2.3 Sizes of polymer chains

A function of both temperature and bending resistance, the persistence length of a filament sets the scale of its thermal undulations. As will be seen in Sec. 2.5, the persistence lengths of the polymers and filaments in the cell span an immense range, from a thousand times smaller to a thousand times larger than the cellular length scale of a micron. If the contour length of the filament is much smaller than its persistence length, the filament can be viewed as a relatively stiff rod undergoing only limited excursions from its equilibrium shape. In contrast, a filament with a short persistence length compared to its contour length may appear highly convoluted and display a large array of configurations.

The curve drawn in Fig. 2.11 might represent a filament with a contour length L_c many times its persistence length ξ_p. The configuration is not excessively convoluted, but would become more so as L_c grows much larger than ξ_p. The direction of the curve, as characterized by the unit tangent vector $\mathbf{t}(s)$ at arc length s, changes constantly, such that its correlation function $<\mathbf{t}(s)\bullet\mathbf{t}(0)>$ decays exponentially with s as $\exp(-s/\xi_p)$. Over small distances $s << \xi_p$ (positions 1 and 2 on Fig. 2.11) the tangent vector undergoes just a modest change in direction, while over large distances $s >> \xi_p$ (positions 1 and 3), the directions are uncorrelated. Clearly, very flexible polymers sample an extensive collection of contorted shapes with erratically changing directions. Do the configurations in this collection have any large scale characteristics, or are they just an unruly mob of rapidly changing tangents and curvatures? If the ensemble of configurations do have common or universal features, upon what properties of the filaments do they depend?   We discuss discuss several polymer families, characterized by their connectivity and interactions, to answer these questions.

Ideal chains and filaments

Our first investigation of polymer geometry is based upon the continuous filament model introduced in Sec. 2.2. From among the several different observables that characterize the size of a polymer configuration, we choose to evaluate the end-
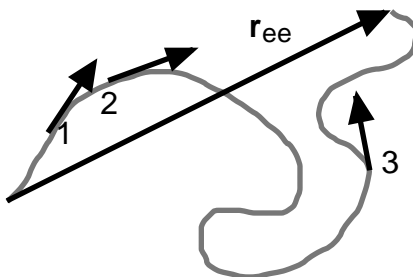

Fig. 2.11. Representative configuration of a filament whose contour length is many times its persistence length ξ_p. Positions 1 and 2 are separated by an arc length s with $s < \xi_p$, while positions 1 and 3 have $s >> \xi_p$. The displacement vector between the ends of the filament is denoted by $\mathbf{r}_{ee}$.

to-end displacement vector $\mathbf{r}_{ee} = \mathbf{r}(L_c) - \mathbf{r}(0)$, where $\mathbf{r}(s)$ denotes the position of the filament at arc length s (see Fig. 2.11). The mean square value of $\mathbf{r}_{ee}$ is then

$$<\mathbf{r}_{ee}^2> = <[\mathbf{r}(L_c) - \mathbf{r}(0)]^2>. \tag{2.24}$$

Integrating the unit tangent vector $\mathbf{t}(s)$ of Eq. (2.4)

$$\mathbf{r}(s) = \mathbf{r}(0) + \int_0^s du\, \mathbf{t}(u), \tag{2.25}$$

permits Eq. (2.24) to be recast as

$$<\mathbf{r}_{ee}^2> = \int_0^{Lc} du \int_0^{Lc} dv <\mathbf{t}(s)\bullet\mathbf{t}(0)>. \tag{2.26}$$

According to Eq. (2.23), the correlation function $<\mathbf{t}(s)\bullet\mathbf{t}(0)>$ decays exponentially as $\exp(-s/\xi_p)$, leaving us to evaluate

$$<\mathbf{r}_{ee}^2> = \int_0^{Lc} du \int_0^{Lc} dv \exp(-|u-v|/\xi_p). \tag{2.27}$$

The condition that the argument of the exponential must be negative can be enforced by breaking the integral into two identical pieces where one integration variable is kept less than the other:

$$<\mathbf{r}_{ee}^2> = 2 \int_0^{Lc} du \int_0^{u} dv \exp(-[u-v]/\xi_p), \tag{2.28}$$

It is straightforward to solve this integral using a few changes of variables

$$2 \int_0^{Lc} \exp(-u/\xi_p)\, du \int_0^{u} dv \exp(v/\xi_p) = 2 \int_0^{Lc} du \exp(-u/\xi_p) \bullet \xi_p \bullet [\exp(u/\xi_p) - 1\,]$$

$$= 2\xi_p^2 \int_0^{Lc/\xi_p} dw\,[1 - \exp(-w)]. \tag{2.29}$$

Evaluating the last integral gives

$$<\mathbf{r}_{ee}^2> = 2\xi_p L_c - 2\xi_p^2 [1 - \exp(-L_c/\xi_p)\,]. \tag{2.30}$$

This equation simplifies in two limits. If $\xi_p \gg L_c$, Eq. (2.30) reduces to $<\mathbf{r}_{ee}^2>^{1/2} = L_c$ using the approximation $\exp(-x) \sim 1 - x + x^2/2...$ valid at small x; the filament appears rather rod-like with an end-to-end displacement close to its contour length. At the other extreme where $\xi_p \ll L_c$, Eq. (2.30) is approximately

$$<\mathbf{r}_{ee}^2> \simeq 2\xi_p L_c \qquad (\text{if } L_c \gg \xi_p), \tag{2.31}$$

implying that, over long distances compared to the persistence length, $<\mathbf{r}_{ee}^2>^{1/2}$ grows like the square root of the contour length, not as the contour length itself. In other words, long polymers appear convoluted, and their average linear dimension increases much more slowly than their contour length.
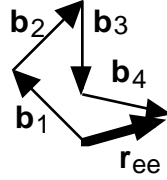
Fig. 2.12. End-to-end displacement vector $\mathbf{r}_{ee}$ resulting from a chain with 4 segments.

Let's now repeat this calulation in a discrete representation to relate the geometry of a continuous polymer to its monomeric constituents. The filament is replaced by a chain of N segments each of which is described by a vector $\mathbf{b}_i$ having the same length and orientation as the segment. From all N vectors along the chain, one can construct the end-to-end displacement $\mathbf{r}_{ee}$ from

$$\mathbf{r}_{ee} = \sum_{i=1,N} \mathbf{b}_i, \qquad (2.32)$$

as illustrated graphically in Fig. 2.12. Taking the ensemble average over all chains with the same number of links N, the mean squared end-to-end displacement $<\mathbf{r}_{ee}^2>$ is

$$<\mathbf{r}_{ee}^2> = \sum_i \sum_j < \mathbf{b}_i \cdot \mathbf{b}_j>. \qquad (2.33)$$

Now we specialize to the case where all segments of the chain have the same length b, although their orientations differ. In a random chain, bond vector $\mathbf{b}_i$ can assume any orientation independent of $\mathbf{b}_j$, with the result that $<\mathbf{b}_i \cdot \mathbf{b}_j>$ vanishes. Thus, the only terms surviving in the double sum of Eq. (2.31) are the diagonal elements $i = j$, each of which equals b^2, so that a chain with random orientations obeys

$$<\mathbf{r}_{ee}^2> = Nb^2 \qquad \text{(random chain).} \qquad (2.34)$$

An alternate expression makes use of the contour length, $L_c = Nb$, of the chain

$$<\mathbf{r}_{ee}^2> = L_c b. \qquad (2.35)$$

This expression is the same as that found in the continuum description in the limit where $L_c >> \xi_p$, namely $<\mathbf{r}_{ee}^2> = 2\xi_p L_c$, except that the persistence length ξ_p has been replaced by $b/2$. In other words, both descriptions show that the linear dimension of very flexible filaments increases as the square root of the contour length. The scaling behavior $<\mathbf{r}_{ee}^2>^{1/2} \sim N^{1/2}$ or $L_c^{1/2}$ in Eqs. (2.31) and (2.34) is referred to as *ideal* scaling. Note that our determination of the ideal scaling exponent does not depend on the dimension of space in which the chain resides: random chains in two dimensions (*i.e.*, confined to a plane) or three dimensions both exhibit the same scaling behavior.

Even if the bond geometry is somewhat restricted, ideal scaling still applies if the chains are permitted to intersect themselves. In the freely rotating chain model, successive chains elements $\mathbf{b}_i$ and $\mathbf{b}_{i+1}$ are forced to have the same polar angle α, although the bonds may swivel around each other. This model is solved in the

problem set [see also Flory (1953), p. 414], and obeys

$$\langle \mathbf{r}_{ee}^2 \rangle = Nb^2 (1 - \cos\alpha) / (1 + \cos\alpha), \qquad (2.36)$$

in the large N limit. Now, Eq. (2.36) has the same scaling exponent for $\langle \mathbf{r}_{ee}^2 \rangle$ as a function of N as does Eq. (2.34), namely $N^{1/2}$, demonstrating that self-intersecting freely rotating chains are ideal. Further, Eq. (2.36) reduces to (2.34) when the chain is measured on a length scale of $b [(1 - \cos\alpha) / (1 + \cos\alpha)]^{1/2}$, suggesting that an *effective bond length* B_{eff} can be defined for freely rotating chains via

$$B_{eff} = b [(1 - \cos\alpha) / (1 + \cos\alpha)]^{1/2}. \qquad (2.37)$$

The parametrizations of $\langle \mathbf{r}_{ee}^2 \rangle$ employed most commonly for ideal chains with N segments are

$$\langle \mathbf{r}_{ee}^2 \rangle = \begin{cases} NB_{eff}^2 \\ L_c \ell_K \\ 2L_c \xi_p \end{cases} \qquad (2.38)$$

where the Kuhn length, ℓ_K, is defined in analogy with the monomer length: $\langle \mathbf{r}_{ee}^2 \rangle = N_K \ell_K^2$ and $L_c = N_K \ell_K$, with N_K the number of Kuhn lengths in the contour length.

Self-avoiding linear chains

Our treatment of random chains places no restriction on the interaction between chain segments: nothing in the mathematical representation of the chains prevents the displacement vectors from crossing one another. However, physical systems have an excluded volume that enforces self-avoidance of the chain, as illustrated in Fig. 2.13 for two-dimensional chains. This steric interaction among the chain elements is important for chains in one-, two- and three-dimensional systems. As an illustration, consider the simple situation in which a chain lies along the x-axis. Self-avoidance forbids the chain from reversing on itself from one step to the next, so that the end-to-end distance must be just the contour length Nb: *i.e.*, $\langle \mathbf{r}_{ee}^2 \rangle^{1/2} \sim N^1$ for a straight chain in one dimension. But Eq. (2.34) shows that $\langle \mathbf{r}_{ee}^2 \rangle^{1/2}$ for ideal chains scales like $N^{1/2}$,

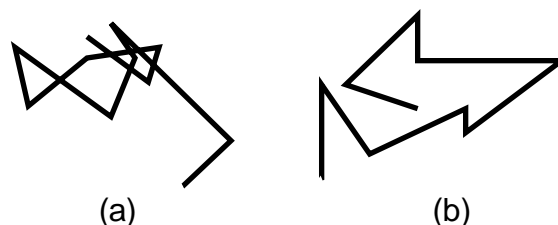(a)   (b)

Fig. 2.13. Self-avoidance changes the scaling properties of chains in one-, two- and three-dimensional systems. In the two-dimensional configurations displayed here, (a) is a random chain and (b) is a self-avoiding chain.

independent of embedding dimension. Thus, we conclude that in one dimension, self-avoidance of a chain dramatically affects its scaling properties: N^1 for self-avoiding chains and $N^{1/2}$ for ideal chains. Similar conclusions can be drawn for chains in two and three dimensions, although the scaling exponents are different.   As shown by Flory, rather general arguments lead to the prediction that the scaling exponents of self-avoiding linear chains should obey (see Sec. 6.4)

$$\nu_{FL} = 3 / (2+d), \hspace{5cm} (2.39)$$

where *d* is the embedding dimension. Eq. (2.39) gives ν_{FL} = 1, 3/4, 3/5 and 1/2, in one to four dimensions, respectively, predictions which have been shown to be exact or nearly so. As the ideal scaling exponent cannot be less than 1/2, Eq. (2.39) is not valid in more than four dimensions; hence, the effects of self-avoidance are irrelevant in four or more dimensions and the scaling is always ideal.

Branched polymers

The polymers discussed in most of this text are linear chains; however, there are many examples of polymers with extensive side branches. The scaling behavior of such *branched polymers* should not be the same as single chains, since branching adds more monomers along the chain length as illustrated in Fig. 2.14(a). Because a branched polymer has more than 2 ends, the end-to-end displacement has to be replaced by a different measure of the polymer size, such as the radius of gyration, R_g (see end-of-chapter problems). The radius of gyration for branched polymers is found to have a scaling form

$$<R_g^{\,2}>^{1/2} \sim N \; , \hspace{5cm} (2.40)$$

where *N* is the number of polymer segments and ν = 0.64 and 0.5 in two and three dimensions, respectively (see Sec. 6.4). In comparison, self-avoiding linear chains have scaling exponents of 3/4 and 0.59, respectively [see Eq. (2.39)], meaning that the spatial region occupied by branched polymers grows more slowly with *N* than does that of linear chains; *i.e.*, linear chains are less dense than branched polymers. Fluid membranes also behave like branched polymers at large length scales (see Sec. 6.4).
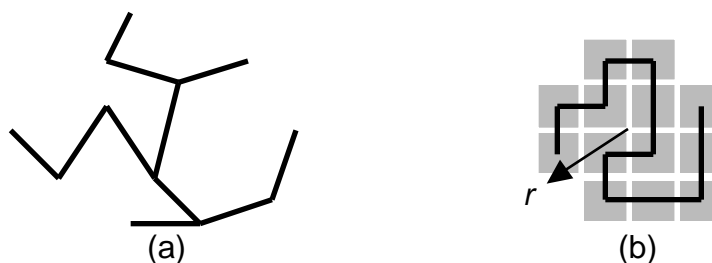

Fig. 2.14. Sample configurations of a branched polymer (a) and a dense chain (b) in two dimensions. To aid the argument in the text, the chain in (b) consists of linked squares which, when packed tightly together, cover an area $\sim r^2$ in two dimensions.

Table 2.1.   Exponents for the scaling law $<R_g^2>^{1/2} \sim N^\nu$ for ideal (or random) chains, self-avoiding chains and branched polymers, as a function of embedding dimension d. Collapsed chains have the highest density and obey $<R_g^2>^{1/2} \sim N$.

Configuration	$d = 2$	$d = 3$	$d = 4$
Ideal chains	1/2	1/2	1/2
Self-avoiding chains	3/4	0.59	1/2
Branched polymers	0.64	1/2	
Collapsed chains	1/2	1/3	1/4

Collapsed chains

        None of the chain configurations described so far in this section is as compact as it could be. Consider a system of identical objects, say squares in two dimensions or cubes in three dimensions, having a length b to the side such that each object has a "volume" of b^d in d dimensions, and N of these objects have a volume Nb^d. The configuration of the N objects with the smallest surface area is the most compact or the most *dense* configuration, as illustrated in Fig. 2.14(b), and we denote by r the linear dimension of this configuration. Ignoring factors of   and the like, the total volume Nb^d of the most compact configuration is proportional to r^d, so that r itself scales like

        $r \sim N^{1/d}$ (dense).   (2.41)

Polymers can be made to collapse into their most dense configurations by a variety of experimental means, including changes in the solvent, and it is observed that the collapse of the chains occurs at a well-defined phase transition.

        The scaling exponents of all the systems that we have considered in this section are summarized in Table 2.1. If the chains are self-avoiding, $1/d$ represents the lower bound on the possible scaling exponents, and the straight rod scaling of $<R_g^2>^{1/2} \sim N^1$ represents the upper bound. One can see from the table that random or self-avoiding chains, as well as branched polymers, exhibit scaling behavior that lies between these extremes.