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Conformational statistics of polymers: a unifying approach comprising broken rods, blobs, and simple random walks

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Various approaches have been proposed for the conformational behaviour of macromolecules with mixed statistics, i.e. chain molecules which are described by different statistics on different length scales. An example is the concentration blob model where the chain experiences excluded volume effects on a small length scale whereas these effects are screened on large length scales. In the present work, I propose a generic model for the description of chain statistics which includes the blob model as a special case. The chain is treated as a succession of n segments. These segments are steps of an uncorrelated random walk. The conformational behaviour of each segment is determined by the exponent ν relating the average extension of the segment to its contour length. Explicit expressions are given for the mean squared end-to-end distance R^2 and the radius of gyration R_g of the chain for arbitrary n and ν. For $\nu = 1$ the transition from rigid rod ($n = 1$) to broken rod ($n > 1$) behaviour is described. The case $1/2 < \nu < 1$ yields a general description of chain statistics in the blob model. The models proposed comprise two cases: model I, where all subsegments have the same length; and model II, where the breaking points between two segments are distributed randomly along the chain. It is shown under which conditions the widely used relation $R_g^2 = R^2/6$ loses its validity. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The conformational behaviour of polymers is usually discussed in terms of random walk models. There are several approaches. On the one hand the concept of the continuous chain, where the polymer is represented by a continuous curve in space, has been proven to be successful[1]. On the other hand many results have been obtained by treating the polymer as a chain of bonds with finite length. For the latter approach there are two possibilities: either each bond is thought to represent a chemical bond of the real polymer[2], in which case the chemical structure prescribes the angles between two successive bonds; or the two end-points of a subsequence containing m chemical bonds are taken to define a fictitious bond[3]. If m is large enough the resulting random walk can be discussed in terms of the Pearson walk[4] or as a random walk on a lattice[3].

With the aid of such coarse-grained random walk models one seeks to derive how the extension of the chain depends on the contour length L or the number of random walk steps N and how this dependence is affected by certain constraints such as excluded volume conditions or solvent quality. The degree of extension is described by the mean squared end-to-end distance R^2 and by the radius of gyration R_g. Relations such as $R^2 \propto N^{2\nu}$ are often used. $\nu = 1/2$ for the simple random walk (RW) which is realized when excluded volume effects are absent or screened, e.g. under theta conditions and in the melt. $\nu = 3/5$ for the self-avoiding random walk (SAW) which is a model for a polymer in a good solvent. These radii are used to compare theoretical predictions with the results from scattering experiments via analysis of the scattered intensity at low angles[1].

There are many cases where it has proven useful to treat the conformational behaviour of polymers on an intermediate level lying between the level of chemical fine structure and the level where the chain is described by one or two parameters. An example is the blob model for semidilute polymer solutions where the polymer chains overlap[3,5,6]. One chain is represented by a succession of virtual blobs. Inside a blob the chain interacts with itself via excluded volume effects—it is swollen ($\nu = 3/5$). Over distances larger than the blob size this interaction is screened by the presence of the other chains, i.e. on a large scale the chain behaves as a simple RW ($\nu = 1/2$).

Another example is given by the class of polymers consisting of stiff or semiflexible segments connected by flexible joints. Such systems have been synthesized[7,8] and are realized in nature, e.g. when DNA undergoes the coil-to-helix transition[9,10]. Locally the chain can be treated as a rigid or semirigid rod ($\nu = 1$), whereas on a large scale the RW case is recovered. Theories for such systems have been developed in numerous papers[11–16]. For both classes, the blobs and the broken rods, one might introduce the term 'mixed statistics' in the sense that the statistical description using ν depends on the length scale being considered.

In the following, I propose a model which comprises and generalizes some of the random walk models discussed above. Explicit expressions for R^2 and R_g are given. The model incorporates the standard concentration blob model and a generalization for blobs with differing sizes. By straightening the segments in the blobs ($\nu \rightarrow 1$) the conformational statistics of a broken rod with constant or varying segment length are obtained. How this model is related to existing approaches[11–16] will be discussed below.

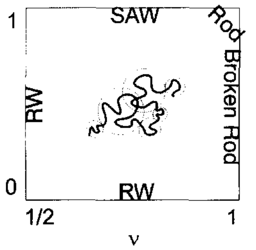

Figure 1 Sketch of the various types of random walk model which are described in the appropriate limit by the present model. n is the number of subsegments and ν is the exponent for the random walk statistics inside a subsegment. The subsegments are not correlated, as is indicated by the blob-picture in the middle of the box ($n = 6$, $\nu = 3/4$)

THE MODEL

I consider a chain made of N monomers of length a, i.e. the contour length is $L = Na$. This chain is divided into n segments of contour lengths b_i. Thus segment i consists of b_i/a monomers. Inside a segment the chain obeys random walk statistics determined by the exponent ν, i.e. $r_i^2 = a^2(b_i/a)^{2\nu}$. r_i^2 is the mean squared end-to-end distance of segment i. The segments are not correlated, i.e. $R^2 = \Sigma r_i^2$. Two cases can be discerned: model I where all segments are of the same length $b = L/n$; and model II in which the points where the segments are connected by flexible joints (breaking points) are located randomly along the contour length of the chain. *Figure 1* shows how this approach comprises some of the standard random walk models. With $n = 1$ the standard self-avoiding walk (SAW) is described, $R^2 \propto N^{2\nu}$. The case of a rod is given by $n = 1$ and $\nu = 1$. The case $n > 1$ and $\nu = 1$ yields the $(n - 1)$-fold broken rod. In the limit $1/n \rightarrow 0$ one obtains the simple RW case when looking at a length scale larger than L/n. For the description to be sensible it is presupposed that $N \gg n$. In the following the chain segments are treated as continuous chain segments; thus the summation over the monomers can be replaced by integration. In this case, the radius of gyration is given by

$$R_g^2 = \frac{1}{2L^2}\int_0^L\int_0^L \left\langle \vec{r}^2(s_1, s_2)\right\rangle \mathrm{d}s_1\mathrm{d}s_2 \tag{1}$$

where s_i is the curvilinear distance measured along the contour of the chain. $\vec{r}(s_1, s_2)$ is the vector between the points of the chain at s_1 and s_2. The averaging $\langle . \rangle$ is performed with respect to all conformations.

Model I: constant segment length $b = L/n$

This case is depicted for $n = 4$ and three different values of ν in *Figure 2a*. R^2 is trivially given by

$$R^2(n, \nu) = na^2\left(\frac{b}{a}\right)^{2\nu} = N^{2\nu}a^2n^{1-2\nu} \tag{2}$$

which reduces to $R^2 = Na^2$ for $\nu = 1/2$ and $R^2 = nb^2$ for $\nu = 1$. The radius of gyration is derived using equation (1), after separating into contributions from inside segment i and between two different segments i, j:

$$\left\langle \vec{r}^2(s_1, s_2)\right\rangle = \begin{cases} a^2\left(\frac{N}{n}\right)^{2\nu}(\alpha_1 - \alpha_2)^{2\nu} & \text{for } i = j \\ a^2\left(\frac{N}{n}\right)^{2\nu}\left[(1-\alpha_1)^{2\nu} + \alpha_2^{2\nu} + (|j-i| - 1)\right] & \text{for } i \neq j \end{cases} \tag{3}$$

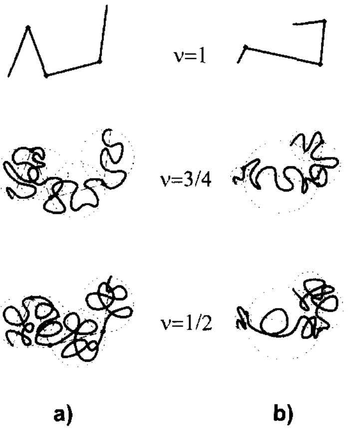

Figure 2 Realization of a random walk with $n = 4$ subsegements (a) of equal length (model I) and (b) of arbitrary lengths with fixed overall contour length (model II). The three cases $\nu = 1$ (straight segments), $\nu = 3/4$ (SAW in two dimensions) and $\nu = 1/2$ (simple RW) for the statistics inside the segments are depicted. For the sake of better visualization the end-to-end distance of the segments was taken to be the same in the three cases, and not the total contour length L

with the reparametrization $s_{1,2} = \frac{Na}{n}(i - 1 + \alpha_{1,2})$. $i, j = 1, \ldots, n$ and $\alpha_{1,2} \in [0, 1]$. After integrating with respect to $\alpha_{1,2}$ and summing over i and j, one obtains:

$$R_g^2(n, \nu) = \frac{a^2}{6}\left(\frac{N}{n}\right)^{2\nu}\left[n - 3\frac{2\nu - 1}{2\nu + 1} + \frac{1}{n}\,\frac{2\nu - 1}{\nu + 1}\right] \tag{4}$$

For $\nu = 1/2$ equation (4) reduces to $R_g^2 = Na^2/6$ which is a well known result for simple random walks. The radius of gyration of an SAW is found to be

$$R_g^2(1, \nu) = \frac{a^2N^{2\nu}}{2(2\nu + 1)(\nu + 1)}.$$

For $\nu = 1$ and $n = 1$ one recovers the result for a rigid rod, $R_g^2 = L^2/12$.

Model II: varying segment lengths b_i

The total contour length $L = Na$ is kept constant. But, in contrast to model I, the $(n - 1)$ breaking points where two segments join are randomly distributed along the contour. The probability of finding a breaking point in a given interval of the contour is assumed to be proportional to the length of this interval. The expressions for R^2 and R_g^2 which are derived in the following are averages over all possible realizations of segment lengths b_i, subject to the condition that $\Sigma b_i = L$. An example of this model is given in *Figure 2b* for the case of $n = 4$ subsegments. In model II R^2 is defined by

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

where the averaging is performed with respect to all possible distributions of the $(n - 1)$ breaking points along the contour. Respecting that these points are indistinguishable and performing the respective n-fold integral, one obtains:

$$R^2(n, \nu) = N^{2\nu}a^2\frac{\Gamma(n + 1)\Gamma(2\nu + 1)}{\Gamma(2\nu + n)} \tag{6}$$

$\Gamma(x)$ is the Gamma function[17] with $\Gamma(x) = (x - 1)\Gamma(x - 1)$ and $\Gamma(1) = 1$. For $\nu = 1/2$ one obtains $R^2 = Na^2$. Inserting $\nu = 1$ leads to $R^2 = 2L^2/(n + 1)$.

The radius of gyration is derived with use of equation (1). When computing $\langle \vec{r}^2(s_1, s_2)\rangle$ the average has to be taken over all possible angles between the subrods as in model I and, additionally, over all possible positions of the breaking points. First the latter averaging is considered. An expression for the probability of finding k_1 of k (breaking) points in a given interval of length $|s_2 - s_1|$, where $s_2, s_1 \in [0, L]$, is found by noting that the situation described is a realization of the Bernoulli process[18]. In the present case the respective probability density function reads

$$P_{k_1}(s_1, s_2) = \begin{pmatrix} k \\ k_1 \end{pmatrix} L^{-k}(|s_2 - s_1|)^{k_1}(L - |s_2 - s_1|)^{k-k_1} \tag{7}$$

$\langle \vec{r}^2(s_1, s_2)\rangle$ is obtained by performing the weighed sum using the weights given by equation (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 (breaking) points, where $k_1 = 0, 1, \ldots, k$. These quantities are known from equation (6) when $N^{2\nu}$ is replaced by $(|s_2 - s_1|/a)^{2\nu}$ and $k \equiv n - 1$ by k_1. When using equation (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

$$\begin{aligned} R_g^2(n, \nu) = {} & \frac{1}{2L^2}\int_0^L \int_0^L \sum_{i=0}^{k} \begin{pmatrix} k \\ i \end{pmatrix} L^{-k}(|s_2 - s_1|)^i \\ & \times (L - |s_2 - s_1|)^{k-i} \frac{|s_2 - s_1|^{2\nu}}{a^{2\nu-2}} \frac{\Gamma(i+2)\Gamma(2\nu+1)}{\Gamma(2\nu+i+1)} \\ & \times \mathrm{d}s_1 \mathrm{d}s_2 \end{aligned} \tag{8}$$

I did not succeed in proving that equation (8) can be reduced to the following expression, but I conjecture that $R_g^2(n, \nu)$ is given by

$$R_g^2(n, \nu) = N^{2\nu}\frac{a^2}{6}\frac{\Gamma(n+3)\Gamma(2\nu+1)}{\Gamma(2\nu+2+n)} \equiv R^2(n+2, \nu)/6 \tag{9}$$

This conjecture stands on firm grounds. First, for $\nu = 1/2$ it is obviously true. Second, for the case $\nu = 1$ it is shown in Appendix A that equation (8) is equivalent to equation (9). Thirdly, by interchanging integration and summation and rearranging the resulting terms, the conjecture, equation (8), can be reduced to ascertain that the following equation holds:

$$\begin{aligned} & \begin{pmatrix} k+3 \\ 3 \end{pmatrix}^{-1} \sum_{l=0}^{k} \frac{2\nu+k+1}{2\nu+l+1}\frac{2\nu+k+2}{2\nu+l+2}(-1)^l \sum_{m=0}^{l}(-1)^m \\ & \times \frac{\Gamma(2\nu+k+1)}{\Gamma(2\nu+m+1)}\frac{m+1}{(k-l)!(l-m)!} = 1 \end{aligned} \tag{10}$$

Equation (10) was checked to be true numerically for $k = 0$ to 20 and ν from 0 to 5 in steps of 0.1. For $\nu = 1/2$, equation (9) reduces to $R_g^2 = Na^2/6$, which is the correct result. For $\nu = 1$ one obtains $R_g^2 = L^2/(3n+9)$, which yields for $n = 1$ the correct rigid rod result $R_g^2 = L^2/12$. For $n = 1$ one obtains

$$R_g^2(1, \nu) = \frac{a^2 N^{2\nu}}{2(2\nu+1)(\nu+1)},$$

which agrees—as it should—with the result derived for $n = 1$ in model I.

DISCUSSION

Before the above results are related to existing theories, some words are in order about the use of the present results in the blob approach. It must be recalled that two different blob models have been proposed. The so-called concentration blob model was used by deGennes to discuss the conformational behaviour of semidilute polymer solutions where the chains overlap[3]. The models presented here correspond, for $\nu = 3/5$, to the deGennes picture in which the segments inside the blobs obey excluded volume statistics whereas different blobs are not correlated. Our approach yields the respective radius of gyration R_g of a single chain in semidilute solution. R_g can be obtained experimentally by small-angle neutron scattering when a small amount of the chains is tagged by deuteration. The respective value may be compared to the corresponding theoretical predictions, equations (4) and (9), when relating n to the concentration of polymer in the solution[3]. Thus, it might even be possible to check whether the model of equal blob size or the model of varying blob sizes is more appropriate. The present approach must not be confused with the thermal blob approach put forward by Weill and des Cloiseaux[6,19]; see also the recent work by Dondos[20]. In that model, the situation is reversed; on a small length scale the chain exhibits Gaussian statistics whereas excluded volume effects become effective on a larger length scale. An expression for R_g in the thermal blob approach is given by Weill and des Cloiseaux[19].

Some models have been proposed for the description of polymers with mixed statistics[11–16]. Khokhlov and Semenov used the model of the freely jointed chain (the broken rod in my terminology) in order to discuss the liquid-crystalline ordering in solutions of semiflexible polymers[11]. Since they were mainly interested in the respective phase diagram, no expressions for R and R_g were derived. Mansfield investigated the broken wormlike chain model[12]. His approach is similar to the one presented here in that he considers a chain made of freely joined subsegments which are flexible. The difference consists in the fact that Mansfield treats the flexibility of the segments by using of the Kratky–Prod or wormlike chain model where the segment is characterized by its contour length and its persistence length λ^{-1}. It is found that the introduction of breaking points leads to a modification of λ only in the respective equation for R_g of the wormlike chain. This result cannot be compared with the present results since the wormlike chain and the chain with critical exponent ν treat the flexibility and excluded volume constraints on different levels which agree only in some limiting cases. Another model similar to the present one has been put forward by Huber[14]. He discusses the statistics of block copolymers made of rigid rods connected by flexible (Gaussian) segments. The distance distribution function of any two monomers of the polymer can be given explicitly but, in general, it is not possible to find closed expressions for the respective sums over all monomers. Thus, Huber calculated the quantities of interest numerically. Finally, Muroga considered the same model as Huber but with more success[13,15,16]. He derived a closed expression for R_g. For the special case that the length of the flexible segments between the rigid rods is reduced to zero, the Muroga expressions coincides with equation (4) above, with $\nu = 1$.

APPENDIX A

In the following it will be shown how the conjectured equation (9) is derived from equation (8) for the case $\nu = 1$. Inserting $\nu = 1$ and interchanging integration and summation in equation (8) yields

$$R_g^2(n) = 2L^2 \sum_{i=0}^{k} \binom{k}{i} \frac{1}{i+2} \sum_{j=0}^{k-i} \binom{k-i}{j} (-1)^j (i+j+3)^{-1} \times (i+j+4)^{-1}$$

After interchanging the summation one obtains

$$R_g^2(n) = 2L^2 \sum_{i=0}^{k} \frac{(-1)^i}{(i+3)(i+4)} \sum_{j=0}^{i} \frac{(-1)^j}{(j+2)} \binom{k}{j} \binom{k-j}{i-j}^{-1}$$

$$= 2L^2 \sum_{i=0}^{k} (-1)^i \frac{k!}{(k-i)!(i+4)!} = \frac{L^2}{3(k+4)}$$

which is identical to equation (9) for $\nu = 1$.

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