Predicting Optimal Lengths of Random Knots

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Abstract

In thermally fluctuating long linear polymeric chain in solution, the ends come from time to time into a direct contact or a close vicinity of each other. At such an instance, the chain can be regarded as a closed one and thus will form a knot or rather a virtual knot. Several earlier studies of random knotting demonstrated that simpler knots show their highest occurrence for shorter random walks than more complex knots. However up to now there were no rules that could be used to predict the optimal length of a random walk, i.e. the length for which a given knot reaches its highest occurrence. Using numerical simulations, we show here that a power law accurately describes the relation between the optimal lengths of random walks leading to the formation of different knots and the previously characterized lengths of ideal knots of the corresponding type.

**keywords:** knots, polymers, scaling laws, DNA, random walks.

A random walk can frequently lead to the formation of knots and it was proven that as the walk becomes very long the probability of forming nontrivial knots upon closure of such a walk tends to one. Many different simulation approaches were used to study random knotting. Probably the most fundamental one is by simulation of ideal random chains where each segment of the chain is of the same length and has no thickness. In ideal random chains the neighboring segments are not correlated with each other and thus show the average deflection angle of \(90^\circ\). Ideal random chain behavior is interesting from physical point of view as it reflects statistical behavior of long
polymer chains in so-called melt phase and in θ solvents where excluded volume effect vanishes [8]. Highly diluted polymer chains in θ solvents are unlikely to interact with each other and therefore upon circularization will form mainly knots rather than links. In thermally fluctuating long linear polymers the ends of the same chain can come from time to time into a close vicinity of each other. This can lead to a cyclization of the polymer whereby the end closure frequently traps a nontrivial knot on the chain. By studying knotting in simulated ideal random chains we thus can gain insight into knotting of real polymer chains in θ solvents and in the dense melt phase frequently used for the preparation of such synthetic polymeric materials like fabrics, paints or adhesives [9]. However, ideal chains do not reflect the behavior of real polymer chains in good solvent. Intramolecular interactions cannot be neglected in these conditions, but can be well approximated by introducing an effective diameter. When such a constraint is introduced into simulated chains one can also model knotting of polymers in good solvents like for example knotting of DNA molecules in typical reaction buffers used for biochemical experiments [4]. Our simulations can be adjusted to both situations and we shall present here results for random chains with and without an effective diameter.

Several earlier studies of random knotting showed that simpler knots reach a maximum of their occurrence for shorter length of random walks than this required for the formation of more complex knots [5, 6, 10]. In considering the equilibrium ensemble of closed walks, these studies showed that the relative frequency of occurrence of each type of knot first increases with the length of the chain, then passes through a maximum and finally decreases exponentially at very long chains. However, these earlier studies did not attempt to establish a relation between the type of a knot and the optimal length of a random walk leading to the maximal occurrence of this knot. If we consider a thermally fluctuating polymer with ends that can stick to each other with the energy much smaller than $kT$, then from time to time these ends will stay in contact for a short period and at this moment the polymer will form a trivial or nontrivial knot. In this study, we characterize statistical ensembles of fluctuating linear polymers in order to find specific lengths (expressed in number of statistical segments) at which a given type of knot or rather a virtual knot reaches its highest occurrence.

Recently we have characterized ideal geometric configurations of knots corresponding to the shortest trajectories of flexible cylindrical tube with uniform diameter to form a given knot [11]. The ratio of the length to diameter of the tube forming ideal configuration of a given knot is a topological invariant and we call it here the length of ideal knots. Ideal knots turned out to be good predictors of statistical behavior of random knots. So for example the writhe of ideal configuration of a given knot was equal to the average writhe of thermally fluctuating polymer forming a given random knot [11]. We showed also that electrophoretic migrations of various types of knotted DNA molecules
of the same molecular weight or their expected sedimentation constants were practically proportional to the length of the corresponding ideal knots [12, 13]. Therefore we decided here to check whether the length of ideal knots is related to the length of ideal random chains for which different knots reach their highest occurrence. To this aim we used the following simulation procedure. \(2 \times 10^9\) random walks of 170 segments were started and each time the growing end approached the starting end to a distance smaller than the length of one segment the configuration was saved upon which the walk was continued for the remaining number of steps. Each vector (segment) of the chain was randomly chosen from uniformly distributed vectors pointing from the center to the surface of the unit sphere. Thus some of the random walks showed one or more approaches of the growing and starting ends and we collected \(2 \times 10^9\) random walks for every number of segments between 5 and 170. Each saved configuration with nearby ends was then closed with a connecting segment and the type of the formed knot was determined by the calculation of its Alexander polynomial [7, 14, 15, 16].

For random linear walks to efficiently form different knots a compromise has to be met between the length optimizing their close approach and the length which is sufficient to form a knot of a given type. The present analysis differs from earlier studies [4, 5, 10] where the statistics was based only on equilibrium knotting of closed walks. In our case, we consider the formation of knots through the approach of the terminal segments of linear chains. Therefore not only closed chains, but also linear chains are taken into account in our statistics.

Figure 1 shows the occurrence profiles of different knots with up to six crossings as a function of the length of random walk which leads to the formation of these knots. It is visible that trefoil knots show their highest occurrence for 25 ± 1 segments while 41 knots form most frequently for 42 ± 1 segments. The formation of more complicated knots happens much less frequently than this of simpler knots, therefore in the insert in Figure 1 a change of scale is applied to better visualize the occurrence of more complicated knots. We observed that the obtained probabilities values for different knots can be well fitted with the function

\[
P_k(N) = a(N - N_0)^b \exp\left(\frac{-N^c}{d}\right)
\]

where for each knot \(a, b\) and \(d\) are free parameters, \(c\) is an empirical constant equal to 0.18, \(N_0\) is the minimal number of segments required to form a given type of knot [17] without the closing segment and \(N\) is the number of segments in the walk. Our fitting function was adapted from Katritch et al. 2000[18] but modified to take into account the probability of cyclization. Table 1 lists the positions of maximal occurrence for the analyzed types of knots. In order to concentrate on the position of the maximum for different knots and not on their actual probability values we decided to present probability profiles for each knot upon normalizing them by assigning a value 1 to the respective maximum of probabilities.
Figure 1: Probability of forming a given knot among all random walks of a given size is plotted as a function of the number of segments in the walk. Note the change of the scale between the main panel and the insert. Diagrams of the corresponding knots are drawn to visualize the differences between analyzed types of knots. The notations accompanying the drawn diagrams correspond to those in standard tables of knots [21], where the main number indicates the minimal number of crossings possible for this knot type and the index indicates the tabular position amongst the knots with the same minimal crossings number. Formed knot types were recognized by computing their Alexander polynomial. Since Alexander polynomial does not distinguish between left-handed and righthanded knots of the same type, we have to group them together and therefore the drawn diagrams of the knots do not show the handedness. This polynomial has sometimes the same value for different knots like for example knot 6_1 and 9_46 [22]. However within groups of knots with the same Alexander polynomial more complicated knots have such a low occurrence that their effect on the position of the maximum of the simplest knot within the group can be neglected.
Figure 2 presents normalized probability profiles for the analyzed knots. It is visible that different knots show now quite similar type of profiles (e.g. knot $5_1$ and $5_2$) whereby the differences in the position of maximum between knots with different minimal number of crossings can be easily perceived. It may be surprising that we observed here such a short optimal length for analyzed knots while earlier studies showed that several hundred segments are needed to observe maximum occurrence of a given knot among closed walks of a given size \cite{5, 10, 19}. This is simply due to the fact that our system takes into account the probability of cyclization.

Figure 2: Normalized probability profiles for the analyzed knots.

In Figure 3 we show the relation between the optimal length of random knots and the length of the corresponding ideal knots. This relation is well approximated by a power law function. Upon fitting the free parameters of this function in the simulation data obtained for the knots with up to 7 crossings, we decided to check if by knowing the length of ideal configurations of more complicated knots we can predict positions of the maximum of occurrence for the corresponding random knots. As the statistics of random knotting gets poor for knots with increasing crossing number we limited verifications of our predic-
tions to these knots with eight crossings which at their maxima of occurrence were represented more than 500 times out of $2 \times 10^9$ random walks with a given number of segments. Analysis of our simulation data (Figure 3) positively verified our predictions for optimal sizes of random walks leading to the formation of these knots.

Figure 3: Relation between the length of the ideal geometric representations of knots [23] and positions of maximal occurrence for the corresponding random knots. The lower curve: the optimal length of random knots with an effective diameter set to zero. The simulation data for the knots with up to seven crossings were fitted with a power law function and the best fit curve was extrapolated. Data points for eight crossing knots for which we obtained good statistics coincide with the extrapolated curve. The upper curve: data points of maximal occurrence of knots for random chains with an effective diameter set to 0.05 of the segment length. In both cases a power law function adequately describes the relation between the optimal length of random knots and the length of ideal knots of a given type. Best fit parameters for both cases are indicated.

As already mentioned, ideal random chains have no thickness and this causes that they reflect the behavior of polymers in the melt phase where thin polymers have practically no exclusion volume [7, 8]. However when polymers are suspended in a good solvent, like DNA in aqueous solution, the exclusion volume of polymers becomes not negligible and this strongly decreases the probability of forming knots [7]. It was observed that the higher the effective diameter of
the polymer the lower the probability of forming knots by random cyclization 
[4, 7, 19]. We decided therefore to investigate whether a power law relation 
between the length of ideal knots and the optimal length of randomly knotted 
chains also holds for chains with an exclusion volume. To this aim from our 
original set of $2 \cdot 10^9$ ideal random walks for every segment length from 5 to 100 
we selected the walks which never showed a closer approach between any pair 
of non neighboring segments than the considered effective diameter (terminal 
segments of the chain are considered as neighboring ones). Subsequently we 
analyzed all configurations with approached ends for the types of formed knots 
and calculated the probabilities of various knots among all random chains which 
fulfilled the criteria of a given effective diameter. We observed that as the ef-
fective diameter grows the probability of forming various knots decreases and 
positions of the maximum move toward longer chains. Figure 3 (dashed line) 
shows the relation between the length of ideal knots and the optimal length of 
corresponding random knots formed by chains with the effective diameter being 
set to 0.05 of the segment length. The effective diameter 0.05 corresponds to 
this of diluted solutions of DNA molecules in about 100 mM NaCl [4]. In the 
case of DNA each segment in the random chain corresponds to 300 base pair 
long region [20]. It is visible that the data can be again approximated by a 
power law function. Fact that lengths of ideal knots shows a correlation with 
the optimal sizes of corresponding random knots formed by chains with a given 
effective diameter provides another example that ideal knots are good predictors 
of physical behavior of real knots [11].

Post factum it might seem to be obvious that knots requiring higher length of 
the rope to tie them should require higher length of a random walk to reach 
their highest occurrence. However until recently the minimal length of the rope 
to tie a given knot was not known. In addition the relation between the optimal 
length of random walk producing a given knot and the length of ideal knot was 
not yet proposed in the literature. On the other hand a simple expectation 
would dictate that the shorter the length of ideal knot the higher the prob-
ability of its formation. So for example trivial knots are more frequent than 
trefoils and these are more frequent than $4_1$ knots. However this does not hold 
for $5_1$ and $5_2$ knots. Ideal knot $5_1$ is slightly shorter than ideal $5_2$ knot (which 
is consistent with the optimal size of random walks leading to the formation 
of corresponding knots), but $5_2$ knot formation by random walks is circa twice 
more frequent than formation of $5_1$ knot. Therefore the values of random knots 
probabilities (in contrast to the positions of the maxima) are not related by a 
relatively simple growing function to the values of lengths of the corresponding 
ideal knots. 

What can be the possible applications resulting from the determination of the 
optimal size of knots? For chemical cyclization of polymer chains we can use 
linear polymer of a specific length and thus promote formation of a given type 
of knot. Materials with interesting properties could be formed by this way.
Table 1: Optimal sizes $O_s$ of random walks (in number of segments) leading to the formation of corresponding knots, the length/diameter ratio $L_D$ values of ideal configurations of these knots $K_n$ [23] and the values of the parameters in the fits of the observed probabilities (see Fig. 1). The presented data are limited to knots with up to 7 crossings since obtained by us, statistics for more complex knots is less good.

| $K_n$ | $O_s$ | $L_D$ | $a$ | $b$ | $d$ | $N_0$ |
|-------|-------|-------|-----|-----|-----|-------|
| 3     | 25±1  | 16.33 | (1.84±0.01)×10$^{-1}$ | 1.57±0.01 | 0.165±0.001 | 5     |
| 4     | 42±1  | 20.99 | (0.45±0.01)×10$^{-1}$ | 2.24±0.01 | 0.134±0.001 | 6     |
| 5     | 54±2  | 23.55 | (1.28±0.02)×10$^{-2}$ | 2.65±0.01 | 0.121±0.001 | 7     |
| 5     | 56±2  | 24.68 | (2.31±0.04)×10$^{-2}$ | 2.77±0.01 | 0.118±0.001 | 7     |
| 6     | 74±2  | 28.30 | (0.78±0.03)×10$^{-2}$ | 3.75±0.02 | 0.095±0.001 | 7     |
| 6     | 75±2  | 28.47 | (0.74±0.03)×10$^{-2}$ | 3.67±0.02 | 0.096±0.001 | 7     |
| 6     | 76±2  | 28.88 | (0.39±0.02)×10$^{-2}$ | 3.69±0.02 | 0.097±0.001 | 7     |
| 7     | 89±3  | 30.70 | (4.09±0.47)×10$^{-7}$ | 3.95±0.06 | 0.083±0.001 | 8     |
| 7     | 92±3  | 32.41 | (1.72±0.16)×10$^{-3}$ | 4.33±0.05 | 0.088±0.001 | 8     |
| 7     | 92±3  | 31.90 | (9.43±0.85)×10$^{-4}$ | 4.03±0.05 | 0.092±0.001 | 8     |
| 7     | 97±3  | 32.53 | (5.55±0.67)×10$^{-4}$ | 4.25±0.06 | 0.087±0.001 | 8     |
| 7     | 97±3  | 32.57 | (1.32±0.09)×10$^{-3}$ | 4.24±0.04 | 0.089±0.001 | 8     |
| 7     | 98±3  | 32.82 | (1.71±0.14)×10$^{-3}$ | 4.36±0.04 | 0.086±0.001 | 8     |
| 7     | 95±3  | 32.76 | (8.82±0.96)×10$^{-4}$ | 4.31±0.06 | 0.087±0.001 | 8     |

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