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Single Polymer Chain

Takamasa Sakai

Graduate School of Engineering, The University of Tokyo, Tokyo, Japan

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1.1 General Features

A polymer gel is a three-dimensional network of polymer chains containing a large amount of solvent (Figure 1.1). When a network structure is formed only by chemical bonding, all the polymer chains are included in a single molecule; one large macromolecule traps a large number of solvent molecules. Let us calculate the molecular weight of a polymer gel. For example, 100 g of a gel with a polymer concentration of 5% contains 5 g of polymer networks. In other words, one molecule has a weight of 5 g. Because the molecular weight is given by the sum of Avogadro's number of weights of individual molecules, the molecular weight of the polymer gel is 3×10^{24} g/mol, which is extremely large. When one stretches a piece of polymer gel, all the chains forming this extremely large macromolecule are stretched, which is why the mechanical properties of polymer gels are predicted based on the simple sum of the contributions of single polymers connected to neighboring chains via crosslinks. Thus, learning the characteristics of a single polymer chain is important for understanding polymer gels. This chapter introduces some methodologies for extracting the universal characteristics of a single polymer chain.

1.1.1 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 of four 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,

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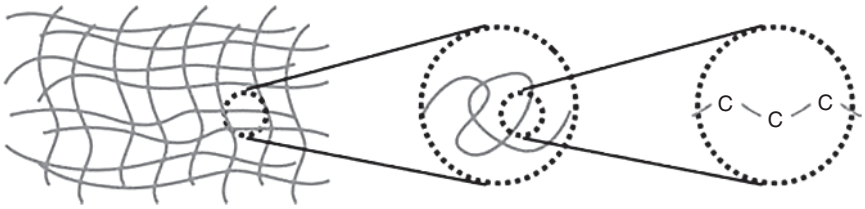

Figure 1.1 Schematic diagram of polymer gels. The polymer network consists of polymer chains connected to neighboring chains via crosslinks.

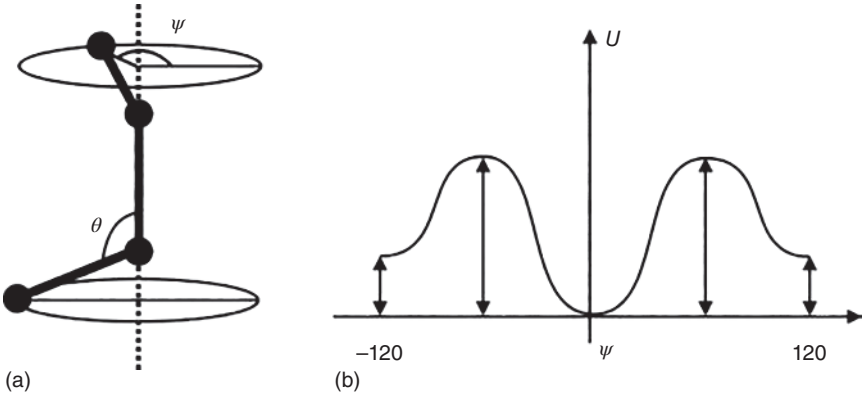

Figure 1.2 Conformation of local structures containing four carbon atoms (a) and the energy landscape (b).

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.

1.1.2 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 of interest, 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.

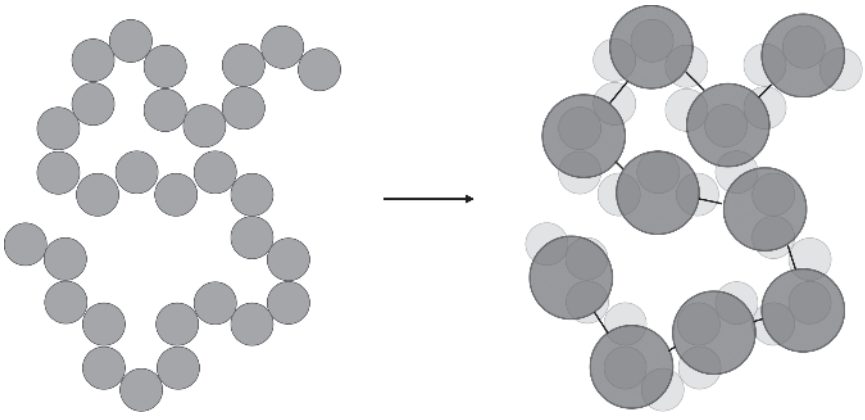

Figure 1.3 Coarse-graining of monomeric units in a polymer chain.

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.

1.1.3 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 ($\mathbf{a}_i$) of size a, the end-to-end distance ($\mathbf{r}$) of the chain is written as follows:

$$\mathbf{r} = \mathbf{a}_1 + \mathbf{a}_2 + \cdots + \mathbf{a}_N \tag{1.1}$$

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:

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

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 of r ($\langle r^2\rangle^{1/2}$). Let us return to the three-dimensional problem from here. For a general three-dimensional vector $\mathbf{r}$, $\langle \mathbf{r}^2\rangle$ is calculated as follows:

$$\begin{aligned} \langle \mathbf{r}^2\rangle &= \mathbf{r}\cdot\mathbf{r} = (\mathbf{a}_1+\mathbf{a}_2+\cdots+\mathbf{a}_N)(\mathbf{a}_1+\mathbf{a}_2+\cdots+\mathbf{a}_N) \\ &= \sum_{i=1}^{N}{\mathbf{a}_i}^2+\sum_{i=1}^{N}\sum_{k\neq i}^{N}\mathbf{a}_i\mathbf{a}_k = Na^2 \end{aligned} \tag{1.3}$$

Here, $\mathbf{a}_i\mathbf{a}_k = 0$ (if $i \neq k$) since each jump vector is uncorrelated ($\langle\cos\theta\rangle = 0$ 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.

1.2 Statistics of a Single Polymer Chain

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

In Section 1.1.3, 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

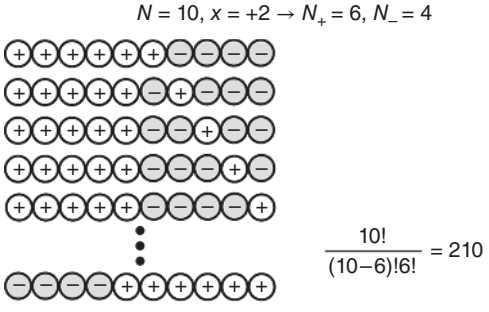

Figure 1.4 Number of situations that reach x in N steps ($N = 10$, $x = +2$).

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:

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

The last two terms are reduced to the following:

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

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

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

$$\begin{aligned}\ln\left(\frac{W(N,x)}{2^N}\right) &= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+s\right) \\ &\quad + \sum_{s=1}^{x/2}\ln\left(\frac{N}{2}+1-s\right) \\ &= \ln N! - N\ln 2 - 2\ln\left(\frac{N}{2}\right)! - \sum_{s=1}^{x/2}\ln\frac{\left(\frac{N}{2}+s\right)}{\left(\frac{N}{2}+1-s\right)} \end{aligned} \tag{1.11}$$

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 between s 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 of large s, which is unlikely, and only considering the case where $s \ll N$, 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:

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

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

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 ∞:

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

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

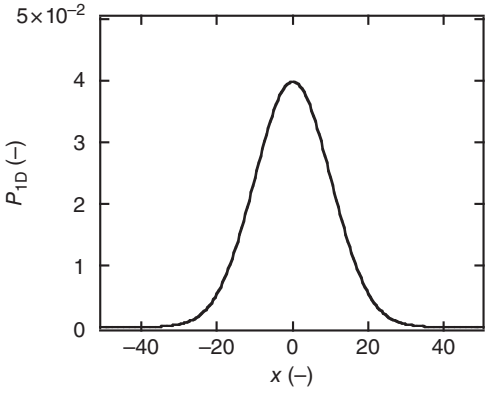

Figure 1.5 Probability density distribution function of the one-dimensional Gaussian distribution (P_{1D} with $a = 1$, $N = 100$).

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 ($\langle x \rangle$) of 0 and a variance ($\langle x^2 \rangle$) of N (Figure 1.5). The general Gaussian distribution is expressed as follows:

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

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, $\langle x \rangle = 0$ and $\langle x^2 \rangle = a^2 N$, resulting in the following:

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

1.2.2 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 $\mathbf{r} = (r_x, r_y, r_z)$ is expressed as follows:

$$P_{3D}(N, \mathbf{r}) \mathrm{d}r_x \, \mathrm{d}r_y \, \mathrm{d}r_z = P_{1D}(N, r_x) \mathrm{d}r_x \cdot P_{1D}(N, r_y) \mathrm{d}r_y \cdot P_{1D}(N, r_z) \mathrm{d}r_z \tag{1.22}$$

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

$$\langle \mathbf{r}^2 \rangle = \langle {r_x}^2 \rangle + \langle {r_y}^2 \rangle + \langle {r_z}^2 \rangle = Na^2$$
$$\langle {r_x}^2 \rangle = \langle {r_y}^2 \rangle = \langle {r_z}^2 \rangle = \frac{Na^2}{3} \tag{1.23}$$

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

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

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

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

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 $|\mathbf{r}|$ differs greatly between one dimension and three dimensions. In one dimension, the probability distribution ($\mathbf{r} \neq 0$) is written as follows since the distance between the ends being $|\mathbf{r}|$ only occurs in two cases: the cases of $-r$ and $+r$.

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

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

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

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 $|\mathbf{r}|$ occurs everywhere on the spherical shell with radius $|\mathbf{r}|$. Thus, the probability distribution can be written as follows:

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

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 $r = 0$,

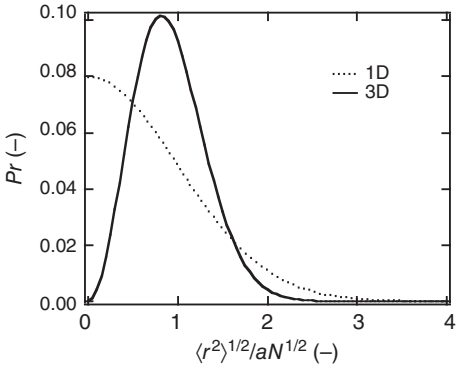

Figure 1.6 Probability distribution of end-to-end distances of one-dimensional and three-dimensional random walks.

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 itself in one dimension and three dimensions. In three-dimensional space, only $r_x = r_y = r_z = 0$ satisfies $|\mathbf{r}| = 0$, whereas there are many combinations of r_x, r_y, r_z that satisfies ${r_x}^2 + {r_y}^2 + {r_z}^2 = |\mathbf{r}|^2$, when $|\mathbf{r}| \neq 0$. This difference in multiplicity causes the major difference in the one-dimensional and three-dimensional probability distributions.

1.2.3 Force Needed to Stretch an Ideal Chain

We then consider the force required to stretch an ideal chain. Under constant temperature and pressure, the total free energy of an ideal chain is written using enthalpy (U) and entropy (S).

$$F = U - TS \tag{1.29}$$

The change in total free energy when the end-to-end distance is extended to r is written as follows:

$$\Delta F = \Delta U - T\Delta S = \{U(N, \mathbf{r}) - U(N, 0)\} - T\{S(N, \mathbf{r}) - S(N, 0)\} \tag{1.30}$$

Here, it should be noted that the reference state is $\mathbf{r} = 0$, which is discussed in detail later. Based on the definition, entropy is expressed as the following:

$$S = k \ln \Omega \tag{1.31}$$

where Ω is the number of possible conformations of the ideal chain with a number of monomers equal to N and an end-to-end vector of $\mathbf{r}$. In contrast, by definition, Ω can be written as follows:

$$P_{3D}(N, \mathbf{r}) = \frac{\Omega(N, \mathbf{r})}{\int \Omega(N, \mathbf{r}) \mathrm{d}\mathbf{r}} \tag{1.32}$$

From Eqs. (1.31) and (1.32), one obtains the following:

$$S = k \ln \left(P_{3D}(N, \mathbf{r}) \cdot \int \Omega(N, \mathbf{r}) \mathrm{d}\mathbf{r} \right) \tag{1.33}$$

In contrast, there is no enthalpy change (ΔU) during stretching because the large deformation can be achieved by rotation around the bond axis without changing the bond lengths or bond angles. (Indeed, there is a weak energy term derived from the interactions between polymer segments, but it does not exist under the assumptions of an ideal chain.) Therefore, the energy change during the deformation mainly stems from the entropy change. This so-called entropic elasticity is completely different from the energy elasticity, which stems from the enthalpy changes of metals and ceramics. Taken together, the energy change from the deformation is given by the following:

$$\begin{aligned} -\frac{\Delta F}{T} &= S(N,\mathbf{r}) - S(N,0) = k\ln\left(P_{3D}(N,\mathbf{r})\int \Omega(N,\mathbf{r})\mathrm{d}\mathbf{r}\right) \\ &\quad - k\ln\left(P_{3D}(N,0)\int \Omega(N,\mathbf{r})\mathrm{d}\mathbf{r}\right) \\ &= k\ln\frac{P_{3D}(N,\mathbf{r})}{P_{3D}(N,0)} + k\left\{\ln\int \Omega(N,\mathbf{r})\mathrm{d}\mathbf{r} - \ln\int \Omega(N,\mathbf{r})\mathrm{d}\mathbf{r}\right\} \\ &= k\ln\frac{P_{3D}(N,\mathbf{r})}{P_{3D}(N,0)} \end{aligned} \tag{1.34}$$

Notably, $\int \Omega(N,\mathbf{r})\mathrm{d}\mathbf{r}$ is the total number of possible conformations and corresponds to 2^N in the one-dimensional problem described earlier, and this value does not depend on $\mathbf{r}$. Substituting Eq. (1.25) into Eq. (1.34), we obtain Eq. (1.35):

$$-\frac{\Delta F}{T} = k\ln\frac{P_{3D}(N,\mathbf{r})}{P_{3D}(N,0)} = k\ln\frac{\left(\frac{3}{2\pi Na^2}\right)^{3/2}\exp\left(-\frac{3r^2}{2Na^2}\right)}{\left(\frac{3}{2\pi Na^2}\right)^{3/2}} = -\frac{3kr^2}{2Na^2} \tag{1.35}$$

Finally, applying $R_0 = aN^{1/2}$, the following equation is obtained:

$$\Delta F = \frac{3kTr^2}{2Na^2} = \frac{3kT}{2}\left(\frac{r}{R_0}\right)^2 \tag{1.36}$$

Next, let us calculate the force, f, required to stretch the chain. f is obtained by differentiating the free energy change (ΔF) with displacement (r):

$$f = \frac{\partial \Delta F}{\partial r} = -T\frac{\partial S}{\partial r} = \frac{3kT}{{R_0}^2}r \tag{1.37}$$

The force is proportional to the strain, so the elasticity of the polymer follows Hooke's law. An ideal chain is a spring with a spring constant of $3kT/{R_0}^2$. This spring softens as the polymer becomes longer or the temperature decreases. Notably, the primary component of the spring constant is kT, which is the energy of simple thermal motion. Figure 1.7 is a schematic picture showing a physical representation of this phenomenon. Many children (monomers) are holding hands with each other, and each is moving freely (thermal motion). Let us consider increasing the distance between the flags being held by the children at each end by little bit. When the distance between the ends is short, it may be possible to easily separate the flags to a certain extent, but as the flags are pulled apart more and more, the resistance will increase. Imagining that if the

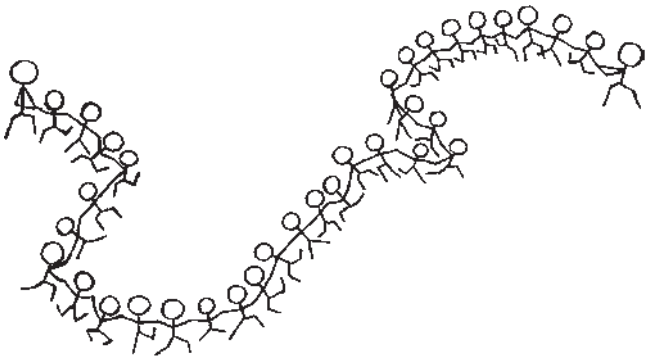

Figure 1.7 Schematic picture of a thermally fluctuating polymer chain.

movement of the children gets faster intuitively suggests that the necessary force becomes greater. Essentially, the same phenomenon occurs when stretching a polymer chain. The elastic energy of the polymer originates from the thermal fluctuations of the monomer units.

Importantly, this spring has a finite length and can be extended to a maximum of aN. As mentioned earlier, the applicability of the Gaussian distribution is limited for small deformations (Eq. (1.13)). When stretched beyond a certain point, the force diverges to values greater than what are predicted. The maximum stretchability is roughly predicted by the Kuhn model from the initial length ($aN^{1/2}$) and maximum length (aN) [5]. This equation expects that longer polymers will be more stretchable.

$$\lambda_{\max} = \frac{aN}{R_0} = \frac{aN}{aN^{1/2}} = N^{1/2} \tag{1.38}$$

Here, let us return to Eq. (1.30) again and think about why the reference condition is $r = 0$. At first glance, this appears contradictory to Eq. (1.28) and Figure 1.6. The end-to-end distance with the highest probability in three dimensions is approximately $aN^{1/2}$, and from the principle of entropy elasticity, the reference state is likely to be approximately $r = aN^{1/2}$. The reference state of $r = 0$ seems to correspond to the one-dimensional results rather than the results in three dimensions. Indeed, this is the essence of the problem. Once the two ends of the polymer are fixed and stretched, the end-to-end vector $\mathbf{r}$ is deformed only in the initial vector direction, and the axial direction will not change. Therefore, the multiplicity of $4\pi r^2$ is lost, reducing the problem to one dimension, which is why the reference state of $r = 0$. From this result, the following strange behavior is expected. When one encounters a polymer in three-dimensional space, the most stable end-to-end distance is $aN^{1/2}$. Once one pinches both ends of the chain, the chain automatically shrinks to 0 because the most stable state is $r = 0$.

Here, we introduce an example in which this phenomenon causes problems. Consider simulating a polymer network using the statistical results of the ideal chain. In three-dimensional space, ideal polymers have an average end-to-end distance of $aN^{1/2}$. We distribute ideal chains so that an average distance between

them is roughly $aN^{1/2}$ and crosslink them. This situation is similar to the situation in which prepolymers with functional groups at both ends are crosslinked by crosslinking agents. We then apply Eq. (1.36), which is the potential for single polymer strands, to each polymer chain. At that moment, the polymer chain automatically shrinks, and the polymer network collapses. In this way, if one simply applies the results based on an ideal chain, one will obtain a practically unrealistic outcome. Similar problems occur when predicting the mechanical properties of polymer networks from the mechanical properties of a single polymer chain.

Since the analytical methods shown in this section can be handled as mathematical equations, it is possible to discuss even coefficients. However, difficult mathematical formulas that are not intuitive must be solved. Additionally, although it is possible to obtain exact solutions under certain limited conditions, solving these equations will not readily provide a rough grasp of more universal behavior. For example, analytically determining the relationship between force and displacement for real polymer chains is practically impossible. On the other hand, the idea of scaling enables us to consider the behavior of polymers in the form of a power law. The scaling theory was first applied to polymer physics by Pierre-Gilles de Gennes. The scaling theory is highly suitable for "coarse-graining" the polymeric system. Using scaling theory, the universal properties of polymers have been predicted and experimentally demonstrated. In this book, analytical description, scaling description, or both are shown to be necessary. In Section 1.3, we introduce the scaling rules for an ideal chain as an introduction of scaling theory.

1.3 Scaling of a Single Polymer Chain

Roughly speaking, the scaling rule is a power law relationship expressing how the parameter of interest changes when other parameters are changed. As an example, let us consider the relationship between the radius (r) and the volume (V) of a sphere:

$$V = \frac{4}{3}\pi r^3 \tag{1.39}$$

What is the essence of this formula? Of course, although it is important for young people to remember the exact equation, it is rare for adults to estimate the exact volume of a ball. There is little possibility of encountering the following problem:

If the radius of a sphere is doubled, by what factor does the volume increase?

When solving this problem, it is not convenient to calculate the volume of the two spheres and then calculate the ratio. Instead, we only use the fact that the volume is the cube of the radius, and $2^3 = 8$. This example gives us a conceptual understanding of the power law relationship, and scaling theory focuses only on the power law relationship. The scaling law between the radius and the volume of the sphere is written as follows:

$$V \sim r^3 \tag{1.40}$$

The coefficient is eliminated, and the formula is dramatically simplified. As a result, this equation expresses the relationship between the volume of the 3D

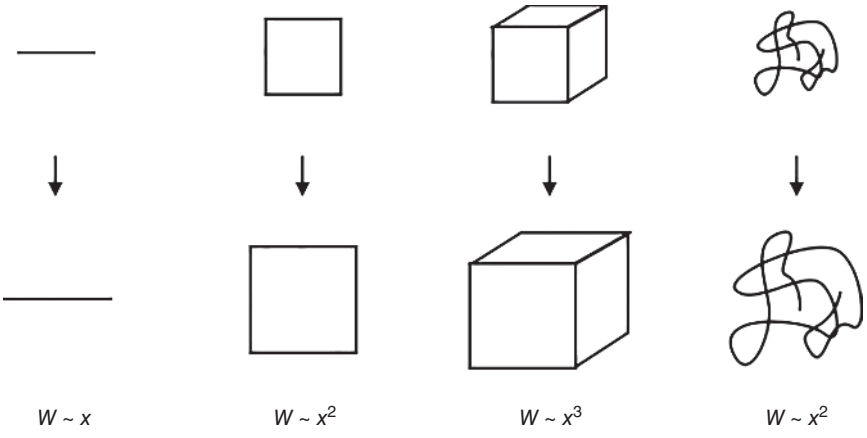

Figure 1.8 Relationship between the weight (W) and length (x) of D-dimensional objects.

object and the representative length. In this way, fine information is lost, and the relationship is generalized. This universality of the scaling fits polymer physics, and it describes the universal rules of polymer chains independent of polymeric species. Indeed, many scaling laws of polymers have been predicted and experimentally validated. Because this book only introduces important scaling laws for understanding polymer gels, I recommend reading the original textbook of de Gennes if you want to learn more. You can find at least two scaling rules earlier in this book. One is scaling for $\langle r^2 \rangle$ of an ideal chain, which is given by Eq. (1.3) as follows:

$$\langle r^2 \rangle \sim N \tag{1.41}$$

From this scaling rule, we can see the characteristics of the ideal chain. In general, an isotropic D-dimensional object has the following relationship between the characteristic length, x, and the weight, w (Figure 1.8):

$$w \sim x^D \tag{1.42}$$

For example, in one dimension, the weight is proportional to the length, and in three dimensions, the weight is proportional to the cube of the length. How does this apply to the ideal chain? Given that the degree of polymerization is proportional to the weight of a polymer chain ($w \sim N$), the following equation is obtained:

$$w \sim N \sim \langle r^2 \rangle \sim x^2 \tag{1.43}$$

The scaling rule reveals that the weight of an ideal chain is proportional to the square of the length. Thus, an ideal chain has a two-dimensional structure despite being an isotropic three-dimensional object. Objects having fractal structures have such extended dimensions, so-called the fractal dimension. Therefore, an ideal chain has a two-dimensional fractal structure.

1.3.1 Stretching of an Ideal Chain

Another important scaling rule that has already been addressed is the relationship between displacement and force in stretching of an ideal chain ($f \sim r$). In this section, scaling theory is applied to determine the force required to stretch an ideal chain. According to de Gennes, this scaling relationship is obtained from the following two conditions:

1. The length (R) after stretching depends only on tension (f), temperature (T), and the initial length (R_0).
2. Since tension (f) is constant at any point along the chain, R must be a linear function of N.

Condition 1 is used for the dimension analysis, which is based on the idea that when the unit systems of the left and right sides are compatible, the equality of the sides is physically correct. This analysis is useful for investigating the relationship between correlating parameters. Many physics teachers will tell you that formula can easily be predicted based on the units of the parameters. An example of dimension analysis is predicting that the formula for speed divides the distance by the time based on the units of speed (m/s). For dimension analysis, let us summarize the units of each physical quantity shown in Condition 1.

$$R\,(\mathrm{m}),\ \ f(\mathrm{N}),\ \ \ T(\mathrm{K}),\ \ \ R_0(\mathrm{m})$$

Since R and R_0 have the same unit system, they seem to be easy to handle, and f and T will require more consideration. For T, the units can be converted to that of energy (J = N m) in the form of kT with Boltzmann's constant (k). For f, multiplying with R forms the work (N m), which involves applying a force of f and stretching the chain by R. Notably, the initial length is 0 since it becomes a one-dimensional problem at the moment both ends are grasped. Based on these considerations, we obtain the following expression by setting the ratio of the length on the left side and the ratio of the energy on the right side:

$$\frac{R}{R_0} \sim \frac{fR}{kT} \tag{1.44}$$

Since this scaling rule is dimensionless on both sides, the dimensions of both sides are of course consistent. However, this equation does not show all possible relationships. Because both sides are dimensionless, even if one multiplies the right side, one can obtain a dimensionally correct expression. Expression (1.44) is a special case ($x = 1$) of the expression shown as follows:

$$\frac{R}{R_0} \sim \left(\frac{fR}{kT}\right)^x \tag{1.45}$$

Since an expression including this arbitrary exponent is obtained from Condition 1, the value of x in the equation derived from Condition 1 is estimated by Condition 2. Let us look at Condition 2 before determining the final scaling rule. What Condition 2 says is extremely simple. That is, "when a chain is divided in half, the force applied to both ends of each half is still f, so the elongation of each half is one-half of that of the whole chain. Therefore, the chain elongation should be

proportional to the degree of polymerization ($R \sim N$)." By applying this condition to Eq. (1.45), x can be determined. Since f and kT do not depend on R or N, they are excluded from the equation, leaving only the relevant physical quantities (R and N).

$$\frac{R}{R_0} \sim R^x \tag{1.46}$$

Rearranging the formula and applying $R_0 \sim N^{1/2}$, we obtain the following:

$$R \sim {R_0}^{\frac{1}{1-x}} \sim N^{\frac{1}{2(1-x)}} \tag{1.47}$$

According to Condition 2 ($R \sim N$), $x = 1/2$. By substituting $x = 1/2$ into Eq. (1.45), the following equation is obtained:

$$f \sim \frac{kT}{{R_0}^2} R \sim \frac{kT}{a^2 N} R \tag{1.48}$$

Although the calculation itself is simple, Eq. (1.48) is almost the same as Eq. (1.37). Let us turn our attention to the following problem. Considering only the unit system, it should be possible to set fR_0 instead of fR as the impulse in Eq. (1.45). Can we still obtain the same conclusion? In fact, the same expression can be obtained. In this way, if one can imagine, one can predict the correct scaling rule without having to solve difficult mathematical problems. This simplicity is an advantage of scaling theory, and at the same time, it can be said that the difficulty in visualizing the problem is the bottleneck. Scaling theory is particularly powerful for complex problems and is compatible with polymer gels with complex structures. Becoming comfortable with scaling theory by learning the various scaling laws in this book will be of great help.

1.3.2 Real Chains

An ideal chain could be modeled as a simple random walk such that the overlapping of monomers is allowed. However, the overlapping of monomers is of course not allowed in reality. A model chain with an excluded volume is called a real chain. Notably, a real chain is a chain modeled by simply adding the excluded volume effect to an ideal chain, but it is still different from chains that actually exist. Real chains are described in a model called a self-avoiding random walk (SAW) [6]. In a SAW, passing through a previously occupied trajectory is inhibited. Although only one condition, in which overlapping is not permitted, is added, the analysis of a SAW is substantially more difficult. For example, the one-dimensional problem cannot be simply extended as it can in ideal chains because the nature of the SAW changes substantially depending on the dimensions of the lattice. For example, in one dimension, there are only two straight paths forward, the plus and minus directions. Intuitively, the number of cases increases qualitatively in 2D and 3D. Even in the two-dimensional and three-dimensional SAWs, it is rare for both chain ends to be close to each other because of the excluded volume effect.

Correlations between close events are relatively easier to consider in the context of processes that are described probabilistically, such as SAW, but to consider

correlations between distant events is extremely difficult. For example, the condition "go forward, but do not to step on the occupied lattice point one step ahead" can be relatively easily formulated, while it is extremely difficult to formulate the condition "do not step on any lattice point that is currently occupied." Despite the difficulty, the statistical properties of SAW have been revealed using various mathematical methodologies. For example, the root-mean end-to-end distance ($\langle r^2 \rangle = {R_F}^2$) in three-dimensional space can be expressed as follows:

$$R_F = aN^{3/5} \tag{1.49}$$

For the derivation, solving difficult mathematical problems or using simulations is necessary. It may seem that compared with $R_0 = aN^{1/2}$ for an ideal chain, this equation is not very different. However, for example, when $a = 3$ Å and $N = 100$, $R_0 = 30$ Å and $R_F = 48$ Å, the difference is a factor of approximately 1.5, which suggests that the effect of overlapping inhibition is reasonably large.

1.3.3 Stretching of a Real Chain

Finally, let us consider the force needed to stretch a real chain. Similar to an ideal chain, the following physical quantities are likely related to this phenomenon:

$$R\,(\mathrm{m}), f\,(\mathrm{N}), T\,(\mathrm{K}), R_F\,(\mathrm{m})$$

The difference between the real chain and the ideal chain is only in the reference, which changed from R_0 to R_F. A similar expression is predicted for an ideal chain:

$$\frac{R}{R_F} \sim \left(\frac{fR}{kT}\right)^x \tag{1.50}$$

Here, unlike in the case of an ideal chain, we assume the chain shows spring-like behavior and resulting Hooke's law ($f \sim R$). Focusing only on the relationship between f and R, we obtain

$$R^{1-x} \sim f^x \tag{1.51}$$

To satisfy Hooke's law, it is necessary for x to equal 1/2. By substituting $x = 1/2$ into Eq. (1.50), the following equation is obtained:

$$f \sim \frac{kT}{{R_F}^2} R \sim \frac{kT}{a^2 N^{6/5}} R \tag{1.52}$$

Equation (1.52) is almost identical to that of an ideal chain, and the only difference is due to the difference between R_0 and R_F. In the case of an ideal chain, when a small force f is applied, R is proportional to N (indeed, the scaling rule was derived from this condition). This relationship indicates that the chain was stretched by tension. On the other hand, in real chains, R is proportional to the power greater than the unity of N ($R \sim N^{6/5}$). This power suggests that the tension is not constant in the chain, and the force applied to the chain is transmitted by the interactions between the units in the real chain as well.

Prior to considering stretching with a large force, we introduce a blob, which is an important concept in polymer physics. Up to this point, we considered f

as a product with reference length and as having the same units as energy or impulse. Pincus, on the other hand, introduced a virtual segment (elastic blob) with a length of ξ defined as the following [7]:

$$\xi \approx \frac{kT}{f} \tag{1.53}$$

As is obvious from the formula, ξ is the length required to give the same impulse as the thermal energy ($k_B T$) from the force f. According to the expression, ξ diverges to infinity at the limit of small forces and becomes 0 at the limit of large forces. ξ is the length at which the impulse given by the external force becomes comparable to the thermal energy. Based on Eq. (1.53), we can estimate the measure of the "small force," which is the condition described by Eq. (1.52). When the applied force is small, ξ is a chain size (not infinite), and the energy given by the force is sufficiently small compared with thermal energy; the thermal motion is not influenced by the applied force. Under this condition, the conformation of the chain is not greatly affected by the external force, and the initial statistics (the statistics of a real chain) are preserved. The initial statistics are disturbed from the point of $\xi = R_F$ because the force ($=kT/R_F$) gives impulses comparable to the thermal energy. When such a force is applied, the conformation of the chain is disturbed, and the initial statistics can no longer be used. Thus, Eq. (1.52) holds at a small f as expressed by the following equation:

$$\xi > R_F \leftrightarrow f < \frac{kT}{R_F} \tag{1.54}$$

Next, let us consider the case when a large force f is applied ($\xi \ll R_F$). First, we focus on a monomer unit in the real chain. Does a great change occur in its correlation with neighboring units? In fact, even when a large force is applied, short-range correlations between neighboring units are hardly affected, which is similar to the situation depicted in Figure 1.7; the children in the middle of the line rarely notice that they are being stretched. Instead, the correlations between groups of units are influenced by the force. The group here is the elastic blob. Inside a blob of size ξ, thermal energy dominates energy from an external force, and inside the blob, the initial conformation is preserved. On the other hand, the correlation between blobs is governed by the applied force. Therefore, under strong stretching, the blobs line up in the stretching direction (Figure 1.9). Assuming that the number of monomer units contained inside the blob is g_p, ξ

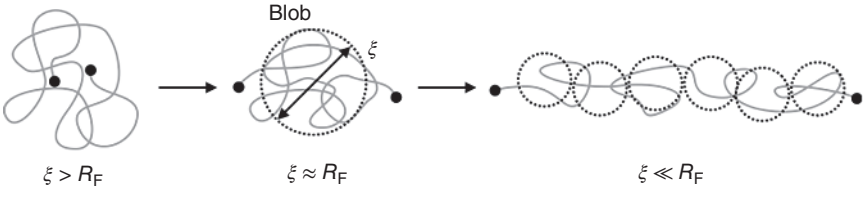

Figure 1.9 Schematic picture of stretching a real chain.

is written as follows:

$$\xi \approx a g_{\mathrm{p}}{}^{3/5} \tag{1.55}$$

Given that the number of blobs is N/g_{p}, the end-to-end distance of a chain is the following:

$$R \approx \xi \cdot \frac{N}{g_{\mathrm{p}}} \approx \xi \cdot N \cdot \left(\frac{\xi}{a}\right)^{-5/3} \approx aN\left(\frac{fa}{kT}\right)^{2/3} \tag{1.56}$$

Now, we rearrange this expression to isolate force f:

$$f \approx \frac{kT}{a}\left(\frac{R}{aN}\right)^{3/2} \tag{1.57}$$

This equation predicts that the force will be proportional to $R^{3/2}$ under a large deformation. However, this power law was not clearly observed in the stretching of a polymer chain as measured by atomic force microscopy (AFM). On the other hand, this scaling rule can be extended to the stretching of gels (Chapter 5), and that rule shows good agreement with experiments [8–10]. Based on these experimental results, the molecular weight of the polymer chain must be sufficiently long to observe the power law predicted by Eq. (1.57).

Column 1: Miscible Gels and Immiscible Gels

In this book, we discuss transparent gels, in which the constituent polymer chains are miscible with the solvent. On the other hand, in turbid gels like "tofu," not all constituent polymers are miscible. In this case, some polymers are phase-separated without solvation, forming an aggregated structure, of which size reaches the visible light region, resulting in turbidity. Therefore, turbid gels can be called immiscible gels or sponge-like gels. Immiscible gels are in between miscible gels and sponges. One of the major differences between miscible and immiscible gels is the solvent retention ability. In immiscible gels, the osmotic pressure is relatively small, because the amount of solvated component is small, leading to poor solvent retention. Therefore, when an immiscible gel is compressed, the solvent is extracted out of the gel. You may know water is easily extracted from tofu; on the other hand, it is hardly extracted from a transparent jelly.

Another difference is that immiscible gels are inherently heterogeneous due to phase separation. In this book, we started the description of polymer gels from that of a polymer chain followed by that of polymer solutions. Thus, this book implicitly treats homogeneous miscible gels. For immiscible gels, mesoscale-sized modeling may be more suitable than molecular models shown in this book; it is better to adopt the prediction based on the mesoscale fibrous structure and the mechanical properties of fibers. Of course, turbid gels like tofu are not just a sponge, but also have properties in between miscible and immiscible gels. Therefore, one needs to consider which character will appear with respect to each physical property.

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