APPENDIX C - PERSISTENCE LENGTH

Consider an ideal chain with N segments each of length a, such that the contour length L_c is

$$L_c = Na. \tag{C.1}$$

If the orientation of each element on the chain is independent of any other element, then the ensemble average of the end-to-end displacement r_{ee} is equal to

$$<r_{ee}^2> = Na^2. \tag{C.2}$$

As discussed in Chap. 3, $<r_{ee}^2>$ for all ideal chains has the same scaling form, namely

$$<r_{ee}^2> \sim N^1, \tag{C.3}$$

although the prefactor in front of the N^1 is not universal. For example, DNA is much stiffer than an alkane chain, and hence DNA has a much larger $<r_{ee}^2>$ for a given contour length Na than does an alkane. However, it is still true for both DNA and alkanes, under physical conditions in which the chains are ideal, that doubling the length of the chain increases $<r_{ee}^2>$ by just a factor of 2. As a technical aside, conventionally one measures the radius of gyration r_g ($<r_g^2>$ = mean square displacement of all segments from the center-of-mass of the chain), and then obtains r_{ee} from $<r_{ee}^2> = 6 <r_g^2>$.

In this section, we address two issues:
• how to parametrize $<r_{ee}^2>$ for stiff chains
• how to relate $<r_{ee}^2>$ to the elastic stiffness of a chain.

C.1 Parametrizations for $<r_{ee}^2>$

There a number of ways to parametrize the functional form of $<r_{ee}^2>$ for chains that are not completely flexible, but are nevertheless ideal.

Effective bond length, B_{eff}

Keeping N as the number of monomers, Eq. (C.2) is written in terms of a new parameter, the effective bond length B_{eff}. The expression for the contour length remains as before and contains no information about B_{eff}.

$$<r_{ee}^2> = NB_{eff}^2 \qquad\qquad\qquad (C.4a)$$

$$L_c = Na. \qquad\qquad\qquad (C.4b)$$

Kuhn length $\mathcal{L}_K$

In Kuhn's approach, both $<r_{ee}^2>$ and L_c are written in a self-consistent form, at the expense of introducing two parameters.

$$<r_{ee}^2> = N_K\mathcal{L}_K^2 \qquad\qquad\qquad (C.5a)$$

$$L_c = N_K\mathcal{L}_K. \qquad\qquad\qquad (C.5b)$$

In this representation, the Kuhn length $\mathcal{L}_K$ of a stiff chain is longer than, say, the length of the chemical monomer in the chain, but there are fewer segments of length $\mathcal{L}_K$ in the chain. That is, $N_K < N$.

Persistence length ξ_p

The persistence length ξ_p has a somewhat different conceptual origin than the Kuhn length, in that it measures the length along the chain over which the tangent vectors of the chain become decorrelated. The persistence length for ideal chains is half of the Kuhn length if $L_c >> \mathcal{L}_K$:

$$\xi_p = \mathcal{L}_K / 2 \qquad \text{if } L_c \gg \mathcal{L}_K \qquad (C.6)$$
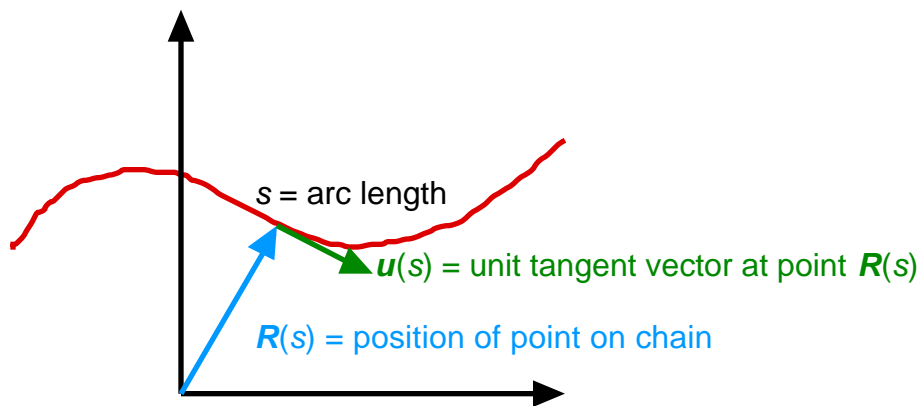
so that

$$<r_{ee}^2> = 2N_p\xi_p^2 \qquad (C.7a)$$
$$\text{if } L_c \gg \mathcal{L}_K$$
$$L_c = N_p\xi_p. \qquad (C.7b)$$

In Eq. (C.7), N_p is the contour length of the chain expressed in units of the persistence length. As shown in Sec. C.3, these expressions are not particularly accurate for extracting the persistence length for short chains, and one must use other, equally simple, expressions.

C.2 Flexible rods

In Chap. 3, the scaling behavior of polymers was obtained by viewing the polymer chain as a system of discrete elements. In this section, we view the chain as a smooth and continuous rod or string, with an arc length parameter s that runs from 0 at one end of the rod, to L_c at the other end.

s = arc length

$\boldsymbol{u}(s)$ = unit tangent vector at point $\boldsymbol{R}(s)$

$\boldsymbol{R}(s)$ = position of point on chain

At any point along the rod, a unit tangent vector can be obtained from the derivative of the coordinate position $\boldsymbol{R}(s)$ with respect to s

$$\boldsymbol{u}(s) = \partial\boldsymbol{R}/\partial s. \qquad (C.8)$$

If the rod is stiff, then $\boldsymbol{u}$ changes only slowly in orientation with respect to s, whereas if the rod is highly flexible, then $\boldsymbol{u}$ changes rapidly.

The properties of flexible rods are derived and summarized in Doi and Edwards (1986). The simplest expression for the bending energy of a continuous, flexible rod has the quadratic form

$$E_{bend} = (\kappa_f/2) \int_0^{L_c} ds (\partial u/\partial s)^2 \tag{C.9}$$

where L_c is the contour length and κ_f is the flexural rigidity of the rod (units of energy • length). This form for E_{bend} is called the Kratky-Porod model. The conformations of the rod at non-zero temperature can be obtained from the conventional Boltzmann weight

$$[probability] \sim \exp\left\{ -(\beta\kappa_f/2) \int_0^{L_c} ds (\partial u/\partial s)^2 \right\} \tag{C.10}$$

where $\beta = (k_B T)^{-1}$ as usual.

For a rod described by Eq. (C.10), it is found that the orientation of the unit tangent vector becomes decorrelated according to [see Doi and Edwards (1986)]

$$\langle u(s) \cdot u(0) \rangle = \exp(-s/\xi_p), \tag{C.11}$$

where ξ_p is the persistence length, which is given in terms of the flexural rigidity κ_f by

$$\xi_p = \beta\kappa_f. \tag{C.12}$$

Note that the persistence length is temperature-dependent, as one might expect: at low temperature, the persistence length tends to infinity. Note as well that ξ_p is a linear function of the flexural rigidity. The exponential decay in the correlation of $u(s)$ contained in Eq. (C.11) implies that the difference in the orientation of u is

$$\langle [u(s) - u(0)]^2 \rangle = 2s/\xi_p \tag{C.13}$$

at small values of s.

Lastly, the expectation $<r_{ee}^2>$ is related to the persistence length through

$$<r_{ee}^2> = 2\xi_p L_c - 2\xi_p^2 [1 - \exp(-L_c / \xi_p)]. \tag{C.14}$$

Eq. (C.14) reduces to a simpler expression in the limit where the contour length is much longer than the persistence length

$$<r_{ee}^2> = 2\xi_p L_c \qquad \text{if } L_c >> \xi_p. \tag{C.15}$$

Comparing Eq. (C.15) with (C.5) shows that the persistence length is half the Kuhn length for long chains

$$\xi_p = \mathcal{L}_K / 2 \qquad \text{if } L_c >> \xi_p. \tag{C.16}$$

C.3 Simulation of ideal chains

How well does the behavior of a small discrete chain reflect the results for flexible rods presented in Sec. C.2? In this section, various expressions from the theory of flexible rods are used to obtain several values for the persistence length, and the results are shown to be in good agreement.

We simulate an ideal segmented chain in three dimensions with the following characteristics:
•the chain has N segments, each with the same length a
•the chain has a bending energy given by

$$\beta H = (\kappa_f/a) \sum_{i=1}^{N-1} (1 - \boldsymbol{a}_i \cdot \boldsymbol{a}_{i+1}) \tag{C.17}$$

where κ_f is the flexural rigidity, as before. The (dimensionless) bond vector $\boldsymbol{a}_i$ of the discrete chain plays the same role as the unit tangent vector $\boldsymbol{u}$ of the flexible rod. In the small angle limit, Eqs. (C.9) and (C.17) agree. The value of the persistence length can be predicted or extracted by several means, and we compare the results below for the specific case of a 20 segment chain with $\beta\kappa_f = 4.0a$. The simulation uses 2,000 independent configurations.

Bending resistence

The persistence length is related to the bending resistence *via* Eq. (C.12). For the situation under consideration, Eq. (C.12) predicts

$$\xi_p = 4.0a. \tag{C.18}$$

Difference in orientations of **a**

The expectation of the difference in orientations along the chain, $<[a(s)-a(0)]^2>$, is predicted to increase linearly with the difference in segment number, according to Eq. (C.13). Data are shown below for several nearby segments; $s/a = 1$ represents nearest neighbor segments, $s/a = 2$ represents next nearest-neighbor segments *etc.*

| s/a	$<[a(s)-a(0)]^2>$
0	0.0
1	0.499
2	0.868
3	1.146
4	1.349

Since Eq. (C.13) should be most accurate for small s/a , then we see that $s/a = 1$ predicts the value of the persistence length to be

$$\xi_p = 4.0a. \tag{C.19}$$

Product of orientations of **a**

The expectation of the product $a_i \cdot a_{i+1}$ vanishes if the two segments are widely separated along the contour of the chain. A semi-log plot of $<a_i \cdot a_{i+1}>$ against s reveals the exponential decay predicted by Eq. (C.11). From the slope of the graph, the persistence length is found to be

$$\xi_p = 3.6a. \tag{C.20}$$
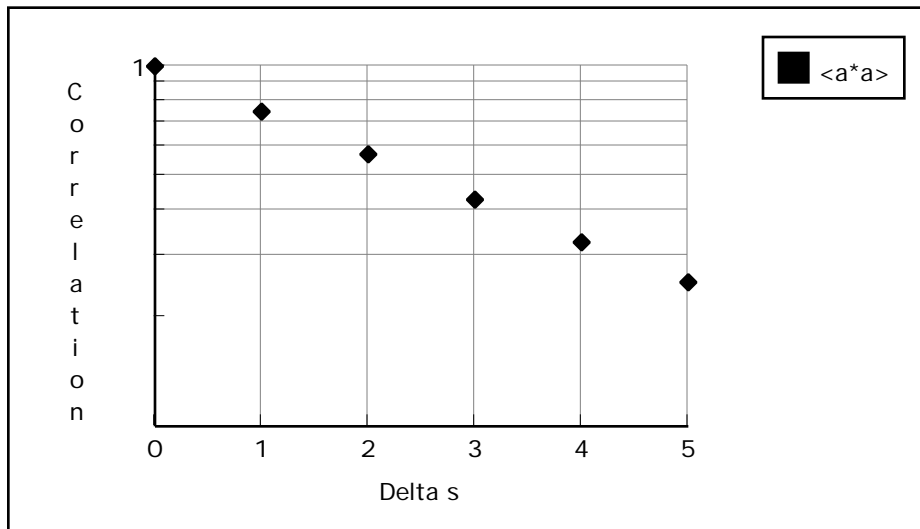
End-to-end distance

Some care must be used in extracting ξ_p from the end-to-end distance of short chains. Using Eq. (C.14), we find that $<r_{ee}^2> = 116.6a^2$ corresponds to

$$\xi_p = 3.5a, \qquad\qquad\qquad\qquad\qquad\qquad (C.21)$$

in agreement with the tangent correlations. However, simply dividing the Kuhn length by two leads to the less accurate value of $\xi_p = 2.9a$.

Summary

The four values of the persistence length, as determined from Eqs. (C.11) to (C.14) are seen to be in general agreement in the simulated chain:

$\xi_p = 4.0a$ from bending resistence
$\xi_p = 4.0a$ from $<[a(s)-a(0)]^2>$ at $s = 1$
$\xi_p = 3.6a$ from $<a_i \bullet a_{i+1}>$
$\xi_p = 3.5a$ from $<r_{ee}^2>$ (C.14)

Reference
M. Doi and S. F. Edwards *The Theory of Polymer Dynamics* (Oxford University Press, 1986), pgs. 316-318.