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Random Walk with Persistence

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The exact analytic result is obtained for the Fourier transform of the generating function $F(\mathbf{R}, s) = \sum_{n=0}^{\infty} s^n P(\mathbf{R}, n)$, where $P(\mathbf{R}, n)$ is the probability density for the end-to-end distance $\mathbf{R}$ in n steps of a random walk with persistence. The moments $\langle R^2(n) \rangle$, $\langle R^4(n) \rangle$, and $\langle R^6(n) \rangle$ are calculated and approximate results for $P(\mathbf{R}, n)$ and $\langle R^{-1}(n) \rangle$ are given.

KEY WORDS: Persistent random walk; polymers; generating function.

1. INTRODUCTION

In the context of random walk models for polymer chains, one is interested in properties such as the moments $\langle R^{2l} \rangle$ of the end-to-end distance $\mathbf{R}$ (for $l \geqslant 2$) and the probability density $P(\mathbf{R}, n)$.[1,2] In this paper, such analytic results will be derived for a random walk with persistence.

In the free flight model, a polymer is represented as a chain of n segments $\mathbf{r}_k$, $k = 1,..., n$, each with a constant length $|\mathbf{r}_k| = b$, but with a random orientation. In the parlance of stochastic processes,[3] $\mathbf{r}_k$ is a "white process" as a function of the discrete time k. Thus, the end-to-end distance,

$$\mathbf{R}(n) = \sum_{k=1}^{n} \mathbf{r}_k \tag{1}$$

being the sum of uncorrelated random variables $\mathbf{r}_k$, is a Markov process. We now consider a model with persistence, namely the kth segment $\mathbf{r}_k$, $k = 2,..., n$, has the same direction as the segment $\mathbf{r}_{k-1}$ with probability p, and has a random orientation otherwise (probability $1 - p$). In this case, $\mathbf{r}_k$ itself is a Markovian process and therefore $\mathbf{R}_n$ alone is no longer

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Markovian. This complication can be dealt with by considering the pair $(\mathbf{R}_n, \mathbf{r}_n)$, which again defines a Markov process.

In the free flight model, subsequent segments are uncorrelated, and the correlation length is therefore equal to b. In the model with persistence, the correlation length is defined as

$$a = b/(1-p) = n_c b \tag{2}$$

The free flight model corresponds to the particular case $p = 0$. For a polymer length much larger than a, we expect the end-to-end distance to be close to Gaussian. We will study this approach to the Gaussian regime on the basis of exact results for $\langle R^2(n) \rangle$, $\langle R^4(n) \rangle$, and $\langle R^6(n) \rangle$.

In Section 2, we derive the analytic result for

$$F(\mathbf{k}, s) = \int d\mathbf{R} \exp(i\mathbf{k} \cdot \mathbf{R}) \sum_{n=0}^{\infty} s^n P(\mathbf{R}, n) \tag{3}$$

for a random walk with persistence. In Section 3, we present the results for $\langle R^2 \rangle$, $\langle R^4 \rangle$, and $\langle R^6 \rangle$ and discuss their convergence to the Gaussian limit. In Section 4, we discuss the continuum of the random walk with persistence.

2. RANDOM WALK WITH PERSISTENCE

Both for the sake of generality and for conceptual simplicity, we will consider, instead of a continuum of possible orientations $\Omega(\theta, \phi)$ of the segments $\mathbf{r}_k$, a finite number of orientations Ω_i, $i = 1,..., N$, in a general space. For example, Ω_i may correspond to a number of allowed polar angles in a two-dimensional space, or it may refer to the orientation of a vector in a many-dimensional space. A continuum of orientations, such as appropriate for the polymer problem in three-dimensions, will be obtained by taking a suitable limit.

At each step, an orientation is chosen. With a probability p, it is equal to the previous orientation, while it is any of the $N-1$ remaining orientations with probability $(1-p)/(N-1)$. Associated with each orientation we have a segment vector $\mathbf{b}_i$. The quantity of interest is the probability density for the end-to-end distance $\mathbf{R}$ as a function of the number of segments n. As discussed in the introduction, $\mathbf{R}(n)$ is not a Markov process, but a Markov process is obtained by including in the description the orientation i of the last segment.

The probability density $P(\mathbf{R}, i, n)$ for an end-to-end vector $\mathbf{R}$ after n segments, with i being the orientation of the last segment, obeys the following master equation:

$$P(\mathbf{R}, i, n) = pP(\mathbf{R} - \mathbf{b}_i, i, n-1) + \sum_{i' \neq i} \frac{1-p}{N-1} P(\mathbf{R} - \mathbf{b}_i, i', n-1) \tag{4}$$

We will consider the following initial condition

$$P(\mathbf{R}, i, 0) = N^{-1}\delta(\mathbf{R}) \tag{5}$$

Note that (4) has a structure analogous to the BGK model in kinetic theory[5] and to the Anderson–Kubo model in nuclear magnetic resonance,[6] except for the fact that the time variable n is discrete. See also Ref. 7 for a very similar model of a random walk with restricted reversals. The exact solution of (4) can be easily obtained by Fourier "Laplace" inversion. For the transform of the end-to-end probability density $P(\mathbf{R}, n)$

$$F(\mathbf{k}, s) = \sum_{n=0}^{\infty} s^n \int d\mathbf{R}\, [\exp(i\mathbf{k}\cdot\mathbf{R})]\, P(\mathbf{R}, n) \tag{6}$$

with

$$P(\mathbf{R}, n) = \sum_{i=1}^{N} P(\mathbf{R}, i, n) \tag{7}$$

we find

$$F(\mathbf{k}, s) = \left[\left(\frac{1}{N} - \frac{1-p}{N-1}\right) \Sigma(\mathbf{k}, s)\right] \Big/ \left[1 - \frac{1-p}{N-1}\,\Sigma(\mathbf{k}, s)\right] \tag{8}$$

with

$$\Sigma(\mathbf{k}, s) = \sum_{i=1}^{N} \left[1 - \left(p - \frac{1-p}{N-1}\right) s \exp(i\mathbf{k}\cdot\mathbf{b}_i)\right]^{-1} \tag{9}$$

Even though the inverse transformation leading to $P(\mathbf{R}, n)$ cannot be performed, this result allows one to investigate various limits and particular cases.

Let us now apply (8) to the problem of a polymer chain in three dimensions. We have to take the limit in the case of a continuum of orientations. This leads to the following correspondences:

$$\begin{aligned} N &\Leftrightarrow N \to \infty \\ i &\Leftrightarrow \Omega = (\theta, \phi) \\ \mathbf{b}_i &\Leftrightarrow \mathbf{b}(\Omega) = (b \sin\theta \cos\phi,\, b \sin\theta \sin\phi,\, b \cos\theta) \\ \frac{1}{N}\sum_{i=1}^{N} &\Leftrightarrow \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \end{aligned} \tag{10}$$

We thus obtain from (8) and (9)

$$F(\mathbf{k}, s) = \left[pkb + 2p \arctan\left(\frac{1+ps}{1-ps} \tan\frac{kb}{2}\right)\right] \times \left[(p+1)\, kb + 2(p-1) \arctan\left(\frac{1+ps}{1-ps} \tan\frac{kb}{2}\right)\right]^{-1} \tag{11}$$

$F(\mathbf{k}, s)$ is a function of $k = |\mathbf{k}|$, as was to be expected on the basis of spatial isotropy.

3. MOMENTS OF THE END-TO-END DISTANCE

By expanding $F(\mathbf{k}, s)$ about $\mathbf{k} = 0$, we find

$$F(\mathbf{k}, s) = \sum_{l=0}^{\infty} A_{2l}(s)\, k^{2l} \tag{12}$$

and, by comparison with (6),

$$A_{2l}(s) = \frac{(-1)^l}{(2l+1)!} \sum_{n=0}^{\infty} s^n \langle R^{2l}(n) \rangle \tag{13}$$

Hence, such an expansion allows one to obtain explicit results for the moments of the end-to-end distance.

This procedure quickly becomes tedious as l increases, but can be handled by a symbolic manipulator. We obtain

$$\langle R^2(n) \rangle = nb^2 \frac{1+p}{1-p} - 2pb^2 \frac{1-p^n}{(1-p)^2} \tag{14}$$

$$\begin{aligned} \langle R^4(n) \rangle = {} & \frac{5}{3} b^4 n^2 \frac{(1+p)^2}{(1-p)^2} \\ & + \frac{16}{3} b^4 n^2 \frac{p^{n+1}}{(1-p)^2} + 4b^4 np^{n+1} \frac{1+p}{(1-p)^3} \\ & + \frac{8}{3} b^4 p \frac{(1-p^n)}{(1-p)^4} (p^2 + p + 1) \\ & - \frac{2}{3} b^4 n \frac{1+p}{(1-p)^3} (p^2 + 10p + 1) \end{aligned} \tag{15}$$

$$\langle R^6(n)\rangle = \frac{35}{9}b^6n^3\frac{(1+p)^3}{(1-p)^3} + \frac{88}{9}b^6n^4\frac{p^{n+1}}{(1-p)^2}$$
$$+\frac{128}{9}b^6n^3\mathrm{p}^{n+1}\frac{1+p}{(1-p)^2}$$
$$-\frac{2}{9}b^6n^2\frac{p^{n+1}}{(1-p)^4}(35p^2-58p+35)$$
$$-\frac{4}{9}b^6np^{n+1}\frac{1+p}{(1-p)^5}(29p^2+62p+29)$$
$$-\frac{32}{3}b^6p\frac{1-p^n}{(1-p)^6}(p^4+p^3+p^2+p+1)$$
$$-\frac{14}{3}b^6n^2\frac{(1+p)^2}{(1-p)^4}(p^2+5p+1)$$
$$+\frac{4}{9}b^6n\frac{1+p}{(1-p)^5}(4p^4+63p^3+46p^2+63p+4) \qquad (16)$$

The result (14) is in agreement with the general result for the second moment of the end-to-end distance of a random walk with "first-order correlations" (see Ref. 9). Approximate results for $\langle R^4\rangle$ and $\langle R^6\rangle$ have been obtained by computer simulation in Ref. 10. All the results in Table II of that paper agree within the simulation error with the analytic results (15) and (16).[2]

In the limit $p\to 0$, the results (14)–(16) reduce to those for the free flight model[1,2]:

$$\langle R^2(n)\rangle_{\mathrm{FF}} = nb^2 \qquad (17)$$
$$\langle R^4(n)\rangle_{\mathrm{FF}} = [\tfrac{5}{3}n(n-1)+n]\,b^4 \qquad (18)$$
$$\langle R^6(n)\rangle_{\mathrm{FF}} = [(35/9)\,n(n-1)(n-2)+7n(n-1)+n]\,b^6 \qquad (19)$$

On the other hand, for n large, or more precisely for n much larger than n_c [cf. (2)], **R** converges to a Gaussian random variable with the following relations between the moments:

$$\langle R^4(n)\rangle_{\mathrm{G}} = \tfrac{5}{3}\langle R^2(n)\rangle_{\mathrm{G}}^2 \qquad (20)$$
$$\langle R^6(n)\rangle_{\mathrm{G}} = (35/9)\langle R^2(n)\rangle_{\mathrm{G}}^3 \qquad (21)$$

[2] There seems to be something systematically wrong with the results of Table I in Ref. 10.

In order to investigate the convergence to the Gaussian limit, we have plotted the ratios $\langle R^4\rangle/(5/3)\langle R^2\rangle^2$ and $\langle R^6\rangle/(35/9)\langle R^2\rangle^3$ as a function of $n/n_c = L/a$ for several values of p in Figs. 1 and 2 ($L = nb$).

Another quantity of interest in polymer statistics, which arises when evaluating hydrodynamic interactions between the polymer beads, is the average $\langle R^{-1}(n)\rangle$. In the Gaussian limit, one has

$$\langle 1/R(n)\rangle_G = [6/\pi\langle R^2(n)\rangle]^{1/2} \tag{22}$$

To calculate corrections to this limit, one can expand the probability $P(\mathbf{R}, n)$ in a series of Hermite polynomials as follows ($\mu^2 = 3R^2/\langle R^2\rangle$):

$$\begin{aligned} P(\mathbf{R}, n) = \left(\frac{3}{2\pi\langle R^2\rangle}\right)^{1/2} \exp\left(-\frac{\mu^2}{2}\right)\bigg[1 &+ \frac{1}{3!}(\langle\mu^2\rangle - 3)\frac{H_3(\mu)}{\mu} \\ &+ \frac{1}{5!}(\langle\mu^4\rangle - 10\langle\mu^2\rangle + 15)\frac{H_5(\mu)}{\mu} \\ &+ \frac{1}{7!}(\langle\mu^6\rangle - 21\langle\mu^4\rangle + 105\langle\mu^2\rangle - 105)\frac{H_7(\mu)}{\mu} + \cdots\bigg] \end{aligned} \tag{23}$$

To evaluate the coefficients of H_3, H_5, and H_7, the expressions (14)–(16)

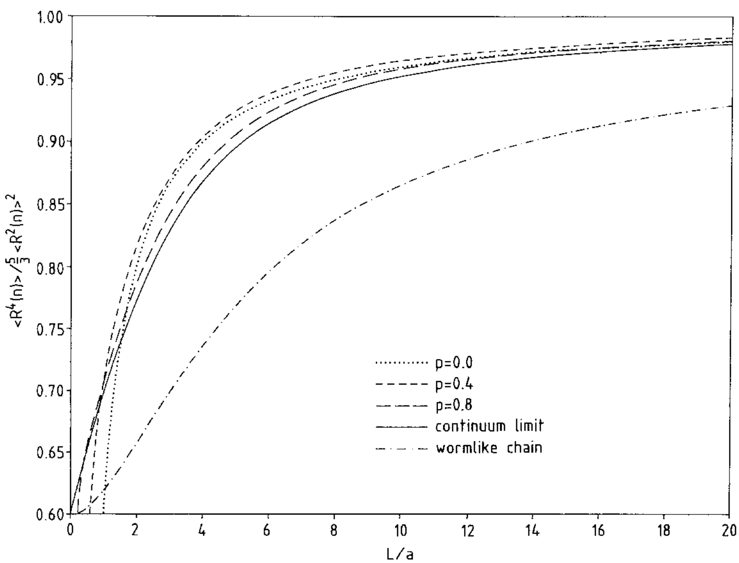

Fig. 1. Convergence of the fourth moment to the Gaussian limit, as a function of L/a.

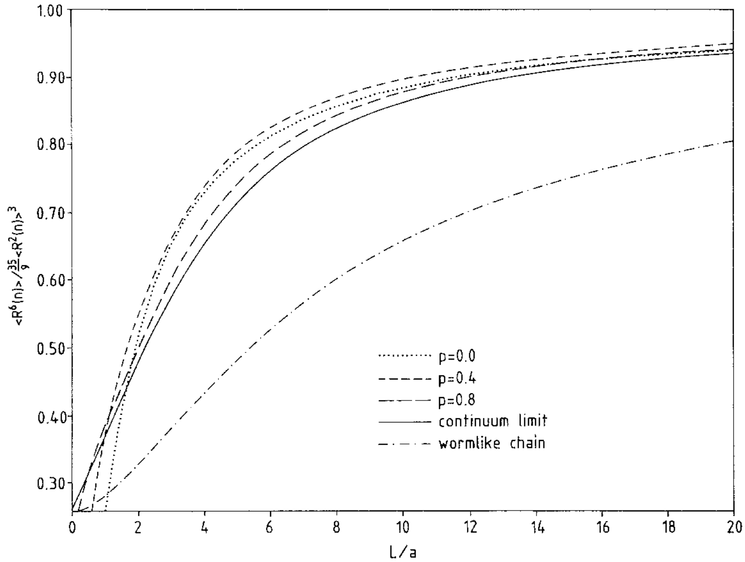

Fig. 2. Convergence of the sixth moment to the Gaussian limit, as a function of L/a.

can be used. A typical probability profile is plotted in Fig. 3. The corresponding expansion for $\langle R^{-1}(n)\rangle$ reads[1]

$$\langle R^{-1}(n)\rangle = \left(\frac{6}{\pi\langle R^2\rangle}\right)^{1/2}\left(\frac{63}{80}\frac{\langle R^4\rangle}{\langle R^2\rangle^2} - \frac{9}{112}\frac{\langle R^6\rangle}{\langle R^2\rangle^3}\right) \tag{24}$$

This result is plotted in Fig. 4 for different values of p. The agreement with the numerical results of Ref. 10 is, as could be expected, not so good, because the series expansion of the probability density $P(\mathbf{R}, n)$ in Hermite polynomials does not converge rapidly enough.

4. THE CONTINUUM LIMIT

A polymer model in polymer statistics for which analytic results can be obtained is the so-called wormlike chain. It can be looked upon as the continuum limit of the free rotation model in which the bond angle θ_0 is converging to 180°, while at the same time the length b of each segment is going to zero and the number of segments to infinity, with $nb = L$ and $b/(1+\cos\theta_0)$ constant. An analogous limit can be formulated for the persistent random walk model:

$$n \to \infty, \quad p \to 1, \quad b \to 0 \qquad \text{with} \qquad nb = L, \quad \frac{b}{1-p} = a \quad \text{const} \tag{25}$$

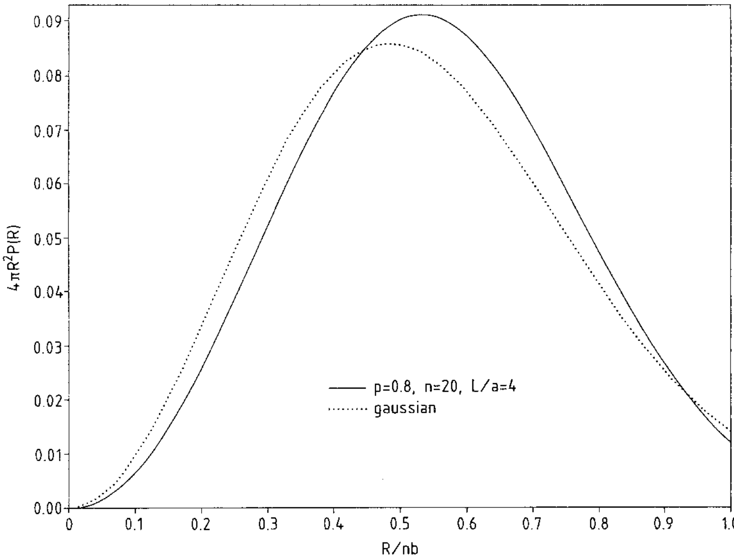

Fig. 3. Radial probability distribution, obtained by expansion in Hermite polynomials, as a function of R/nb.

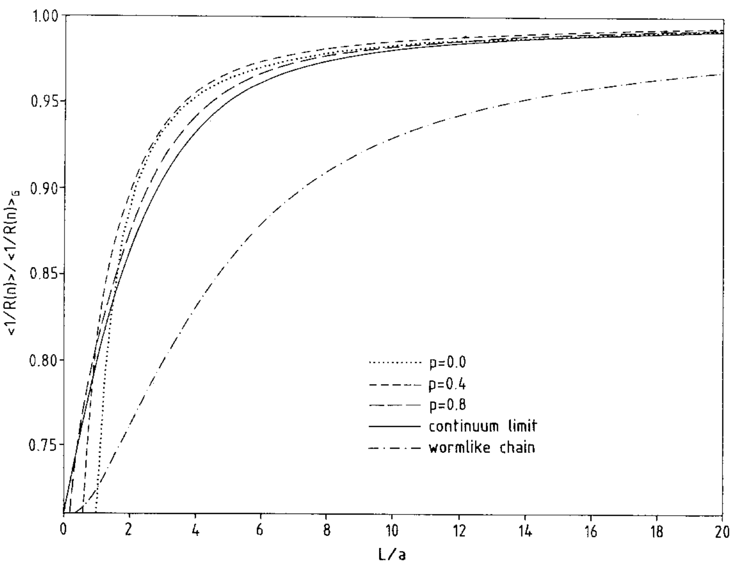

Fig. 4. Convergence of the average inverse end-to-end distance to the Gaussian limit, as a function of L/a.

The evolution equation for the probability density $P(\mathbf{R}, i, L)$ becomes

$$\frac{\partial}{\partial L} P(\mathbf{R}, i, L) = \frac{1}{a(N-1)} \sum_{i' \neq i} P(\mathbf{R}, i', L) - \frac{1}{a} P(\mathbf{R}, i, L) - \mathbf{u}_i \cdot \frac{\partial}{\partial \mathbf{R}} P(\mathbf{R}, i, L) \qquad (26)$$

with

$$\mathbf{u}_i = \lim_{b \to 0} \mathbf{b}_i / b \qquad (27)$$

This equation can be solved by Fourier–Laplace transformation

$$F(\mathbf{k}, z) = \int_0^\infty dL\, [\exp(-zL)] \int d\mathbf{R}\, [\exp(i\mathbf{k} \cdot \mathbf{R})]\, P(\mathbf{R}, L) \qquad (28)$$

with

$$P(\mathbf{R}, L) = \sum_{i=1}^{N} P(\mathbf{R}, i, L) \qquad (29)$$

One finds (using (10)):

$$F(\mathbf{k}, z) = \frac{a \arctan[ak/(1+az)]}{ak - \arctan[ak/(1+az)]} \qquad (30)$$

This result can also be obtained from (11). The moments of the end-to-end distance read

$$\langle R^2(L) \rangle = 2a^2 \left[\frac{L}{a} - 1 + \exp\left(-\frac{L}{a} \right) \right] \qquad (31)$$

$$\langle R^4(L) \rangle = 4a^4 \left\{ \frac{5}{3} \left(\frac{L}{a} \right)^2 - 4\frac{L}{a} + 2 + \left[\frac{4}{3} \left(\frac{L}{a} \right)^2 + 2\frac{L}{a} - 2 \right] \exp\left(-\frac{L}{a} \right) \right\} \qquad (32)$$

$$\langle R^6(L) \rangle = 8a^6 \left\{ \frac{35}{9} \left(\frac{L}{a} \right)^3 - \frac{147}{9} \left(\frac{L}{a} \right)^2 + 20\frac{L}{a} - \frac{20}{3} + \left[\frac{11}{9} \left(\frac{L}{a} \right)^4 + \frac{32}{9} \left(\frac{L}{a} \right)^3 - \frac{1}{3} \left(\frac{L}{a} \right)^2 - \frac{40}{3}\frac{L}{a} + \frac{20}{3} \right] \exp\left(-\frac{L}{a} \right) \right\} \qquad (33)$$

The ratios $\langle R^4 \rangle / (5/3) \langle R^2 \rangle^2$, $\langle R^6 \rangle / (35/9) \langle R^2 \rangle^3$, and $\langle 1/R \rangle / \langle 1/R \rangle_G$ for the present continuum model have also been included in Figs. 1, 2, and 4, as well as the corresponding results for the wormlike chain.

5. CONCLUSION

In this paper, we have shown that the random walk with persistence can, to a certain extent, be treated analytically. Apart from its intrinsic interest, the model can thus be used to test the validity of approximation schemes or to check numerical calculations. From Figs. 1, 2 and 4, it follows that the approach to the Gaussian form is rather insensitive to the value of p, provided that the length $L = nb$ of the polymer is expressed in terms of the correlation length a. Finally, we note that the present model differs strikingly from the wormlike chain.

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