Figure 1.19.** Example of a freely jointed chain (a) and a bead-spring model (b) of 100 steps with the same orientation of each pair of jumps in two dimensions. The bar shows the bond length  $b$ .

properties as a random walk on the cubic lattice:  $\langle \Delta \mathbf{r} \rangle = 0$  and  $\langle \Delta \mathbf{r}^2 \rangle = Nb^2$ . When  $N \gg 1$ , the probability density of the final position  $\mathbf{r}_N$  is given by

$$P(\mathbf{r}_N) = (2\pi Nb^2/3)^{-3/2} \exp\left(-\frac{3(\mathbf{r}_N - \mathbf{r}_0)^2}{2Nb^2}\right) \quad \text{3D random walk} \quad (1.20)$$

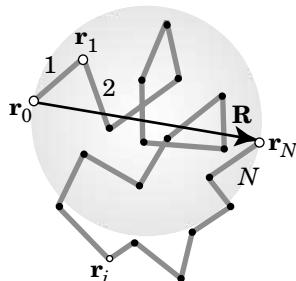
The step length does not have to be fixed to  $b$  either. Suppose the step length has some distribution, but each step follows the same distribution to yield  $\langle \Delta \mathbf{r}_i^2 \rangle = b^2$ . A typical trajectory of this type of random walk is seen in a bead-spring model. With a randomness in the orientation of  $\Delta \mathbf{r}_i$  and a common distribution for all of  $\Delta \mathbf{r}_i$ ,  $\Delta \mathbf{r}_i$  will satisfy Eq. 1.19. If  $\Delta \mathbf{r}_i$  and  $\Delta \mathbf{r}_j$  ( $i \neq j$ ) are not correlated, the final position  $\mathbf{r}_N$  follows the distribution given by Eq. 1.20.

Figure 1.19 compares a freely jointed chain with a fixed bond length  $b$  (also called a **segment length**) and a bead-spring model with  $\langle \Delta \mathbf{r}_i^2 \rangle = b^2$ , both in two dimensions. Examples of a 100-step random walk are shown. The bead-spring model can have greater density fluctuations for the same  $Nb^2$ .

## 1.2.3 Dimensions of Random-Walk Chains

**1.2.3.1 End-to-End Distance and Radius of Gyration** Here, we learn how to assess the dimension or the size of a polymer molecule. We consider a linear chain consisting of  $N$  bonds of length  $b$  (Fig. 1.20). The positions of the joints are denoted by  $\mathbf{r}_i$  ( $i = 0, 1, \dots, N$ ). The two ends of the  $i$ th bond are at  $\mathbf{r}_{i-1}$  and  $\mathbf{r}_i$ . It is convenient to define the **end-to-end vector**  $\mathbf{R}$  by

$$\mathbf{R} \equiv \mathbf{r}_N - \mathbf{r}_0 \quad (1.21)$$



**Figure 1.20.** End-to-end vector  $\mathbf{R}$  is defined by  $\mathbf{R} = \mathbf{r}_N - \mathbf{r}_0$  in the bead-stick model. The sphere with  $\mathbf{R}$  as its diameter contains most of the segments.

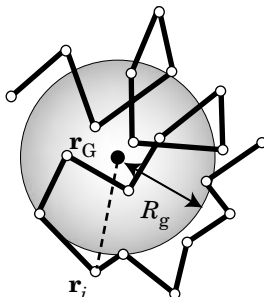
$\mathbf{R}$  is different for each configuration of the chain. Although the chain ends are not necessarily faced outward and therefore  $\mathbf{R}$  does not always span the largest dimension of the chain, its average length is a good measure for the overall chain dimension. The **root-mean-square end-to-end distance**  $R_F$  (or simply **end-to-end distance**) of the chain is the root mean square of  $\mathbf{R}$ :

$$R_F^2 = \langle \mathbf{R}^2 \rangle \equiv \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle \quad (1.22)$$

We can regard the whole chain as roughly being contained in a sphere of diameter  $R_F$ .

Another often used measure of the chain dimension is the **root-mean-square radius of gyration**  $R_g$  (or simply **radius of gyration**). Its square,  $R_g^2$ , is the second moment around the center of mass of the chain. The latter is defined as the mean square of the distance between the beads and the center of mass (Fig. 1.21). Roughly, the chain occupies a space of a sphere of radius  $R_g$ . The center of mass  $\mathbf{r}_G$  of the chain is given as

$$\mathbf{r}_G = \frac{1}{N+1} \sum_{i=0}^N \mathbf{r}_i \quad (1.23)$$



**Figure 1.21.** Center of mass  $\mathbf{r}_G$  and the radius of gyration  $R_g$  in the bead-stick model.



where we assume that beads have the same mass and are connected by massless bonds. Then,  $R_g$  is given by

$$R_g^2 = \left\langle \frac{1}{N+1} \sum_{i=0}^N (\mathbf{r}_i - \mathbf{r}_G)^2 \right\rangle = \frac{1}{N+1} \sum_{i=0}^N \langle (\mathbf{r}_i - \mathbf{r}_G)^2 \rangle \quad (1.24)$$

where the summation and averaging can be interchanged. As the name suggests,  $mR_g^2$  is the moment of inertia ( $m$  represents mass of the molecule) for rotational motion of this molecule around its center of mass.

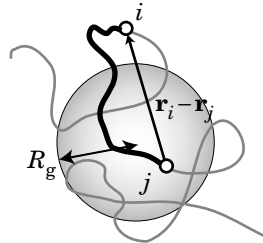
The following formula is useful:

$$R_g^2 = \frac{1}{2} \left\langle \frac{1}{(N+1)^2} \sum_{i,j=0}^N (\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle = \frac{1}{2(N+1)^2} \sum_{i,j=0}^N \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle \text{ any conformation} \quad (1.25)$$

This formula indicates that we can use the mean square distance between two monomers to obtain  $R_g$  in place of first calculating  $\mathbf{r}_G$  and then the mean square distance between  $\mathbf{r}_G$  and each monomer. Because summation with respect to  $i$  and  $j$  is another averaging, we can say that  $R_g^2$  is half of the average square distance between two monomers on the chain (Fig. 1.22).

We can prove the formula by using the following identity:

$$\begin{aligned} \sum_{i,j=0}^N (\mathbf{r}_i - \mathbf{r}_j)^2 &= \sum_{i,j=0}^N [(\mathbf{r}_i - \mathbf{r}_G) - (\mathbf{r}_j - \mathbf{r}_G)]^2 \\ &= \sum_{i,j=0}^N (\mathbf{r}_i - \mathbf{r}_G)^2 - 2 \sum_{i,j=0}^N (\mathbf{r}_i - \mathbf{r}_G) \cdot (\mathbf{r}_j - \mathbf{r}_G) + \sum_{i,j=0}^N (\mathbf{r}_j - \mathbf{r}_G)^2 \quad (1.26) \\ &= 2(N+1) \sum_{i=0}^N (\mathbf{r}_i - \mathbf{r}_G)^2 - 2 \sum_{i=0}^N (\mathbf{r}_i - \mathbf{r}_G) \cdot \sum_{j=0}^N (\mathbf{r}_j - \mathbf{r}_G) \\ &= 2(N+1) \sum_{i=0}^N (\mathbf{r}_i - \mathbf{r}_G)^2 \end{aligned}$$



**Figure 1.22.** The mean square distance between two monomers  $i$  and  $j$  is twice as large as  $R_g^2$ .

where Eq. 1.23 was used. This transformation does not assume any specific chain model. Equation 1.25 applies therefore to any chain conformation.

Note that  $R_F$  is defined for linear chains only, but  $R_g$  can be defined for any chain architecture including nonlinear chains such as branched chains. In this sense,  $R_g$  gives a more universal measure for the chain dimension.

**1.2.3.2 Dimensions of Ideal Chains** Now we obtain  $R_F$  and  $R_g$  for ideal chains whose conformations are given as trajectories of random walkers. They include a random walk on a lattice, a freely jointed chain, a bead-spring model, and any other model that satisfies the requirement of Markoffian property (Eq. 1.19). The bond vector  $\mathbf{r}_i - \mathbf{r}_{i-1}$  of the  $i$ th bond is then the displacement vector  $\Delta\mathbf{r}_i$  of the  $i$ th step. We assume Eq. 1.19 only. Then the end-to-end distance is  $Nb^2$ . To calculate  $R_g$ , we note that a part of the ideal chain is also ideal. The formula of the mean square end-to-end distance we obtained for a random walk applies to the mean square distance between the  $i$ th and  $j$ th monomers on the chain just by replacing  $N$  with  $|i - j|$ :

$$\boxed{\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle = b^2|i - j| \quad \text{ideal chain}} \quad (1.27)$$

From Eqs. 1.25 and 1.27, we can calculate the radius of gyration of the chain as

$$\begin{aligned} 2R_g^2 &= \frac{1}{(N+1)^2} \sum_{i,j=0}^N b^2|i - j| = \frac{2b^2}{(N+1)^2} \sum_{i=0}^N \sum_{j=0}^i (i - j) \\ &= \frac{2b^2}{(N+1)^2} \sum_{i=0}^N \frac{1}{2}i(i+1) = b^2 \frac{N(N+2)}{3(N+1)} \end{aligned} \quad (1.28)$$

Thus, we find for large  $N$  ideal chains with no correlations between bonds have the dimensions of

$$\boxed{R_F^2 = b^2N, \quad R_g^2 = \frac{1}{6}b^2N \quad \text{ideal chain, } N \gg 1} \quad (1.29)$$

The ratio of  $R_F$  to  $R_g$  is  $6^{1/2} \cong 2.45$  for the ideal chain, close to the diameter to radius ratio.

Both  $R_F^2$  and  $R_g^2$  consist of  $x$ ,  $y$ , and  $z$  components. In Section 1.2.2, we have seen this property for  $R_F^2$  already. The  $x$  component of  $R_g^2$  is defined by

$$R_{gx}^2 = \left\langle \frac{1}{N+1} \sum_{i=0}^N (x_i - x_G)^2 \right\rangle = \frac{1}{N+1} \sum_{i=0}^N \langle (x_i - x_G)^2 \rangle \quad (1.30)$$

where  $x_i$  and  $x_G$  are the  $x$  components of  $\mathbf{r}_i$  and  $\mathbf{r}_G$ , respectively. If there is no preferred orientation of the chain,  $\langle (x_i - x_G)^2 \rangle = \langle (\mathbf{r}_i - \mathbf{r}_G)^2 \rangle / 3$ . Then,  $R_{gx}^2 = R_g^2 / 3$ .

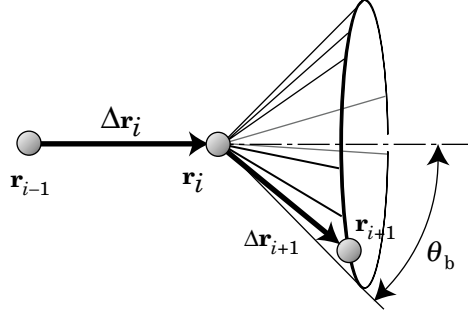


Figure 1.23. Bond vectors in the bead-stick model with a fixed bond angle.

**1.2.3.2 Dimensions of Chains with Short-Range Interactions** Now we lift the condition of  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle = b^2 \delta_{ij}$  and consider a bead-stick model with a restriction on the choice of the bond angle. In Figure 1.23, the angle  $\theta$  between two adjacent bond vectors (bond angle =  $\pi - \theta$ ) is fixed to  $\theta_b (>0)$ , but there is no restriction on the dihedral angle (freely rotating chain; see Table 1.1). The next bead ( $\mathbf{r}_{i+1}$ ) can be anywhere on the circular base of a cone. Then,  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_{i+1} \rangle = b^2 \cos \theta_b$ .

To calculate  $\langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_{i+1} \rangle$ , we first obtain  $\langle \Delta \mathbf{r}_{i+1} \rangle_{\Delta \mathbf{r}_i}$ , the average of  $\Delta \mathbf{r}_{i+1}$  for a given  $\Delta \mathbf{r}_i$ .<sup>1</sup> We decompose  $\Delta \mathbf{r}_{i+1}$  into a component parallel to  $\Delta \mathbf{r}_i$  and a component perpendicular to  $\Delta \mathbf{r}_i$  (see Fig. 1.24). The parallel component is  $(\cos \theta_b) \Delta \mathbf{r}_i$ , common to all dihedral angles. The perpendicular component is different from one orientation to another orientation of  $\Delta \mathbf{r}_{i+1}$ , but the randomness in the dihedral angle makes the perpendicular component uniformly distributed on a plane perpendicular to  $\Delta \mathbf{r}_i$ . Thus,  $\langle \Delta \mathbf{r}_{i+1} \rangle_{\Delta \mathbf{r}_i} = (\cos \theta_b) \Delta \mathbf{r}_i$ . Next, we calculate  $\langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_{i+1} \rangle$  in two steps:  $\langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_{i+1} \rangle = \langle \Delta \mathbf{r}_{i-1} \cdot \langle \Delta \mathbf{r}_{i+1} \rangle_{\Delta \mathbf{r}_i} \rangle$ , where the interior bracket of the right-hand side refers to the average for a given  $\Delta \mathbf{r}_i$  and the exterior bracket refers to that

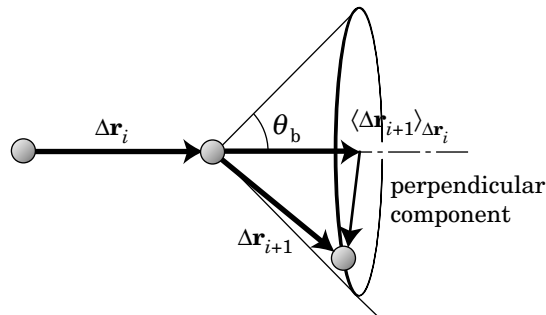


Figure 1.24. Average of  $\Delta \mathbf{r}_{i+1}$  for a given  $\Delta \mathbf{r}_i$ . The perpendicular component averages to zero.

for a given  $\Delta\mathbf{r}_{i-1}$  (or without any condition). Then,  $\langle\Delta\mathbf{r}_{i-1}\cdot\Delta\mathbf{r}_{i+1}\rangle = b^2\cos^2\theta_b$ . Repeating the same procedure, we obtain

$$\langle\Delta\mathbf{r}_i\cdot\Delta\mathbf{r}_j\rangle = b^2\cos^{|i-j|}\theta_b \quad (1.31)$$

The correlation diminishes exponentially with an increasing distance between the two bonds along the chain contour. The displacement in a total  $N$  steps is

$$\begin{aligned} R_F^2 = \langle\Delta\mathbf{r}^2\rangle &= \sum_{i,j=1}^N \langle\Delta\mathbf{r}_i\cdot\Delta\mathbf{r}_j\rangle = \sum_{i,j=1}^N b^2\cos^{|i-j|}\theta_b = b^2\left[N + 2\sum_{i=1}^{N-1}\sum_{j=i+1}^N \cos^{j-i}\theta_b\right] \\ &= b^2N\frac{1+\cos\theta_b}{1-\cos\theta_b} - 2b^2\cos\theta_b\frac{1-\cos^N\theta_b}{(1-\cos\theta_b)^2} \end{aligned} \quad (1.32)$$

When  $N \gg 1$ ,

$$\boxed{R_F^2 = b^2N\frac{1+\cos\theta_b}{1-\cos\theta_b} \quad \text{bond angle} = \pi - \theta_b} \quad (1.33)$$

When  $\theta_b$  is the tetrahedral angle,  $\cos\theta_b = 1/3$ . Then,  $R_F^2 = 2Nb^2$ .

A smaller  $\theta_b$  denotes that the bond vector changes its orientation by a smaller angle, effectively making the chain stiffer. Equation 1.33 demonstrates that a stiffer chain has a longer end-to-end distance, a reasonable result. A restriction on the local correlation of the bond direction does not change the proportionality between  $R_F$  and  $N^{1/2}$ . Thus we can regard the chain as consisting of freely jointed bonds of an effective bond length of  $b_{\text{eff}} = b[(1+\cos\theta_b)/(1-\cos\theta_b)]^{1/2}$ . This equivalence allows us to estimate  $R_g$  in a simple way: From Eq. 1.29,  $R_g^2$  is 1/6 of the value of  $R_F^2$  given by Eq. 1.33. It is possible to obtain an exact formula for  $R_g^2$  that applies to any  $N$ .

As seen in this example, short-range interactions such as the restriction on the bond angle do not deprive the chain of the characteristics of the ideal chain. Other examples of the short-range interactions include a restriction on the dihedral angle. The short-range interactions are only between monomers that are close to each other along the chain backbone. The correlation between the bond orientations decreases with an increasing distance along the backbone, as we saw in Eq. 1.31.

#### 1.2.4 PROBLEMS

**Problem 1.1:** When we obtained Eq. 1.16, we implicitly assumed that  $\Delta x$  and  $\Delta y$  were uncorrelated. This assumption is, however, correct only when  $N \gg 1$ . In each step,  $\Delta x_1$  and  $\Delta y_1$  are correlated; When the random walker moves in the  $y$  direction,  $\Delta x_1 = 0$ . Then,  $\langle\Delta x_1^2\Delta y_1^2\rangle = 0$  is not equal to  $\langle\Delta x_1^2\rangle\langle\Delta y_1^2\rangle = (b^2/2)^2$ . Show that  $\langle\Delta x^2\Delta y^2\rangle = \langle\Delta x^2\rangle\langle\Delta y^2\rangle$  when  $N \gg 1$ .

**Solution 1.1:**

$$\begin{aligned}
\langle \Delta x^2 \Delta y^2 \rangle &= \sum_i \sum_j \sum_k \sum_l \langle \Delta x_i \Delta x_j \Delta y_k \Delta y_l \rangle = \sum_{i=j=k=l} \langle \Delta x_i \Delta x_j \Delta y_k \Delta y_l \rangle \\
&= \sum_{i=j=k=l} \langle \Delta x_i \Delta x_j \Delta y_k \Delta y_l \rangle + \sum_{i=j \neq k=l} \langle \Delta x_i \Delta x_j \Delta y_k \Delta y_l \rangle \\
&= 0 + N(N-1) \langle \Delta x_1^2 \rangle \langle \Delta y_2^2 \rangle = N(N-1)(b^2/2)^2
\end{aligned}$$

$\langle \Delta x^2 \Delta y^2 \rangle$  approaches  $(Nb^2/2)^2 = \langle \Delta x^2 \rangle \langle \Delta y^2 \rangle$  as  $N \rightarrow \infty$ .

**Problem 1.2:** Find a formula similar to Eq. 1.25 that allows us to calculate  $R_g^2$  without explicitly obtaining  $\mathbf{r}_G$  for a linear polymer chain in which mass  $m_i$  of the  $i$ th monomer may be different from monomer to monomer. Here,  $R_g^2$  is the average of the second moment around  $\mathbf{r}_G$ , weighted by the mass of each monomer.

**Solution 1.2:** Let  $M = \sum_{i=0}^N m_i$ , then  $\mathbf{r}_G = \frac{1}{M} \sum_{i=0}^N m_i \mathbf{r}_i$

$R_g^2$  for this polymer chain is defined as

$$R_g^2 = \left\langle \frac{1}{M} \sum_{i=0}^N m_i (\mathbf{r}_i - \mathbf{r}_G)^2 \right\rangle$$

By definition, it is rewritten to

$$R_g^2 = \left\langle \frac{1}{M} \sum_{i=0}^N m_i \mathbf{r}_i^2 - \mathbf{r}_G^2 \right\rangle$$

Since

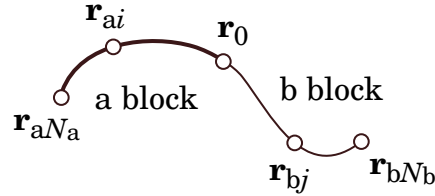
$$\frac{1}{2} \sum_{i,j=0}^N m_i m_j (\mathbf{r}_i - \mathbf{r}_j)^2 = M \sum_{i=0}^N m_i \mathbf{r}_i^2 - (M \mathbf{r}_G)^2$$

we obtain

$$R_g^2 = \frac{1}{2} \left\langle \frac{1}{M^2} \sum_{i,j=0}^N m_i m_j (\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle$$

**Problem 1.3:** In an a–b diblock copolymer, the monomer molecular weights in the two blocks are  $M_{1a}$  and  $M_{1b}$  and the degrees of polymerization are  $N_a$  and  $N_b$  ( $N_a, N_b \gg 1$ ), respectively. The two blocks are ideal chains with a segment

length  $b_a$  and  $b_b$ , respectively. Calculate  $R_g^2$  of the whole chain. Neglect the joint.



**Solution 1.3:**

The molecular weight  $M$  of the whole chain is given by  $M = M_{1a}N_a + M_{1b}N_b$ . Now we use the formula we obtained in Problem 1.2:

$$2M^2R_g^2 = \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} M_{1a}^2 \langle (\mathbf{r}_{ai} - \mathbf{r}_{aj})^2 \rangle + 2 \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} M_{1a}M_{1b} \langle (\mathbf{r}_{ai} - \mathbf{r}_{bj})^2 \rangle + \sum_{i=1}^{N_b} \sum_{j=1}^{N_b} M_{1b}^2 \langle (\mathbf{r}_{bi} - \mathbf{r}_{bj})^2 \rangle$$

where  $\mathbf{r}_{ai}$  and  $\mathbf{r}_{bj}$  are the positions of monomers  $i$  and  $j$  on a block and b block, respectively, with  $\mathbf{r}_{a0} = \mathbf{r}_{b0} = \mathbf{r}_0$  being the joint. In the second term, the mean square distance between monomers on different blocks is

$$\langle (\mathbf{r}_{ai} - \mathbf{r}_{bj})^2 \rangle = \langle (\mathbf{r}_{ai} - \mathbf{r}_0)^2 \rangle + \langle (\mathbf{r}_0 - \mathbf{r}_{bj})^2 \rangle = b_a^2 i + b_b^2 j$$

Thus,

$$2M^2R_g^2 = M_{1a}^2 \sum_{i=1}^{N_a} \sum_{j=1}^{N_a} b_a^2 |i-j| + 2M_{1a}M_{1b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} (b_a^2 i + b_b^2 j) + M_{1b}^2 \sum_{i=1}^{N_b} \sum_{j=1}^{N_b} b_b^2 |i-j|$$

$$\cong M_{1a}^2 b_a^2 \frac{1}{3} N_a^3 + M_{1a}M_{1b} N_a N_b (b_a^2 N_a + b_b^2 N_b) + M_{1b}^2 b_b^2 \frac{1}{3} N_b^3$$

**Problem 1.4:** In the freely rotating chain with bond length  $b$  and bond angle  $\pi - \theta_b$ , the dihedral angle is unrestricted. How do  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_{i+1} \rangle$ ,  $\langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_{i+1} \rangle$ , and  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle$  change from those for the freely rotating chain when the dihedral angles are restricted to *trans*, *gauche* +, and *gauche* -, but the three angles are chosen with equal probabilities?

**Solution 1.4:**

$$\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_{i+1} \rangle = b^2 \cos \theta_b$$

For a given  $\Delta \mathbf{r}_i$ ,  $\langle \Delta \mathbf{r}_{i+1} \rangle_{\Delta \mathbf{r}_i} = (\cos \theta_b) \Delta \mathbf{r}_i$  because the average of the components perpendicular to  $\Delta \mathbf{r}_i$  is zero. Then,  $\langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_{i+1} \rangle = \langle \Delta \mathbf{r}_{i-1} \cdot \Delta \mathbf{r}_i \rangle \cos \theta_b = b^2 \cos^2 \theta_b$ . Likewise,  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle = b^2 \cos^{|i-j|} \theta_b$ . There are no changes.

### 1.3 GAUSSIAN CHAIN

#### 1.3.1 What is a Gaussian Chain?

**1.3.1.1 Gaussian Distribution** We have learned that, in the limit of  $N \rightarrow \infty$ , all ideal chains become identical and follow the normal distribution as long as each step satisfies the same statistics given by Eq. 1.19. We define a **Gaussian chain** by extending the ideality to short parts of the chain. In the Gaussian chain, any two points  $\mathbf{r}_1$  and  $\mathbf{r}_2$  on the chain follow a **Gaussian distribution**  $G(\mathbf{r}_1, \mathbf{r}_2; n)$ . For a given  $\mathbf{r}_2$ , the probability density for  $\mathbf{r}_1$  is given as

$$G(\mathbf{r}_1, \mathbf{r}_2; n) = (2\pi n b^2/3)^{-3/2} \exp\left(-\frac{3(\mathbf{r}_1 - \mathbf{r}_2)^2}{2n b^2}\right) \quad (1.34)$$

where the partial chain between the two points consists of  $n$  ( $n \leq N$ ) segments of segment length  $b$ . We do not limit  $n$  to integers but allow it to change continuously.

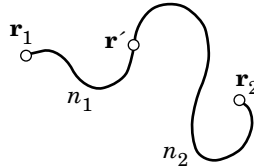
Essentially  $G(\mathbf{r}_1, \mathbf{r}_2; n)d\mathbf{r}_1$  is a **transition probability** for a point  $\mathbf{r}_2$  to move into a small volume  $d\mathbf{r}_1$  around  $\mathbf{r}_1$  in  $n$  steps. Likewise,  $G(\mathbf{r}_1, \mathbf{r}_2; n)d\mathbf{r}_2$  gives a probability for the chain of  $n$  segments with one end at  $\mathbf{r}_1$  to have the other end in a small volume  $d\mathbf{r}_2$  around  $\mathbf{r}_2$ . We can show that  $G(\mathbf{r}_1, \mathbf{r}_2; n)$  satisfies the following multiplication law:

$$\int G(\mathbf{r}_1, \mathbf{r}'; n_1)G(\mathbf{r}', \mathbf{r}_2; n_2) d\mathbf{r}' = G(\mathbf{r}_1, \mathbf{r}_2; n_1 + n_2) \quad (1.35)$$

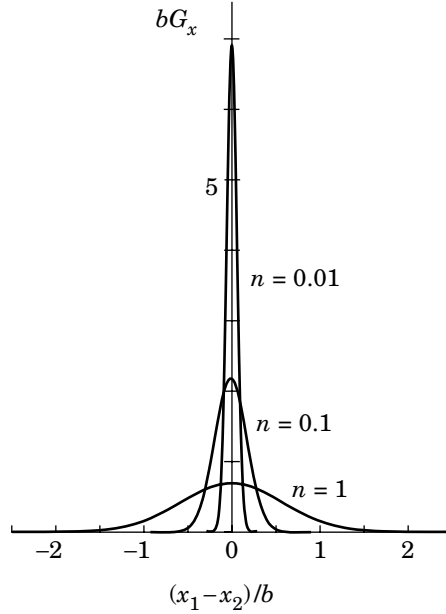
This law states that a Gaussian chain of  $n_1$  segments and another Gaussian chain of  $n_2$  segments can be joined into a single Gaussian chain of  $n_1 + n_2$  segments, as illustrated in Figure 1.25. Alternatively, a Gaussian chain of  $N$  segments can be divided into two parts of  $n$  segments and  $N - n$  segments.

Just as in  $P(\mathbf{r})$  for the three-dimensional random walk on a discrete lattice (Eq. 1.18),  $G(\mathbf{r}_1, \mathbf{r}_2; n)$  consists of three independent factors:

$$G(\mathbf{r}_1, \mathbf{r}_2; n) = G_x(x_1, x_2; n)G_y(y_1, y_2; n)G_z(z_1, z_2; n) \quad (1.36)$$



**Figure 1.25.** Two jointed Gaussian chains with  $n_1$  and  $n_2$  segments are equivalent to a single Gaussian chain with  $n_1 + n_2$  segments.



**Figure 1.26.** As  $n$  decreases to 0,  $G_x$  approaches the delta function at  $x_1 - x_2 = 0$ .

where, for example, the  $x$  component

$$G_x(x_1, x_2; n) = (2\pi mb^2/3)^{-1/2} \exp\left(-\frac{3(x_1 - x_2)^2}{2nb^2}\right) \quad (1.37)$$

is the one-dimensional transition probability from  $x_2$  to  $x_1$  in  $n$  steps. When the Gaussian chain is projected onto  $x, y$  plane, the projection forms a two-dimensional Gaussian chain with  $n$  and  $(2/3)^{1/2}b$ . We can find the segment length,  $(2/3)^{1/2}b$ , by comparing  $G_x G_y$  with Eq. 1.16.

Unlike the ideal random walk, the Gaussian chain is defined also in the limit of  $n \rightarrow 0$ . As shown in Figure 1.26,  $G_x(x_1, x_2; n)$  narrows at around  $x_1 - x_2 = 0$  as  $n$  approaches 0 without changing the area under the curve (normalization). Then,  $G_x(x_1, x_2; 0)$  must be a delta function of  $x_1$  centered at  $x_2$ :

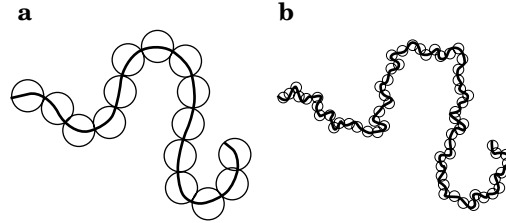
$$G_x(x_1, x_2; 0) = \delta(x_1 - x_2) \quad (1.38)$$

See Appendix A1 for the delta function. The same limiting procedure is applied to  $G_y$  and  $G_z$ . Combining the three factors,

$$G(\mathbf{r}_1, \mathbf{r}_2; 0) = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (1.39)$$

The Gaussian distribution is of the same functional form as the solution of a





**Figure 1.27.** The contour length of a Gaussian chain depends on the number of segments. Compared with panel **a**, panel **b** has a more detailed contour and therefore has a longer contour. The end-to-end distance is common to both.

diffusion equation, which we will learn in Section 3.2. Thus,  $G(\mathbf{r}, \mathbf{r}'; n)$  satisfies

$$\left[ \frac{\partial}{\partial n} - (b^2/6)\nabla^2 \right] G(\mathbf{r}, \mathbf{r}'; n) = \delta(n) \delta(\mathbf{r} - \mathbf{r}') \quad (1.40)$$

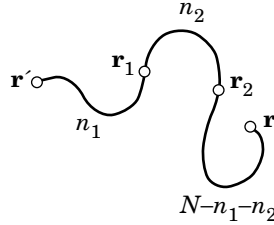
where  $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$  is the Laplacian. The right-hand side is zero except for  $n = 0$ .

**1.3.1.2 Contour Length** Each segment of the Gaussian chain has a root-mean-square length of  $b$ . It may appear that the whole chain of  $N$  segments has a contour length of  $Nb$ , but this is wrong. The contour length is not defined in the Gaussian chain because the choice of  $N$  is arbitrary and the apparent contour length  $Nb$  depends on  $N$ . This situation is illustrated in Figure 1.27. As  $N$  increases and the trajectory becomes more detailed, the path length increases, resulting in an increase of  $Nb$ . What is held unchanged in the Gaussian chain between different choices of  $N$  is  $Nb^2$ . A Gaussian chain should rather be viewed as a hypothetical chain with the end-to-end distance  $R_F$  that, when coarse-grained into  $N$  segments, each segment follows a Gaussian distribution with the mean square end-to-end length of  $R_F^2/N$ .

The Gaussian chain has another unrealistic property. In Eq. 1.34,  $\mathbf{r}_1$  and  $\mathbf{r}_2$  can be separated by more than  $nb$ , although its probability is low when  $n$  is large (see Problem 1.7). Despite this shortcoming, the Gaussian chain is the most preferred model in calculating various physical quantities in theories. It often happens that we can obtain an explicit analytical expression for the quantity in question only in the Gaussian chain model. It is the only model that gives an exact yet simple expression for the density of the chain ends, for instance.

### 1.3.2 Dimension of a Gaussian Chain

**1.3.2.1 Isotropic Dimension** Because a Gaussian chain is ideal, the end-to-end distance and the radius of gyration are given by Eq. 1.29. Here, we use Eq. 1.34 to confirm these dimensions for a Gaussian chain consisting of  $N$  segments of length  $b$ .



**Figure 1.28.** Two points,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ , on the Gaussian chain of  $N$  segments.

A partial chain of a Gaussian chain is also a Gaussian. The mean square distance between two monomers separated by  $n$  segments is calculated as follows:

$$\begin{aligned} \langle (\mathbf{r}_1 - \mathbf{r}_2)^2 \rangle &= \int (\mathbf{r}_1 - \mathbf{r}_2)^2 G(\mathbf{r}_1, \mathbf{r}_2; n) d(\mathbf{r}_1 - \mathbf{r}_2) \\ &= (2\pi n b^2/3)^{-3/2} \int_0^\infty r^2 \exp\left(-\frac{3r^2}{2nb^2}\right) 4\pi r^2 dr = nb^2 \end{aligned} \quad (1.41)$$

The three components of  $\langle (\mathbf{r}_1 - \mathbf{r}_2)^2 \rangle$  are equal:

$$\langle (x_1 - x_2)^2 \rangle = \langle (y_1 - y_2)^2 \rangle = \langle (z_1 - z_2)^2 \rangle = nb^2/3 \quad (1.42)$$

These relationships apply to the whole chain ( $n = N$ ) as well.

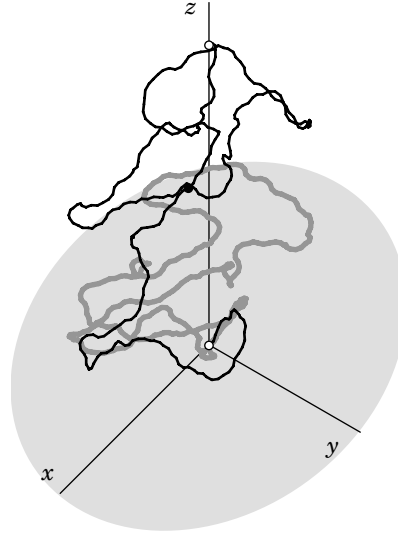
We calculate  $R_g^2$  of the whole chain by first placing  $\mathbf{r}_1$  and  $\mathbf{r}_2$  on the chain, as shown in Figure 1.28, and then taking average of  $\langle (\mathbf{r}_1 - \mathbf{r}_2)^2 \rangle = n_2 b^2$  with respect to  $n_1$  and  $n_2$  (also shown in Fig. 1.28). The random variables  $n_1$  and  $n_2$  are uniformly distributed in  $[0, N]$  and  $[0, N - n_1]$ , respectively. Using a formula similar to Eq. 1.25, we obtain  $R_g^2$  as

$$R_g^2 = \frac{1}{2} \frac{2}{N^2} \int_0^N dn_1 \int_0^{N-n_1} dn_2 \langle (\mathbf{r}_1 - \mathbf{r}_2)^2 \rangle = \frac{1}{N^2} \int_0^N dn_1 \int_0^{N-n_1} n_2 b^2 dn_2 = \frac{1}{6} b^2 N \quad (1.43)$$

The above results are identical to those in Eq. 1.29, as required. Again,  $x$ ,  $y$ , and  $z$  components of  $R_g^2$  are equal.

**1.3.2.2 Anisotropy** The Gaussian chain is isotropic when averaged over many conformations and orientations. In the crudest approximation, we can regard it as a sphere of radius  $R_g$ . The instantaneous shape of the chain, however, does not look like a sphere. We will examine its anisotropic shape here.

In Figure 1.29, a Gaussian chain shown as a dark line is placed with its end-to-end vector on the  $z$  axis. We estimate how much the segments are away from the  $z$  axis. The distance from the  $z$  axis is better represented by the projection of the chain onto the  $x,y$ -plane, which is shown as a gray line. To evaluate the distance,



**Figure 1.29.** Gaussian chain with its end-to-end vector on the  $z$  axis is shown as a dark line. Its projection onto the  $x,y$ -plane is shown as a gray line. The small filled circle on the  $y,z$ -plane is the midpoint of the chain.

we consider the conditional distribution  $G_{0\mathbf{R}}(\mathbf{r}; n)$  for the position  $\mathbf{r}$  of the  $n$ th segment ( $0 \leq n \leq N$ ), when one of the ends is at the origin and the other at  $\mathbf{R} = [0, 0, R_F]$  on the  $z$  axis. It is given by

$$G_{0\mathbf{R}}(\mathbf{r}; n) = \frac{G(\mathbf{r}, 0; n) G(\mathbf{R}, \mathbf{r}; N - n)}{G(\mathbf{R}, 0; N)} \quad (1.44)$$

Note that this probability distribution is already normalized. Using Eq. 1.34, we can rearrange the right-hand side into (Problem 1.8)

$$G_{0\mathbf{R}}(\mathbf{r}; n) = G\left(\mathbf{r}, \frac{n}{N} \mathbf{R}; \frac{n(N - n)}{N}\right) \quad (1.45)$$

We take the segment at the midpoint of the two chain ends,  $n = N/2$ . Its distribution

$$G_{0\mathbf{R}}(\mathbf{r}; N/2) = G(\mathbf{r}, \mathbf{R}/2; N/4) \quad (1.46)$$

is identical to the distribution for the end of the  $N/4$ -segment Gaussian chain with the one end at  $\mathbf{R}/2$ . Because  $\mathbf{R}/2 = [0, 0, R_F/2]$  in our arrangement, the average of  $x^2 + y^2$  is equal to  $2/3$  of the mean square end-to-end distance. It is calculated as

$$\langle x^2 + y^2 \rangle = \frac{N}{4} b^2 \times \frac{2}{3} = \frac{1}{6} N b^2 \quad (1.47)$$

The excursion into  $x$  and  $y$  directions is much shorter than  $R_F = bN^{1/2}$ , the principal extension of the chain in the  $z$  direction. It is premature to say that the Gaussian chain resembles a football, however. The cross section of the Gaussian chain is not circular, as shown below.

Now we rotate the chain around the  $z$  axis until the midpoint  $\mathbf{r}$  sits on the  $y,z$ -plane. We consider how much the midpoint of the half chain, i.e., the quarterpoint of the original chain, extends in the  $x$  direction. As in Eq. 1.46, the probability density of the quarterpoint  $\mathbf{r}_1$  is given by

$$\frac{G(\mathbf{r}_1, 0; N/4)G(\mathbf{r}, \mathbf{r}_1; N/4)}{G(\mathbf{r}, 0; N/2)} = G(\mathbf{r}_1; \mathbf{r}/2; N/8) \quad (1.48)$$

This distribution is equivalent to the one for the end of a Gaussian chain that consists of  $N/8$  segments and has the other end at  $\mathbf{r}/2$ . Because  $\mathbf{r}/2 = [0, y/2, z/2]$ , the mean square of  $x_1$  is calculated as

$$\langle x_1^2 \rangle = \frac{N}{8} b^2 \times \frac{1}{3} = \frac{1}{24} Nb^2 \quad (1.49)$$

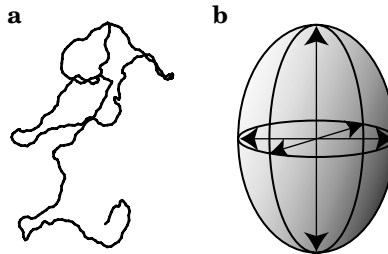
The overall shape of the Gaussian chain is thus approximated by an ellipsoidal body with the lengths of its principal axes in the ratio of

$$R_F: \langle x^2 + y^2 \rangle^{1/2}: \langle x_1^2 \rangle^{1/2} = 1: \frac{1}{\sqrt{6}}: \frac{1}{2\sqrt{6}} \cong 1: 0.4: 0.2 \quad (1.50)$$

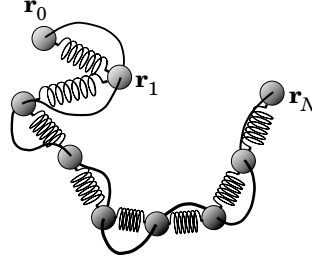
Figure 1.30 depicts the ellipsoid. However, the Gaussian chain in solution does not behave like a solid ellipsoid. The overall shape is constantly changing. At a given time, the shape is different from chain to chain. The overall shape can be either more spherical or more elongated than the one shown in the figure.

### 1.3.3 Entropy Elasticity

**1.3.3.1 Boltzmann Factor** The Gaussian chain of  $N$  segments is physically realized by a bead-spring model consisting of  $N$  independent springs of a force constant



**Figure 1.30.** An instantaneous shape of the Gaussian chain (a) is approximated by an ellipsoid (b).



**Figure 1.31.** Gaussian chain of  $N$  segments is realized by a bead-spring model in which  $N$  springs are connected in series.

$k_{\text{sp}}$  (Fig. 1.31). Let the beads be at  $\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N$ . The potential energy  $U$  of the chain resides in the elastic energy of the springs:

$$U(\mathbf{r}_0, \dots, \mathbf{r}_N) = \frac{1}{2} k_{\text{sp}} \sum_{n=1}^N (\mathbf{r}_n - \mathbf{r}_{n-1})^2 \quad (1.51)$$

The kinetic energy is negligible in a viscous solvent where the motion is overdamped. Then, the Boltzmann distribution with Eq. 1.51 gives the probability (unnormalized) for a specific arrangement of  $\mathbf{r}_0, \dots, \mathbf{r}_N$ :

$$\exp[-U(\mathbf{r}_0, \dots, \mathbf{r}_N)/k_{\text{B}}T] = \prod_{n=1}^N \exp\left[-\frac{k_{\text{sp}}}{2k_{\text{B}}T} (\mathbf{r}_n - \mathbf{r}_{n-1})^2\right] \quad (1.52)$$

where  $k_{\text{B}}$  is the Boltzmann constant and  $T$  the temperature. Each factor,  $\exp[-(k_{\text{sp}}/2k_{\text{B}}T)(\mathbf{r}_n - \mathbf{r}_{n-1})^2]$ , is identical to the Gaussian distribution of a single segment given by Eq. 1.34 with  $n = 1$ , when

$$b^2 = \frac{3k_{\text{B}}T}{k_{\text{sp}}} \quad (1.53)$$

The force constant is equal to  $3k_{\text{B}}T/b^2$ , where  $b^2$  is the mean square length of the spring.

With Eq. 1.53, the Boltzmann factor given by Eq. 1.52 can be rewritten to an expression that does not involve  $k_{\text{sp}}$ :

$$\exp[-U(\mathbf{r}_0, \dots, \mathbf{r}_N)/k_{\text{B}}T] = \exp\left[-\frac{3}{2b^2} \sum_{n=1}^N (\mathbf{r}_n - \mathbf{r}_{n-1})^2\right] \quad (1.54)$$

We can take  $i$  to be continuous and write

$$\exp[-U(\mathbf{r}_0, \dots, \mathbf{r}_N)/k_{\text{B}}T] = \exp\left[-\frac{3}{2b^2} \int_0^N \left(\frac{\partial \mathbf{r}}{\partial n}\right)^2 dn\right] \quad (1.55)$$

This factor gives a statistical weight for each conformation given as a continuous line,  $\mathbf{r}(n)$ .

**1.3.3.2 Elasticity** We model the whole chain by a single spring. Its force constant is given by

$$k_{\text{sp}} = \frac{3k_{\text{B}}T}{R_{\text{F}}^2} = \frac{3k_{\text{B}}T}{Nb^2} \quad (1.56)$$

The two ends of the Gaussian chain behave like two points connected by a spring with a force constant of  $3k_{\text{B}}T/R_{\text{F}}^2$ . Another way to look at this elastic property is described below.

Equation 1.34 allows us to express the entropy  $S$  of the Gaussian chain as a function of the two ends at  $\mathbf{r}$  and  $\mathbf{r}'$ :

$$S = \text{const.} + k_{\text{B}} \ln G = \text{const.} - \frac{3k_{\text{B}}}{2R_{\text{F}}^2} (\mathbf{r} - \mathbf{r}')^2 \quad (1.57)$$

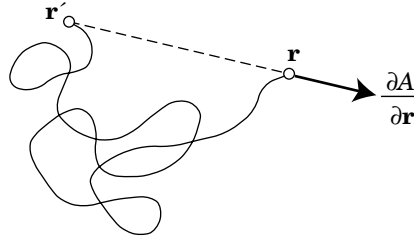
Then, the Helmholtz free energy  $A$  of the chain is calculated as

$$A = \text{const.} + \frac{3k_{\text{B}}T}{2R_{\text{F}}^2} (\mathbf{r} - \mathbf{r}')^2 \quad (1.58)$$

The chain tries to decrease the magnitude of  $\mathbf{r} - \mathbf{r}'$  to minimize  $A$  and thus approach the equilibrium. To hold the end-to-end vector at a nonzero  $\mathbf{r} - \mathbf{r}'$  in Figure 1.32 requires a force of

$$\frac{\partial A}{\partial \mathbf{r}} = \frac{3k_{\text{B}}T}{R_{\text{F}}^2} (\mathbf{r} - \mathbf{r}') \quad (1.59)$$

which is nothing more than the spring force of a force constant  $3k_{\text{B}}T/R_{\text{F}}^2$ .



**Figure 1.32.** Entropy elasticity. To hold the end-to-end vector at  $\mathbf{r} - \mathbf{r}'$ , the Gaussian chain needs to be pulled with a force of  $\partial A / \partial \mathbf{r} = (3k_{\text{B}}T/R_{\text{F}}^2)(\mathbf{r} - \mathbf{r}')$ .

Because of the entropic origin, the above property is called the **entropy elasticity**. It is not limited to Gaussian chains. Any chain that has a finite size, including ideal chains and real chains, has this elasticity. By the same reason, a rubber is elastic. A rubber is a cross-linked polymer. A partial chain between two cross-links behaves elastically, giving rise to the elasticity of the material as a whole.

### 1.3.4 PROBLEMS

**Problem 1.5:** What is the most probable end-to-end distance  $R_{mp}$  of a Gaussian chain? At  $R = R_{mp}$ ,  $R^2 G(R; N)$  maximizes, where  $G(R; N) = G(\mathbf{r}, \mathbf{r}'; N)$  with  $R = |\mathbf{r} - \mathbf{r}'|$ .

**Solution 1.5:** At  $R = R_{mp}$ ,

$$\begin{aligned} 0 &= \frac{\partial}{\partial R} R^2 G(R; N) = \frac{\partial}{\partial R} R^2 (2\pi N b^2/3)^{-3/2} \exp\left(-\frac{3R^2}{2Nb^2}\right) \\ &= (2\pi N b^2/3)^{-3/2} \left(2R - \frac{3R^3}{Nb^2}\right) \exp\left(-\frac{3R^2}{2Nb^2}\right) \end{aligned}$$

Then,  $R_{mp} = b(2N/3)^{1/2} = 2R_g$ .

**Problem 1.6:** What is the second moment of the segments from one of the chain ends in the Gaussian chain? The square root of this second moment gives the “size” of the molecule tethered to a point in space.

**Solution 1.6:** Let  $\mathbf{r}$  be the position of the  $n$ th segment. Then, the second moment around the end at 0 is

$$\frac{1}{N} \int_0^N dn \langle (\mathbf{r} - 0)^2 \rangle = \frac{1}{N} \int_0^N n b^2 dn = \frac{1}{2} N b^2$$

**Problem 1.7:** Calculate the probability for the two ends of a Gaussian chain with the mean square end-to-end distance  $Nb^2$  to be longer than its “fully stretched length”  $Nb$ . How large is the probability when  $N = 5$ ? When  $N = 10$ ?

**Solution 1.7:** The probability  $P$  is given as

$$P = \int_{Nb}^{\infty} 4\pi r^2 (2\pi N b^2/3)^{-3/2} \exp\left(-\frac{3r^2}{2Nb^2}\right) dr$$

With  $t = (3/2N)^{1/2} r/b$ ,

$$P = 4\pi^{-1/2} \int_{(3N/2)^{1/2}}^{\infty} t^2 \exp(-t^2) dt = 2\pi^{-1/2} \left[ (3N/2)^{1/2} \exp(-3N/2) + \text{Erfc}\left((3N/2)^{1/2}\right) \right] (*)$$

Where

$$\operatorname{Erfc}(z) \equiv \int_z^{\infty} \exp(-t^2) dt$$

When  $Z \gg 1$ ,

$$\operatorname{Erfc}(z) \cong (2z)^{-1} \exp(-z^2)$$

Therefore, the first term is dominant in (\*):

$$P \cong (6N/\pi)^{1/2} \exp(-3N/2)$$

At  $N = 5$ ,  $P = 1.7 \times 10^{-3}$ . At  $N = 10$ ,  $P = 1.3 \times 10^{-6}$ .

**Problem 1.8:** Verify Eq. 1.45.

**Solution 1.8:** From Eq. 1.44,

$$\begin{aligned} G_{0\mathbf{R}}(\mathbf{r}; n) &= \frac{(2\pi n b^2/3)^{-3/2} \exp\left(-\frac{3\mathbf{r}^2}{2n b^2}\right) (2\pi(N-n)b^2/3)^{-3/2} \exp\left(-\frac{3(\mathbf{R}-\mathbf{r})^2}{2(N-n)b^2}\right)}{(2\pi N b^2/3)^{-3/2} \exp\left(-\frac{3\mathbf{R}^2}{2N b^2}\right)} \\ &= \left(2\pi \frac{n(N-n)}{N} b^2/3\right)^{-3/2} \exp\left[-\frac{3}{2b^2} \left(\frac{\mathbf{r}^2}{n} + \frac{(\mathbf{R}-\mathbf{r})^2}{N-n} - \frac{\mathbf{R}^2}{N}\right)\right] \\ &= \left(2\pi \frac{n(N-n)}{N} b^2/3\right)^{-3/2} \exp\left[-\frac{3(\mathbf{r} - (n/N)\mathbf{R})^2}{2b^2 n(N-n)/N}\right] = G\left(\mathbf{r}, \frac{n}{N} \mathbf{R}; \frac{n(N-n)}{N}\right) \end{aligned}$$

**Problem 1.9:** Equation 1.45 gives the distribution of an arbitrary point on the Gaussian chain when its ends are at 0 and  $\mathbf{R}$ . Place  $\mathbf{R}$  on the  $z$  axis and calculate the average of  $\langle x^2 + y^2 \rangle$  when  $n$  is swept from 0 to  $N$ .

**Solution 1.9:**

$$\begin{aligned} \langle x^2 + y^2 \rangle &= \frac{1}{N} \int_0^N dn \iint (x^2 + y^2) G_{0\mathbf{R}}(x, y; n) dx dy \\ &= \frac{1}{N} \int_0^N dn \iint (x^2 + y^2) \left(2\pi \frac{n(N-n)}{N} b^2/3\right)^{-1} \\ &\quad \times \exp\left(-\frac{3(x^2 + y^2)}{2[n(N-n)/N]b^2}\right) dx dy \end{aligned}$$



$$\begin{aligned}
&= \frac{1}{N} \int_0^N dn \int_0^{\infty} dx \left( 2\pi \frac{n(N-n)}{N} b^2/3 \right)^{-1/2} \\
&\quad \times \exp\left( -\frac{3x^2}{2[n(N-n)/N]b^2} \right) dx \\
&= \frac{1}{N} \int_0^N dn \int_0^{\infty} dx \left( 2\pi \frac{n(N-n)}{N} b^2/3 \right)^{-1/2} \\
&= \frac{1}{N} \int_0^N dn \int_0^{\infty} dx \left( 2\pi \frac{n(N-n)}{N} b^2/3 \right)^{-1/2} = \frac{1}{9} Nb^2
\end{aligned}$$

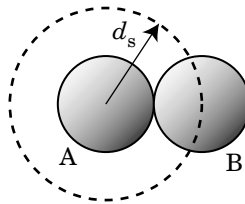
**Problem 1.10:** A Gaussian chain with fluorescent tag on one end and its quencher on the other end is dissolved in a non-quenching solvent. If there is no specific interaction between the two ends other than the fluorescence quenching, how does the fluorescence intensity change with the chain length? The fluorescence is quenched when the quencher is in close proximity.

**Solution 1.10:** The probability  $P$  for the two chain ends to come close is proportional to  $(2\pi Nb^2)^{-3/2}$ . Thus,  $P \propto N^{-3/2}$ . The intensity per molecule increases as  $\text{const.} \cdot N^{-3/2}$ .

## 1.4 REAL CHAINS

### 1.4.1 Excluded Volume

**1.4.1.1 Excluded Volume of a Sphere** The excluded volume makes the real chains nonideal. The dimension of the real chain is different from that of the ideal chain of the same contour length, for instance. Before considering the excluded volume effect in a chain molecule, we look at the effect in a suspension of hard spheres of diameter  $d_s$ . In Figure 1.33, the center-to-center distance between spheres A and B cannot be less than  $d_s$ . In effect, sphere B is excluded by sphere A. The space not available to the center of sphere B is a sphere of radius  $d_s$  indicated by a dashed line. Thus the excluded volume ( $v_e$ ) is eight times the volume of the sphere.



**Figure 1.33.** Excluded volume in a suspension of spheres. The center of sphere B is excluded from the spherical region (dashed line) by sphere A.

Consider a hypothetical process in which the volume excluded by each of the two spheres increases from 0 to  $v_e$ . The space available to the other sphere decreases from the volume  $V$  of the system to  $V - v_e$ . Therefore, the configurational entropy of the sphere changes by

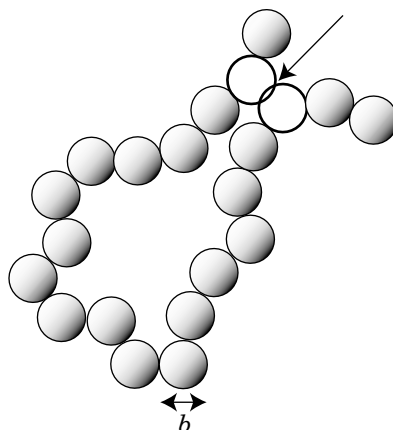
$$\Delta S = k_B \ln \frac{V - v_e}{V} \cong -k_B \frac{v_e}{V} \quad (1.60)$$

where  $v_e \ll V$  is assumed. The change in the Helmholtz free energy is then  $\Delta A/k_B T = -\Delta S/k_B = v_e/V$ .

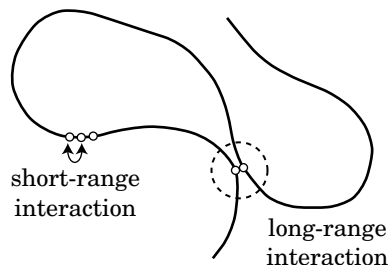
When the system has  $N$  identical spheres in the volume of  $V$ , there are  $N^2/2$  pairs of excluded-volume interaction. Then, the change in the total free energy due to the excluded volume is  $\Delta A/k_B T = (N^2/2)v_e/V$ . The change per sphere,  $(\Delta A/k_B T)/N$ , is proportional to the density  $N/V$ . At low concentrations, the excluded volume is negligible. As the concentration increases and  $Nv_e$  approaches  $V$ , the effect becomes stronger. The same effect appears in the van der Waals equation of state for a real gas; The correction to the volume is equal to the excluded volume.

**1.4.1.2 Excluded Volume in a Chain Molecule** In the polymer solution, the excluded volume does not disappear even in the low concentration limit. Connectivity of monomers makes the situation different from that in the suspension of spheres.

Suppose a polymer chain consisting of  $N$  spheres of diameter  $b$  (pearl-necklace model; see Fig. 1.34). We consider the dilute solution limit in which each chain is isolated from the other chains in the solution. When the chain dimension is  $R$ , these  $N$  spheres are contained in a cube of volume close to  $R^3$ , but no other spheres



**Figure 1.34.** Excluded volume in a chain molecule. The two white beads cannot overlap each other.



**Figure 1.35.** Short-range interaction and long-range interaction on a polymer chain.

will be found there. The free-energy change per chain due to the excluded volume is then  $\Delta A_{\text{ch}}/k_{\text{B}}T = (N^2/2)v_e/R^3$ . Although entropic in origin, we regard the excluded volume as an interaction and we write  $\Delta U_{\text{ch}}/k_{\text{B}}T = (N^2/2)v_e/R^3$ . Because  $v_e \cong b^3$ ,

$$\Delta U_{\text{ch}}/k_{\text{B}}T \cong b^3 N^2/R^3 \quad (1.61)$$

where the numerical coefficient is dropped. Note that  $N^2/R^3$  is equal to the volume  $R^3$  multiplied by the square of the monomer density ( $= N/R^3$ ). Other types of direct interactions between monomers such as van der Waals interactions are included in this expression of  $\Delta U_{\text{ch}}$  because the magnitude of any direct interaction in a given small volume is proportional to the square of the monomer density. Therefore, Eq. 1.61 can be written as  $v_{\text{eff}}(N^2/R^3)$ , in general. Note that the effective excluded volume ( $v_{\text{eff}}$ ) is negative when the attractive interaction dominates, which occurs when the monomers prefer other monomers to solvent molecules. In the following, we take  $v_{\text{eff}} = b^3 > 0$  for simplicity unless otherwise specified.

The interactions we are considering here are between monomers that may be widely apart along the chain contour. To distinguish these interactions from the short-range interactions such as the restriction on the bond angle and the dihedral angle we considered in Section 1.2.3, we call them long-range interactions (Fig. 1.35). The “long” and “short” do not refer to the distance between the monomers in space. They refer to the distance along the backbone of the polymer chain. Unlike the short-range interactions that are always present, the long-range interactions do not manifest themselves unless another monomer happens to come close. It is rather the large probability of this event that makes the long-range interactions dominant in the statistical properties of the polymer chain. The presence of many other monomers in a small volume of  $R^3$ , due to the chain connectivity, gives rise to the dominance of the long-range interactions even in the dilute solution limit.

The excluded volume is not limited to a pair of monomers on the same chain (intra-chain interaction). It exists equally for a pair of monomers on different chains (interchain interaction). At higher concentrations, the interchain interaction is the dominant part of the excluded volume effect.

## 1.4.2 Dimension of a Real Chain

**1.4.2.1 Flory Exponent** It is easy to expect that the excluded volume effect “swells” the chain compared with the dimension it would take were it not for the excluded volume effect. The swelling becomes more serious with an increasing contour length. We can see  $\Delta U_{\text{ch}}/k_{\text{B}}T$  to increase with  $N$  in Eq. 1.61. With  $R \cong bN^{1/2}$ , the dimension of the ideal chain, we have  $\Delta U_{\text{ch}}/k_{\text{B}}T \cong N^{1/2}$ .

When we write the radius of gyration of the real chain consisting of  $N$  monomers as  $R_{\text{g}} = bN^{\nu}$ , the exponent  $\nu$  is greater than 0.5, the exponent for the ideal chain. In fact,  $\nu$  was found to be around 0.59. Using the approximate value,  $0.6 = 3/5$ , is more common:

$$\boxed{R_{\text{g}} \cong bN^{\nu} \quad \nu = 0.59 \text{ or } 3/5 \quad \text{real chains}} \quad (1.62)$$

The numerical coefficient is dropped again. Within this level of approximation, the same formula applies to the end-to-end distance  $R_{\text{F}}$  of the real chain.

The exact exponent was estimated in the **renormalization group theory**.<sup>2</sup> The proof is difficult. Fortunately, however, Flory correctly obtained the approximate  $\nu$  in a simple method.<sup>3</sup> The exponent  $\nu$  is called the **Flory exponent**. Below we briefly review his method.

Flory expressed the free energy of the real chain as a function of the overall dimension of  $R$ . Here,  $R$  is not the average dimension but is allowed to change as the shape of the chain changes. The free energy consists of two terms—one is the entropy due to the freedom for different chain conformations and the other is the interaction mostly due to the excluded volume. In Section 1.3.3, we obtained the entropy term as  $S \cong -k_{\text{B}}R^2/(Nb^2)$  [Eq. 1.57 with  $(\mathbf{r} - \mathbf{r}')^2 = R^2$  and  $R_{\text{F}}^2 = Nb^2$ ; the numerical coefficient is dropped here]. The interaction term is given by Eq. 1.61. Then the free energy of the chain ( $A_{\text{ch}}$ ) is given as

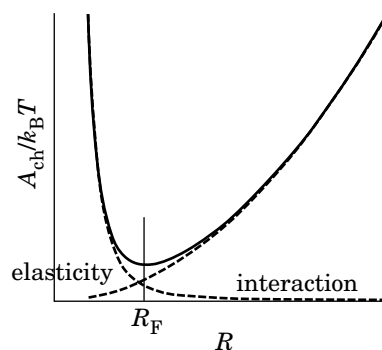
$$\frac{A_{\text{ch}}}{k_{\text{B}}T} \cong \frac{R^2}{Nb^2} + b^3 \frac{N^2}{R^3} \quad (1.63)$$

Figure 1.36 is a sketch of  $A_{\text{ch}}/k_{\text{B}}T$ . The two terms on the right-hand side have the opposite  $R$  dependence. The interaction becomes weaker as the monomer density becomes lower with an increasing  $R$ , but the entropy term gains. As a result, there is a minimum in  $A_{\text{ch}}$ . The  $R$  that minimizes  $A_{\text{ch}}$  is the most probable value of  $R$  for a given  $N$ . The excluded volume chain will have that dimension. Thus  $R_{\text{F}}$  can be obtained from  $\partial(A_{\text{ch}}/k_{\text{B}}T)/\partial R|_{R=R_{\text{F}}} = 0$  as  $R_{\text{F}} \cong bN^{3/5}$ , reproducing Eq. 1.62.

The ratio of  $R_{\text{g}}^2$  to  $R_{\text{F}}^2$  is insensitive to the excluded volume effect. The renormalization group theory gives<sup>2</sup>

$$\frac{6R_{\text{g}}^2}{R_{\text{F}}^2} = 0.952 \quad (1.64)$$

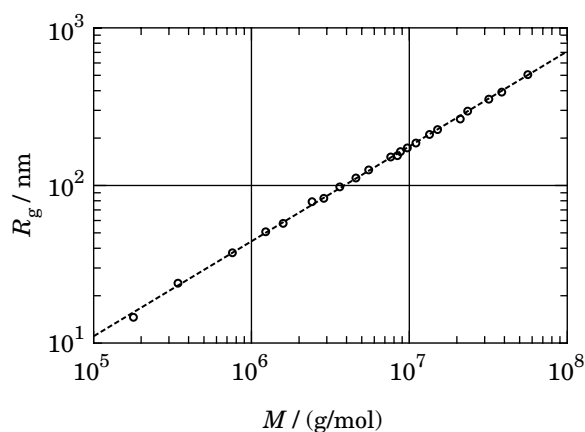
In the ideal chain, the ratio is 1 (Eq. 1.29).



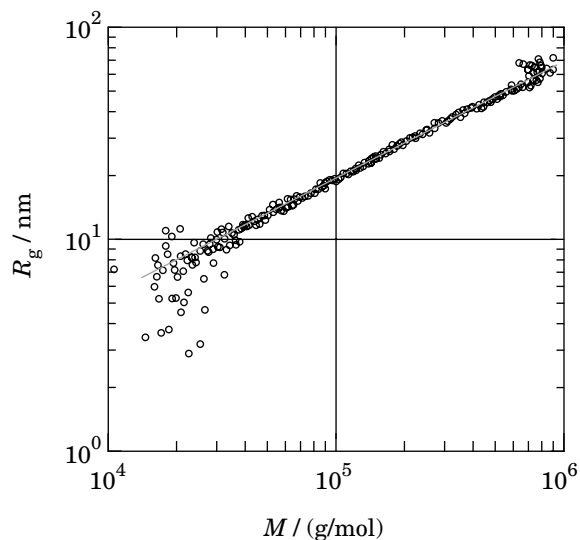
**Figure 1.36.** Free energy of a chain,  $A_{\text{ch}}$ , as a function of the chain dimension  $R$ . The free energy consists of the elastic energy and the interaction.

Note that the chain dimension thus obtained is independent of the temperature. For this reason, the real chains are often called **athermal** chains. The independence results from the fact that both the elasticity and the excluded volume are entropic in origin. The two terms on the right-hand side of Eq. 1.63 are independent of  $T$ . In some polymer solutions, however, the interaction is enthalpic. Dividing the interaction by  $k_B T$  makes the interaction term in Eq. 1.63 reciprocally proportional to  $T$ . Consequently, the polymer chain dimension depends on the temperature. In Section 2.3, we will see this effect.

**1.4.2.2 Experimental Results** Experiments conducted on dilute polymer solutions verified that the chain dimension follows Eq. 1.62. Figure 1.37 shows a



**Figure 1.37.** Radius of gyration  $R_g$  of polystyrene in toluene and benzene, plotted as a function of molecular weight  $M$ . The dashed line is the optimal fit by a power relationship. (From Ref. 2.)



**Figure 1.38.** Radius of gyration  $R_g$  of linear high-density polyethylene in trichlorobenzene, plotted as a function of molecular weight  $M$ . The gray line is the optimal fit by a power relationship. (From Ref. 4.)

typical result for polystyrene in toluene and benzene at around room temperature.<sup>2</sup> The latter is a typical athermal chain. The data were obtained in lightscattering experiments that can measure  $R_g$  and the average molecular weight ( $M$ ) of a polymer chain in a dilute solution, as we will see in Section 2.4. All the data fall on a straight line in the double logarithmic scale. Curve fitting yields

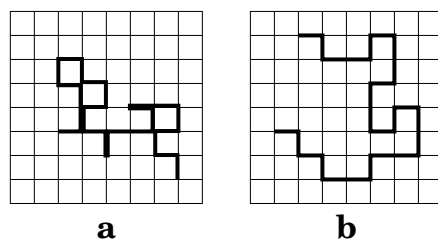
$$R_g/\text{nm} = 0.01234 \times (M/(\text{g/mol}))^{0.5936} \quad \text{polystyrene in toluene and benzene} \quad (1.65)$$

The exponent is in agreement with the theoretically predicted value. At lower molecular weights ( $M < 10^4$  g/mol),  $R_g$  is smaller than the one given by this equation. There is a slight difference in the coefficient and the exponent from solvent to solvent, but the difference is small in a wide range of solvents that dissolve the polymer easily.

The coefficient and the exponent are quite different for other polymers. For instance, linear high-density polyethylene in trichlorobenzene at 135°C has the following  $R_g$ :<sup>4</sup>

$$R_g/\text{nm} = 0.0335 \times (M/(\text{g/mol}))^{0.553} \quad \text{polyethylene in trichlorobenzene} \quad (1.66)$$

Figure 1.38 shows the dependence. The data were obtained by using an on-line lightscattering detector in size exclusion chromatography. In the study,  $R_g$  and  $M$  were measured simultaneously and instantaneously as the polymer was separated in



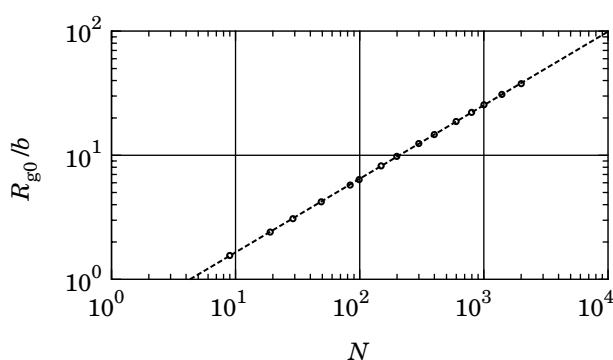
**Figure 1.39.** Polymer chain on a square lattice. a: Random walk for an ideal chain. b: Self-avoiding walk for a real chain.

column chromatography (Section 2.5). Compared with polystyrene of the same  $M$ , polyethylene has a greater  $R_g$  primarily because its monomer molecular weight is lower.

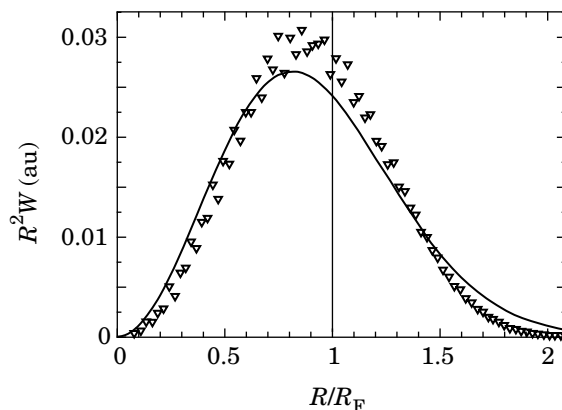
### 1.4.3 Self-Avoiding Walk

A polymer chain with an excluded volume can be modeled by a **self-avoiding walk** (SAW) on the lattice. Unlike the random walker we have seen in Section 1.2 for the ideal chain, this walker is not allowed to visit the sites it has already visited. Its trajectory is close to the conformation of a real chain with excluded volume on the lattice. For the SAW to represent a real chain, the SAW must be equilibrated by moving the chain around on the lattice. Figure 1.39 illustrates a difference between the random walk and the SAW on a square lattice. Apparently, the dimension of the latter is greater; The excluded volume swells the chain. SAW is widely used in computer simulations to calculate properties of the polymer chain that are difficult to obtain in experiments.

Figure 1.40 shows a typical result of the simulation.<sup>5</sup> An  $N$ -step SAW was generated on a cubic lattice of lattice unit  $b$ . After equilibration, the root-mean-square



**Figure 1.40.** Radius of gyration  $R_g$  of a self-avoiding walk on a cubic lattice of lattice unit  $b$ , plotted as a function of the number  $N$  of the steps. The solid line is the optimal fit by a power relationship. (From Ref. 5.)



**Figure 1.41.** Distribution of the end-to-end distance.  $R^2W(\mathbf{R})$  is plotted as a function of  $R/R_F$ . Symbols were obtained in computer simulation; the solid line represents the distribution for the Gaussian chain. (From Ref. 6.)

radius of gyration,  $R_g$ , was calculated over many different arrangements of the chain. Again, the data are on a straight line in the double logarithmic scale. Curve fitting gives

$$\boxed{R_g/b = 0.4205 \times N^{0.5934} \quad \text{SAW on a cubic lattice}} \quad (1.67)$$

Unlike in Figure 1.36, a good fitting persists to  $N$  as small as 9.

A difference between SAW and the Gaussian chain is also evident in the distribution of the end-to-end distance  $R$ . Figure 1.41 compares  $R^2W(\mathbf{R})$ , where  $W(\mathbf{R})$  is the distribution function for  $\mathbf{R}$ . Note that  $4\pi R^2W(\mathbf{R}) dR$  gives the probability to find the end-to-end distance between  $R$  and  $R + dR$ . In the Gaussian chain,  $W(\mathbf{R}) = G(\mathbf{R}, 0; N)$ , where  $G$  is given by Eq. 1.34. The SAW of  $N = 199$  steps was generated on a tetrahedral lattice.<sup>6</sup> In the figure, the Gaussian chain has a broader distribution, especially at large  $R$ . It is one of the shortcomings of the Gaussian chain model to describe the conformation of the real chain.

#### 1.4.4 PROBLEMS

**Problem 1.11:** A self-avoiding walk (SAW) generated on a lattice is slightly different from the trace of a real chain on the same lattice. Explain why.

**Solution 1.11:** The environment for a growing chain end of SAW changes as more monomers are added to the chain and more sites become unavailable to the next monomer.



**Problem 1.12:** Assume that we can use the expression for the mean square distance between the two ends of a real chain ( $R_F^2 = b^2 N^{2\nu}$ ) also for the mean square distance between two monomers, i.e.,  $\langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle = b^2 |i - j|^{2\nu}$ . Calculate  $R_g^2$  of the real chain. In Eq. 1.25, replace the sum with a double integral. What is  $6R_g^2/R_F^2$  for  $\nu = 0.59$ ? Why do you think it is different from the one calculated in a more rigorous theory (renormalization theory)?

**Solution 1.12:**

$$\begin{aligned} R_g^2 &= \frac{1}{2N^2} \int_0^N di \int_0^N dj b^2 |i - j|^{2\nu} = \frac{b^2}{N^2} \int_0^N di \int_0^i dj (i - j)^{2\nu} \\ &= \frac{b^2 N^{2\nu}}{(2\nu + 1)(2\nu + 2)} \\ \frac{6R_g^2}{R_F^2} &= \frac{6}{(2\nu + 1)(2\nu + 2)} \cong 0.87 \end{aligned}$$

The real chain is more rigid over a short distance, which makes a contribution of close pairs of  $i$  and  $j$  greater than it is in the above calculation.

**Problem 1.13:** We can apply Flory's method to find the Flory exponent for the dimension of a two-dimensional excluded-volume chain. In two dimensions, the entropy term is the same as that of the three-dimensional chain, but the interaction term changes to  $\Delta U_{\text{ch}}/k_B T = b^2 R^2 (N/R^2)^2 = b^2 N^2/R^2$ .

**Solution 1.13:**

$$\frac{A_{\text{ch}}}{k_B T} \cong \frac{R^2}{Nb^2} + b^2 \frac{N^2}{R^2}$$

The derivative is zero at the free energy minimum:

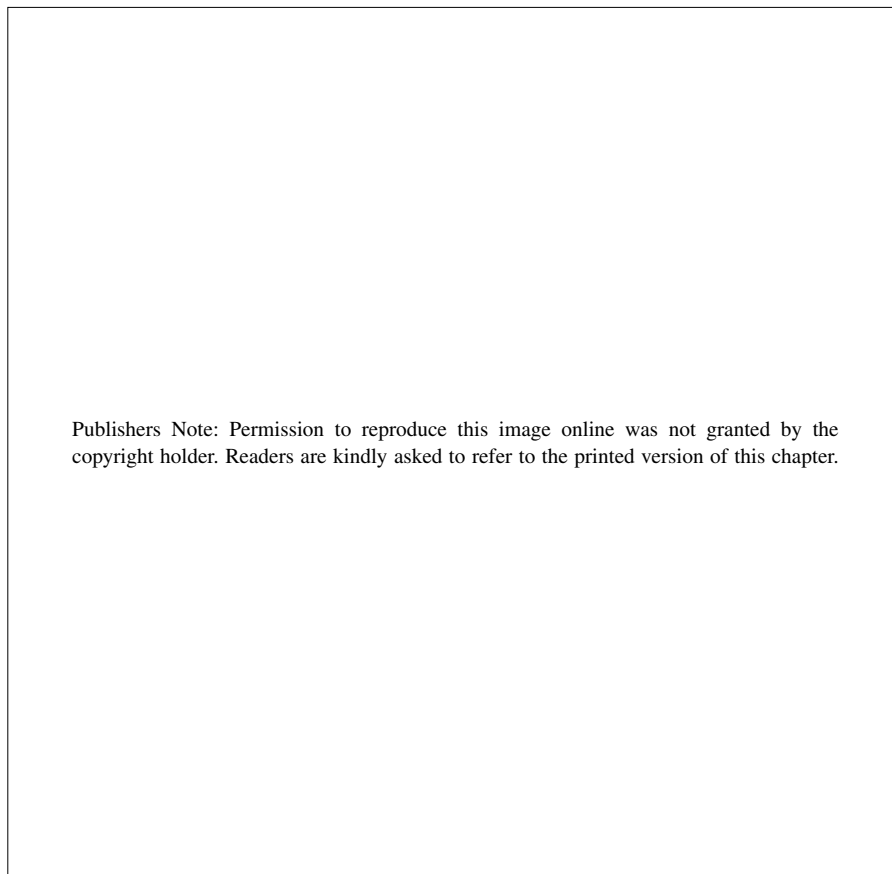
$$0 = \frac{\partial}{\partial R} \frac{A_{\text{ch}}}{k_B T} \cong \frac{2R}{Nb^2} - 2b^2 \frac{N^2}{R^3}$$

From which we obtain  $R = bN^{3/4}$ .

## 1.5 SEMIRIGID CHAINS

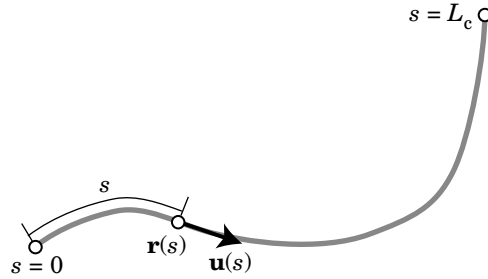
### 1.5.1 Examples of Semirigid Chains

In the preceding sections, we assumed that the polymer chain is flexible and coil-shaped. However, some linear chains have an inherent backbone rigidity. In contrast to flexible chains that look like a cotton thread, the inherently rigid chains resemble a fishing thread. These polymers are called **semirigid** polymers or **semiflexible** polymers. There are several mechanisms that support the backbone rigidity (Fig. 1.42):



**Figure 1.42.** Examples of a wormlike chain. a: Chain with a  $\pi$ -conjugated backbone [poly(*p*-phenylene) and polydiacetylene]. b: Chain with a bulky side chain [poly(*n*-hexyl isocyanate); also helical]. c: Helical chain (double-stranded DNA). d: Polyelectrolyte [poly(styrene sulfonate); ionized in neutral water]. The rigidity is supported by the high density of negative charges on the backbone. (b is from Ref. 7.)

- (a)  $\pi$ -Conjugation in the valence electrons of the main chain. The delocalized electrons prefer a straight backbone. Polyacetylene, poly(*p*-phenylene), and polydiacetylene are typical of these polymers. Side groups ( $\mathbf{R}, \mathbf{R}'$ ) are attached to make these polymers soluble in solvents without compromising the rigidity.
- (b) Bulky side groups. Bulky pendant groups grafted at high density to the main chain force the chain to adopt an extended conformation. Poly(*n*-hexyl isocyanate) belongs to this group.<sup>7</sup>
- (c) Hydrogen bonding. Hydrogen bonding between hydrogen donors and acceptors on the main chain or side groups locks the chain into a specific



**Figure 1.43.** Conformation of a wormlike chain is specified by  $\mathbf{r}(s)$ . Its unit tangential vector is  $\mathbf{u}(s)$ .

arrangement, mostly into a straight conformation. The bonding can be between immediate neighbors or between monomers a few units apart.  $\alpha$ -Helix forming synthetic polypeptides such as poly( $\gamma$ -benzyl-L-glutamate) and double-stranded DNA fragments belong to this category. These polymers may change into flexible coils at high temperatures (helix-coil transition).

- (d) Coulomb repulsions. Same charges distributed along the chain at high density repel each other to extend the otherwise flexible chain. Strong **polyelectrolytes** such as poly(styrene sulfonate) in a neutral, salt-free solution at low concentrations belong to this category.

The rigidity depends on the solvent, temperature, and additives. When the chain is straight, the polymer is called a **rodlike molecule**.

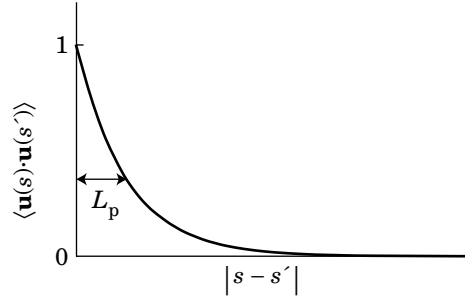
## 1.5.2 Wormlike Chain

**1.5.2.1 Model** In Section 1.2.3, we looked at a freely rotating chain with a fixed bond angle  $\pi - \theta_b$  but an unrestricted dihedral angle. When the bond angle is close to  $\pi$  and the bond length  $b$  is short, this model can represent a semirigid chain, as shown below. The orientation correlation of the  $i$ th stick and the  $j$ th stick was obtained as  $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \cos^{|i-j|} \theta_b$ , where  $\mathbf{u}_i$  is the unit vector parallel to the  $i$ th stick (Eq. 1.31). We now decrease  $\theta_b$ . When  $\theta_b \ll 1$ , the correlation between  $\mathbf{u}$  and  $\mathbf{u}'$  at two points separated by  $l = b|i-j|$  along the contour is  $\langle \mathbf{u} \cdot \mathbf{u}' \rangle = (1 - \theta_b^2/2)^{l/b}$ . We take the limit of  $b \rightarrow 0$  while holding  $2b/\theta_b^2$  unchanged. Then,

$$\langle \mathbf{u} \cdot \mathbf{u}' \rangle = [(1 - b/L)^{1/b}]^l \rightarrow \exp(-l/L) \quad (1.68)$$

where  $L \equiv 2b/\theta_b^2$ , and  $(1 + bx)^{1/b} \rightarrow e^x$  ( $b \rightarrow 0$ ) with  $x = -1/L$  was used.

In the limit, the conformation of the chain is not zigzag but rather a smooth curve in a three-dimensional space, as illustrated in Figure 1.43. This model is called a **wormlike chain** or a **Kratky-Porod model**. A continuous



**Figure 1.44.** Correlation of the tangential vector is lost with an increasing segment distance.

variable  $\mathbf{r}(s)$  describes the conformation, where  $s$  is measured along the contour from one of the chain ends ( $0 < s < L_c$ ). The tangential vector  $\mathbf{u}(s)$  of unit length at  $s$  is given by

$$\mathbf{u}(s) = \frac{d\mathbf{r}(s)}{ds} \quad (1.69)$$

and represents the local orientation of the segment in the semirigid chain. As in the bead-stick model, the correlation between  $\mathbf{u}(s)$  and  $\mathbf{u}(s')$  of two segments at  $s$  and  $s'$  decreases to zero with a growing distance between the two segments along the contour:

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle = \exp(-|s - s'|/L_p) \quad (1.70)$$

where  $L_p$  is called the **persistence length**. The correlation is lost exponentially as shown in Figure 1.44. The wormlike chain is described by two parameters,  $L_p$  and  $L_c$  (the contour length). The chain can be realized in a computer modeling by a bead-stick model of  $L_c/b$  sticks of length  $b$  ( $L_c/b \gg 1$ ) with a bond angle of  $\pi - \theta_b = \pi - (2b/L_p)^{1/2}$ .

**1.5.2.2 End-to-End Distance** We now calculate the end-to-end distance  $R_F$ . The end-to-end vector  $\mathbf{R}$  is related to  $\mathbf{u}(s)$  by

$$\mathbf{R} = \mathbf{r}(L_c) - \mathbf{r}(0) = \int_0^{L_c} \mathbf{u}(s) ds \quad (1.71)$$

Therefore,

$$\langle \mathbf{R}^2 \rangle = \int_0^{L_c} \int_0^{L_c} \langle \mathbf{u}(s) \mathbf{u}(s') \rangle ds ds' = 2 \int_0^{L_c} ds \int_0^s ds' \langle \mathbf{u}(s) \cdot \mathbf{u}(s') \rangle \quad (1.72)$$

With Eq. 1.70, we obtain

$$\boxed{R_F^2 = 2L_p[L_c + L_p(\exp(-L_c/L_p) - 1)] \quad \text{wormlike chain}} \quad (1.73)$$

Two limiting cases are interesting. When  $L_p \gg L_c$ , i.e., the chain is either sufficiently rigid or short,

$$R_F^2 = L_c^2 \left( 1 - \frac{L_c}{3L_p} + \dots \right) \quad (1.74)$$

In the limit of  $L_c/L_p \rightarrow 0$ , the wormlike chain is a rod ( $L_c = R_F$ ). When  $L_c \gg L_p$ , i.e., the chain is sufficiently flexible or long,

$$R_F^2 = 2L_cL_p \left( 1 - \frac{L_p}{L_c} + \dots \right) \quad (1.75)$$

In the limit of  $L_c \rightarrow \infty$ ,  $R_F \propto L_c^{1/2}$ , the same as the ideal chain. Comparison with Eq. 1.29 ( $L_c = bN$ ) gives an effective segment length of  $2L_p$ . The wormlike chain behaves like an ideal chain of a bond length of  $2L_p$  when  $L_c \gg L_p$ . The segment length defined in this way is called the **Kuhn segment length**.

**1.5.2.3 Radius of Gyration** To calculate the radius of gyration of the wormlike chain, we use a slightly different version of Eq. 1.25:

$$R_g^2 = \frac{1}{2L_c^2} \int_0^{L_c} \int_0^{L_c} [\mathbf{r}(s) - \mathbf{r}(s')]^2 ds ds' = \frac{1}{L_c^2} \int_0^{L_c} ds \int_0^s ds' [\mathbf{r}(s) - \mathbf{r}(s')]^2 \quad (1.76)$$

Since  $[\mathbf{r}(s) - \mathbf{r}(s')]^2 = 2L_p[|s - s'| + L_p(\exp(-|s - s'|/L_p) - 1)]$  has been already obtained in Eq. 1.73, it is easy to calculate  $R_g$ . The result is

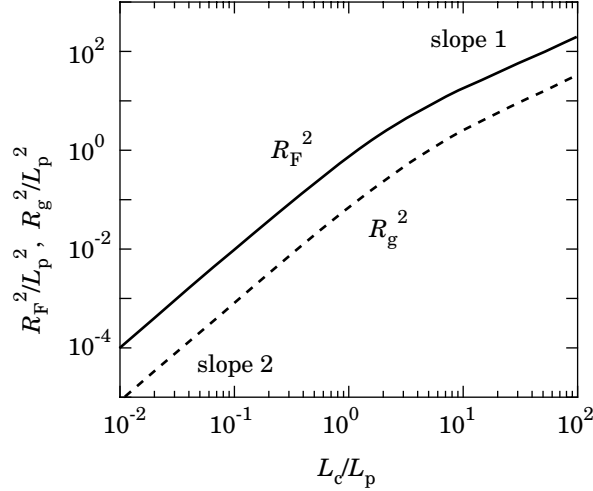
$$\boxed{R_g^2 = \frac{1}{3} L_p L_c - L_p^2 + 2 \frac{L_p^3}{L_c} \left( 1 - \frac{L_p}{L_c} [1 - \exp(-L_c/L_p)] \right) \quad \text{wormlike chain}} \quad (1.77)$$

In the short-chain or the rigid-chain limit ( $L_c/L_p \ll 1$ ),

$$R_g^2 = \frac{1}{12} L_c^2 \left( 1 - \frac{L_c}{5L_p} + \dots \right) \quad (1.78)$$

In the long-chain limit or the flexible-chain limit ( $L_c/L_p \gg 1$ ),

$$R_g^2 = \frac{1}{3} L_p L_c \left( 1 - \frac{3L_p}{L_c} + \dots \right) \quad (1.79)$$



**Figure 1.45.** Mean square end-to-end distance  $R_F^2$  (solid line) and mean square radius of gyration  $R_g^2$  (dashed line) reduced by  $L_p^2$ , plotted as a function of  $L_c/L_p$ .

As in  $R_F^2$ ,  $2L_p = b$  makes the wormlike chain in the asymptote of  $L_c/L_p \gg 1$  have the same  $R_g$  as the ideal chain of the same  $L_c$ .

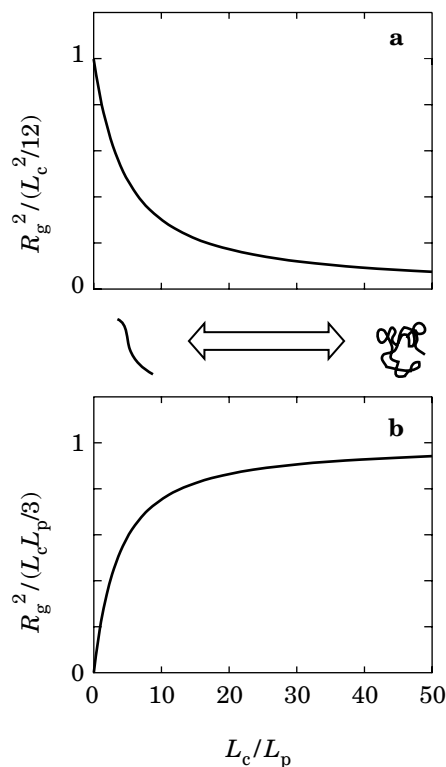
Figure 1.45 shows how  $R_F^2$  and  $R_g^2$  change with  $L_c/L_p$ . The slope shows a crossover from that of a rigid rod (slope = 2) to that of a flexible chain (slope = 1) for both  $R_F^2$  and  $R_g^2$ . The value of  $6R_g^2/R_F^2$  increases from 1/2 to 1 with an increasing  $L_c/L_p$ . The crossover occurs at around  $L_c/L_p \cong 1$ .

Figure 1.46 shows how  $R_g$  changes with  $L_c/L_p$ . Parts a and b are the plots of  $R_g^2/(L_c^2/12)$  and  $R_g^2/(L_p L_c/3)$  as a function of  $L_c/L_p$ , respectively. Figure 1.46a indicates how the chain dimension decreases from that of the rigid rod conformation of the same  $L_c$  as the chain becomes longer or more flexible. Figure 1.46b shows how the chain approaches an ideal chain as  $L_c/L_p$  increases. Because  $L_c \propto M$ , the two plots are essentially the plots of  $R_g^2/M^2$  and  $R_g^2/M$ , respectively, as a function of  $M$ .

**1.5.2.4 Estimation of Persistence Length** As we will learn in Section 2.4, the lightscattering experiments for different molecular weights of a semirigid polymer give the estimates of  $R_g$  and  $M$  for each fraction of the polymer. From the dependence of  $R_g$  on  $M$ , we can estimate  $L_p$ . For this purpose, we rewrite Eq. 1.77 into

$$\frac{R_g^2}{M} = \frac{L_p}{3m_L} - \frac{L_p^2}{M} + \frac{2L_p^3 m_L}{M^2} \left( 1 - \frac{L_p m_L}{M} [1 - \exp(-M/(L_p m_L))] \right) \quad (1.80)$$

where  $m_L = M/L_c$  is the molecular weight per unit length of the chain contour.



**Figure 1.46.** Mean square radius of gyration, reduced by (a)  $L_c^2/12$  and (b)  $L_p L_c/3$ , is plotted as a function of  $L_c/L_p$ . When  $L_c/L_p \ll 1$ , the wormlike chain is rodlike. When  $L_c/L_p \gg 1$ , the wormlike chain is a linear flexible chain.

An example of the lightscattering studies is shown in Figure 1.47 for poly(*n*-hexyl isocyanate) in hexane.<sup>8</sup> The data are on the curve shown in Figure 1.46b. Curve-fitting of the data by Eq. 1.80 gives the estimate of the two parameters as  $L_p = 42$  nm and  $m_L = 715$  g/(mol·nm). In Figure 1.47,  $R_g$  of poly(*n*-hexyl isocyanate) for  $M = 10^5$  g/mol is 31 nm. This value is much greater than those of polystyrene and polyethylene of the same  $M$  (compare Fig. 1.47 with Figs. 1.37 and 1.38).

Examples of  $L_p$  thus estimated are listed in Table 1.3 for some semirigid polymers. The persistence length depends on the solvent, the temperature, the concentration, and, for polyelectrolytes, on the ionic strength and pH.

### 1.5.3 PROBLEMS

**Problem 1.14:** What is  $L_p$  in the freely rotating chain with bond length  $b$  and bond angle  $\pi - \theta_b$ ?

**TABLE 1.3 Persistence Length of Some Semirigid Polymers**

Polymer	Solvent	$L_p$ /nm
poly( <i>p</i> -phenylene) <sup>a</sup>	toluene	13
poly( <i>n</i> -hexyl isocyanate) <sup>b</sup>	hexane	42
DNA <sup>c</sup>	aqueous	~50
poly( $\gamma$ -benzyl-L-glutamate) <sup>d</sup>	DMF	~200

<sup>a</sup>S. Vanhee et al. *Macromolecules* **29**, 5136 (1996).

<sup>b</sup>H. Murakami et al. *Macromolecules* **13**, 345 (1980).

<sup>c</sup>B. Zimm, *Macromolecules* **31**, 6089 (1998).

<sup>d</sup>E. Temyanko et al. *Macromolecules* **34**, 582 (2001).

**Solution 1.14:** For two bonds  $\mathbf{u}_i$  and  $\mathbf{u}_j$  separated by  $s$ ,  $|i - j| = s/b$ . Then,

$$\langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle = (\cos \theta_b)^{s/b} = \exp[(s/b)\ln(\cos \theta_b)]$$

Comparison with Eq. 1.70 gives

$$L_p = \frac{b}{-\ln(\cos \theta_b)}$$

**Problem 1.15:** What is the expectation of the projection of the end-to-end vector  $\mathbf{R}$  onto the tangential vector  $\mathbf{u}_0 = \mathbf{u}(0)$  at the end of a wormlike chain?

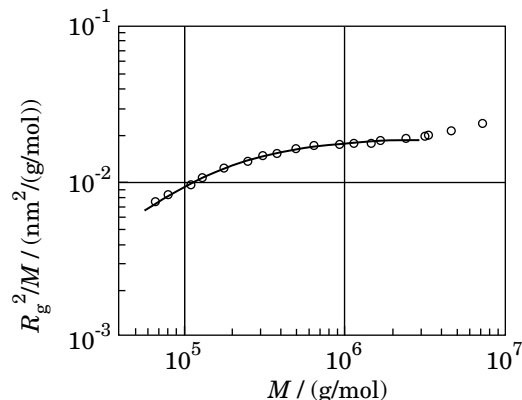
**Solution 1.15:** The projection is given by

$$\begin{aligned} \langle \mathbf{R} \cdot \mathbf{u}_0 \rangle &= \left\langle \int_0^{L_c} \mathbf{u}(s) \, ds \cdot \mathbf{u}_0 \right\rangle = \int_0^{L_c} \langle \mathbf{u}(s) \cdot \mathbf{u}(0) \rangle \, ds \\ &= \int_0^{L_c} \exp(-s/L_p) \, ds = L_p [1 - \exp(-L_c/L_p)] \end{aligned}$$

**Problem 1.16:** Nonreverse random walk (NRRW) is often used in lattice simulations. The random walker can choose any direction except for returning to the preceding site. Otherwise, the walker can return to the site it visited earlier. We can expect that the trajectory is between that of an ideal chain and that of an excluded volume chain. For a cubic lattice of lattice unit  $b$ , assume that the random walker chooses one out of the five directions at random and answer the following questions.

- (1) What is  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_{i+1} \rangle$ ? How about  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle$ ?
- (2) What is the mean square displacement of  $N$  steps when  $N \gg 1$ ?
- (3) The nonreverse condition makes NRRW somewhat rigid. What is the persistence length?





**Figure 1.47.** Mean square radius of gyration reduced by molecular weight  $M$  for different fractions of poly(*n*-hexyl isocyanate) in hexane. The optimal curve fitting by the wormlike chain model is shown as a solid line. (From Ref. 8.)

**Solution 1.16:**

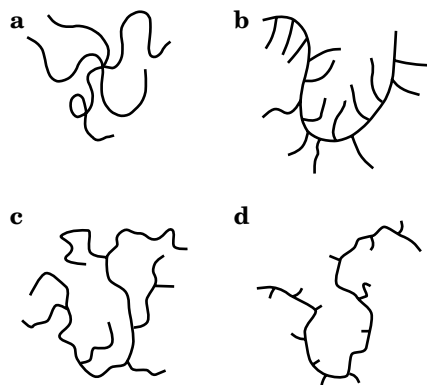
- (1)  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_{i+1} \rangle = b^2/5$ .  $\langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle = b^2/5^{|i-j|}$ .
- (2)  $\langle \Delta \mathbf{r}^2 \rangle = \sum_{i,j=1}^N \langle \Delta \mathbf{r}_i \cdot \Delta \mathbf{r}_j \rangle = \sum_{i,j=1}^N b^2 5^{-|i-j|} = b^2 \left[ N + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N 5^{i-j} \right] \cong \frac{3}{2} b^2 N$
- (3) Equate  $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = (1/5)^{|i-j|}$  with  $\langle \mathbf{u}_i \cdot \mathbf{u}_j \rangle = \exp(-b|i-j|/L_p)$ . Then, we get  $L_p = b/\ln 5$ . It is close to  $(3/4)b$  estimated from (2).

## 1.6 BRANCHED CHAINS

### 1.6.1 Architecture of Branched Chains

There are different architectures in branched chains as shown in Figure 1.48. A **star-branched chain** or **star polymer** (a) consists of a core and arms of a more or less similar length. A two-arm star polymer is essentially a linear polymer. A **comb polymer** (b) consists of a linear-chain backbone and many small combs stemming from trifunctional units distributed along the backbone. The joints may be uniformly spaced. The comb length is more or less uniform. The comb polymer with a uniform distribution of branching points and a uniform distribution of branching length can be prepared by polymerizing monomers that have a long side chain.

Copolymerization of monomers having a side chain with side chain-free monomers is one of the methods to introduce randomness in the branching points. In the **random-branched chain** (Figure 1.48, c and d), branching points are distributed randomly. The branches may have further branches, although its probability is usually low. The branching density can be controlled by changing the mixing ratio of the two types of monomers. It is difficult to pick up the main chain or the



**Figure 1.48.** Architectures of branched polymers: star polymer (a), comb copolymer (b), short-chain branching (c), and long-chain branching (d).

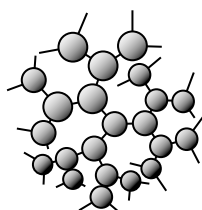
backbone in the random-branched chain. The length of the branches distinguishes long-chain branching (c) from short-chain branching (d). Long-chain branching is sometimes naturally introduced in the chain-reaction polymerization. When the frequency of branching is high, then the chain is called a highly branched chain or **hyperbranched chain**.

There is a different class of branched polymer. In a **dendrimer** shown in Figure 1.49, every repeating unit is trifunctional. Starting at the center, the number of monomers in a layer (generation) increases twofold every generation.

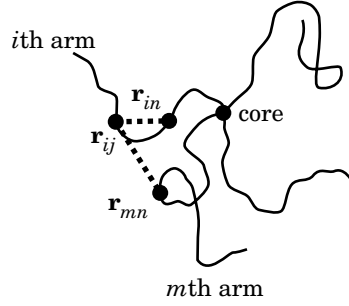
### 1.6.2 Dimension of Branched Chains

The best quantity to characterize the overall dimension of the branched chain is the radius of gyration,  $R_g$ ; The end-to-end distance cannot be well defined for nonlinear chains. The **branching parameter**  $g_g$  is defined as

$$g_g \equiv \frac{R_{gb}^2}{R_{gl}^2} \quad \text{branching parameter} \quad (1.81)$$



**Figure 1.49.** Dendrimer.



**Figure 1.50.** Two monomers can be on the same arm or on different arms.

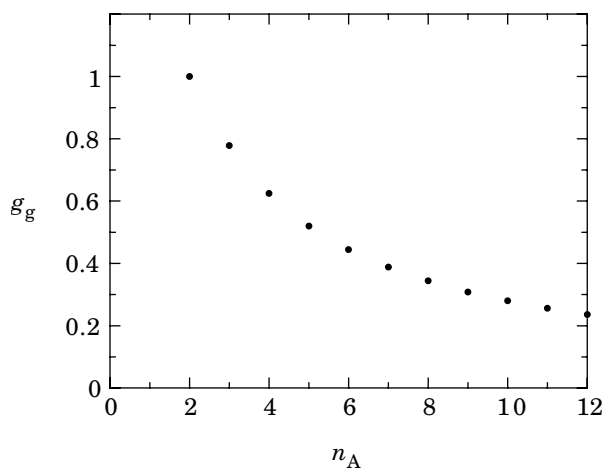
where  $R_{gb}^2$  is the mean square radius of gyration for the branched chain, and  $R_{gl}^2$  is the mean square radius of gyration for the linear chain. The ratio is calculated for the two polymers of the same molecular weight. Branching makes the monomers more congested around the center of mass. Therefore  $g_g \leq 1$ .

For demonstration, we calculate here  $g_g$  for an  $n_A$ -arm star polymer. We assume that each arm is an ideal chain and has the same number of monomers,  $N_1$  ( $N_1 \gg 1$ ). Let  $\mathbf{r}_{ij}$  be the position of the  $j$ th monomer ( $j = 0, 1, \dots, N_1$ ) on the  $i$ th arm ( $i = 1, 2, \dots, n_A$ ), as illustrated in Figure 1.50. The core is at  $\mathbf{r}_{i0}$ . With the use of Eq. 1.25, the mean-square radius of gyration  $R_{gb}^2$  is expressed as

$$R_{gb}^2 = \frac{1}{2n_A^2 N_1^2} \sum_{i,m=1}^{n_A} \sum_{j,n=1}^{N_1} \langle (\mathbf{r}_{ij} - \mathbf{r}_{mn})^2 \rangle \quad (1.82)$$

where the core is not included in the sum. The mean square of the monomer distance is calculated for monomers on the same arm and those on difference arms separately (see Figure 1.50):

$$\begin{aligned} \sum_{i,m=1}^{n_A} \sum_{j,n=1}^{N_1} \langle (\mathbf{r}_{ij} - \mathbf{r}_{mn})^2 \rangle &= \sum_{i=1}^{n_A} \sum_{j,n=1}^{N_1} \langle (\mathbf{r}_{ij} - \mathbf{r}_{in})^2 \rangle + \sum_{i \neq m}^{n_A} \sum_{j,n=1}^{N_1} \langle (\mathbf{r}_{ij} - \mathbf{r}_{mn})^2 \rangle \\ &= \sum_{i=1}^{n_A} \sum_{j,n=1}^{N_1} |j - n| b^2 + \sum_{i \neq m}^{n_A} \sum_{j,n=1}^{N_1} (j + n) b^2 \\ &= b^2 \left[ n_A \sum_{j,n=1}^{N_1} |j - n| + n_A(n_A - 1) \sum_{j,n=1}^{N_1} (j + n) \right] \\ &= \frac{1}{3} b^2 n_A N_1 (N_1 + 1) (3n_A N_1 - 2N_1 - 1) \end{aligned} \quad (1.83)$$



**Figure 1.51.** The branching parameter of a star polymer, plotted as a function of the number of arms,  $n_A$ .

From Eqs. 1.82 and 1.83, we have

$$R_{gb}^2 = \frac{b^2(N_1 + 1)}{6n_A N_1} (3n_A N_1 - 2N_1 - 1) \cong b^2 \frac{N}{n_A} \left( \frac{1}{2} - \frac{1}{3n_A} \right) \quad (1.84)$$

where  $N_1 \gg 1$  was used, and  $N = n_A N_1$  is the total chain length. For linear polymer ( $n_A = 2$ ), the mean-square radius of gyration is  $R_{gl}^2 = b^2 N / 6$ . Thus,

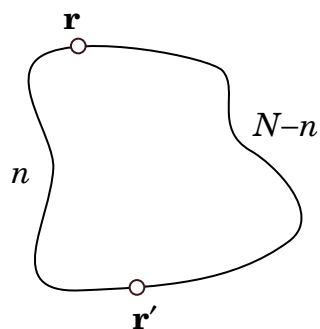
$$g_g = \frac{1}{n_A} \left( 3 - \frac{2}{n_A} \right) \quad \begin{array}{l} \text{branching parameter} \\ n_A\text{-arm star} \end{array} \quad (1.85)$$

Figure 1.51 shows a plot of  $g_g$  as a function of  $n_A$ . As the number of arms increases, the chain becomes more compact and therefore  $g_g$  decreases.

Branching is widely observed in polyolefins. Figure 1.52 shows  $R_g$  of branched polyethylene as a function of molecular weight  $M$  of the polymer.<sup>9</sup> As in Figure 1.38, size-exclusion chromatography with an on-line light-scattering detector was employed to measure  $R_g$  and  $M$  simultaneously for every fraction separated in the chromatography. Different sets of data (distinguished by different symbols in the plot) were obtained by changing the reaction pressure. Each set follows approximately a power law of  $R_g \sim M^{0.59}$ . We can estimate the branching parameter  $g_g$  for each sample by comparing  $R_g$  at some value of  $M$ .

### 1.6.3 PROBLEMS

**Problem 1.17:** Calculate  $R_g$  of a ring polymer (also called a cyclic polymer) consisting of  $N$  segments of length  $b$ . Assume Gaussian statistics for any part of the chain.

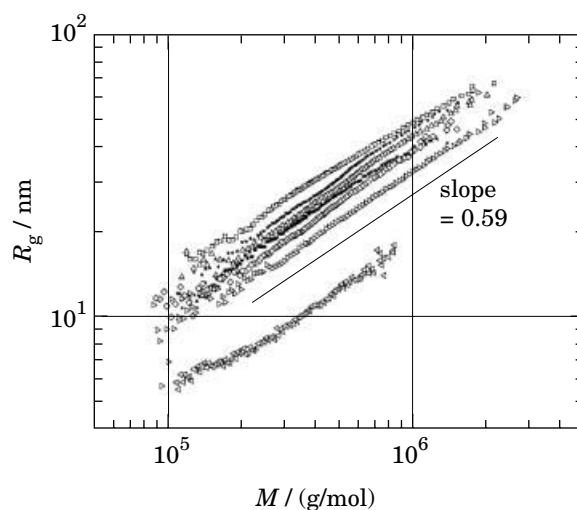
**Solution 1.17:**

Two segments at  $\mathbf{r}$  and  $\mathbf{r}'$  separated by  $n$  segments on one side and  $N - n$  segments on the other side are distributed with a probability proportional to

$$\exp\left(-\frac{3(\mathbf{r} - \mathbf{r}')^2}{2nb^2}\right) \exp\left(-\frac{3(\mathbf{r} - \mathbf{r}')^2}{2(N-n)b^2}\right) = \exp\left(-\frac{3(\mathbf{r} - \mathbf{r}')^2}{2n'b^2}\right)$$

where  $1/n' = 1/n + 1/(N - n) = N/[n(N - n)]$ . When normalized, the probability is given by  $G(\mathbf{r}, \mathbf{r}'; n')$ . The average of  $(\mathbf{r} - \mathbf{r}')^2$  is

$$\begin{aligned} \langle (\mathbf{r} - \mathbf{r}')^2 \rangle &= N^{-1} \int_0^N dn \int d\mathbf{r} (\mathbf{r} - \mathbf{r}')^2 G(\mathbf{r}, \mathbf{r}'; n') \\ &= N^{-1} \int_0^N dn n' b^2 = N^{-1} b^2 \int_0^N dn \frac{n(N-n)}{N} = \frac{1}{6} N b^2 \end{aligned}$$



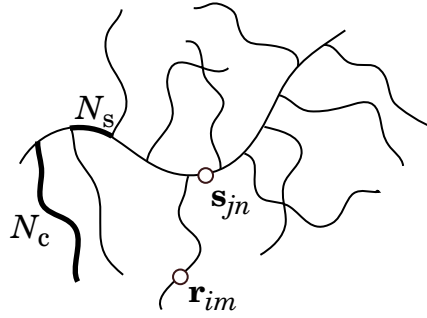
**Figure 1.52.** Radius of gyration  $R_g$  of branched polyethylene prepared at different reaction pressures, plotted as a function of the molecular weight  $M$ . (From Ref. 9.)

Thus,

$$R_{\text{g,ring}}^2 = \frac{1}{2} \langle (\mathbf{r} - \mathbf{r}')^2 \rangle = \frac{1}{12} N b^2$$

**Problem 1.18:** A comb polymer has  $n_A$  anchors along its backbone, interspaced by  $N_s$  monomers. Each comb consists of  $N_c$  monomers. What is  $R_g$  of this comb polymer, when all monomers have an equal mass? Assume that all parts of the comb polymer are ideal, each monomer has a size of  $b$ , and  $N_s, N_c, n_A \gg 1$ .

**Solution 1.18:**



Let  $\mathbf{r}_{im}$  be the position of the  $m$ th monomer on the  $i$ th comb and  $\mathbf{s}_{jn}$  be the position of the  $n$ th monomer on the  $j$ th block on the main chain.  $1 \leq m \leq N_c$ ,  $1 \leq n \leq N_s$ ,  $1 \leq i, j \leq n_A$ . There are a total  $n_A(N_c + N_s)$  monomers in the chain. The mean square distance between the two monomers has four parts:  $S_A$  (two monomers on the same comb),  $S_B$  (two monomers on different combs),  $S_C$  (two monomers on the main chain), and  $S_D$  (one monomer on the comb, the other on the main chain):

$$\begin{aligned} S_A &= \sum_{i=1}^{n_A} \sum_{m,n=1}^{N_c} \langle (\mathbf{r}_{im} - \mathbf{r}_{in})^2 \rangle \cong n_A b^2 \frac{1}{3} N_c^3 \\ S_B &= \sum_{i \neq j}^{n_A} \sum_{m,n=1}^{N_c} \langle (\mathbf{r}_{im} - \mathbf{r}_{jn})^2 \rangle = \sum_{i \neq j}^{n_A} \sum_{m,n=1}^{N_c} b^2 (|i-j|N_s + m + n) \\ &= b^2 \sum_{i \neq j}^{n_A} \left( N_s |i-j| N_c^2 + 2 \sum_{m,n=1}^{N_c} m \right) \cong n_A^2 b^2 N_c^2 \left( \frac{1}{3} N_s n_A + N_c \right) \\ S_C &= \sum_{i,j=1}^{n_A} \sum_{m,n=1}^{N_s} \langle (\mathbf{s}_{im} - \mathbf{s}_{jn})^2 \rangle \cong \frac{1}{3} b^2 (n_A N_s)^3 \\ S_D &= \sum_{i,j=1}^{n_A} \sum_{m=1}^{N_c} \sum_{n=1}^{N_s} \langle (\mathbf{r}_{im} - \mathbf{s}_{jn})^2 \rangle = \sum_{i,j=1}^{n_A} \sum_{m=1}^{N_c} \sum_{n=1}^{N_s} b^2 (|i-j|N_s + m + n) \end{aligned}$$

$$\cong b^2 \left( \frac{1}{3} n_A^3 N_s^2 N_c + \frac{1}{2} n_A^2 N_s N_c (N_s + N_c) \right)$$

We find that  $S_A \ll S_B$ . The means square distance between two monomers is

$$\frac{S_B + S_C + 2S_D}{n_A^2 (N_s + N_c)^2} = b^2 \left[ \frac{1}{3} n_A N_s + \frac{N_c (N_c^2 + N_s N_c + N_s^2)}{(N_s + N_c)^2} \right]$$

Thus,  $R_g^2$  is given by

$$R_g^2 = \frac{1}{2} b^2 \left[ \frac{1}{3} n_A N_s + \frac{N_c (N_c^2 + N_s N_c + N_s^2)}{(N_s + N_c)^2} \right]$$

Note that the second term in the square bracket is negligible when  $n_A N_s \gg N_c$ . The chain dimension is determined by the main chain only.

## 1.7 MOLECULAR WEIGHT DISTRIBUTION

### 1.7.1. Average Molecular Weights

**1.7.1.1 Definitions of the Average Molecular Weights** Nearly all of polymer is a mixture of molecules with a different degree of polymerization. This **polydispersity** is absent in some synthetic oligomers and some polymers of biological origin such as proteins. **Monodisperse** polymers refer to those with a single molecular weight. They are exceptions. Polymers are usually polydisperse and have a molecular weight distribution. A few representative values are used as a typical molecular weight of the polymer. We learn here about average molecular weights.

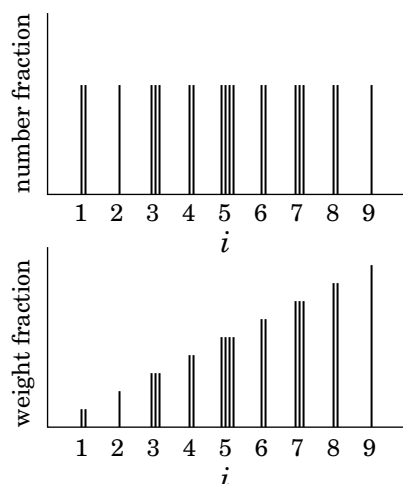
Let the sample of the polymer consist of  $n_i$  chains of exact molecular weight  $M_i$ , where the  $i$ th component has a degree of polymerization  $i$ . The difference between  $M_i$  and  $M_{i+1}$  is the mass of the repeating unit. The **number-average molecular weight**  $M_n$  is defined as

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \quad \text{number-average molecular weight} \quad (1.86)$$

The weight-average molecular weight  $M_w$  is defined as

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \quad \text{weight-average molecular weight} \quad (1.87)$$

Note that  $n_i / \sum n_i$  gives the number fraction of the  $i$ th component and  $n_i M_i / \sum n_i M_i$  is its weight fraction. For  $i \gg 1$ ,  $M_i \propto i$  because the chain ends are only a small part of the long chain; therefore, the weight fraction is given by  $i n_i / \sum i n_i$  as well. It is not necessary that  $n_i$  be the actual number of polymer molecules, but  $n_i$



**Figure 1.53.** Distribution of chain length in a polymer sample. a: Number fraction. b: Weight fraction. The total height of the bars at each  $i$  gives the weight factor to calculate the number average and the weight average, respectively.

must be proportional to the number. Figure 1.53 illustrates the difference between the number fraction and the weight fraction. The total height of the bars at each  $i$  gives the weight factor in calculating the average. In the number average, each polymer chain is counted equally regardless of its length. In the weight average, a longer chain is counted with a greater proportion.

Also used is the z-average molecular weight  $M_z$  further weighted with  $M_i$ :

$$M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2} \quad \text{z-average molecular weight} \quad (1.88)$$

For a perfectly monodisperse polymer,  $M_n = M_w = M_z$ . Otherwise,  $M_n < M_w < M_z$ . The ratio of  $M_w$  to  $M_n$  is often used to express how polydisperse the polymer sample is. The ratio is called **polydispersity index**, often abbreviated as PDI:

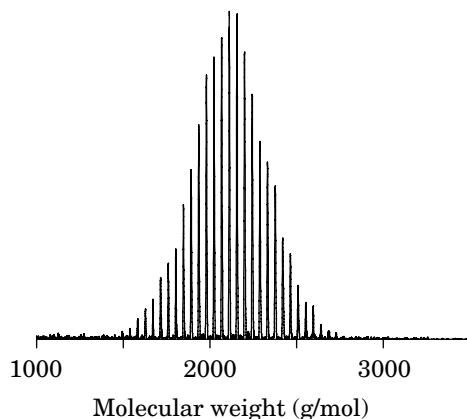
$$\text{PDI} = \frac{M_w}{M_n} = \frac{\sum_i n_i \sum_i n_i M_i^2}{\left(\sum_i n_i M_i\right)^2} \quad \text{polydispersity index} \quad (1.89)$$

Unless the polymer is monodisperse,  $\text{PDI} > 1$ . A sample with a greater PDI has a broader molecular weight distribution.

A continuous version of the molecular weight distribution is also used in the definition of the average molecular weights. The discrete variable  $M_i$  is now replaced by a continuous variable  $M$ , and  $n_i$  is replaced by  $f(M)$ , where  $f(M)dM$  is proportional to the number of polymer molecules with molecular weights between  $M$  and







**Figure 1.54.** Example of a mass spectrum of a polymer obtained in MALDI-TOF mass spectrometry. Poly(ethylene glycol) of a nominal molecular weight of 2,000 g/mol is shown. (From Ref. 10.)

$M + dM$ . Now the three definitions of the average molecular weight are

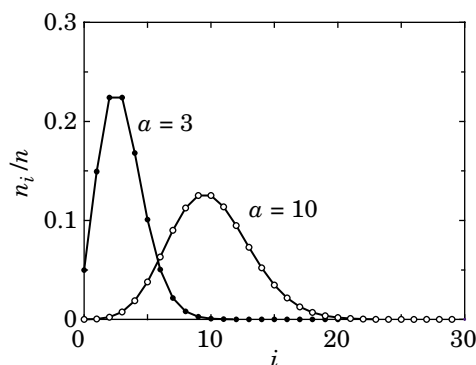
$$M_n = \frac{\int Mf(M) dM}{\int f(M) dM} \quad (1.90)$$

$$M_w = \frac{\int M^2f(M) dM}{\int Mf(M) dM} \quad (1.91)$$

$$M_z = \frac{\int M^3f(M) dM}{\int M^2f(M) dM} \quad (1.92)$$

**1.7.1.2 Estimation of the Averages and the Distribution** Osmometry (membrane or vapor pressure) counts the number of independently moving units (polymer chains) per volume and therefore can be used to estimate  $M_n$ . A proton NMR spectrum can also give  $M_n$ . If the polymer is end-functionalized, titration can give an estimate of  $M_n$ . In Section 2.4, we will learn that light scattering gives an estimate of  $M_w$ .

Recently, mass spectroscopy has been increasingly applied to the analysis of the molecular weight distribution of polymers. Development of a soft ionization method that allows a whole polymer chain to be ionized without fragmentation has facilitated the application. The method is called matrix-assisted laser desorption ionization (MALDI) and usually coupled with time-of-flight (TOF) mass analyzer. Figure 1.54 shows an example of the mass spectrum.<sup>10</sup> The sample is poly(ethylene glycol) of a nominal molecular weight of 2,000 g/mol. The peaks are interspaced by the monomer molecular weight of 44 g/mol. The width of each peak is due to the presence of isotopes (mostly  $^{13}\text{C}$ ). The application has been limited, however, to



**Figure 1.55.** Poisson distribution. The number fraction  $n_i/n$  is shown for  $a = 3$  and 10.

polymers with a narrow molecular weight distribution or with molecular weights less than a few tens of thousand g/mol. Ions consisting of a single molecule but with multiple charges and ions consisting of more than one polymer molecules cause significant ghost peaks at twice as large  $m/z$ , half as large  $m/z$ , and so forth. A sample with a broad molecular weight distribution makes these ghost peaks overlap. Furthermore, there is a question of the molecular weight-dependent ionization efficiency.

Size exclusion chromatography has been the mainstay in the analysis of the molecular weight distribution. Although the resolution is poorer than that of mass spectrometry by orders of magnitude, the chromatographic separation gives an unbiased molecular weight distribution. We will learn about the chromatographic method in Section 2.5.

## 1.7.2 Typical Distributions

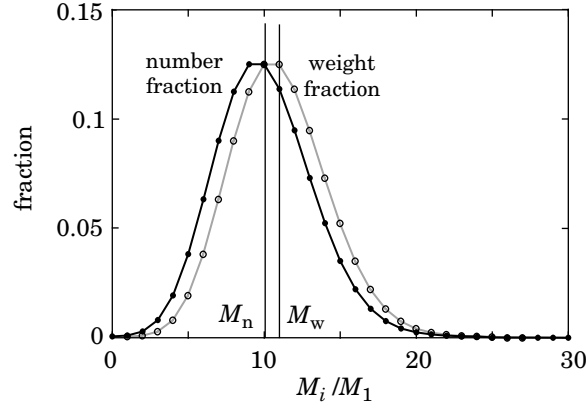
**1.7.2.1 Poisson Distribution** We now calculate the average molecular weights for some typical distributions of a linear polymer. The examples are a **Poisson distribution** and an **exponential distribution** in a discrete space and a **log-normal distribution** in a continuous space.

In the Poisson distribution, the number fraction of the  $i$ th component is given by

$$n_i/n = e^{-a} a^i / i! \quad (i = 0, 1, 2, \dots) \quad (1.93)$$

where  $n$  is the total number of chains and  $a$  is a constant. A greater  $a$  makes the distribution heavier at larger values of  $i$ . Figure 1.55 shows the Poisson distributions with  $a = 3$  and 10. For simplicity, we assume that  $M_i = iM_1$ , where  $M_1$  is the monomer molecular weight. Then,  $M_n$  is calculated as

$$M_n = \sum_{i=0}^{\infty} M_i n_i/n = M_1 e^{-a} \sum_{i=0}^{\infty} i a^i / i! = M_1 e^{-a} a \sum_{i=1}^{\infty} a^{i-1} / (i-1)! = M_1 a \quad (1.94)$$



**Figure 1.56.** Number fraction and weight fraction of the Poisson distribution.  $M_n$  and  $M_w$  are also indicated.

The constant  $a$  is the number-average degree of polymerization. Likewise,

$$\sum_{i=0}^{\infty} M_i^2 n_i/n = M_1^2 e^{-a} \left[ a^2 \sum_{i=2}^{\infty} a^{i-2}/(i-2)! + a \sum_{i=1}^{\infty} a^{i-1}/(i-1)! \right] = M_1^2 (a^2 + a) \quad (1.95)$$

Thus  $M_w = (1 + a)M_1$ . Note that  $M_n$  and  $M_w$  differ only by  $M_1$ . Therefore,

$$\text{PDI} = 1 + \frac{1}{a} = 1 + \frac{M_1}{M_n} \quad (1.96)$$

PDI decreases toward 1 as  $M_n$  increases. Figure 1.56 shows  $M_n$  and  $M_w$  together with its parent Poisson distribution with  $a = 10$ . If  $a = 1,000$ , then  $\text{PDI} = 1.001$ . Polymers prepared in living polymerization are known to have a distribution close to the Poisson distribution.

**1.7.2.2 Exponential Distribution** In the exponential distribution, the number fraction of the  $i$ th component is given by

$$n_i/n = (1 - a)a^{i-1} \quad (i = 1, 2, \dots) \quad (1.97)$$

where  $a$  is a constant ( $a < 1$ ).  $n_i$  decreases with an increasing  $i$ . With  $M_i = iM_1$ ,  $M_n$  is calculated as

$$M_n = \sum_{i=1}^{\infty} M_i n_i/n = M_1 (1 - a) \sum_{i=0}^{\infty} i a^{i-1} = \frac{M_1}{1 - a} \quad (1.98)$$

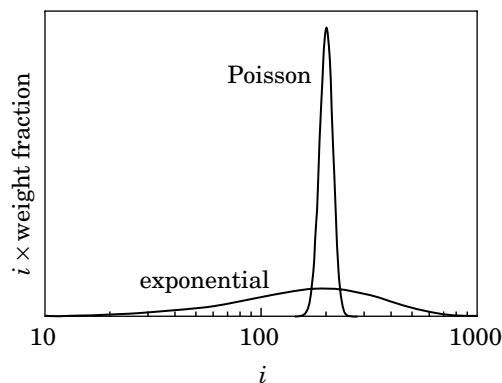


Figure 1.57. Poisson distribution and exponential distribution with the same  $M_w$ .

To have a high molecular weight,  $a$  must be close to 1. Likewise,

$$\sum_{i=1}^{\infty} M_i^2 n_i / n = M_1^2 (1 - a) \sum_{i=0}^{\infty} i^2 a^{i-1} = M_1^2 \frac{1 + a}{(1 - a)^2} \quad (1.99)$$

which gives  $M_w = M_1(1 + a)/(1 - a)$ . Thus the polydispersity is

$$\text{PDI} = 1 + a = 2 - \frac{M_1}{M_n} \quad (1.100)$$

As  $M_n$  increases, PDI increases to 2. Polymers prepared in condensation polymerization follows this distribution. In the latter,  $a$  is the probability for the reactive end to add another monomeric unit, not the terminator.

Figure 1.57 compares the weight fraction distribution of the Poisson distribution and the exponential distribution with the same  $M_w$ . The abscissa is on a logarithmic scale; therefore, the ordinate is the weight fraction  $\times i$ . The difference in the width between the two distributions is large.

**1.7.2.3 Log-Normal Distribution** Size-exclusion chromatography (Section 2.5) is widely used to obtain a continuous distribution of the molecular weight. The direct signal from the detector is proportional to the mass of the polymer in the relevant fraction, and the signal plotted as a function of time is close to the weight fraction on a logarithmic scale of  $M$ . Therefore, we usually display  $d\Sigma/d \ln M$  as a function of  $\ln M$ , where  $\Sigma$  is the cumulative weight fraction defined as

$$\Sigma(M) \equiv \int_0^M Mf(M) dM \quad (1.101)$$

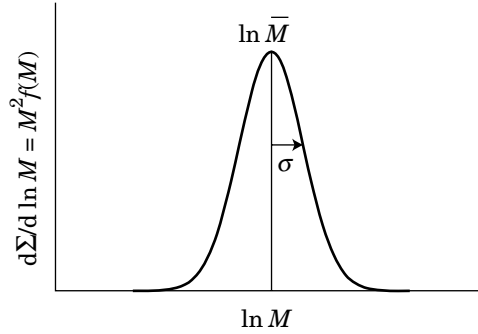


Figure 1.58. Log-normal distribution.

Then, what is displayed is  $M^2f(M)$ . The log-normal distribution is a normal distribution for  $M^2f(M)$  with a random variable of  $\ln M$ :

$$M^2f(M) = (2\pi\sigma^2)^{-1/2} \exp\left[-(\ln M - \ln \bar{M})^2/2\sigma^2\right] \quad (1.102)$$

where  $\bar{M}$  is the peak molecular weight on the log scale and  $\sigma^2$  is the variance. The weight distribution function is normalized:

$$\int Mf(M)dM = \int M^2f(M)d \ln M = 1 \quad (1.103)$$

The distribution is shown in Figure 1.58. We notice that the log-normal distribution has almost the same shape as that of the Poisson distribution or the exponential distribution. The similarity is due to the law of large numbers.

Other relevant integrals are calculated as follows:

$$\begin{aligned} \int f(M) dM &= (2\pi\sigma^2)^{-1/2} \int \exp\left[-(\ln M - \ln \bar{M} + \sigma^2)^2/2\sigma^2 - \ln \bar{M} + \sigma^2/2\right] d \ln M \\ &= (1/\bar{M})\exp(\sigma^2/2) \end{aligned} \quad (1.104)$$

$$\begin{aligned} \int M^2f(M) dM &= (2\pi\sigma^2)^{-1/2} \int \exp\left[-(\ln M - \ln \bar{M} - \sigma^2)^2/2\sigma^2 + \ln \bar{M} + \sigma^2/2\right] d \ln M \\ &= \bar{M} \exp(\sigma^2/2) \end{aligned} \quad (1.105)$$

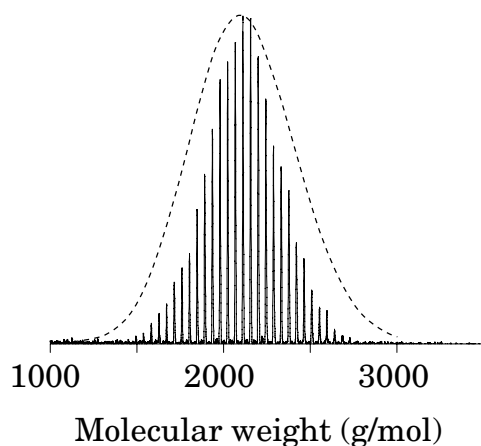
Thus,

$$M_n = \bar{M} \exp(-\sigma^2/2), \quad M_w = \bar{M} \exp(\sigma^2/2), \quad \text{PDI} = \exp(\sigma^2) \quad (1.106)$$

### 1.7.3 PROBLEMS

**Problem 1.19:** The peak of the molecular weight distribution in Fig. 1.54 is around 2,100 g/mol. Compare the plot in the figure with the Poisson distribution with this peak molecular weight.

**Solution 1.19:** The dashed line was calculated for  $DP = 48$ .



**Problem 1.20:** Find the molecular weight of the polymer that maximizes the number fraction in the Poisson distribution (Eq. 1.93). Assume that  $i \gg 1$ .

**Solution 1.20:**

$$\ln(n_i/n) = -a + i \ln a - \ln i! \cong -a + i \ln a - i(\ln i - 1)$$

At the peak,

$$0 = \frac{\partial}{\partial i} \ln(n_i/n) = \ln a - (\ln i - 1) - 1 = \ln(a/i)$$

The value of  $i$  that gives the peak is  $a$ . The peak molecular weight is  $aM_1$ .

**Problem 1.21:** Show that the polydispersity of an  $n_A$ -arm star polymer,  $PDI_{\text{star}}$ , is related to the polydispersity of the arm,  $PDI_{\text{arm}}$ , as

$$PDI_{\text{star}} = 1 + \frac{PDI_{\text{arm}} - 1}{n_A}$$

**Solution 1.21:** Let  $f(M)$  be the normalized number distribution of the molecular weight of each arm. The molecular weight  $M_{\text{star}}$  of the star polymer is the sum

of the molecular weights  $M_j$  of the arm ( $j = 1, \dots, n_A$ ):

$$M_{\text{star}} = \sum_{j=1}^{n_A} M_j$$

From definition,

$$\text{PDI}_{\text{star}} = \frac{\int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} \left( \sum_{j=1}^{n_A} M_j \right)^2}{\left( \int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} \sum_{j=1}^{n_A} M_j \right)^2}$$

The denominator and the numerator are calculated respectively as

$$\begin{aligned} \int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} \sum_{j=1}^{n_A} M_j &= \sum_{j=1}^{n_A} \int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} M_j \\ &= \sum_{j=1}^{n_A} \int M_j f(M_j) dM_j = n_A \int M_1 f(M_1) dM_1 \\ \int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} \left( \sum_{j=1}^{n_A} M_j \right)^2 &= \sum_{i,j=1}^{n_A} \int f(M_1) dM_1 \dots \int f(M_{n_A}) dM_{n_A} M_i M_j \\ &= n_A \int M_1^2 f(M_1) dM_1 + n_A(n_A - 1) \left( \int M_1 f(M_1) dM_1 \right)^2 \end{aligned}$$

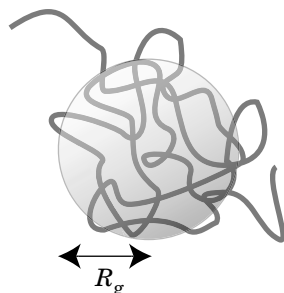
Then,

$$\begin{aligned} \text{PDI}_{\text{star}} &= \frac{n_A \int M_1^2 f(M_1) dM_1 + n_A(n_A - 1) \left( \int M_1 f(M_1) dM_1 \right)^2}{\left( n_A \int M_1 f(M_1) dM_1 \right)^2} \\ &= \frac{1}{n_A} \frac{\int M_1^2 f(M_1) dM_1}{\left( \int M_1 f(M_1) dM_1 \right)^2} + 1 - \frac{1}{n_A} = 1 + \frac{1}{n_A} (\text{PDI}_{\text{arm}} - 1) \end{aligned}$$

## 1.8 CONCENTRATION REGIMES

### 1.8.1 Concentration Regimes for Linear Flexible Polymers

In a crude approximation, each linear polymer chain occupies a space of a sphere or a cube of a linear dimension of  $R_g$ , as illustrated in Figure 1.59. Each



**Figure 1.59.** A polymer chain has a volume approximately of a sphere of radius  $R_g$ .

monomer occupies a volume of  $\sim b^3$ . The volume fraction of the monomers in this volume is

$$\frac{Nb^3}{R_g^3} \cong \frac{Nb^3}{(bN^\nu)^3} = N^{1-3\nu} \quad (1.107)$$

The exponent  $1 - 3\nu$  is  $-1/2$  for an ideal chain and  $-4/5$  (or  $-0.77$  for  $\nu = 0.59$ ) for a real chain. The monomer volume fraction decreases as the chain becomes longer. The real chain is expanded; therefore, the decrease is steeper than that of the ideal chain. The monomer volume fraction is low in the sphere. It is 0.029 at  $N = 100$  and 0.0049 at  $N = 1,000$  for the real chain.

At low concentrations, these spheres or cubes are separated from each other. As the concentration  $c$  (mass concentration; expressed in g/mL, for instance) increases, they become congested and eventually touch each other. At the so-called **overlap concentration** ( $c^*$ ), the whole volume of the solution is packed with these spheres. The overall concentration of the solution is equal to the concentration in the sphere given by Eq. 1.107 at the chain overlap. Thus  $c^* \sim N^{1-3\nu}$ . More quantitative definitions of  $c^*$  are usually used:

$$c^* \left( \frac{4\pi}{3} R_g^3 \right) = \frac{M}{N_A} \quad (1.108)$$

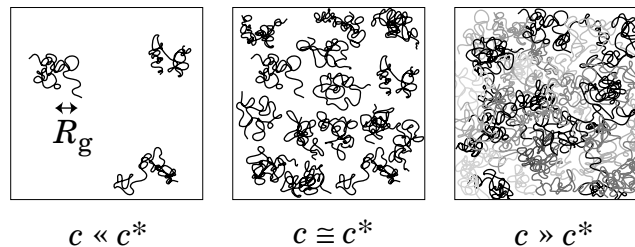
$$c^* (\sqrt{2} R_g)^3 = \frac{M}{N_A} \quad (1.109)$$

$$c^* [\eta] = 1 \quad (1.110)$$

where  $M/N_A$  is the mass of each chain, with  $N_A$  being the Avogadro's number. The last equation relies on the intrinsic viscosity  $[\eta]$  of the polymer, which we will further discuss in Section 3.3.

Figure 1.60 depicts three ranges of concentration  $c$ :  $c \ll c^*$ ,  $c \cong c^*$ , and  $c \gg c^*$ . When  $c$  is below  $c^*$ , the solution is called **dilute**. At  $c \ll c^*$ , the chains are separated





**Figure 1.60.** Concentration regimes for solutions of linear flexible polymers: dilute solution,  $c \ll c^*$ ; solution at the overlap concentration  $c \cong c^*$ ; semidilute solution,  $c \gg c^*$ .

from each other and behave more or less independently. The polymer chain interacts primarily with the solvent molecules. The solution is close to an ideal solution. The situation is different at concentrations above  $c^*$ . The solution in this regime is called **semidilute**. At  $c \gg c^*$ , chains are overlapped and entangled. Their mobility is greatly reduced compared with the chains in dilute solutions. The thermodynamic properties of the semidilute solutions are greatly different from those of an ideal solution extrapolated to the same concentration. In polymer solutions, deviation from the ideal solution takes place at a low concentration in terms of the volume fraction or the mass concentration. The existence of the semidilute regime is characteristic of the polymer solutions. At a higher concentration  $c^{**}$ , the solution enters a so-called **concentrated** regime in which each segment of the polymer chain does not have a sufficient space available. Typically, the volume fraction of the polymer at  $c^{**}$  is between 0.2 and 0.3. For a polymer of a sufficiently high molecular weight, there is a broad range of concentrations between  $c^*$  and  $c^{**}$ . For polystyrene of  $M = 3 \times 10^5$  g/mol that has  $R_g = 21$  nm, for instance, Eq. 1.108 gives  $c^* = 0.013$  g/mL, and  $c^{**}$  is 0.2 to 0.3 g/mL.

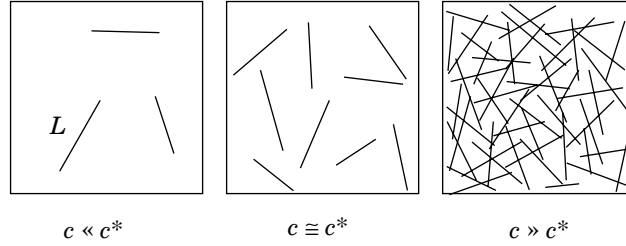
We rely on  $R_g$  to define  $c^*$ . This provision allows us to apply the same definition to solutions of nonlinear polymers such as star polymer, a branched polymer, and a spherical polymer. As chains become more spherical,  $R_g$  decreases compared at the same molecular weight. Then, the overlap occurs at a higher concentration.

### 1.8.2 Concentration Regimes for Rodlike Molecules

The concentration regimes are different for rigid-chain polymers. Here we consider solutions of rodlike molecules (the contour length  $L \gg L_p$ ). A thin rodlike molecule of length  $L$  occupies a volume of  $L^3$  to allow tumbling of the molecule without colliding with other molecules. The overlap concentration  $c^*$  is then given by

$$c^* L^3 = \frac{M}{N_A} \quad (1.111)$$

The dilute solution, the solution at  $c^*$ , and the semidilute solution are illustrated in Figure 1.61. Compared with a linear flexible chain,  $c^*$  is much lower. Because



**Figure 1.61.** Concentration regimes for solutions of rodlike polymers: dilute solution,  $c \ll c^*$ ; solution at the overlap concentration  $c \cong c^*$ ; semidilute solution,  $c \gg c^*$ .

$L \sim M$ ,  $c^* \sim M^{-2}$ . As expected, the effect of neighboring polymer molecules is more evident in its motion, rather than it is in the thermodynamic properties.

At higher concentrations, the solution loses isotropy and turns into a nematic liquid crystal. In the nematic phase, the molecules are more or less aligned along one axis, but their centers are still randomly distributed.

### 1.8.3 PROBLEMS

**Problem 1.22:** How does  $c^*$  of a wormlike chain with  $L_p$  and  $L_c$  depend on the molecular weight  $M$ ?

**Solution 1.22:**

$$c^* \cong \frac{M}{N_A} R_g^{-3} = \frac{m_L}{N_A} R_g^{-3} L_c$$

where  $m_L = M/L_c$  is the molecular weight per length along the chain contour and therefore independent of  $M$ . When  $L_c \ll L_p$ ,  $R_g \cong L_c$ . Therefore,  $c^* \sim L_c/L_c^3 \sim L_c^{-2} \sim M^{-2}$ . When  $L_c \gg L_p$ ,  $R_g \cong (L_c L_p)^{1/2}$ . Therefore,  $c^* \sim L_c/(L_c L_p)^{3/2} \sim (L_p^3 L_c)^{-1/2} \sim M^{-1/2}$ .

**Problem 1.23:** The overlap concentration can also be defined for a solution of a polydisperse polymer. We impose the condition that the whole volume of the solution be filled with cubes of volume equal to (radius of gyration)<sup>3</sup> for each chain. Find the concentration  $c_i$  of component  $i$  at the chain overlap.

**Solution 1.23:** Let  $n_i$  chains of component  $i$  be present in the solution of volume  $V$ . At the chain overlap,

$$a \sum_i n_i R_{g,i}^3 = V$$

where  $a$  is a constant and  $R_{g,i}$  is the radius of gyration for component  $i$ . In the solution of a single component  $i$ , the condition is given by

$$an_i^* R_{g,i}^3 = V$$

where  $n_i^*$  is the number of chains at the overlap in the monodisperse solution. Thus,

$$\sum_i \frac{n_i}{n_i^*} = 1$$

which is identical to

$$\sum_i \frac{c_i}{c_i^*} = 1$$

where  $c_i^*$  is the overlap concentration for the solution of monodisperse polymer  $i$ , and  $c_i$  is the concentration of component  $i$  in the solution.