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From rigid rod to random walk. Some exact results*

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Summary

The conformational behaviour of a macromolecule is described by a random walk of fixed contour length which consists of n straight segments, where n=1,2,.... Two cases are discussed: (i) the segments are of equal length; (ii) the points where the random walk changes its direction are randomly distributed along the contour. Analytical expressions for the mean squared end-to-end distance R and for the radius of gyration R_g are presented. When deriving R_g it is assumed that the mass of the chain is distributed uniformly along the contour.

Introduction

A vast literature exists on the theory of random walks and its application to the conformational statistics of macromolecules, see, e.g., references 1 - 5. In this Note two basic types of random walks are discussed. Analytical expressions for the root mean squared end-to-end distance R and the radius of gyration R_g are derived. The following approach for the discussion of the conformational behaviour of a (semiflexible) macromolecule is used: a random walk of contour length L changes its direction k times (k=0,1,2,...). The k=0 case represents the rigid rod, whereas the case k>>1 coincides with the classical random walk. Two different models are treated:
Model I. The k points where the random walk changes its direction are distributed equidistantly along the contour.
Model II. These k points are distributed randomly along the contour.
Expressions for R and R_g will be given for both cases. When deriving R_g it is assumed that the (scattering) mass of the polymer is smeared along its contour length. This approach must be contrasted with the assumption that the mass of the macromolecule is concentrated in beads and is justified when the chain is considered on a length scale which is much larger than the dimension of the monomeric units. In principle, the derivation of R and R_g is straightforward. But, since the calculations are somewhat tedious and since explicit expressions are given describing the crossover from rigid rod to random walk behaviour the results are presented here.
Models which are related to Model I and II, respectively, have been discussed in the Literature: the broken wormlike chain model of semiflexible polymers (6), rods joined by flexible coils (7,8), and the randomly broken chain (9). From the experimentalist's point of view such models are relevant when discussing the conformational (and thus scattering) behaviour of (i) stiff molecules with flexible links being built in (10,11) and of (ii) biomolecules undergoing a rod-to-coil transition (12,13).

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Results

Model I. The random walk consists of $n=k+1$ straight segments of length $b=L/n$. It is assumed that there is no directional correlation between the segments, i.e. excluded volume effects are neglected. The mean squared distance is then given by:

$$R^2(n) = L^2/n \equiv nb^2 \tag{1}$$

The squared radius of gyration for a continuous distribution of mass along the contour is defined in the present case as follows:

$$R_g^2(n) = \left(2L^2\right)^{-1} \int_0^L \int_0^L \left\langle \vec{r}^{\,2}(s_1, s_2) \right\rangle ds_1 ds_2 \tag{2}$$

s_i (i=1,2) is the curvilinear distance measured along the chain and $\vec{r}(s_1, s_2)$ is the vector between the points of the chain at s_1 and s_2. The averaging is performed with respect to all configurations. After some algebra one finds:

$$R_g^2(n) = \frac{nb^2}{6}\left[1 - n^{-1} + \left(2n^2\right)^{-1}\right] \tag{3}$$

For $n=1$, i.e. the rigid rod, Eq. (3) yields $R_g^2=L/12$. For $n>>1$ one obtains $R_g^2 = nb^2/6 \equiv R^2/6$. These results for the limiting cases are well known. It is interesting to compare Eq. (3) with the appropriate expression for a random walk with n steps of length b where the mass of the chain is located at the junction of two segments and at the end points. In this case the following relation is obtained:

$$R_g^2(n) = \frac{nb^2}{6} \frac{1 + 2/n}{1 + 1/n} \tag{4}$$

Model II. The k points (P) where the random walk changes its direction are distributed randomly along the contour. The probability of finding such a point in a given interval along the contour is proportional to the length of this interval and independent of the positions of the rest of these points. $R^2(n)$ is given by

$$R^2(n) = \left\langle \sum_{i=1}^{n} r_i^2 \right\rangle \tag{5}$$

r_i is the length of the i-th segment. The averaging is performed with respect to all distributions of the points P. Respecting that these points are indistinguishable and performing the respective n-fold integral one obtains:

$$R^2(n) = 2L^2(n+1)^{-1} \equiv 2nl^2\left(1 + n^{-1}\right)^{-1} \tag{6}$$

where $l=L/n$ is the average length of a segment.

For the derivation of $R_g(n)$ we use again the definition (2). When computing $\langle \vec{r}^2(s_1,s_2) \rangle$ the average has to be taken with respect to all possible angles between the segments, as before, and with respect to all possible positions of the points P. First the latter averaging is considered. An expression for the probability of finding k_1 of k points P in a given interval of length $|s_2 - s_1|$, where $s_1, s_2 \in [0,L]$ is found by noting that the described situation is a realization of the Bernoulli process (14). In the present case the respective probability density function reads

$$P_{k_1}(s_1,s_2) = \binom{k}{k_1} L^{-k} \left(|s_2 - s_1|\right)^{k_1} \left(L - |s_2 - s_1|\right)^{k-k_1} \tag{7}$$

$\langle \vec{r}^2(s_1,s_2) \rangle$ is obtained by performing the weighted sum using the weights given by Eq. (7) with respect to the mean squared end-to-end distances of the random walks with contour length $|s_2 - s_1|$ with k_1 points P, where $k_1 = 0,1,...,k$. These quantities are known from Eq. (6) when replacing L by $|s_2 - s_1|$ and $k \equiv n-1$ by k_1. When using (6), the averaging with respect to all possible orientations of the segments has implicitly been performed. The squared radius of gyration is then given by:

$$R_g^2(n) = L^{-2} \int_0^L \int_0^L \left[\sum_{i=0}^{k} \binom{k}{i} L^{-k} \left(|s_2 - s_1|\right)^{i+2} \left(L - |s_2 - s_1|\right)^{k-i} (i+2)^{-1} \right] ds_1 ds_2 \tag{8}$$

Interchanging summation and integration and rearranging the occuring sums one finally obtains:

$$R_g^2(n) = \frac{L^2}{3(n+3)} \equiv \frac{R^2(n)}{6} \frac{1+n^{-1}}{1+3n^{-1}} \tag{9}$$

For $n=1$ and for $n>>1$ the limiting cases discussed above are recovered.
Modell II is related to the randomly broken chain discussed in Ref. (9). There the points P occur with a certain probability along the chain whereas our Model II the number of points P is fixed.

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