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Average density of chain atoms at points along the contour of freely jointed chains

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Abstract

The density of chain atoms in the volume element dV centered on atom i has been obtained for short and long freely jointed (FJ) chains. The Gaussian distribution function is used for long chains, and Treloar's corrections to this distribution are imposed for short chains. For long FJ chains, the density of chain atoms is a maximum when atom i is located midway along the contour of the chain, and it is a minimum when atom i is any of the three atoms at either end of the chain. The ratio of these densities is 2. Short FJ chains can exhibit qualitatively different behavior, with the site of the maximum density shifting from the middle to the end of the chain when the number of bonds decreases from 8 to 7. This shift is imposed by the strong deviations from the Gaussian distribution when n is small.

Keywords: Conformation; Crosslinking; End effects

1. Introduction

Conformational end effects in a freely jointed (FJ) chain are subtle. They can appear to be present or absent, depending on the conformation-dependent physical property used to search for them. The mean square end-to-end distance, $\langle r^2\rangle$, is an example of a property that detects no end effects, because a FJ chain with n bonds of length l has a characteristic ratio, defined as $C_n \equiv \langle r^2\rangle/nl^2$ [1], that is equal to one at all values of n. Furthermore, the mean square end-to-end distance of the FJ subchain between atoms i and j, $\langle r_{ij}^2\rangle = |j-i|l^2$, is independent of the position of the subchain, $(i+j)/2$, within the chain.

A different conclusion is obtained from the average density, denoted ρ_i, of the n chain atoms about chain atom i. This average density may become important in models that consider crosslinked FJ chains [2]. The probability that chain atom i can instantaneously form a short intramolecular crosslink depends on the density of the other atoms in its vicinity. It is worthwhile to inquire whether this probability depends on the location of atom i along the contour of a FJ chain. One approach to this question uses the volumes specified by the mean square radius of gyration of all chain atoms about atom i, denoted $\langle s_i^2\rangle$ [3].

$$\langle s_i^2\rangle = \left[\frac{1}{2} - \frac{i}{n}\left(\frac{n-i}{n+1}\right)\right] nl^2 \tag{1}$$

If ρ_i is identified with the average density of chain atoms in this volume, i.e. $n/\langle s_i^2\rangle^{3/2}$, it depends on the position of atom i within the chain [3]. Eq. (1) implies that ρ_i is smaller when atom i is one of the ends of the chain than when atom i is located midway along the contour of the chain, i.e. $\rho_0 = \rho_n < \rho_{n/2}$. The ratio $\rho_0/\rho_{n/2}$ is equal to $(2/3)^{3/2}$ when $n=2$, and it monotonically approaches $(1/2)^{3/2}$ as $n \to \infty$.

This result for ρ_i is exact for FJ chains of all n when the density is averaged over the finite volume defined by $\langle s_i^2\rangle$. This volume can be quite large. For a FJ chain, $\langle s_i^2\rangle$ is larger (by a factor of 3/2 to 3, depending on n) than the mean square radius of gyration of the $n+1$ atoms about their center of mass [3]. It therefore becomes of interest to inquire whether the conclusions about the position dependence of ρ_i need modification if the volume over which the density is averaged becomes smaller than $\langle s_i^2\rangle^{3/2}$. As this volume shrinks, the limit for ρ_i is the density of chain atoms in an infinitesimally small volume element, dV, centered on chain atom i. Information required for the calculation of ρ_i in this limit can be extracted from the distribution function for the

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end-to-end vector, $W(\mathbf{r})$, of a FJ chain. The result depends in a striking manner on whether n is large or small.

2. Freely jointed chains with large n

The implementation is simpler for FJ chains with large n because $W(\mathbf{r})$ assumes a more complicated form when n is small. In the limit as $n\to\infty$, the starting point is the Gaussian distribution.

$$\lim_{n\to\infty} W(\mathbf{r}) = \left(\frac{3}{2\pi n l^2}\right)^{3/2} \exp\left(-\frac{3r^2}{2nl^2}\right) \tag{2}$$

The fact that this approximation overestimates $W(\mathbf{r})$ at extensions approaching nl is of no consequence in the current application of Eq. (2) because we are only interested in the behavior when $\mathbf{r}=\mathbf{0}$.

Eq. (2) can be applied to each FJ subchain of $|j-i|$ bonds from chain atom i to chain atom j.

$$\lim_{|j-i|\to\infty} W(\mathbf{r}_{ij}) = \left(\frac{3}{2\pi|j-i|l^2}\right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2|j-i|l^2}\right) \tag{3}$$

Assume temporarily that n is large enough so that the inaccuracy of this expression at small $|j-i|$ is not important to the final result. (This assumption, which is badly in error at small n, will be relaxed in the next section.) Application to the first atom in the FJ chain, using $i=0$, leads to the renormalized sum of the distributions for each of the n possible $\mathbf{r}_{ij}$ with $j>0$ about this atom.

$$X(\mathbf{r})_{i=0} \equiv \frac{1}{n}\sum_{j=1}^{n} W(\mathbf{r}_{0j})$$

$$= \frac{1}{n}\left(\frac{3}{2\pi l^2}\right)^{3/2} \sum_{j=1}^{n}\left(\frac{1}{j}\right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2jl^2}\right) \tag{4}$$

here the $\mathbf{r}$ in $X(\mathbf{r})_{i=0}$ denotes the position in three-dimensional space at which the distribution functions for the n subchains have been summed. If i can index any chain atom, $0\le i\le n$, the number of bonds in each subchain is $|j-i|$ instead of j.

$$X(\mathbf{r})_i = \frac{1}{n}\left(\frac{3}{2\pi l^2}\right)^{3/2}\left[\sum_{j=0}^{i-1}\left(\frac{1}{i-j}\right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2(i-j)l^2}\right) + \sum_{j=i+1}^{n}\left(\frac{1}{j-i}\right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2(j-i)l^2}\right)\right] \tag{5}$$

For the special case of the density of chain atoms at the site occupied by chain atom i, each r_{ij}^2 is equal to zero and the exponentials are all equal to one.

$$X(\mathbf{0})_i = \frac{1}{n}\left(\frac{3}{2\pi l^2}\right)^{3/2}\left[\sum_{j=0}^{i-1}\left(\frac{1}{i-j}\right)^{3/2} + \sum_{j=i+1}^{n}\left(\frac{1}{j-i}\right)^{3/2}\right] \tag{6}$$

At a specified large value of n, the maximum value of $X(\mathbf{0})_i$ is at $i=n/2$, and $X(\mathbf{0})_i$ decreases continuously as i departs from this position. The size of the end effect can be represented by the ratios of the $X(\mathbf{0})_i$ for a terminal atom and an atom located midway along the contour of the FJ chain.

$$\frac{X(\mathbf{0})_0}{X(\mathbf{0})_{n/2}} = \frac{\sum_{j=1}^{n} j^{-3/2}}{2\sum_{j=n/2+1}^{n}[j-(n/2)]^{-3/2}} \tag{7}$$

This ratio approaches 1/2 in the limit as $n\to\infty$. The density of chain atoms at the site of a terminal atom is 1/2 of the density of chain atoms at the site of the atom midway along the contour of the long FJ chain. If the volume in which the density is measured increases from $\mathrm{d}V$ to $\langle s_i^2\rangle^{3/2}$, the ratio $\rho_0/\rho_{n/2}$ decreases from 1/2 to $(1/2)^{3/2}$. The qualitative end effects are similar, but the quantitative end effect is more severe if the density is averaged over the larger volume, $\langle s_i^2\rangle^{3/2}$, instead of the infinitesimally small volume, $\mathrm{d}V$.

3. Freely jointed chains with small n

In FJ chains with n small enough so that they do not achieve the behavior expected in the limit as $n\to\infty$, the end effect can be qualitatively different from the one specified by Eq. (7). The complication arises because Eq. (2) badly overestimates the value of $W(\mathbf{0})$ when n is small [4,5]. The correction of the result in Eq. (7) for these short subchain effects can be obtained by substituting the inaccurate value from Eq. (2) with the $W(\mathbf{r})$ reported by Treloar [4,5]. As described by Flory [6], these corrections are $W(\mathbf{0})=0$ for $n=1$ and 2, along with the values of $W(\mathbf{0})$ calculated from Eq. (8) for $n>2$.

$$W_n(\mathbf{r}) = \left[\frac{n(n-1)}{8\pi r l^2}\right]\sum_{t=0}^{\tau}\frac{(-1)^t}{t!(n-t)!}\left[\frac{n-(r/l)-2t}{2}\right]^{n-2} \tag{8}$$

The number of terms in the sum is given by the value of τ specified in Eq. (9).

$$\frac{n-(r/l)}{2} - 1 \le \tau < \frac{n-(r/l)}{2} \tag{9}$$

Fig. 1 depicts the values of $X(\mathbf{0})_i$ for a FJ chain of 12 bonds as the corrections are applied successively to subchains of 1–12 bonds. Fig. 1(a) shows that the largest change occurs when the Gaussian approximation to $X(\mathbf{0})_i$ (no corrections) is modified to account for the fact that $W_n(\mathbf{0})$ must be zero when $n=1$. This correction strongly reduces all values of $X(\mathbf{0})_i$, but the reduction is only half as severe for the terminal atoms (which participate in only one

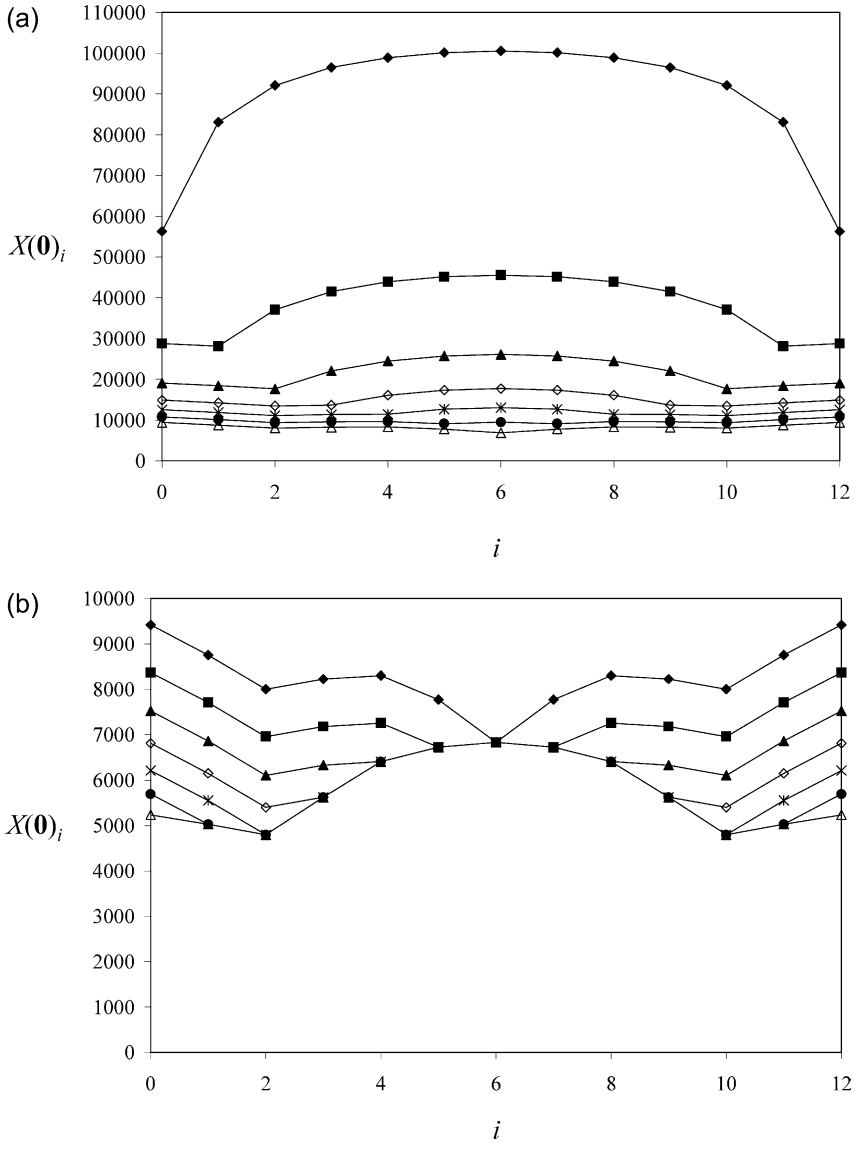

Fig. 1. Values of $X(\mathbf{0})_i$ (multiplied by $10^6\ l^3$) for a FJ chain of 12 bonds as Treloar's corrections are applied to successively longer subchains. Fig. 1(a) depicts the result when no corrections are applied (Gaussian approximation, top curve) and also the results when the corrections are applied successively to subchains with lengths up to 1–6 bonds, reading from the curve second from the top to the curve at the bottom. Fig. 1(b) depicts the results when the corrections are applied successively to subchains with lengths up to 6–12 bonds, reading from top to bottom for the terminal atoms. Both panels contain data for the case where the corrections are applied through subchains of 6 bonds, i.e. the bottom curve in Fig. 1(a) is the same as the top curve in Fig. 1(b).

subchain of a single bond) as for the interior atoms (which participate in two such subchains). This difference causes the minimum value of $X(\mathbf{0})_i$ to shift from the terminal atoms to the penultimate atoms. (Since $X(\mathbf{0})_1$ is 2.3% smaller than $X(\mathbf{0})_0$, the difference in these numbers is not readily apparent on the scale used for Fig. 1(a).) All of the $X(\mathbf{0})_i$ continue to decrease in size as the corrections are imposed for successively longer subchains up to a length of 6 bonds, as shown in Fig. 1(a). However, when the corrections are applied to still longer subchains, with lengths varying from 6 to 12 bonds, qualitatively different behavior is seen, as depicted in Fig. 1(b). Since the atom in the middle of the chains, with $i=6$, cannot be the terminus of any subchain of length 7–12 bonds, the value of $X(\mathbf{0})_6$ is unaffected by these additional corrections. Similarly, the values of $X(\mathbf{0})_5$ and $X(\mathbf{0})_7$ are affected by the correction for subchains of seven bonds, but are unaffected by corrections for longer subchains. Finally, when the correction is imposed for $W_n(\mathbf{0})$ for a chain of 12 bonds, it is of consequence only for $X(\mathbf{0})_i$ for the terminal beads. Therefore, the very first correction, which imposed the correct value of $W_1(\mathbf{0})$, is less important for the terminal beads than for internal beads, but the very last correction, imposing the correct value of $W_n(\mathbf{0})$, is important only for the terminal beads and is irrelevant for the internal atoms.

The second column in Table 1 presents the ratios of $X(\mathbf{0})_0$ to $X(\mathbf{0})_i$ for the chain atom located closest to the midway point along the contour of the chains when n is in the range

Table 1
The end effect detected by $X(\mathbf{0})_i$ in freely jointed chains, using Treloar's corrections for short subchains, except for the last line

N	$X(\mathbf{0})_{end}/X(\mathbf{0})_{middle}$	$X(\mathbf{0})_{min}/X(\mathbf{0})_{max}$	n_{min}	n_{max}
5	2.626	0.381	2, $n-2$	0, n
6	1.563	0.640	2, 3, $4=n-2$	0, n
7	1.175	0.744	2, $n-2$	0, n
8	0.965	0.781	2, $n-2$	$n/2$
9	0.895	0.762	2, $n-2$	$(n\pm1)/2$
10	0.811	0.735	2, $n-2$	$n/2$
11	0.800	0.720	2, $n-2$	$(n\pm1)/2$
12	0.766	0.702	2, $n-2$	$n/2$
13	0.745	0.691	2, $n-2$	$(n\pm1)/2$
14	0.725	0.679	2, $n-2$	$n/2$
⋮	⋮	⋮	⋮	⋮
∞ [a]	0.500	0.500	0, 1, 2, $n-2$, $n-1$, n	$n/2$
∞ [b]	0.500	0.500	0, n	$n/2$

[a] The limit as $n\to\infty$, using Treloar's corrections to the Gaussian distribution.
[b] The limit as $n\to\infty$, using the uncorrected Gaussian distribution.

5–14. All $W(\mathbf{0})$ for these finite FJ chains have been calculated using Treloar's correction to the Gaussian distribution for all of the subchains. With these corrections, the end effect is found to be qualitatively different for long and short FJ chains. The value of $X(\mathbf{0})_{end}/X(\mathbf{0})_{middle}$ is less than one only when $n>7$. For shorter FJ chains, the density of chain atoms is larger about the terminal atom than about the atom located midway along the contour of the chain. This situation arises because the severe corrections for very short subchains, which reduce the value of $W(\mathbf{0})$, are twice as important for $X(\mathbf{0})_{midpoint}$ as for $X(\mathbf{0})_{end}$, since the number of relevant subchains also differs by a factor of two.

Another difference in the behavior of short and long FJ chains is seen in Fig. 2, which depicts the values of $X(\mathbf{0})_i/X(\mathbf{0})_{middle}$ for FJ chains with 6–9 bonds. For the two shortest FJ chains, $X(\mathbf{0})_i$ passes through a distinct minimum at intermediate i within the range $0<i<n/2$. No such minimum is implied by the expression for $X(\mathbf{0})_i$ in the limit as $n\to\infty$, Eq. (6). This qualitative difference in the behavior of short and long FJ chains is not observed if the densities of chain atoms are averaged over the larger volumes specified by $\langle s_i^2\rangle^{3/2}$ [3].

The presence of the local minimum in $X(\mathbf{0})_i/X(\mathbf{0})_{middle}$ when n is small suggests another measure of the finite chain length effect in FJ chains. That measure is the ratio of the minimum and maximum values of $X(\mathbf{0})_i$, without regard to the value of i at which the minima and maxima occur. These numbers are presented in the third column of Table 1, and the locations of the minima and maxima are specified in the final two columns. The location of the maximum probability is especially sensitive to n, shifting from the end to the middle of the chain when n increases from 7 to 8. In contrast, the minimum probability retains much the same location, always being found within two chain atoms of the nearest chain end. The values of $X(\mathbf{0})_{min}/X(\mathbf{0})_{middle}$ pass through a maximum at $n=8$. According to this measure, the end effect becomes more severe as n moves away from 8 in either direction.

The Treloar corrections for short FJ chains contain an interesting implication for the behavior of $X(\mathbf{0})_i$ near the ends of very long chains, in the limit is $n\to\infty$. Without these corrections, the minimum values of $X(\mathbf{0})_i$ occur at the two terminal atoms, $i=0$ and n. When these corrections are applied, they cause $W(\mathbf{0})$ to be equal to zero for FJ subchains of one or two bonds, with the consequence that the minimum values of $X(\mathbf{0})_i$ (in the long chain limit) now appear in identical fashion at six atoms, $i=0$, 1, 2, $n-2$, $n-1$, and n. The values of $X(\mathbf{0})_i$ for $i=0$, 1, and 2 receive nonzero contributions only from

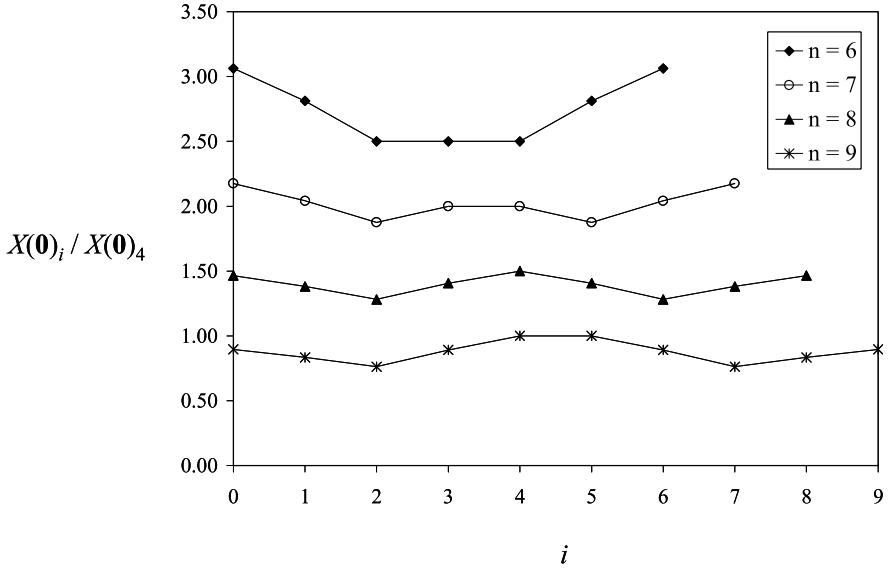

Fig. 2. Values of $X(\mathbf{0})_i/X(\mathbf{0})_{middle}$ for freely jointed chains with 6, 7, 8 and 9 bonds when the exact distribution functions described by Treloar are used. A vertical offset of $0.5(9-n)$ separates the four curves.

atoms indexed with $j=i+2$, $i+3,\ldots,\infty$, and are therefore identical. When we move to $X(\mathbf{0})_3$, there is an additional nonzero contribution from the atom indexed with $i=0$, and therefore $X(\mathbf{0})_3 > X(\mathbf{0})_2 = X(\mathbf{0})_1 = X(\mathbf{0})_0$. This result is incorporated in the last two lines of Table 1.

4. Conclusion

Treloar's corrections to the Gaussian distribution show that the density of chain atoms in the infinitesimally small volume element, dV, centered on chain atom i depends strongly on n. The minimum in this distribution at any value of n is always located at a chain atom within two atoms of the nearest chain end. The location of the maximum in the distribution is subject to stronger variation, shifting from a terminal chain atom to the middle of the chain when the number of bonds in the FJ chain increases from 7 to 8.

In the limit of large n, the density of chain atoms is twice as large about the atom located midway along the contour of the chain as about either atom at the end of a chain. Long FJ chains show qualitatively the same end effects if the density is averaged over an infinitesimally small volume, dV, or in the finite volume defined by $\langle s_i^2 \rangle^{3/2}$. However, the quantitative end effect is more pronounced if the averaging of the density is performed in the larger volume. The value of $\rho_0/\rho_{n/2}$ is either 1/2 or $(1/2)^{3/2}$, depending on whether dV or $\langle s_i^2 \rangle^{3/2}$ is the volume used for the averaging of the density. The probability for formation of an intramolecular crosslink by chain atom i in a long unperturbed chain should be bracketed by these two results, because it probably depends on the density of chain atoms within a volume element that is larger than dV but smaller than $\langle s_i^2 \rangle^{3/2}$. The results have a similar implication for cyclization probabilities, because the formation of an intramolecular crosslink introduces a ring into the chain.

Acknowledgements

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