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Topological constraints on polymer rings and critical indices

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Abstract. — Ring polymers in two and three dimensions have been simulated by closed Gaussian random walks. The effects of topological constraints is studied. In two dimensions, the non self crossing condition leads to an excluded volume effect and the critical index $v$ so observed is in good agreement with the predictions of the renormalization group theory. In three dimensions, the condition of absence of knots should lead to new effects. However, it is observed that the probability of knot formation increases very slowly with the number of segments and consequently no comparable estimate could be made of any critical index.

1. Introduction. — At present time, rather well defined samples of polymers of high molecular weights with a low polydispersity can be prepared. As a consequence, the properties of solutions of linear polymers have been widely studied not only experimentally but also theoretically.

It also appears that in the near future it will be possible to get in a similar way, well defined ring polymers of high molecular weights.

Thus, the following question arises. « In which respect, will differences be observed between the properties of similar solutions of linear and ring polymers? »

In order to answer this, we must study the effect of topological restrictions.

Clearly, the effect of these restrictions will be more important and more striking in the absence of excluded volume interactions. We know for instance that at the 0 point, two chains interact only weakly. In a first approximation, we may assume that linear chains behave rather independently, and the second virial coefficient vanishes for solutions of linear polymers. However, if the solution is made of similar simple ring polymers, topological constraints will prevent these rings from penetrating each other as was remarked several years ago by Delbrück [1].

Thus, we may expect a priori very different behaviours.

In this article, the polymer chains will be simulated by closed random walks. The topological restrictions will be

— in two dimensions, the exclusion of any crossing
— in three dimensions, the exclusion of any knot.

We shall study Gaussian random walks in space and the probability of having a polygonal closed chain with sides $u_1, ..., u_N$ will be assumed to be

\[
P(u_1, ..., u_N) \propto \delta(u_1 + \cdots + u_N) \times 
\exp \left\{ - \sum_{j=1}^{N} u_j^2/2 \right\} . \tag{1.1}
\]

The reason for preferring Gaussian chains to chains drawn on a lattice is threefold.

1) Our chains are infinitely thin and we take into account only the effect of knot formation avoiding any finite excluded volume effect.
2) The model is completely isotropic.
3) The effects depending on small distances are eliminated. It is also hoped that the effect of knot formation will be felt earlier because the minimum number of steps required to form a knot is much smaller for Gaussian walks than for walks on a lattice.

We consider Gaussian rings made of $N$ links in a space of dimension $d$. Let $Z_N$ be the number of
configurations of Gaussian rings without self intersection for \(d = 2\), or without a knot for \(d = 3\) and \((Z^N)_0\), the number of configurations of the corresponding free Gaussian rings (i.e. without topological constraints). When a proper cut-off is introduced, these quantities are finite and, for large \(N\) and at least for \(d = 2\), we expect the following behaviour

\[
Z_N = AN^{-\nu} \mu^N \quad (1.2)
\]

\[
(Z_N)_0 = A_0 N^{-d/2} \mu_0^N. \quad (1.3)
\]

The ratio \(\frac{Z_N}{(Z^N)_0}\) remains finite in the continuous limit and this is the quantity which is calculated here. Thus, for large \(N\), \(\frac{Z_N}{(Z^N)_0}\) should behave as follows

\[
\frac{Z_N}{(Z^N)_0} = A_1 N^{-(\nu - 1/2d)} \mu_N. \quad (1.4)
\]

Actually, for \(d = 3\), very little is known concerning the probability \(P_N\) that a ring is unknotted (simple ring or trivial knot) but the same kind of behaviour can be expected for \(d = 3\) as for \(d = 2\), with different constants and a different index \(\nu\).

Now consider the size of these rings.

Putting

\[
\mathbf{r}_j = u_1 + \cdots + u_j
\]

we define the size \(R_N\) of a ring \((N\) even) by setting

\[
R_N^2 = \frac{2}{N} \sum_{j=1}^{\frac{N}{2}} (r_{j+N/2} - r_j)^2. \quad (1.5)
\]

Let \(\langle R_N^2 \rangle\) be the mean square size of Gaussian rings without self intersection for \(d = 2\) or without a knot for \(d = 3\) and \(\langle R_N^2 \rangle_0\) the mean square size of the corresponding free rings.

For large \(N\), we expect the following behaviour

\[
\langle R_N^2 \rangle \simeq BdN^{2\nu-1}
\]

\[
\langle R_N^2 \rangle_0 = \frac{d}{4} N^2
\]

and we shall study particularly

\[
\langle R_N^2 \rangle_0 \approx 4 BN^{2\nu-1}.
\]

For \(d > 3\), there are no topological constraints.

A calculation in two-dimensional space for non crossing Gaussian walks was carried out first as an introduction to the three-dimensional case. Actually the non crossing condition has the same effect as an excluded surface (i.e. two-dimensional volume) proportional to the mean square length of a link. These results are discussed in section 3 and compared with the predictions of renormalization group theory.

In three dimensions, our numerical work leads to a good estimation of \(\mu\) namely \(\mu \approx 0.996\) but the value of \(\nu\) is difficult to predict. The trouble is that the probability \(P_N\) of having rings without a knot decreases rather slowly with \(N\) as indicated on figure 7. Thus, for \(N \sim 200\) which is a rather large number, \(P_N\) remains equal to about 0.5 in spite of the fact that eq. (1.2) is probably valid in the asymptotic region \(N \rightarrow \infty\), \(P_N \rightarrow 0\), but we are far from this limit.

2. Generation of Gaussian rings. — We construct Gaussian rings step by step by finding values for \(u_1, u_2, \ldots, u_j\) successively.

Let \(\mathbf{r}_j = u_1 + \cdots + u_j\), \(\mathbf{r}_0 = 0\).

We find

\[
P(u_j; u_{j-1}, \ldots, u_1) = \frac{1}{2\pi l^2} \times
\]

\[
\exp \left\{ -\left( \frac{1}{2} \sum_{j=1}^{N} k_j^2 + \frac{l^2}{2N} \left( \sum_{j=1}^{N} k_j \right)^2 \right) \right\}. \quad (2.1)
\]

which can be easily deduced from eq. (1.1).

Then we calculate the conditional probability for \(u_j\) when \(u_1, \ldots, u_{j-1}\) are given. This function will be denoted \(P(u_j; u_{j-1}, \ldots, u_1)\).

We make the transformation

\[
x = (-2 l^2 \ln v_1)^{1/2} \cos (2 \pi v_2)
\]

\[
y = (-2 l^2 \ln v_1)^{1/2} \sin (2 \pi v_2). \quad (2.5)
\]

The random vector \(\mathbf{r}_j\) with coordinates \((x_j, y_j)\) having the desired probability (2.3) can therefore be obtained from

\[
x_j = \left( \frac{N-j}{N-j+1} \right) x_{j-1} + \left( -2 l^2 \frac{N-j}{N-j+1} \ln v_1 \right)^{1/2} \cos (2 \pi v_2)
\]

\[
y_j = \left( \frac{N-j}{N-j+1} \right) y_{j-1} + \left( -2 l^2 \frac{N-j}{N-j+1} \ln v_1 \right)^{1/2} \sin (2 \pi v_2). \quad (2.6)
\]

The random vector \(\mathbf{r}_j\) with coordinates \((x_j, y_j)\) having the desired probability (2.3) can therefore be obtained from

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\]

\[
y_j = \left( \frac{N-j}{N-j+1} \right) y_{j-1} + \left( -2 l^2 \frac{N-j}{N-j+1} \ln v_1 \right)^{1/2} \sin (2 \pi v_2). \quad (2.6)
\]
(For three dimensions, we generate \( z_j \) in a similar manner.) Thus \( r_1 \) is almost freely chosen, \( r_2 \) contains a small component directed toward the starting point; \( r_3, r_4, \ldots \) and so on are more and more restricted and finally \( r_N \) is determined by the fact that we must come back to the starting point because the ring is closed. We take \( N \) even, \( N = 2m \), so that the average \( \frac{1}{m} \sum_{j=1}^{m} (r_{j+m} - r_j)^2 \) gives a better estimate of the size of the ring.

3. Two-dimensional results. — We consider plane rings made of \( N \) links. For large \( N \), the probability \( \mathcal{Z}_N \) that the Gaussian rings are non intersecting is

\[
\mathcal{Z}_N \approx A_1 N^{-(2n-1)} \mu^N_1. \tag{3.1}
\]

The values obtained for \( \mathcal{Z}_N \) are given in table I. For a given \( N \), \( t_N \) is the total number of rings which have been constructed and \( b_N \) the number of those rings which are non-intersecting. \( \mathcal{Z}_N \) has been fitted by a function of the form (1.4) in the following manner. First a rough estimate of \( \mu_1 = \lim \frac{\ln \mathcal{Z}_N}{N} \) has been obtained. Then for various values of \( \mu_1 \) the quantity \( \ln \mathcal{Z} - N \ln \mu_1 \) has been plotted versus \( \ln N \). For a well chosen value of \( \mu_1 \), all the points nearly lie on a straight line and this criterion defines all the parameters.

The result is

\[
\mathcal{Z}_N = 3.13 N^{-0.43(0.785)}^N. \tag{3.2}
\]

Thus, for \( v \) we find the value

\[
v' = 0.715. \tag{3.5}
\]

Table I. — The number of Gaussian random rings in two dimensions with various number of segments; \( N \) is the number of segments, \( t_N \) is the total number of rings constructed of which \( b_N \) are non self intersecting. The probability of no self-intersection is \( \mathcal{Z}_N = b_N/t_N \) with an error [9]

\[
\Delta \mathcal{Z}_N \approx \{ b_N(t_N - b_N)/t_N^2 \}^{1/2}.
\]

The error in average mean square size is

\[
\Delta (\langle R_N^2 \rangle / \langle R_N^2 \rangle_0) \approx \{ 3 dbN/2 \}^{-1/2}
\]

with \( d = 2 \).

On the other hand, the ratio \( \langle R_N^2 \rangle / \langle R_N^2 \rangle_0 \) has been calculated for various values of \( N \) and the results are given in table I.

In agreement with the expected result

\[
\langle R_N^2 \rangle / \langle R_N^2 \rangle_0 \approx 4 BN^{2n-1} \tag{3.3}
\]

we find, for large \( N \)

\[
\langle R_N^2 \rangle / \langle R_N^2 \rangle_0 = 0.4774 N^{0.4833} \tag{3.4}
\]

and therefore for \( v \) the approximate value

\[
v'' = 0.741. \tag{3.5}
\]

The values of \( v' \) and \( v'' \) obtained here show clearly that the no intersection condition is equivalent to an excluded volume effect.

For \( d = 2 \), Flory's formula \( v_F = \frac{3}{d(d+2)} \) gives \( v_F = 0.75 \) and we find that the values obtained for \( v' \) and \( v'' \) are smaller.

However, it is known that Flory's formula gives, for \( v \), an estimation which is slightly too large. A better estimate for \( v \) can be obtained as follows.

For \( 4 \geq d \geq 1 \), we try to represent \( v \) by an approximate formula of the form

\[
v_d = \frac{A + Bd}{C + Dd + Ed^2} \tag{3.5}
\]

and we determine the coefficients by using four known results [3]

\[
v_{d-1} \approx \frac{1}{2} \left( \frac{3}{d} + \frac{1}{d-1} + \cdots \right)
\]

\[v_3 = 0.588\]

\[v_1 = 1.
\]

For \( d = 2 \), the preceding formula gives

\[v_2 = 0.736\]

and this value lies just between \( v' \) and \( v'' \).

Thus, the agreement between the computer experiments and the theoretical expectations is rather good.

4. Knot invariants. — The problem of deciding whether a knot (for a single ring) or a link (for two or more rings) is present has been already considered by Edwards [4] and by Vologodskii et al. [5].

Thus the lacing number of two rings (1 and 2) is given by

\[
I = \frac{1}{4\pi} \int (dr_1 \wedge dr_2).r_{12}
\]

which is invariant under ring manipulations. If it is different from zero, we know that the rings cannot be separated without cutting one of them. The invariant can be easily found by projecting the two
rings on a plane. The rings are oriented and, on the projection, we mark the double point as +1 if the priority of the overpass from the right is observed and -1 if it is not. The lacing number \( I \) is half the sum of all the marks of the intersections of one ring with the other one (Figs. 1, 2).

Fig. 1. — The sign of an over or underpass; it is +1 or -1 according as the priority to right overpass is observed or not.

Fig. 2. — Two closed laced chains with the lacing number zero.

One would like to find a similar invariant for describing the lacing of one ring with itself. Thus, from a single ring, one may create two rings by doubling it along all its length. In this way, it is possible to derive an invariant for a single ring. However, this invariant is not really useful here because its value does not depend only on the configurations of the knots in the ring but also on other analytic properties of the ring [6].

Therefore, when dealing with single rings, we have to rely on the algebraic invariants derived by Alexander [7] and Alexander and Briggs [8]. The simplest one is the Alexander polynomial \( \Delta(x) \). In particular, its value for \( x = -1 \) is different for different prime knots and easily calculable on a computer. Without going into mathematical details which can be found in references [9] or [5], we shall present in section 5 the process used for calculating \( \Delta(-1) \).

Actually \( \Delta(-1) \) (and even \( \Delta(x) \)) is not sufficient to distinguish in all cases a knotted ring from an unknotted one. An example of a knotted ring [5, 10] with \( \Delta(x) = +1 \) is given on figure 3. It cannot be distinguished from the trivial knot (i.e. unknotted ring) by its \( \Delta(x) \) which is 1. Such ambiguous cases are however complicated and occur only for long chains. We shall assume without further apology that the ring is unknotted if its \( \Delta(-1) = 1 \).

5. Three-dimensional rings. Calculating the algebraic invariant \( \Delta(-1) \). — We choose the projection of the knot on a plane in such a way that every multiple point is a double point. At every double point, the part of the curve passing below is called an underpass, and the other one is called an overpass. Usually, any of the three projections, namely on \( x, y; y, z \) and \( z, x \) planes, will do. To reduce computer time, we choose the projection with the smallest number, say \( n \), of double points. Taking any point, not multiple, of the knot as the origin and assigning arbitrarily a direction of travel on the knot, we ignore the overpasses and number consecutively the underpasses as \( 1, 2, ..., n \). Now the overpassing arc (i.e. the section of the curve) lying between the underpasses \( j - 1 \) and \( j \) (mod. \( n \)) is assigned the number \( j \). Thus two integers are assigned to every double point, the number of the underpass and the arc number of the overpass. Let us denote them as \( j \) and \( \text{arc}(j) \),

\[
1 \leq \text{arc}(j) \leq n, \quad j = 1, 2, ..., n.
\]

Now, an \( n \times n \) matrix \( M \) with integer elements is built as follows. The rows of \( M \) corresponding to
the underpasses $j = 1, 2, ..., n$ are constructed one by one. Consider the row $j$. If arc $(j) = j$ or
\[ \text{arc}(j) = j + 1 \pmod{n} \]
then put $M(j, j) = 1$, and $M(j, j + 1) = -1$; otherwise put $M(j, j) = M(j, j + 1) = 1$, and
\[ M(j, \text{arc}(j)) = -2. \]
All the other elements in the $j$-th row are put equal to zero. The absolute value of any $(n-1) \times (n-1)$ minor of $M$ is the value of $\Delta(-1)$.

The time taken for the evaluation of an $n \times n$ determinant on a computer varies as $n^3$. To reduce this time, we take advantage of the special structure of the matrix $M$. We may proceed as follows.

i) If arc $(j) = j$, or arc $(j) = j + 1 \pmod{n}$, add column $j$ to column $j + 1 \pmod{n}$; then all the elements of the row $j$ except one vanish; we remove the $j$th row and $j$th column, and we renumber the rows and columns.

ii) If arc $(j) = \text{arc}(j + 1)$, whereas arc $(k) \neq j + 1$ for any $k$, then we add column $j$ to column $j + 2 \pmod{n}$; we remove the rows and columns numbered $j$ and $j + 1$ and we renumber the remaining ones. A similar operation can be performed when
\[ \text{arc}(n) = \text{arc}(1), \]
whereas arc $(k) \neq 1$ for any $k$.

The above operations are performed in any order and as many times as possible. They reduce considerably the size of the matrix $M$ and hence the computer time. If $n < 3$, the chain is not knotted and $\Delta(-1) = 1$.

Simple knots are usually distinguishable by the value of their $\Delta(-1)$. For example, out of the 84 knots, which in their plane projections have the minimum number of crossings less than or equal to nine [7, 8], only six pairs are indistinguishable by their $\Delta(-1)$. Thus one may sort out different knots according to their $\Delta(-1)$. However, this was not of interest to us. We sorted knots having $\Delta(-1) \neq \pm 1$ from those having $\Delta(-1) = \pm 1$.

6. Discussion of the results. — For three dimensions, table II lists the number of chains generated together with those having $\Delta(-1) = 1$. The number of segments varies from 10 to 270. On figures 7, 9 and 10 we plot respectively $z_N$, $\ln z_N + 0.004 N$ and $\ln \langle R^2 \rangle$ as functions of $\ln N$, while figure 8 is a plot of $\ln z_N$ as a function of $N$.

For two dimensions, the curves on figures 5 and 6 are nearly straight lines and furnish the values of $\nu$ announced in section 3. For three dimensions the reader is free to draw any conclusions he likes.

We would like to thank R. Conte and J. Raynal for help in programing.

![Figure 5](image_url)

**Fig. 5.** — $\ln z_N - N \ln (0.785)$ as a function of $\ln N$ for two dimensions.

![Figure 6](image_url)

**Fig. 6.** — $\ln \langle R^2 \rangle$ as a function of $\ln N$ for two dimensions.
Fig. 7. — $\bar{\chi}_N$ as a function of $\ln N$ for three dimensions.

Fig. 8. — $\ln \chi_N$ as a function of $N$.

Fig. 9. — $\ln [\chi_N + 0.004 N]$ as a function of $\ln N$ for three dimensions.

Fig. 10. — $\ln \left[ \langle R_N^2 \rangle / \langle R_N^2 \rangle_+ \right]$ as a function of $\ln N$ for three dimensions.

References


