

# THE SPATIAL DISTRIBUTION AND MOMENTS OF CIRCULAR FREELY JOINTED CHAIN

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## ABSTRACT

The spatial distribution function and second moments of circular freely jointed chain are derived based on an analytical method. The circular Gauss chain, which is simple for long chains, is compared with the circular freely jointed chain, which is exact for short chains. It is shown that the Gauss chain model predicts a more compact configurational distribution than the exact freely jointed chain. The two chain models, however, become closer to each other when the chain length increases. It is found that the difference of the mean square radius of gyration calculated with these two chain models is a constant, independent of the chain length.

## INTRODUCTION

Theories of Gauss chain for circular polymers have been developed in the past by a number of authors<sup>[1, 2, 3]</sup>, but there is not yet a parallel treatment on circular freely jointed chain. The later chain model, however, is also theoretical interesting for the reasons that first it can be exactly solved into a close form and secondly it is a precise model when the polymer is not long enough to approach the Gauss chain limit<sup>[4]</sup>. An initial study is reported here on circular freely jointed chain. Such a theory is relevant to some synthetic and natural ring polymers, such as cyclic polystyrene<sup>[5]</sup> and circular DNAs<sup>[6]</sup>, etc. Because Gauss chain enjoys analytical simplicity while freely jointed chain is favored for its precision, emphasis is put below on comparisons between these two chain models.

## SPATIAL DISTRIBUTION AND GAUSS CHAIN

Both Gauss and freely jointed chains consist of a number of links, each of which corresponds to the Kuhn statistical segment of a polymer<sup>[4]</sup>. The property of primary importance to the configurational statistics of polymers is the spatial distributions of all links in the chain with respect to a selected link, say the first one. In what follows, these symbols will be used:  $b$  is the length of a link,  $n$  the total number of links in a circular chain,  $k$  is either the number of links in a linear chain or the serial number of the  $k$ th link in a circular chain (in the later case  $k < n$ ), and  $r$  is either the end-to-end distance of a linear chain or the distance between the start-point of the first chain and the endpoint of the specified  $k$ th link in a circular chain.

Supposing that  $s_k$  is the end-point of the  $k$ th link in a circular polymer,  $s_k$  together with the start-point of the first link divide the circular chain into two linear chains, one with  $k$  links and another with  $n-k$  links. For both Gauss and freely jointed chains under unperturbed condition, the fluctuations of the two linear chains are independent of one another, and therefore, the distribution probability

of the  $k$ th link in the circular chain is the jointed probability of the distributions of the two linear chains<sup>[1]</sup>. More precisely, let the spatial distribution function of the contour point  $s_k$  be  $P_0(r, k:n)$  and the distribution functions of the end-to-end vectors of the two linear chains be, respectively,  $p_c(r, k)$  and  $p_c(r, n-k)$ ,  $p_0(r, n:k)$  will be proportional to the product of  $p_c(r, k)$  and  $p_c(r, n-k)$ :

$$P_0(r, k:n) \propto p_c(r, k) p_c(r, n-k) \quad (1)$$

This relationship is the basis of our later developments.

Let us first collect a few results known for the Gauss chain<sup>[3]</sup> before discussing the freely jointed chain. The distribution function of the end-to-end vector of a linear Gauss chain is

$$p_c(r, k) = \left( \frac{3}{2\pi k b^2} \right)^{3/2} \exp \left( -\frac{3r^2}{2kb^2} \right) \quad (2)$$

The spatial distribution function of the  $k$ th link in a circular Gauss chain is

$$\begin{aligned} P_0(r, k:n) &= C p_c(r, k) p_c(r, n-k) \\ &= \left( \frac{3n}{2\pi b^2 k(n-k)} \right)^{3/2} \exp \left( -\frac{3nr^2}{2b^2 k(n-k)} \right) \end{aligned} \quad (3)$$

where the distribution function has been normalized. The mean square  $r$  in a circular Gauss chain is

$$\langle r^2 \rangle = \int_0^\infty r^2 P_0(r, k:n) 4\pi r^2 dr = b^2 k(n-k)/n \quad (4)$$

The mean square radius of gyration of a circular Gauss chain is

$$\langle s^2 \rangle = nb^2/12 \quad (5)$$

### THE CIRCULAR FREELY JOINTED CHAIN

The distribution function of the end-to-end vector of a linear freely jointed chain has been derived by Treloar as follows:<sup>[4,7]</sup>

$$p_c(r, k) = \frac{k(k-1)}{8\pi r b^2} \sum_{t=0}^{\tau} \frac{(-1)^t 2^{2-k}}{t!(k-t)!} (k-r/b-2t)^{k-2} \quad (6)$$

where  $\tau$  is defined as

$$(k-r/b)/2-1 \leq \tau \leq (k-r/b)/2 \quad (7)$$

and

$$p_c(r, k) = 0 \quad \text{if } r/b > k \quad (8)$$

According to Eq.(1), the spatial distribution function of the  $k$ th link in a circular freely jointed chain can be expressed as

$$P_0(r, k:n) = \frac{k(k-1)(n-k)(n-k-1)}{C_{n,k} (8\pi r b^2)^2} \sum_{t=0}^{\tau} \frac{(-1)^t 2^{2-k}}{t!(k-t)!} (k-r/b-2t)^{k-2}$$

$$\times \sum_{t'=0}^{\tau'} \frac{(-1)^{t'} 2^{k+2-n}}{(n-k-t')!} (n-k-r/b-2t')^{n-k-2} \quad (9)$$

where  $\tau$  is defined by Eq.(7),  $\tau'$  is defined by

$$(n-k-r/b)/2-1 \leq \tau' \leq (n-k-r/b)/2 \quad (10)$$

and the factor  $C_{n,k}'$  is to normalize the distribution function :

$$\int_0^{\infty} P_0(r, k; n) 4\pi r^2 dr = 1 \quad (11)$$

Form Eq.(8) it can be shown that

$$P_0(r, k; n) = 0 \quad \text{if } r/b > \min(k, n-k) \quad (12)$$

where  $\min(k, n-k)$  means the smaller one of  $k$  and  $n-k$ . We will only consider the cases with  $n-k \geq k$ , i.e.  $k \leq n/2$ , since for those with  $k \geq n/2$  similar results should be obtained by simply reversing the order of the links in the circular chain. Eqs.(7) and (10) define the upper limits of  $\tau$  and  $\tau'$ . Let  $J$  and  $J'$  be the largest values that  $\tau$  and  $\tau'$  can take, respectively. Because neither  $(k-r/b)$  nor  $(n-k-r/b)$  is permitted to be negative,  $J$  and  $J'$  are determined by

$$J = \begin{cases} k/2-1 & \text{if } k \text{ is even} \\ (k-1)/2 & \text{if } k \text{ is odd} \end{cases}$$

$$J' = \begin{cases} (n-k)/2-1 & \text{if } n-k \text{ is even} \\ (n-k-1)/2 & \text{if } n-k \text{ is odd} \end{cases}$$

In the calculations of the normalization factor and other integrals with the distribution function, it is convenient to define an integer  $l$  as follows :

$$l = \begin{cases} n/2-k-t & \text{if } n \text{ is even} \\ (n-1)/2-k-t & \text{if } n \text{ is odd} \end{cases} \quad (13)$$

Let  $C_{n,k}'$  be represented by the following expression :

$$C_{n,k}' = C_{n,k} k(k-1)(n-k)(n-k-1) / (\pi b^3) \quad (14)$$

then, the normalization factor  $C_{n,k}$  is calculated to be

$$C_{n,k} = \frac{2^{-n}}{(n-3)!} \sum_{t=0}^J \frac{(-1)^t}{t!(k-t)!} \left\{ \frac{(n-k-2)!}{(k-2t)!} \sum_{t'=0}^{l-1} \frac{(-1)^{t'}}{t'!(n-k-t')!} \sum_{s=0}^{n-k-2} \frac{(n-4-s)!(n-2k-2t'+2t)^s}{(n-k-2-s)!(n-k-2t)^{k+s+2-n}} \right. \\ \left. + \sum_{t'=1}^{J'} \frac{(-1)^{t'}(k-2)!(n-k-2t')!}{t'!(n-k-t')!} \sum_{s=0}^{k-2} \frac{(n-4-s)!(2k+2t'-n-2t)^s}{(n-k-2-s)!(k-2t)^{s+2-k}} \right\} \quad (15)$$

The statistical properties of the circular freely jointed chain can be calculated with the distribution function of Eq.(9). In order to index different links, we

will use  $r_k$  to indicate explicitly the distance between the starting point of the first link and the end-point of the  $k$ th link. The various moments of  $r_k$  are defined by the following formula :

$$\langle r_k^{2m} \rangle = \int_0^\infty r^{2m} P_0(r, k; n) 4\pi r^2 dr \quad (16)$$

An examination of Eq.(9) reveals that the above expression includes a total of  $(J+1)(J'+1)$  single integrals, each of which has the following form :

$$I_{t,t'} = \int_0^\alpha x^{2m} (k-2t-x)^{k-2} (n-k-2t'-x)^{n-k-2} dx \quad (17)$$

where  $x=r/b$ ,  $t=0, \dots, J$ ,  $t'=0, \dots, J'$ , and  $\alpha = \min(k-2t, n-k-2t')$ . Since neither  $(k-2t-x)$  nor  $(n-k-2t'-x)$  is permitted to be negative, the upper limit of integral Eq.(17) is  $\alpha$  instead of infinity. As  $t$  takes all its allowed values,  $I_{t,t'}$  have to be distinguished according to  $t'$  being smaller or larger than 1 defined by Eq.(13): if  $t' < 1$ , the upper limit of integral Eq.(17) takes  $(n-k-2t')$ , otherwise takes  $(k-2t)$ . These rules have been used in the calculation of  $C_{n,k}$  in Eq.(15), in that case the power of  $x$  in Eq.(17) is zero.

The second moment  $\langle r_k^2 \rangle$  is calculated according to Eq.(16) by specifying  $m=1$ , the result is

$$\begin{aligned} \langle r_k^2 \rangle &= \frac{2b^2}{2^n C_{n,k} (n-3)!} \sum_{t=0}^J \frac{(-1)^t}{t! (k-t)!} \\ &\times \left\{ \sum_{t'=0}^{t-1} \frac{(-1)^{t'} n! (k-2t)^{k+1}}{t'! (n-k-t')!} \sum_{s=0}^{n'} \frac{(n-4-s)!}{(n-2-s)!} \sum_{u=0}^{n'-s} \frac{(n-3-s-u)!}{(n-1-s-u)!} \right. \\ &\quad \left. \sum_{v=0}^{n'-s-u} \frac{(n-2-s-u-v)! (n+2t-2k-2t')^{s+u+v}}{(n'-s-u-v)! (n-k-2t')^{s+u+v-n'}} \right. \\ &+ \sum_{t'=t}^{J'} \frac{(-1)^{t'} k! (n-k-2t')^{n-k+1}}{t'! (n-k-t')!} \sum_{s=0}^{k'} \frac{(n-4-s)!}{(n-2-s)!} \sum_{u=0}^{k'-s} \frac{(n-3-s-u)!}{(n-1-s-u)!} \\ &\quad \left. \sum_{v=0}^{k'-s-u} \frac{(n-2-s-u-v)! (2k+2t'-2t-n)^{s+u+v}}{(k'-s-u-v)! (k-2t)^{s+u+v-k'}} \right\} \quad (18) \end{aligned}$$

where  $n' = n-k-2$ ,  $k' = k-2$ . After obtaining the second moments for all pairs of links, one can readily calculate the mean square radius of gyration of the circular freely jointed chain by the following formula :

$$\langle s^2 \rangle = \frac{1}{2n^2} \sum_{k=1}^n \sum_{k'=1}^n \langle r_{kk'}^2 \rangle = \frac{1}{n^2} \sum_{k=1}^n (n-k) \langle r_k^2 \rangle \quad (19)$$

It is noted that  $\langle r_1^2 \rangle \equiv 1$  and all other  $\langle r_k^2 \rangle$  are given by Eq.(18).

While being possible to calculate the higher moments for the circular

freely jointed chain by choosing  $m > 1$  in Eq.(17), we found that it is impossible to calculate the mean reciprocal distance  $\langle r_k^{-1} \rangle$  because the integral of Eq.(17) becomes divergent when choosing  $m = -1/2$ . This is an intrinsic limitation of the distribution function for circular freely jointed chain. The same problem is not found in the circular Gauss chain.

We now use the above results to discuss the properties of circular freely jointed chain. Fig.1 shows the radial distribution of freely jointed chains. In the calculation of the distribution function according to Eq.(9), it is most convenient to consider  $r$  in separate regions so that the terms with different  $t$  and  $t'$  needed to be calculated can be determined in advance. For example, when  $n$  is even and  $J \geq J'$ , one can find that the calculation of  $P_0(r, k:n)$  in the following regions need to consider these terms with  $t$  and  $t'$  specified below:

$$\begin{aligned} r > kb: & \quad \text{no term, i.e. } P_0(r, k:n) = 0 \\ kb \geq r > (k-2)b & \quad t=0; \quad t'=0, \dots, J'-J \\ (k-2)b \geq r > (k-4)b & \quad t=0, 1; \quad t'=0, \dots, J'-J+1 \\ & \quad \dots \dots \dots \\ 2b \geq r \geq 0 & \quad t=0, \dots, J; \quad t'=0, \dots, J' \end{aligned}$$

Fig.1 (a) shows the radial distributions of the links with  $k=2, 3, 4, 6, 8$  and  $10$  in a circular freely jointed chain of  $n=20$ ; these results are compared with the end-to-end radial distributions of linear chains with  $k=2, 3, 4, 6, 8$  and  $10$ . Note that in the linear chain with  $k=2$ , the radial distribution function is a linear function as  $r/b$  is within  $(0, 2)$ , outside this region  $p_c(r, 2)=0$ . It is observed that the radial distribution of the distance vector between two links in a circular chain is more narrow than that of similar pair of links in a linear chain. Such a result implies that the average configuration of a circular chain is more compact than that of an equal-length linear chain. In fact, this result holds not only for freely jointed chain, but also for other chains, including Gauss chain.

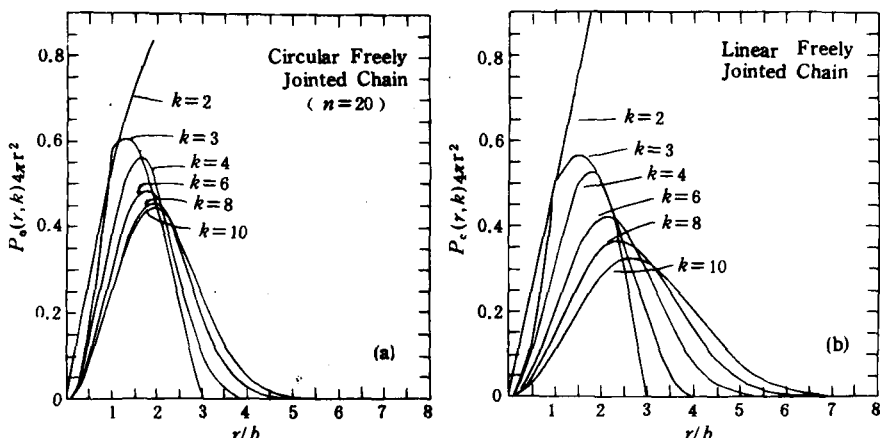


Fig.1 The radial distributions of different links in (a) circular and (b) linear freely jointed chains. Refer to text for the definitions  $n$  and  $k$ .

Figs.2(a) and (b) compare the radial distributions of freely jointed chain

with that of circular Gauss chain of similar lengths. It is found that for a circular chain of 8 links (Fig.2 (a)), the radial distribution of freely jointed chain is significantly different from that of Gauss chain. But the differences become smaller as the total number of links increases, for example, when  $n$  increases to 40 (Fig.2 (b)), the two chain models show quite close radial distributions. The Gauss chain always predicts a more compact configurational distribution than the exact freely jointed chain, and the deviations are more evident for short chains.

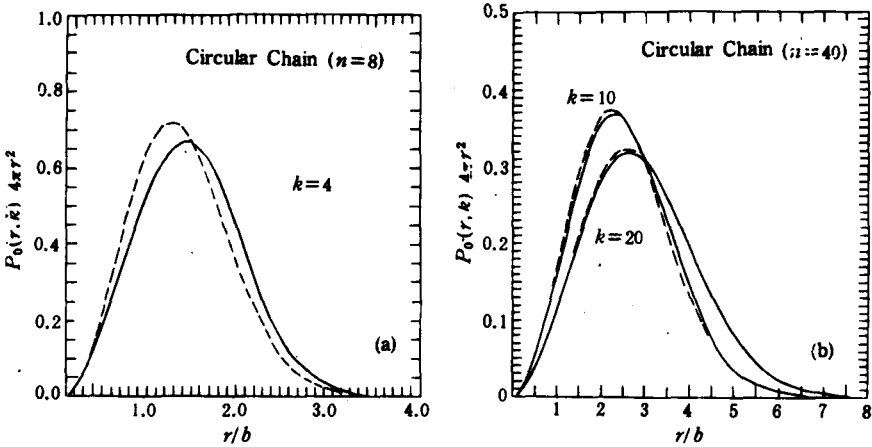


Fig.2 Comparisons between the radial distributions of circular freely jointed chain and Gauss chain at a smaller chain length (a) and a larger chain length (b).

Figs.3 (a) and (b) show the mean square distance (second moment) between the first link and other links in circular freely jointed chains with  $n=10$  and 20, respectively. These results are compared in the same graphs with circular Gauss chains of similar lengths. Note that for freely jointed chain and Gauss chain,  $\langle r_1^2 \rangle$  is respectively equal to and smaller than  $b^2$ . To all links, the second moments in circular Gauss chain are always smaller than that of corresponding links in freely jointed chain, such a fact in another way indicates the former chain

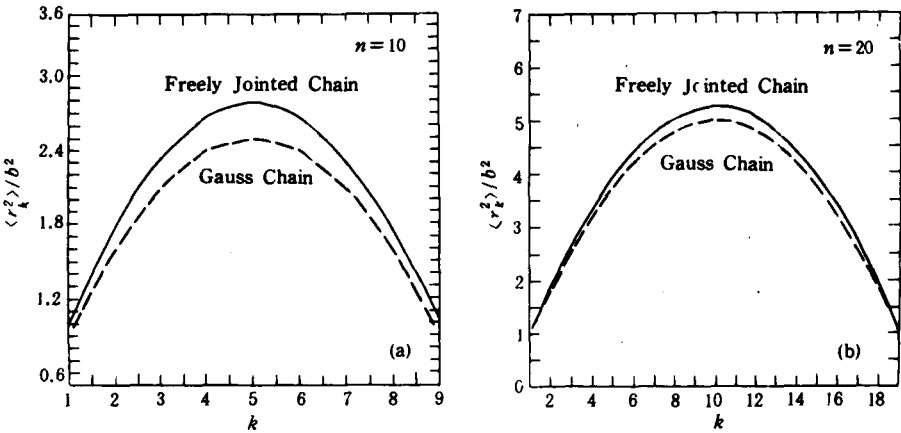


Fig.3 The comparison of the link-to-link mean square distances ( $\langle r_{1..k}^2 \rangle$ ) in circular freely jointed chain and Gauss chain at two selected chain lengths

being more compact than the later.

Fig.4 shows the mean square radii of gyration of circular freely jointed and Gauss chain as a function of the total number of links. It is found that to both chain models, the mean square radius of gyration is a linear function of  $n$ , the total number of links. Due to the fact that the average configurations of these two chain models are different even at similar chain length, the plot of the mean square radius of gyration of freely jointed chain appears on the above of that of Gauss chain. Interestingly, the two plots have exactly similar slope but with different intercepts.

### CONCLUSION

We have derived the analytical expressions of the spatial distribution of the circular freely jointed chain, and with the distribution function obtain the second moments of the chain. It is shown that the Gauss chain predicts a more compact configurational distribution than the exact freely jointed chain. The errors produced by Gauss chain is significant for short chains, but for long chains the two chain models give approximately similar results. The mean square radius of gyration predicted by these two chain models has a constant deviation, independent of the chain length. This may be explained by the fact that for shorter chains, individual links have larger deviations between the two chain models but the total number of links is smaller, while for long chains, individual links have smaller deviations between the two chain models but the number of links is large, the sum of the deviations of all links then becomes exactly independent of the total number of links.

### Keywords :

Freely Jointed Chain; Gauss Chain; Spatial Distribution

**Acknowledgment** The author is grateful to Professor Wilma Olson for her support at the Department of Chemistry, Rutgers University, U.S.A., where most of this work was done.

### REFERENCES

- [1] Zimm, B.Z. and Stockmayer, W.H., *J. Chem. Phys.*, **1949**, *17*, 1301.
- [2] Casassa, E.F., *J. Polymer Sci., Part A* **1965**, *3*, 605.
- [3] Burchard, W. in "Cyclic Polymers" (ed. J. A. Semlyen), Elsevier Applied Science Publishers, Essex, England, **1986**, p.43.
- [4] Flory, P.J., "Statistical Mechanics of Chain Molecules", Interscience Publisher, New York, **1969**, p.1.
- [5] Semlyen, J. A., In "Cyclic Polymers" (ed. J. A. Semlyen), Elsevier Applied Science Publishers, Essex, England, **1986**, p.1.
- [6] Wang, J. C., in "Cyclic Polymers" (ed. J. A. Semlyen), Elsevier Applied Science Publishers, Essex, England, **1986**, p.225.
- [7] Treloar, L. R. G., *Trans. Faraday Soc.*, **1946**, *42*, 77.

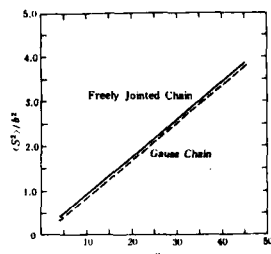


Fig.4 The mean square radii of gyration of circular freely jointed chain and circular Gauss chain as a function of total number of links in the chains