2.4 Chain configurations and elasticity

Averaged quantities such as the tangent correlation function or $<r_{ee}^2>$ provide only limited information about the behavior of chains or filaments. In this section, we develop a more complete picture of chain geometry by determining the probability distribution for the length of their end-to-end displacements.   These distributions confirm that it is highly unlikely for a random chain to be found in a fully stretched configuration: the most likely value of r_{ee}^2 for a freely jointed chain is not far from its mean value of Nb^2. That the chain has an average size much smaller than its contour length is a reflection of its entropy: there are far more configurations available for r_{ee} ~ $N^{1/2}b$ than there are for the fully extended situation r_{ee} = Nb. Because of this, as the chain is made to straighten out by an external force, its entropy decreases and work must be done on the chain to stretch it: in other words, the chain behaves elastically because of its entropy.

Random chain in one dimension

Consider the set of one-dimensional random chains with three segments, as shown in Fig. 2.15: each chain starts off at the origin, and a link in the chain can point to the right or the left. As each link has 2 possible orientations, there are a total of 2^3 = 8 possible configurations for the chain as a whole. Using $C(\mathbf{r}_{ee})$ to denote the number of configurations with a particular end-to-end displacement $\mathbf{r}_{ee}$, the eight configurations are distributed according to:

$$C(+3b) = 1 \quad C(+1b) = 3 \quad C(-1b) = 3 \quad C(-3b) = 1. \tag{2.42}$$

The reader will recognize that these values of $C(\mathbf{r}_{ee})$ are equal to the binomial coefficients in the expansion of $(p+q)^3$; *i.e.*, the values are the same as the coefficients $N! / i!j!$ in the expansion

$$(p + q)^N = \textstyle\sum_{i=0,N} \{N! / i!j!\}\, p^i q^j, \tag{2.43}$$

where $j = N - i$. Is this fortuitous? Not at all; the different configurations in Fig. 2.15 just reflect the number of ways that the left- and right-pointing vectors can be arranged. So, if there are i vectors pointing left, and j pointing right, such that $N = i + j$, then the total number of ways in which they can be arranged is just the binomial coefficient

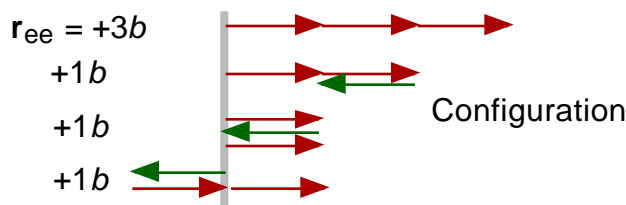$$C(i, j) = N! / i!\, j!. \tag{2.44}$$

Fig. 2.15. Configurations for a one-dimensional chain with three segments of equal length b. Only half of the allowed configurations are shown, namely those with $\mathbf{r}_{ee} > 0$.

One can think of the configurations in Fig. 2.15 as random walks in which each step (or link) along the walk occurs with probability 1/2. Thus, the probability $\mathscr{P}(i, j)$ for there to be a configuration with (i, j) steps to the (left, right) is equal to the product of the total number of configurations [$C(i, j)$ from Eq. (2.44)] with the probability of an individual configuration, which is $(1/2)^i (1/2)^j$:

$$\mathscr{P}(i, j) = \{N! / i! \, j!\} (1/2)^i (1/2)^j. \tag{2.45}$$

Note that the probability in Eq. (2.45) is appropriately normalized to unity, as can be seen by setting $p = q = 1/2$ in Eq. (2.43)

$$\sum_{i=0,N} \mathscr{P}(i, j) = \sum_{i=0,N} \{N! / i! j!\} (1/2)^i (1/2)^j = (1/2 + 1/2)^N = 1. \tag{2.46}$$

What happens to the probability distribution as the number of steps becomes larger and the distribution consequently appears more continuous? The probability distribution for a one-dimensional chain with $N = 6$ is shown in Fig. 2.16, where we note that the end-to-end displacement $\mathbf{r}_{ee} = (j - i) = (N - 2j)$ changes by 2 for every unit change in i or j. The distribution is peaked at $\mathbf{r}_{ee} = 0$, as one would expect, and then falls off towards zero at large values of $|\mathbf{r}_{ee}|$ where $i = 0$ or N. As becomes ever more obvious for large N, the shape of the curve in Fig. 2.16 resembles a Gaussian distribution, which has the form

$$\mathscr{P}(x) = (2\pi\sigma^2)^{-1/2} \exp[-(x-\mu)^2 / 2\sigma^2]. \tag{2.47}$$

Normalized to unity, this expression is a probability density (*i.e.*, a probability per unit value of x) such that the probability of finding a state between x and $x + dx$ is $\mathscr{P}(x)dx$.
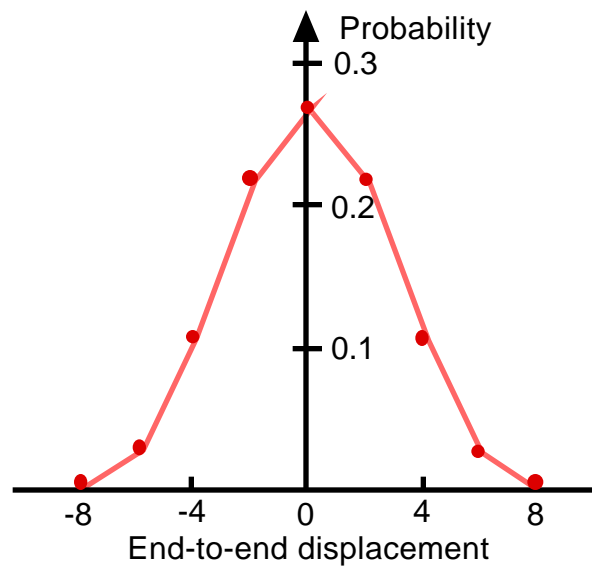

Fig. 2.16. Probability distribution from Eq. (2.45) for a one-dimensional chain with six segments.

The mean value μ of the distribution can be obtained from

$$\mu = <x> = \int x \, \mathscr{P}(x) \, dx, \tag{2.48}$$

and its variance σ^2 is

$$\sigma^2 = < (x - \mu)^2 > = <x^2> - \mu^2, \tag{2.49}$$

as expected. Eq. (2.47) is the general form of the Gaussian distribution; the values of μ and σ are specific to the system of interest. For one Cartesian component of $\mathbf{r}_{ee}$ in a random chain, $\mu = 0$ because the vectors $\mathbf{r}_{ee}$ are isotropically distributed; taken together, $\mu = 0$ and $<x^2> = Nb^2$ imply

$$\sigma^2 = Nb^2 \quad \text{(one dimension)}, \tag{2.50}$$

for random chains.   Proofs of the equivalence of the Gaussian and binomial distributions at large N can be found in most statistics textbooks.   However, the Gaussian distribution provides a surprisingly accurate approximation to the binomial distribution even for modest values of N, as can be seen from Fig. 2.16.

Random chain in three dimensions

By projecting their configurations onto a set of Cartesian axes, as illustrated in Fig. 2.17, three-dimensional random chains can be treated as three separate one-dimensional systems. For example, the x-component of the end-to-end displacement, $r_{ee,x}$, is just the sum of the individual monomer vectors as projected onto the x-axis:

$$r_{ee,x} = \sum_i b_{i,x} \quad , \tag{2.51}$$

where $b_{i,x}$ is the x-projection of the monomer vector $\mathbf{b}_i$. For freely-jointed chains, the component $b_{i,x}$ is independent of the component $b_{i+1,x}$, so the projections form a random walk in one dimension, although the x-axis projections are of variable lengths even if all monomers have the same b. If the number of segments is large, the probability distribution with variable segment length has the same form as the
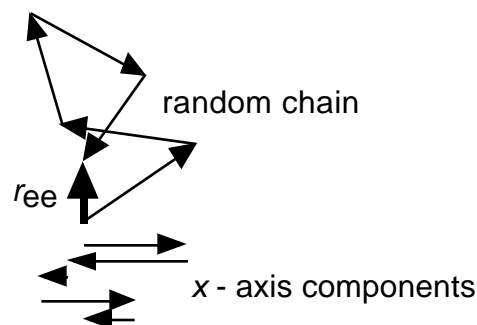

random chain

r_{ee}

x - axis components

Fig. 2.17. Projection of the segments of a two-dimensional chain onto the x-axis.

distribution with uniform segment length (Chap. 1 of Reif, 1965),

$$\mathscr{P}(x) = (2\ \sigma^2)^{-1/2}\ \exp(-r_{ee,x}^2\ /\ 2\sigma^2), \tag{2.52}$$

with a variance given by $\sigma^2 = N<b_x^2>$.

Now $<b_x^2>$ refers to the expectation of the projection of the individual steps on the x-axis. Because of symmetry, we anticipate that the mean projections are independent of direction, so

$$<b_x^2> = <b_y^2> = <b_z^2> = b^2/3, \tag{2.53}$$

the last equality arising from $<b_x^2> + <b_y^2> + <b_z^2> = <b^2> = b^2$ for steps of constant length. Hence, the variance in Eq. (2.52) is

$$\sigma^2 = Nb^2/3 \qquad \text{(for three dimensions).} \tag{2.54}$$

Returning to the properties of three-dimensional chains, the probability of finding the end-to-end displacement in a volume $dx\,dy\,dz$ centered on the position (x,y,z) is $\mathscr{P}(x,y,z)dx\,dy\,dz$, where $\mathscr{P}(x,y,z)$ is the product of the probability distributions in each of the Cartesian directions

$$\mathscr{P}(x,y,z) = \mathscr{P}(x)\ \mathscr{P}(y)\ \mathscr{P}(z) = (2\ \sigma^2)^{-3/2}\ \exp[-(x^2+y^2+z^2)\ /\ 2\sigma^2], \tag{2.55}$$

where σ^2 is still given by Eq. (2.54), and where $x\ \ r_{ee,x}$, *etc.* Eq. (2.55) says that, of all possible chain configurations, the most likely set of coordinates for the tip of the chain is (0,0,0), which is the origin or tail of the chain; it does *not* say that the most likely
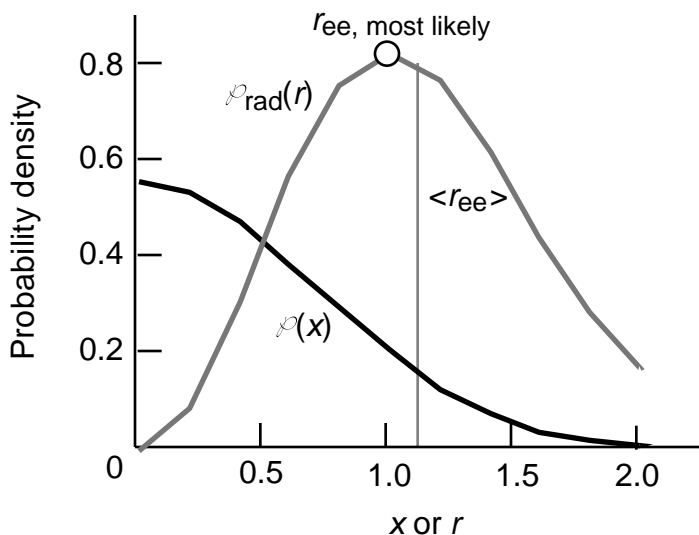

Fig. 2.18. Probability distributions for random chains in three dimensions. Two cases are shown: the three-dimensional distribution, Eq. (2.57), as a function of $r = r_{ee}$, and the x-axis projection, Eq. (2.52), as a function of $x = r_{ee,x}$ ($\sigma^2 = 1/2$ in both distributions).

value of r_{ee} is zero. Indeed, the distribution of the magnitude of $\mathbf{r}_{ee}$ must reflect the fact that many different coordinate positions have the same r. The probability for the chain having a radial end-to-end distance between r and $r + dr$ is $\mathscr{P}_{rad}(r)dr$, where $\mathscr{P}_{rad}(r)$ is the probability per unit length obtained from

$$\mathscr{P}(x,y,z)dx\,dy\,dz = \mathscr{P}_{rad}(r)dr, \tag{2.56}$$

so that

$$\mathscr{P}_{rad}(r) = 4\ r^2\ (2\ \sigma^2)^{-3/2}\ \exp(-r^2/2\sigma^2). \tag{2.57}$$

It's the extra factor of r^2 outside of the exponential that shifts the most likely value of r_{ee} away from zero. Eq. (2.57), as well as the projection of the chain on the x-axis, is plotted in Fig. 2.18. We can equate to zero the derivative of $\mathscr{P}_{rad}(r)$ with respect to r to find the most likely value of r_{ee}. A summary of the results for ideal chains in three dimensions is:

$$r_{ee,\ most\ likely} = (2/3)^{1/2}\ N^{1/2}b, \tag{2.58}$$

$$<r_{ee}> = (8/3\ )^{1/2}\ N^{1/2}b, \tag{2.59}$$

and, of course,

$$<\mathbf{r}_{ee}^{\ 2}> = Nb^2. \tag{2.60}$$

Note that r_{ee} in Eqs. (2.58) and (2.59) is the scalar radius $r_{ee} = (\mathbf{r}_{ee}^{\ 2})^{1/2}$.

Entropic elasticity

The probability distribution functions, as illustrated in Fig. 2.18, confirm our intuition that far more chain configurations have end-to-end displacements close to the mean value of r_{ee} than to the chain contour length L_c. Being proportional to the logarithm of the number of configurations, the entropy S of a chain must decrease as the chain is stretched from its equilibrium length. Now the free energy of an ensemble of chains is $F = E - TS$, which is simply $F = -TS$ for freely jointed chains, since their configurations all have vanishing energy E. Thus, S decreases and F increases as the chain is stretched at non-zero temperature; in other words, work must be done to stretch the chain, and the chain is elastic by virtue of its entropy.

Viewed as a spring obeying Hooke's law, the effective force constant of the chain can be extracted by comparing the distributions for the end-to-end displacement of the chain with that of a spring, whose fluctuations can be calculated using statistical mechanics. Now, a Hookean spring has a potential energy $V(x)$ equal to $k_{sp}x^2/2$, where x is the displacement from equilibrium and k_{sp} is the force constant of the spring. Aside from an overall normalization factor, the probability distribution $\mathscr{P}(x)$ for the spring displacement x is proportional to the usual Boltzmann factor $\exp(-E/k_BT)$, which

becomes, for the Hooke's Law potential

$$\mathscr{P}(x) \sim \exp(-k_{sp}x^2 / 2k_B T). \tag{2.61}$$

The probability distribution for the displacement of an ideal chain from Eq. (2.52) is $\mathscr{P}(x) \sim \exp(-x^2 / 2\sigma^2)$, again aside from an overall normalization factor. Comparing the functional form of the two distributions at large x gives $k_{sp} = k_B T / \sigma^2$, where $\sigma^2 = Nb^2/d$ for ideal chains embedded in d dimensions [the dimensionality can be seen from Eqs. (2.50) and (2.54)]. Hence, in three dimensions, we expect

$$k_{sp} = 3k_B T / Nb^2 = 3k_B T / 2\xi_p L_c \qquad \text{(three dimensions)}, \tag{2.62}$$

using $L_c = Nb$ and $\xi_p = b/2$ for an ideal chain. Observe that k_{sp} increases with temperature, which is readily demonstrated experimentally by hanging a weight from an elastic band, and then using a device (like a hair dryer) to heat the elastic. The weight will be seen to rise as the elastic heats up, since k_{sp} rises simultaneously and provides greater resistance to the stretching of the elastic by the weight.

Highly stretched chains

The Gaussian probability distribution, Eq. (2.52), gives a good description of chain behavior at small displacements from equilibrium. It predicts, from Eq. (2.62), that the force f required to produce an extension x in the end-to-end displacement is $f = (3k_B T / 2\xi_p L_c)x$, which can be rewritten as

$$x/L_c = (2\xi_p / 3k_B T) \, f. \tag{2.63}$$

If the chain segments are individually inextensible, the force required to extend the chain should diverge as the chain approaches its maximal extension, $x/L_c \rightarrow 1$. Such a divergence is not present in Eq. (2.63), indicating that the Gaussian distribution must be increasingly inaccurate and ultimately invalid as an inextensible chain is stretched towards its contour length.

Of course, the Gaussian distribution is only an approximate representation of freely jointed chains; fortunately, the force-extension relation of rigid, freely-jointed rods can be obtained analytically. For those familiar with the example, the problem is analogous to the alignment of spin vectors in an external field, where the spin vectors represent the projection of the polymer segments along the direction of the applied field. It is straightforward to show (Kuhn and Grün, 1942; James and Guth, 1943; see also Flory, 1953, p. 427) that the solution has the form

$$x/L_c = \mathscr{L}(2\xi_p f / k_B T), \tag{2.64}$$

where $\mathscr{L}(y)$ is the Langevin function

$$\mathscr{L}(y) = \coth(y) - 1/y. \tag{2.65}$$

Note that x in Eq. (2.64) is the projection of the end-to-end displacement along the direction of the applied force. For small values of f, Eq. (2.64) reduces to the Gaussian expression Eq. (2.63); for very large values of f, the Langevin function tends to 1 so that x asymptotically approaches L_c in Eq. (2.64), as desired.

The force-extension relation of freely-jointed rods provides a reasonably accurate description of biopolymers. Its weakness lies in viewing the polymer as a chain of rigid segments: thick filaments such as microtubules and DNA surely look more like continuously flexible ropes than chains of rigid rods. A more appropriate representation of flexible filaments can be derived from the Kratky-Porod energy expression, Eq. (2.13), and is referred to as the worm-like chain (WLC). Although the general form of the WLC force-extension relationship is numerical, an accurate interpolation formula has been obtained by Marko and Siggia (1995):

$$\xi_p f / k_B T = (1/4)(1 - x/L_c)^{-2} - 1/4 + x/L_c. \qquad (2.66)$$

Again, the force diverges in this expression as $x/L_c \rightarrow 1$, as desired. Eq. (2.66) and the freely-jointed chain display the same behavior at both large and small forces, although their force-extension curves may disagree by as much as 15% for intermediate forces.