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Knots in finite memory walks

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Abstract. We investigate the occurrence and size of knots in a continuum polymer model with finite memory via Monte Carlo simulations. Excluded volume interactions are local and extend only to a fixed number of successive beads along the chain, ensuring that at short length scales the excluded volume effect dominates, while at longer length scales the polymer behaves like a random walk. As such, this model may be useful for understanding the behavior of polymers in a melt or semi-dilute solution, where exactly the same crossover is believed to occur. In particular, finite memory walks allow us to investigate the role of local interactions in the transition from highly knotted ideal polymers to almost unknotted self-avoiding polymers. Even though knotting decreases substantially when a few next-nearest neighbor interactions are considered, we find that the knotting probability of a polymer chain of modest length of 500 steps only decays slowly as a function of the range of the excluded volume interaction. In this context, we also find evidence that for length scales up to the interaction length the knotting behavior of the finite memory walk resembles that of a self-avoiding walk (effectively suppressing small knots), while for larger length scales it resembles that of a random walk.

1. Introduction

Knots are known since the dawn of mankind for their utility and aesthetics, but have only been described in mathematical terms rather recently. Arguably, the foundations of modern knot theory have been laid by two Scottish physicists in the 1870s and 1880s: Lord Kelvin, who devised an atomic theory based on the idea of vortex atoms made from ether \cite{Kelvin} and Peter Tait, who started to tabulate knots in an attempt to account for all vortex atoms \cite{Tait}.

A variant of Tait’s classification scheme \cite{Tait} is still used today and categorizes knots according to the minimum number of crossings of a closed loop in a projection onto a plane. Apart from the so-called unknot, an unknotted circle, there is one knot with three, one with four (see figure \ref{fig:3-4knots}), two knots with five crossings, three knots with six and so on. This number increases, however, exponentially and there are, e.g., already more than one million distinct knots with more than 16 crossings \cite{Hoste}. It is therefore not surprising that there is still no algorithm which is able to distinguish between all knots. As knots are only mathematically defined in closed loops, the termini of open chains are typically connected in a prescribed way before knot detection takes place \cite{Reidemeister}.

In the 1960s interest in knots among natural scientists was revived by the Frisch-Wasserman-Delbrück conjecture \cite{Frisch} \& \cite{Wasserman}. This conjecture essentially states that all polymers (just like macroscopic strings) will eventually become knotted if they are just long enough. This was proved in the case of self-avoiding walks on the lattice by Sumners and Whittington \cite{Sumners}. The
Figure 1. From left to right: Unknot, Trefoil (3₁) and Figure-Eight-Knot (4₁). The index was introduced by Alexander and Biggs to distinguish between knots with the same crossing number.

The theoretical work of the 1960s eventually led to the discovery and creation of knots in DNA [10–15], proteins [16–24] and polymers [25; 26], and a multitude of simulation work e.g. [27–45] to better understand their properties. Intriguingly, two of the basic model classes have already been addressed in the first two simulations, respectively simple random walks and self-avoiding walks in 1974 and 1975 [27; 28].

Simple random walks (also known as ideal chains), either on the lattice or in the continuum, are the simplest model of a polymer as there are no interactions at all between monomers. In this case, although the short distance behavior may depend on details such as the lattice, the large distance behavior converges to Brownian motion, and all such models belong to the same universality class.

Self-avoiding walks are a more realistic model of polymers which incorporate the excluded volume interaction. On the lattice they are defined as the subset of random walks that are strictly self-avoiding, i.e., no two monomers can occupy the same lattice site. It is widely believed that dilute solutions of polymers in a good solvent, self-avoiding walks on a lattice, and a wide variety of related models on the lattice and in the continuum with sufficiently strong excluded volume interaction, are all in the same universality class.

One key observable which characterises the behavior of a polymer model is the mean-square end-to-end distance, and the dependence of this observable on the number of monomers, \( N \), is given by

\[
\langle R_e^2 \rangle = DN^{2\nu},
\]

where \( D \) is a model- and lattice-dependent constant, and \( \nu \) is a universal critical exponent which is identical for all models in the same universality class. For simple random walks, \( \nu = 1/2 \), as expected for Brownian motion, while for three-dimensional self-avoiding walks \( \nu = 0.587597(7) \) [46].

Random walks [27] knot readily as it is easy to create loops and knots on a very local scale. Typically, six to seven segments suffice for a simple trefoil [35]. This behavior changes drastically if repulsive excluded volume interactions are considered [28], which model polymers in good solvent conditions. Local entanglements disappear and the probability of observing knots becomes almost zero for chains of comparable size. Even though these knots are localized as well [37; 39], they are typically larger than knots in random walks. The transition from highly knotted ideal chains to almost unknotted self-avoiding polymers was first investigated in 1991 by Koniaris and Muthukumar [30; 47] who determined knotting probabilities as a function of chain thickness.

However, isolated polymers are not the only system of interest, and in particular polymer melts and semi-dilute polymer solutions are of great theoretical, experimental, and industrial interest. Polymer melts consist of a dense system of self-avoiding polymer fragments that nonetheless behave like simple random walks at large length scales (i.e. \( \nu = 1/2 \), even
though corrections to scaling exist even for large chains [48]. Similarly, the blob model of semi-dilute polymers suggests that they behave like self-avoiding walks within blobs, but the blobs themselves for a particular chain diffuse in accordance with Brownian motion. The interplay between these two length scales determines the overall exponent $\nu$ in this case.

One model which performs such an interpolation between self-avoiding walks at short lengths, and simple random walks at greater lengths, is that of finite memory walks, where excluded volume interactions still occur, but only between monomers separated within a fixed cut-off distance $r$ along the chain.

These walks have been considered on various lattices, and have been useful in proving upper bounds on the connective constant [49–51]. This is because self-avoiding walks are a strict subset of finite memory walks for any cut-off $r$, and the number of finite memory walks can be exactly calculated for small values of $r$. More recently, the case with $r = 2$ on the lattice, so-called non-backtracking random walks, have been proved to converge to Brownian motion [52].

It is perfectly natural to extend this idea to polymer models with more complicated excluded volume interactions, either on- or off-lattice. In this work we consider an off-lattice variant of finite memory walks, and investigate the effect of the internal length scale $r$ on the knotting behavior of the polymer.

2. Model and Algorithms

2.1. A continuum finite-memory walk

We investigate a continuous variant of a finite-memory walk [49–51]. Adjacent beads along the chain are connected with fixed bonds of length $1\sigma$. Excluded volume interactions are defined via a repulsive Weeks-Chandler-Anderson (WCA) potential:

$$ U_{WCA}(d) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{d} \right)^{12} - \left( \frac{\sigma}{d} \right)^{6} + \frac{1}{4} \right], & \text{if } d < d_{\text{min}} = 2^{1/6}\sigma \\ 0, & \text{else} \end{cases} $$

Excluded volume interactions are only considered between beads of a distance along the chain of up to $r$ bonds. $r = 0$ refers to a random walk with no excluded volume interactions, and in our case $r = 1$ also corresponds to the pure random walk because the bond length is fixed. For $r = 2$ next-nearest neighbors interact, and for a polymer with $N$ monomers $r = N - 1$ corresponds to a fully self-avoiding polymer.

For $r = 3$, three interactions need to be accounted for in the determination of energy change $\Delta E$ in the Metropolis criterion.
2.2. Implementation of the pivot algorithm

Configurations are sampled with the fastest known method for polymers in a good solvent, a Markov chain Monte Carlo approach called the pivot algorithm \[53\] \[54\]. As computer time is dominated by the determination of knot type we use the standard implementation of the pivot algorithm \[54\] rather than exploiting recent implementations which are asymptotically faster \[46\] \[55\] \[56\]. Typically, a pivot center is chosen randomly and one arm of the chain rotated around the center by an arbitrary angle. For a fully self-avoiding polymer, all interactions between monomers of the rotated arm with the other arm need to be accounted for in the Metropolis criterion. Interactions between beads belonging to the same arm do not change and need not be considered. Likewise, for random walks \((r = 0, 1)\) all moves are accepted automatically as there is no interaction energy and thus no change in energy. For next-nearest neighbor interactions \((r = 2)\), we only determine the change in energy between the bead succeeding the pivot center on the rotated arm with the bead preceding the pivot center. For arbitrary \(r\), we determine interactions of the first \(r\) beads with their interaction partners on the other arm including the pivot center (for \(r = 3\), see figure 2).

2.3. Knot detection

In this manuscript, we apply a variant of the Alexander polynomial \[57\], as detailed in reference \[5\], which allows us to distinguish (though not unambiguously) between simple knots. As knots are only mathematically well-defined in closed curves \[5\] \[6\], the ends of linear chains need to be connected in a well-defined manner first, before the knot type is determined. In this work, we apply a closure in which two lines emerge from the termini along the respective connection lines from the center of mass of the chain to the termini \[19\]. Then, the two lines are connected far away from the chain. Even though knots can in principle be created by the specific closure, knotting probabilities vary only little when different closures are applied \[5\] \[39\]. The size of the knot is determined by deleting monomers first from one side until the Alexander polynomial changes, which fixes one of the ends of the knotted subchain as the last monomer before the change occurred. Monomers are then successively deleted from the remaining end of the subchain until the Alexander polynomial changes again. The number of monomers in the knotted subchain provide a measure of the extent of the knot.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Mean square end-to-end distance \(\langle R^2 \rangle\) as a function of chain length for random walk \((r = 0)\), finite-memory walk \((r = 5, r = 30)\) and self-avoiding polymer.}
\end{figure}
3. Results

3.1. Scaling

First, we would like to verify that our finite-memory walks indeed scale like random walks in the limit of long chains. From fitting the data in figure 3 we obtain scaling exponents of $\nu = 0.50$ for $r = 5$ and $\nu = 0.51$ for $r = 30$. Interestingly, our results for rather modest chain sizes are already compatible with the critical exponents for random walks ($\nu = 0.50$) and can clearly be distinguished from the Flory exponent for self-avoiding polymers ($\nu = 0.587597(7)$). (For our rather modest chain sizes we have obtained $\nu \approx 0.59$.) Nevertheless, the mean square end-to-end distance of the finite memory walk is still significantly larger than the corresponding value of a random walk and resembles the result obtained for our fully self-avoiding polymer, which leads to an increase in the non-universal amplitude in the scaling law of equation 1.

3.2. Knot probability

As shown in figure 3, the probability of observing a knot quickly decreases to almost half the value observed for a random walk ($r = 0, 1$) when a few neighboring excluded volume interactions are considered. However, the knotting probability only decreases gradually afterwards and it takes $r = 30$ to decrease the probability to about 13%. Likewise, full excluded volume interactions are required to obtain the knotting behavior of a self-avoiding polymer, which is almost always unknotted ($P(\text{knot}) = 0.0014$). For comparison we have also plotted the probability for observing a trefoil knot ($3_1$). While for the random walk the knots predominantly have larger crossing numbers, we observe that the complexity of knots decreases with $r$, until for $r = 30$ almost all knots are simple trefoil knots.

3.3. Distribution of knot sizes

Figure 5 shows the distribution of knot sizes for configurations, which contain a simple trefoil knot. As indicated in the introduction the most likely size of a trefoil knot in a random walk is only around six or seven segments as it is very easy to create loops on a local scale if

![Figure 4](image-url)  
**Figure 4.** Probability of observing any knot for a finite-memory walk of size 500 and a trefoil knot as a function of interaction range $r$. $r = 0$ or 1 corresponds to a random walk. The probability $P$ of observing a knot in a self-avoiding polymer is almost zero ($P(\text{knot}) = 0.0014$). The lines are guides to the eye. Errors are smaller than symbol sizes.
Figure 5. a) Size distributions of trefoil knots for a random walk \((r = 0)\), finite memory walks \((r = 10\) and \(r = 30)\) and a fully self-avoiding polymer \((r = 499)\). In all cases, the chain consists of 500 monomers. All curves are normalized to one. b) Same as above but with a semi-logarithmic scale. In addition, all histogram entries have been divided by the total number of walks instead of the total number of trefoil \((3_1)\) knots.

beads do not repel each other. For a fully self-avoiding polymer, the local stiffness emerging from the excluded volume interactions shifts the most likely size of a trefoil knot to larger values. Finite memory walks on the other hand exhibit a rather unexpected and peculiar behavior. In figure 5b, there are almost no knots of size up to \(r\), while for larger knot sizes the behavior resembles that of a random walk. This feature becomes even more pronounced when we divide our histogram by the total number of walks (with fixed \(r\)) (figure 5b). Then the probability on the ordinate corresponds to the probability of observing a knot of a particular size. In this representation the knotting probability for \(r = 30\) follows closely that of a self-avoiding walk up to sizes of 30 and then quickly emulates the knotting behavior of random walks for larger sizes.
4. Discussion and conclusions
In this work we study the influence of local excluded volume interactions on knottedness in polymer chains by investigating the occurrence and size of knots in continuous finite memory walks. This allows us to study the transition from highly knotted random walks to almost unknotted self-avoiding walks as a function of the extent of local interactions. Local excluded volume interactions stiffen the chain and reduce knotting substantially even though the chain still behaves like an ideal chain from the point of view of scaling. However, after the strong initial decay in the probability of finding knots as a function of the extent of local interactions, the decay flattens and it takes self-avoidance in the whole chain to obtain the knotting probability of the fully self-avoiding polymer. The strong localization of entanglements and knots observed for random walks is softened and shifted to larger lengths. We find evidence that for length scales up to interaction range $r$ the finite memory walk behaves like a self-avoiding walk (prohibiting knots of sizes smaller than $r$), while for larger length scales the knotting behavior resembles that of a random walk. Finite-memory walks offer the possibility of tuning knotting properties of polymer chains while retaining the scaling properties of random walks (in contrast to self-avoiding walks with reduced excluded volume throughout the chain). They are thus interesting candidates for the structural description of single chains in a polymer melt or a semi-dilute polymer solution, which will be investigated in future work.

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