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Knots in polymers

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Abstract. Knots and topological entanglements play an important role in the statistical mechanics of polymers. While topological entanglement is a global property, it is possible to study the size of a knotted region both numerically and analytically. It can be shown that long-range repulsive interactions, as well as entropy favor small knots in dilute systems. However, in dense systems and at the Θ-point in two dimensions the uncontracted knot configuration is the most likely.

Keywords. Polymer loops; self-avoiding walks; topology; knots.

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1. Introduction

Knots and links naturally appear in long polymers [1] and play an important role in biological processes [2]. The simplest statistical–mechanical model of a polymer is a self-avoiding walk either on a lattice or in continuous space. It faithfully represents the properties of dilute solutions of long polymers in good solvents. Thus, the numerical study of knots is frequently reduced to the study of self-avoiding loops (SALs). It can be shown [2,3] that the probability of finding a knot in a SAL approaches 1 as the number of monomers N in the loop increases. Nevertheless, the knots are rare in polymers of moderate size. Figure 1 (from ref. [4]) depicts a trefoil knot that has been found by examining randomly generated 64-step SALs on a cubic lattice. Probability of finding a knot in such a short SAL is 0.00002. Only for the number of monomers N of order 10^5 the majority of closed loops are knotted [4,5]. Since most numerical studies are performed with N of a few thousands, they are in fact performed in the range where knotted configurations are an exception rather than the rule among SALs with unrestricted topologies.

Since knots and other topological entanglements may present an obstacle to biological processes (see, e.g., ref. [6]), in many cases it would be advantageous if there existed a possibility to recognize a knot locally, i.e. without examining the entire closed loop. This is possible if the knotted region is localized rather than spread out over the entire chain. If a method can be found to identify the number of monomers N_k forming the 'knotted part' of the N-monomer loop, then we may

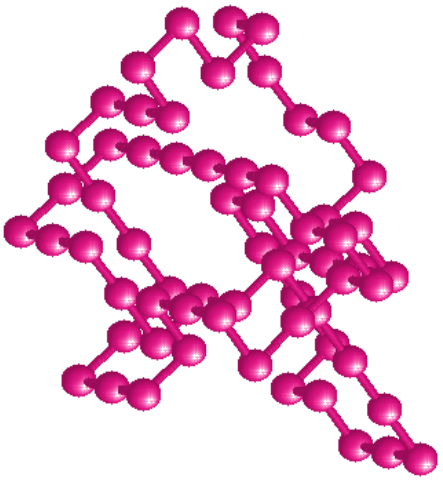

Figure 1. A trefoil knot in a 64-step self-avoiding loop on a cubic lattice.

inquire as to the N-dependence of N_k. We will say that the knot is delocalized if $N_k \sim N$. If N_k is independent of N, we will call it a strongly localized knot, while in the case of $N_k \sim N^t$ with $0 < t < 1$, we will denote it as weakly localized.

Position and size of tight knots, such as a simple knot on a rope, are easily recognized visually both in theoretical constructions [7], and in actual experiments with knots on DNA [8]. However, in general situations we need mathematical tools to identify the presence of a knot. The mathematical knot theory provides a large number of invariants for classification of the knots [9]. Unfortunately, they are not 'absolute': Every invariant eventually fails to distinguish between some of the (complicated) different topologies. However, in practical calculations they are more than sufficient to correctly identify simple knots. In fact the oldest (and simplest) invariant, Alexander polynomial [10], provided the first quantitative insight into the frequency of appearance of knots in random loops [11]. By their very nature, these mathematical methods use the entire closed loop to determine the presence of a knot, and provide no indication regarding the position or the size of the 'knotted region'. The lack of ability to rigorously define N_k led the entire research of knot sizes to use very indirect methods.

2. Knot size detection – methods and results

Delocalized knots may be expected to influence the radius of gyration R_g of a loop. Indeed an early study of R_g revealed that for fixed N, R_g decreases with increasing complexity of the knot [12]. However, later studies [13] demonstrated that the ratios of R_g of loops with different (fixed) topologies approach 1 as N increases. This is a strong indicator that the knots are localized, since in such a case there is no difference between loops with various topologies for sufficiently large N. Grosberg *et al* [14] estimated the free energy of a knotted polymer under an assumption that

the knot is either spread out over the entire polymer or is concentrated in a small area, and concluded that for each knot type for sufficiently large N the knotted region becomes localized.

The most direct method of estimating N_k was devised by Katrich *et al* [15]: They determined whether a particular part of a loop is knotted by removing finite segments of a loop, attaching them to semi-infinite straight lines and checking (by standard knot recognition techniques) whether the new closed (via infinity) loop contains a knot. By selecting segments of different lengths from different parts of the loop, they established the size of the smallest segment that is still knotted. Unfortunately, this method sometimes produces false identifications – sometimes a segment of an unknotted loop forms a knot when it is connected to semi-infinite straight lines. This introduces a degree of uncertainty into the recognition process, which must be tolerated if the method is to be used. It is impossible to perform an 'objective' check of the accuracy of the method since there is no other method to compare it with. One may imagine that the error rate is larger when the knots are less tight and include larger number N_k of monomers. This effect may distort the distribution of the sizes of the knotted region. Katrich *et al* investigated loops formed by random walks (without self-avoidance) and concluded that $N_k \ll N$, although it was difficult to establish how strongly the knots are localized.

If knots are localized they can be viewed as finite size corrections. In the absence of knots of finite size corrections in SALs usually have a very small amplitude, and the power-law relation $R_g = aN^\nu$ holds true even for moderate Ns. However, in the presence of a knot the corrections become significant. We may attempt to correct that relation by replacing N by $N - N_k$. Thus by measuring R_g as a function of N we may extract the values of N_k for various values of N. Such data can be extracted, e.g., from the results of ref. [13]. We used such an approach in a slightly different numerical study [16]: We considered a polymer attached to two walls by its ends. The stretching force f exerted on the polymer by the walls was measured as a function of the separation R between the walls. Figure 2 depicts two examples of a stretched polymer with trefoil knot tied on it (from ref. [16]). When a polymer is strongly stretched it forms a linear sequence of 'blobs' [17], and the number of monomers N_b in each blob depends on f. On length-scales smaller than the size of a blob, the polymer behaves as if there is no external force. We note that in the presence of a knot the knotted region must be restricted to a single blob. Thus by increasing f we effectively consider systems with decreasing values of N [18], and we may assume that $N_k \sim N_b^t$. By considering finite size effects in force-separation curves we were able to show [16] that the knots are weakly localized, i.e. in SALs $N_k \sim N^t$ with $t = 0.4 \pm 0.1$.

3. Simplified cases

Since we encounter such difficulties in identifying knotted regions, it may be useful to consider few cases for which clear answers can be provided. For instance, in a charged polymer loop the interplay between Coulomb interactions and irreducible topological constraints leads to strongly localized (tight) knots, while the composite knots are factored and separated as depicted in figure 3 (from ref. [19]). This can

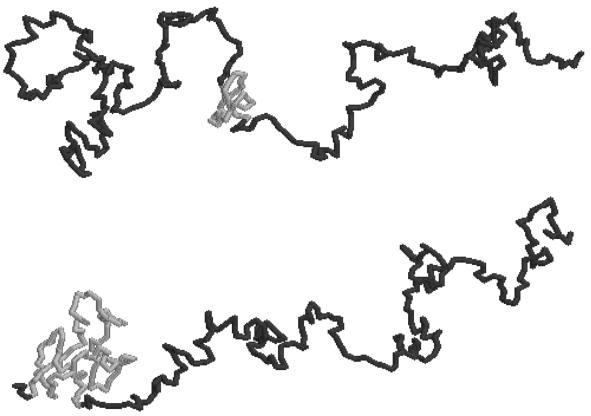

Figure 2. Two examples of a stretched polymer with $N = 334$ with trefoil knot on it. Grey segments indicate the knotted region.

be demonstrated both by semi-quantitative arguments and by numerical simulations [19]. It can also be shown, that such behavior survives even for screened Coulomb interaction, until the screening length λ becomes shorter than a critical value λ_c (which is proportional to $\sqrt{N}$). For $\lambda < \lambda_c$ the polymer is dominated by the bending rigidity (which was generated on the short-length scales by the Coulomb interactions) and the knot becomes delocalized.

Another simple approach to topological entanglements is to replace the real entanglement by a ring sliding on a polymer and enforcing a contact between one pair of monomers [20]. The ring can slide from one pair to another. Such a ring, called slip-link, forces a polymer loop to behave as figure-8. Several slip-links may create complex figures. Although this is not a real topological entanglement, it provides us with an indication as to what entanglements may do. For instance we find that a single slip-link on a SAL, forces figure-8 geometry (in two- and three-space dimensions) to look like a very large loop to which a very small and tight loop has been attached. This is analogous to the strongly localized case of a knot. (Our theoretical predictions in two dimensions (2D) have been confirmed both by numerical simulation [20] and by an interesting experiment of figure-8 chain placed on a vibrating surface [21].) In dense or Θ-point solution figure-8 becomes weakly localized [22].

In two dimensions we can make an additional step towards understanding the entanglements [20,22]: Imagine a knotted polymer loop pressed by a strong potential to a two-dimensional plane. The loop will attempt to eliminate all possible accidental intersections of lines except for the bare minimum of intersections that remain because of the presence of the knot. The two-dimensional picture will look like a projection of a knot into 2D with a minimal number of intersections. It can also be viewed as a two-dimensional network. The scaling behavior of 2D networks has been studied in great detail by Duplantier and his co-workers [23]. Their results can be applied to the case of 2D knots, with modifications resulting from the fact that a number of monomers can redistribute between the segments of the network. (One also needs to treat separately the cases when one or more segments

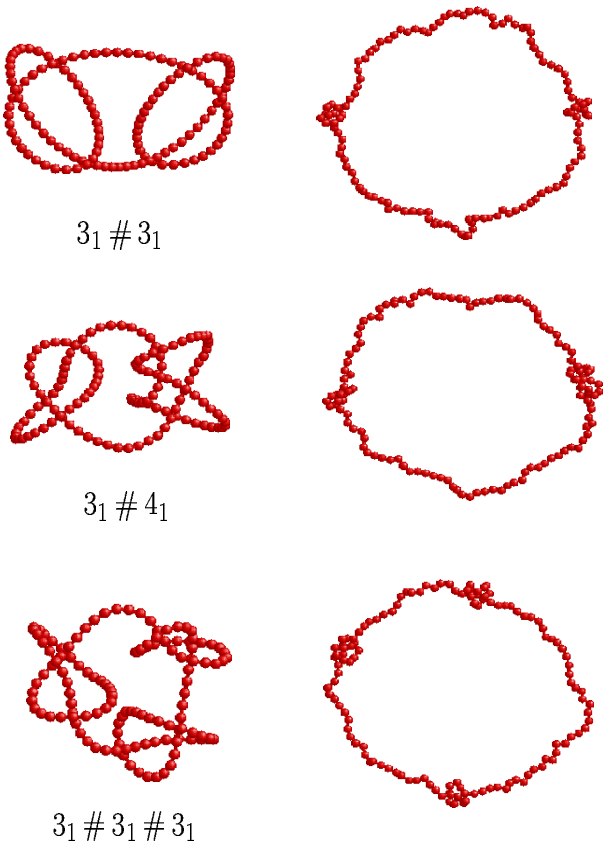

Figure 3. Polymer loops with composite knots (knot type [9,10] is indicated near each picture). Left column depicts clearly the type of the knot. Right column depicts low-temperature configurations of the system with monomers repelling each other via Coulomb potential. (The figures in the right column have been scaled down.)

become very short and we effectively have a network of different topology and different number of bonds and vertices.) By analysing such 2D networks we arrived at a conclusion that 2D knot is strongly localized in dilute good solvent regime [20] and becomes delocalized in dense and Θ-point conditions [22]. The prediction regarding the dense phase is consistent with the numerical results of ref. [24]. However, our prediction regarding the behavior at the Θ-point is at variance with [24].

4. Discussion

Statistical mechanics of knotted polymers presents a fascinating challenge of local detection of the knotted region. Both indirect measurements of the size of the

knotted region and investigations of simplified systems indicate, that at least in dilute systems the knot is localized. One can therefore view a composite knot as a collection of interacting localized objects. If the knots are weakly localized, the components of a composite knot may have long range interactions. If a convenient method for detecting position of the knotted region can be found, one may attempt to investigate such a 'gas' of components. Unfortunately, the simplified objects presented in the previous section (figure-8, 2D knots) will not be of much use for this purpose, and we will probably need to work with true three-dimensional knots. The method of Katrich *et al* [15] was originally employed to study knots in random walk loops. It seems as a good candidate method for the study of the size and position of knotted regions in simple and complex knots, provided the error rate of the method can be controlled. Marcone *et al* [25] have recently attempted to use such a method to study polymer loops in both dilute good solvent regime, and in collapsed regime with some surprising results: In the good solvent regime their exponent t is almost two times larger than the one obtained in ref. [16]. Clearly more detailed studies are needed to resolve such contradictions.

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