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Single Polymer Chain

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1.1 Conformation of a Polymer Chain

A polymer chain is a linear molecule containing a large number of atoms. Prior to considering the shape of a polymer chain, let us focus on the local structure of a polymer composed offour carbons (Figure 1.2). When a carbon–carbon single bond is present between the monomers, the distance between each monomer is approximately 1.5 Å. Additionally, if carbons are connected by a single bond, the bond angle θ is essentially constant at 109.5°. Even if the bond length and bonding angle are constant, rotation around the bond axis, represented by ψ, is allowed, resulting in conformational flexibility. In fact, the value of ψ takes the trans ($\psi = 0°$) or gauche ($\psi = \pm 120°$) stable angles due to steric hindrance.

Let us increase the number of carbons to 100 and consider the shape of the resulting polymer chain. For example, if all the bonds take trans conformations, the polymer chain takes an elongated form with an end-to-end distance of approximately 25 nm. Conversely, if all bonds are in gauche conformations, the polymer chain takes a helical structure, and the end-to-end distance becomes very short. Although these structures can be realized by some specific macromolecules or under specific conditions, conventional polymers contain both trans and gauche forms and have highly complicated structures. However, by applying coarse-graining concepts, sufficiently long polymer chains can be approximated to a model chain regardless of the details of the monomer unit.

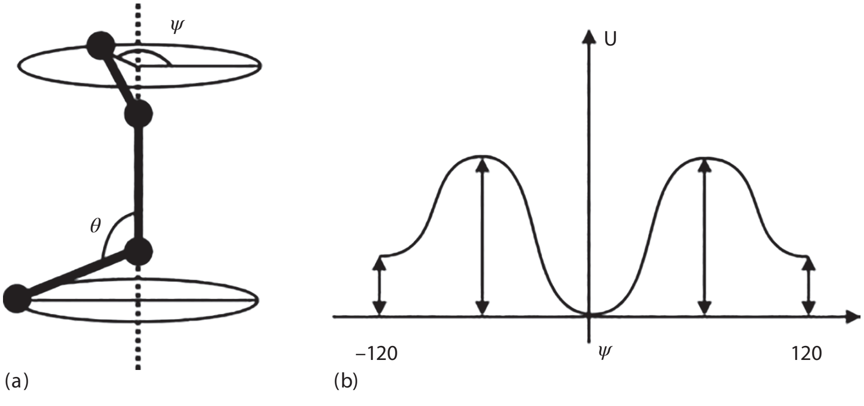

Figure 1.2 Conformation oflocal structures containing four carbon atoms (a) and the energy landscape (b).

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1.2 Coarse-Graining of a Polymer Chain

Here, we introduce "coarse-graining," which is an important concept in discussing polymers. Coarse-graining is one methodology for extracting the universal characteristics of a phenomenon. Roughly speaking, coarse-graining methods intentionally shift focus away from the trivial matters for the characteristics ofinterest, simplify the problem, and provide the universal characteristics. Let us see an example of coarse-graining for polymer chains. The first coarse-graining is "setting the bond length as constant and the bond angle as freely rotational." This assumption represents a considerable "jump" from the discussion earlier. In principle, the bonding angle should be constant at approximately 109.5°, and the local conformation should be trans or gauche.

However, one simple idea justifies this coarse graining. The idea is to combine some monomers together and to make a "segment." Figure 1.3 shows a schematic of making a segment from three monomers; as a result, a polymer chain can be visualized as a sequence of segments. As shown in Figure 1.3, the bonds between neighboring segments can take various angles relative to the bonds between monomers, and the individual properties of each monomer can be masked. Masking the individual properties of each monomer is of great importance in polymer physics, because only under such conditions can we extract the universal properties of the polymer chain. The length of the smallest segment that has freely rotating bonds is called the segment length, which is intrinsic to each monomer unit. Conversely, by taking the appropriate segment with the segment length, the end-to-end distance of a polymer chain is determined by considering a series of segments connected by freely rotating bonds. For simplicity, this book considers polymer chains as consisting of monomers that act as segments with freely rotating bonds, following the method of de Gennes [1]. In other words, the monomer length is the same as the segment length, and the degree of polymerization is the same as the number of segments.

1.3 Free Rotation Model

Chains consisting of segments with free rotation can be addressed using the free rotation chain model. Assuming that a polymer chain consists of N vectors (a_i) of size a, the end-to-end distance (r) of the chain is written as follows:

$$r = a_1 + a_2 + \cdots + a_N \tag{1.1}$$

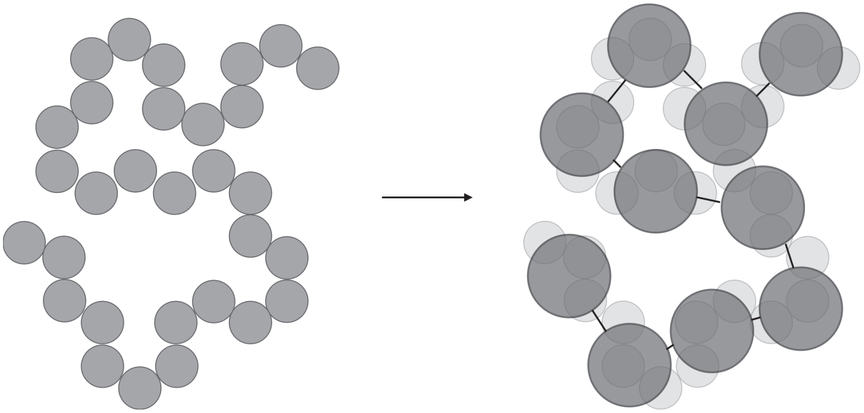

Figure 1.3 Coarse-graining of monomeric units in a polymer chain.

Since it may be difficult to start with a three-dimensional problem, let us first consider the problem in one dimension. The one-dimensional version of this problem is actually given by the familiar problem as follows:

A point proceeds $+a$ or $-a$ with equal probabilities in one step. How far is the point from the origin after N steps?

This problem is equivalent to tossing coins in high school mathematics. In this case, the displacement, r, can be calculated as an expected value as follows:

$$\begin{aligned} r &= a\left(-N\binom{N}{0}\left(\frac{1}{2}\right)^{N} - (N-2)\binom{N}{1}\left(\frac{1}{2}\right)^{N-1}\left(\frac{1}{2}\right)\right. \\ &\qquad \left. + \cdots + (N-2)\binom{N}{1}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^{N-1} + N\binom{N}{0}\left(\frac{1}{2}\right)^{N}\right) \\ &= a\left[N\left\{-\binom{N}{0}\left(\frac{1}{2}\right)^{N} + \binom{N}{0}\left(\frac{1}{2}\right)^{N}\right\}\right. \\ &\qquad \left. + (N-2)\left\{-\binom{N}{1}\left(\frac{1}{2}\right)^{N-1}\left(\frac{1}{2}\right) + \binom{N}{1}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)^{N-1}\right\} + \cdots\right] = 0 \end{aligned} \tag{1.2}$$

The result of $r = 0$ is not essential. This answer is obvious from the expression of Eq. (1.2); the situations in which a point reaches $-r$ and r have equal probabilities and cancel each other. In both cases, the end-to-end distance should be considered, r. The absolute value of the displacement must be considered to correctly evaluate the size. In general, the absolute value of the displacement is obtained by the square root of the root mean square ofr ($<r^2>^{1/2}$). Let us return to the three-dimensional problem from here. For a general three-dimensional vectorr, $<r^2>$is calculated as follows:

$$\begin{aligned}<r^2>= r\cdot r &= (a_1 + a_2 + \cdots + a_N)(a_1 + a_2 + \cdots + a_N) \\ &= \sum_{i=1}^{N} a_i{}^2 + \sum_{i=1}^{N}\sum_{k\neq i}^{N} a_i a_k = Na^2 \end{aligned} \tag{1.3}$$

Here, $a_i a_k = 0$ (if $i \neq k$) since each jump vector is uncorrelated ($<\cos\theta>=0$ because the average value of bond angle is 90°). Given that the polymer chains are isotropic, the polymer chains are considered spheres of diameter $aN^{1/2}$. In a one-dimensional problem, some people may feel uncomfortable that vectors can overlap each other. Although the overlap is highly reduced in the three-dimensional space, overlap between the monomer units is permitted under this model. This polymer chain is called an ideal chain [2–4]. This concept is analogous to an ideal gas having no volume. Of course, the overlapping of monomers is not allowed in real polymers; this model is incorrect except in special cases. Despite this assumption being unrealistic, it is the foundation for many theoretical models because the end-to-end distance of an ideal chain follows the Gaussian distribution. The Gaussian distribution is a simple and useful statistical model and thus provides physical quantities in simple forms with less difficulty than other methods. Section 1.2 shows that the Gaussian distribution successfully describes the end-to-end distance of an ideal chain.

1.4 Statistics of a Single Polymer Chain

1.4.1 End-to-End Distance of a 1D Random Walk

In Section 1.3, the average end-to-end distance of an ideal chain was determined based on the distribution of end-to-end distances. This section considers the probability that an ideal chain has a specific distance of x. Again, let us start with a one-dimensional problem. Assuming that the number of steps the point proceeded in the + direction is N_+ and that in the − direction is N_- in the previously mentioned one-dimensional problem, the following equations are obtained:

$$N = N_+ + N_- \tag{1.4}$$

$$x = N_+ - N_- \tag{1.5}$$

For simplicity, we can assume that the length of a step is unity and estimate the number of situations ($W(N, x)$) in the case that the point reaches x after N steps. Because sets of N_+ and N_- for arriving at x are uniquely determined from Eqs. (1.4) and (1.5), $W(N, x)$ is estimated as the number of arrangements of N_+ pieces of "+" and N_- pieces of "−" (Figure 1.4):

$$W(N, x) = \binom{N}{N_+} = \frac{N!}{(N - N_+)!\,N_+!} = \frac{N!}{\left(\frac{N+x}{2}\right)!\left(\frac{N-x}{2}\right)!} \tag{1.6}$$

On the other hand, the total number of possible paths in N steps is 2^N, which is calculated as the total number of situations that can occur when selecting one of the two choices N times. Thus, the probability of reaching x after N steps is expressed as follows:

$$\frac{W(N,x)}{2^N} = \frac{N!}{2^N\left(\frac{N+x}{2}\right)!\left(\frac{N-x}{2}\right)!} \tag{1.7}$$

Calculating the exact value for all N is a very painful task; however, if we make a proper approximation at a sufficiently large limit of N, this equation leads to a Gaussian distribution. Let us calculate this value following the method of Rubinstein and Colby [4]. First, the natural logarithm is taken of both sides of the equation:

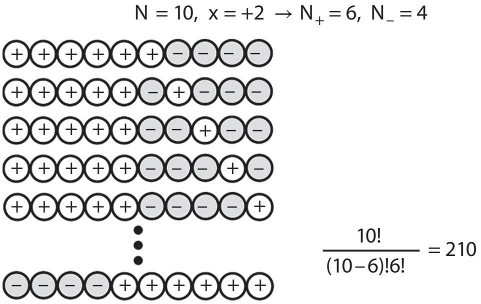

Figure 1.4 Number of situations that reach *x* in *N* steps ($N = 10$, $x = +2$).

$$\ln\left(\frac{W(N,x)}{2^N}\right) = \ln N! - N\ln 2 - \ln\left(\frac{N+x}{2}\right)! - \ln\left(\frac{N-x}{2}\right)! \tag{1.8}$$

The last two terms are reduced to the following:

$$\ln\left(\frac{N+x}{2}\right)! = \ln\left[\left(\frac{N}{2}+\frac{x}{2}\right)\left(\frac{N}{2}+\frac{x}{2}-1\right)\cdots\left(\frac{N}{2}+2\right)\left(\frac{N}{2}+1\right)\cdot\left(\frac{N}{2}\right)!\right]$$
$$= \ln\left(\frac{N}{2}\right)! + \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+s\right) \tag{1.9}$$

$$\ln\left(\frac{N-x}{2}\right)! = \ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+1-s\right) \tag{1.10}$$

By substituting Eqs. (1.9) and (1.10) into Eq. (1.8), one obtains the following:

$$\ln\left(\frac{W(N,x)}{2^N}\right) = \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+s\right) + \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+1-s\right)$$

$$= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2} \ln \frac{\left(\frac{N}{2}+s\right)}{\left(\frac{N}{2}+1-s\right)} \tag{1.11}$$

The fourth term in Eq. (1.11) can be rewritten as the following:

$$\ln \frac{\left(\frac{N}{2}+s\right)}{\left(\frac{N}{2}+1-s\right)} = \ln \frac{\left(1+\frac{2s}{N}\right)}{\left(1+\frac{2-2s}{N}\right)} = \ln\left(1+\frac{2s}{N}\right) - \ln\left(1+\frac{2-2s}{N}\right) \tag{1.12}$$

Here, we apply an important approximation of the relationship betweens and N. The maximum value of s is N/2, and the number of situations corresponding to this case is only 1. In most cases, s stays close to the origin (see one-dimensional walks), making it sufficiently smaller than N. Here, by ignoring the case oflarge s, which is unlikely, and only considering the case where $s << N$, the expression can be further transformed using a Taylor expansion ($\ln(1+y) \approx y$).

$$\ln\left(1+\frac{2s}{N}\right) - \ln\left(1+\frac{2-2s}{N}\right) \cong \frac{2s}{N} - \frac{2-2s}{N} = \frac{4s}{N} - \frac{2}{N} \tag{1.13}$$

Using Eq. (1.13), Eq. (1.11) can be transformed to the following:

$$\begin{aligned}
\ln\left(\frac{W(N,x)}{2^N}\right) &= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\left(\frac{4s}{N} - \frac{2}{N}\right) \\
&= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \frac{4}{N}\sum_{s=1}^{x/2} s + \frac{2}{N}\sum_{s=1}^{x/2} 1 \\
&= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \frac{4}{N}\frac{\left(\frac{x}{2}\right)\left(\frac{x}{2}+1\right)}{2} + \frac{2}{N}\frac{x}{2} \\
&= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \frac{x^2}{2N}
\end{aligned} \tag{1.14}$$

Equation (1.14) can be reduced using the following Starling approximation:

$$N! \cong \sqrt{2\pi N}\left(\frac{N}{e}\right)^N \quad \text{for} \quad N>>1 \tag{1.15}$$

$$\begin{aligned}
\ln\left(\frac{W(N,x)}{2^N}\right) &= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \frac{x^2}{2N} \\
&= \ln\left(\sqrt{2\pi N}\left(\frac{N}{e}\right)^N\right) - N\ln 2 - 2\ln\left(\sqrt{\pi N}\left(\frac{N}{2e}\right)^{N/2}\right) - \frac{x^2}{2N} \\
&= \ln\sqrt{2\pi N} + N\ln\frac{N}{e} - N\ln 2 - \ln \pi N - N\ln\frac{N}{2e} - \frac{x^2}{2N} \\
&= \ln\left(\sqrt{\frac{2}{\pi N}}\right) - \frac{x^2}{2N}
\end{aligned} \tag{1.16}$$

As a result, the probability is given by the following:

$$\frac{W(N, x)}{2^N} = \sqrt{\frac{2}{\pi N}} \exp\left(-\frac{x^2}{2N}\right) \tag{1.17}$$

If we consider x to be a continuous value and this function to be a continuous function, Eq. (1.17) corresponds to a probability density distribution function. To investigate the function, let us integrate it from $-\infty$ to ∞:

$$\int_{-\infty}^{\infty} \frac{W(N, x)}{2^N} dx = \sqrt{\frac{2}{\pi N}} \int_{-\infty}^{\infty} \exp\left(-\frac{x^2}{2N}\right) dx = \sqrt{\frac{2}{\pi N}} \cdot \sqrt{2\pi N} = 2 \tag{1.18}$$

Since this calculation corresponds to calculating "the sum of probabilities," it is natural that the value of the integral is 1. The doubled integral value comes from the procedure of converting discrete x to continuous x. As shown in Table 1.1, in the lattice space, when N is an even number, the probability that x becomes odd is 0. On the other hand, if N is an odd number, the probability that x will be even is 0. Therefore, for any case, as x is changed to 1, 2, 3, …, the probability alternates between a finite value and 0 (Table 1.1). The integral value of 2 comes from simply changing the discontinuous function to a continuous function.

Table 1.1 Number of situations reaching *x* in *N* steps.

	x	−4	−3	−2	−1	0	1	2	3	4
W (N, x)	N = 3	0	1	0	3	0	3	0	1	0
	N = 4	1	0	4	0	6	0	4	0	1

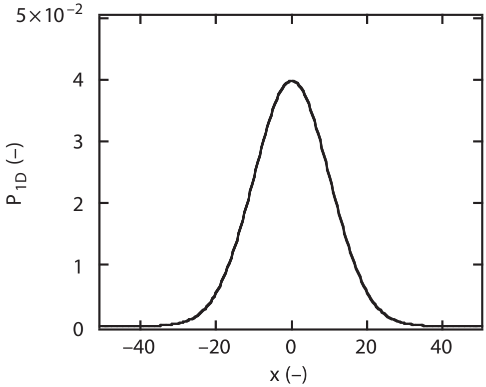

Figure 1.5 Probability density distribution function of the one-dimensional Gaussian distribution (P_{1D} with $a = 1$, $N = 100$).

By standardizing Eq. (1.17) by 2, the probability density function of a one-dimensional random walk ($P_{1D}(N, x)$) is obtained.

$$P_{1D}(N, x) = \frac{1}{\sqrt{2\pi N}} \exp\left(-\frac{x^2}{2N}\right) \tag{1.19}$$

This equation is the same as the Gaussian distribution with an average ($<x>$) of 0 and a variance ($<x^2>$) of N(Figure 1.5). The general Gaussian distribution is expressed as follows:

$$f(x) = \frac{1}{\sqrt{2\pi <x^2>}} \exp\left(-\frac{(x - <x>)^2}{2<x^2>}\right) \tag{1.20}$$

At the end of the one-dimensional problem, let Eq. (1.20) be expanded to an arbitrary step length. When the step length is a, $<x> = 0$ and $<x^2> = a^2N$, resulting in the following:

$$P_{1D}(N, x) = \frac{1}{\sqrt{2\pi a^2 N}} \exp\left(-\frac{x^2}{2a^2N}\right) \tag{1.21}$$

1.4.2 End-to-End Distance of a 3D Random Walk

Let us expand the 1D discussion to three dimensions. In 3D space, the probability that one end is at the origin and the other at $r = (r_x, r_y, r_z)$ is expressed as follows:

$$P_{3D}(N, r)dr_x\, dr_y\, dr_z = P_{1D}(N, r_x)dr_x \cdot P_{1D}(N, r_y)dr_y \cdot P_{1D}(N, r_z)dr_z \tag{1.22}$$

By obtaining the root mean square of r from Eq. (1.3) and assuming the spatial isotropy, the following equation is obtained:

$$\begin{aligned} &<r^2> = <r_x{}^2> + <r_y{}^2> + <r_z{}^2> = Na^2 \\ &<r_x{}^2> = <r_y{}^2> = <r_z{}^2> = \frac{Na^2}{3} \end{aligned} \tag{1.23}$$

Here, we focus on the x-axis component. From Eqs. (1.21) and (1.23), the following equation is obtained:

$$P_{1D}(N, r_x) = \frac{1}{\sqrt{2\pi <r_x{}^2>}} \exp\left(-\frac{r_x{}^2}{2<r_x{}^2>}\right) = \sqrt{\frac{3}{2\pi Na^2}} \exp\left(-\frac{3r_x{}^2}{2Na^2}\right) \tag{1.24}$$

The y- and z-axis components are estimated in similar ways and substituted into Eq. (1.22).

$$\begin{aligned} P_{3D}(N, r) &= P_{1D}(N, r_x) \cdot P_{1D}(N, r_y) \cdot P_{1D}(N, r_z) \\ &= \left(\frac{3}{2\pi Na^2}\right)^{3/2} \exp\left(-\frac{3(r_x{}^2 + r_y{}^2 + r_z{}^2)}{2Na^2}\right) \\ &= \left(\frac{3}{2\pi Na^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2Na^2}\right) \end{aligned} \tag{1.25}$$

Compared with Eq. (1.21), the probability density functions in one dimension and three dimensions are almost the same. However, the probability distribution that the distance between both ends becomes $|r|$ differs greatly between one dimension and three dimensions. In one dimension, the probability distribution ($r \neq 0$) is written as follows since the distance between the ends being $|r|$ only occurs in two cases: the cases of $-r$ and $+r$.

$$\mathrm{Pr}_{1D}(N, |r|) = 2\sqrt{\frac{1}{2\pi N a^2}} \exp\left(-\frac{r^2}{2Na^2}\right) = \sqrt{\frac{2}{\pi N a^2}} \exp\left(-\frac{r^2}{2Na^2}\right) \tag{1.26}$$

Because there is only one situation for $r = 0$, the probability distribution is given by

$$\mathrm{Pr}_{1D}(N, |r|) = \sqrt{\frac{1}{2\pi N a^2}} \exp\left(-\frac{r^2}{2Na^2}\right) \tag{1.27}$$

In the case of three dimensions, we need to consider a multiplicity factor of $4\pi r^2$ because the end-to-end distance of $|r|$ occurs everywhere on the spherical shell with radius $|r|$. Thus, the probability distribution can be written as follows:

$$\mathrm{Pr}_{3D}(N, |r|) = 4\pi r^2 \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2Na^2}\right) \tag{1.28}$$

Figure 1.6 shows the probability distributions of one-dimensional and three-dimensional end-to-end distances. Their shapes are completely different from each other; in one dimension, there is a local maximum in the vicinity of $r = 0$,

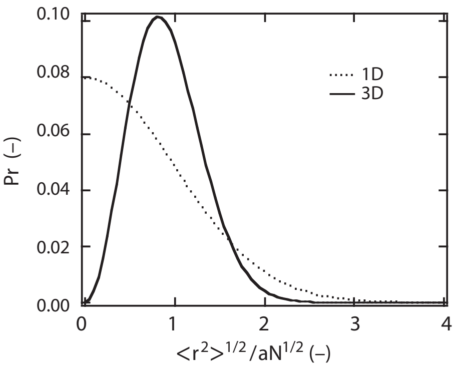

Figure 1.6 Probability distribution of end-to-end distances of one-dimensional and three-dimensional random walks.

whereas in three dimensions, there is a local maximum in the vicinity of $aN^{1/2}$. Notably, the probability that the random coil returns to the vicinity of the origin is almost 0 in three dimensions. This difference is obviously due to the multiplication factor of $4\pi r^2$, as there was no significant difference in the probability density distribution itselfin one dimension and three dimensions. In three-dimensional space, only $r_x = r_y = r_z = 0$ satisfies $|r| = 0$, whereas there are many combinations of r_x, r_y, r_z that satisfies $r_x{}^2 + r_y{}^2 + r_z{}^2 = |r|^2$, when $|r| \neq 0$. This difference in multiplicity causes the major difference in the one-dimensional and three-dimensional probability distributions.