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# The entropic cost to tie a knot

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**Abstract.** We estimate by Monte Carlo simulations the configurational entropy of $N$-step polygons in the cubic lattice with fixed knot type. By collecting rich statistics of configurations with very large values of $N$ we are able to analyse the asymptotic behaviour of the partition function of the problem for different knot types. Our results confirm that, in the large $N$ limit, each prime knot is localized in a small region of the polygon, regardless of the possible presence of other knots. Each prime knot component may slide along the unknotted region contributing to the overall configurational entropy with a term proportional to $\ln N$. Furthermore, we discover that the mere existence of a knot requires a well defined entropic cost that scales exponentially with its minimal length. In the case of polygons with composite knots it turns out that the partition function can be simply factorized in terms that depend only on prime components, with an additional combinatorial factor that takes into account the statistical property that by interchanging two identical prime knot components in the polygon the corresponding set of overall configurations remains unaltered. Finally, the above results allow one to conjecture a sequence of inequalities for the connective constants of polygons whose topology varies within a given family of composite knot types.

**Keywords:** loop models and polymers, mechanical properties (DNA, RNA, membranes, bio-polymers) (theory), polymers, copolymers, polyelectrolytes and biomolecular solutions

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**Contents**





## 1. Introduction

A long, flexible polymer chain in good solvent can be highly self-entangled [1, 2] and if a ring closure reaction occurs, or if its extremities are held tied by some device, the entanglement can be trapped as a knot [3, 4]. Moreover, because of the excluded volume interaction, a knotted molecule cannot change its topological status without breaking and reconnecting chemical bonds. This, for example, is the situation one encounters in biological systems, where special enzymes, called topoisomerases, can pass one strand of the double stranded circular DNA through another, and knot or unknot the molecule to facilitate elementary cellular processes [5, 6]. In general, however, there is no spontaneous transition between different knot types, and in the most common experimental situations the topology of the ring does not change in time. Clearly, the presence of topological constraints limits the configurational space available to the ring, with a consequent reduction of the entropy of the system compared to the topologically unconstrained case [7]. It is then interesting to precisely quantify this entropy loss and to determine how it depends on the particular topology (i.e. knot type) considered.

Unfortunately, most of the theoretical studies performed so far refer to the ensemble in which the rings may assume all the topologies. The reason is that polymer rings in good solvent can be modelled as self-avoiding polygons (SAPs or simply polygons), which are in turn mapped to a magnetic system at its critical point and studied by renormalization group techniques [1, 8, 9]. This approach has led to the well established result that the number $Z(N)$ of $N$-steps SAPs grows for large $N$ as

$$Z(N) \simeq A\mu^N N^{\alpha-2} \tag{1}$$

where the amplitude $A$ and the connective constant $\mu$ are non-universal quantities that depend on the microscopic features of the chain, while $\alpha$ is a universal exponent given by $\alpha = 2 - d\nu$, where $d$ is the dimensionality of the space and $\nu$ the metric exponent [9]. In $d = 3$ dimensions, numerical simulations [10] give for self-avoiding loops the estimate $\nu \simeq 0.587\,597(7)$, and consequently $\alpha \simeq 0.237\,209(21)$, in agreement with field theoretical results [8]. Since for the subset of SAPs with a given knot type $k$ the above mentioned mapping is no longer valid, there is no field theory argument to establish a scaling similar to (1) for $Z_k(N)$. However, it is reasonable to expect [11, 12, 4] that

$$Z_k(N) \simeq A_k \mu_k^N N^{\alpha_k - 2} \tag{2}$$

where $\mu_k$ and $\alpha_k$ are, respectively, the connective constant and the entropic exponent of the subset of SAPs with fixed knot type $k$. For a generic knot type $k$ there is no rigorous relation between $\mu_k$ and $\mu$, but in the case of *unknotted polygons* (i.e. SAPs with trivial topology, $k = \emptyset$) it is possible to prove rigorously that $\mu_\emptyset < \mu$ [7], whereas numerical estimates of $\alpha_\emptyset$ suggest the intriguing identity $\alpha = \alpha_\emptyset$ [12, 13], although results presented so far are not sharp enough to rule out completely a possible, although small, discrepancy between the two entropic exponents, i.e. $\alpha_\emptyset \simeq \alpha$. One among the results presented here concerns the improvement of the estimate $\alpha - \alpha_\emptyset$ and of the ratio $A_\emptyset/A$ (see section 2), this one performed, to our knowledge, for the first time.

Note that equations (1) and (2) with $k = \emptyset$ have interesting implications for the probability of realizing an unknot in the ensemble with unrestricted topology, $P_\emptyset(N) \equiv Z_\emptyset(N)/Z(N)$. Indeed, from (1) and (2) with $k = \emptyset$ one gets

$$P_\emptyset \simeq \frac{A_\emptyset}{A}\left(\frac{\mu_\emptyset}{\mu}\right)^N N^{\alpha_\emptyset - \alpha} = \frac{A_\emptyset}{A} \mathrm{e}^{-N/N_0} N^{\alpha_\emptyset - \alpha} \tag{3}$$

and since $\mu_\emptyset < \mu$ we get the well known result that the unknotting probability goes to zero exponentially fast with $N$ [7]. The parameter $N_0 = 1/\ln(\mu/\mu_\emptyset)$ gives a typical number of steps above which the unknot probability is reasonably low or, in other words, the occurrence of knots is no longer negligible. Previous numerical estimates for polygons on the cubic lattice gave $N_0 \approx 2 \times 10^5$ [14]–[16].

Since for polymer rings with a generic fixed knot type $k$ neither analytical tools nor rigorous arguments are available, one has to rely entirely on numerical approaches and scaling arguments in the analysis of the above issues. By using the BFACF algorithm [17, 18] (the acronym comes from the initials of the authors) coupled to a multiple Markov chain sampling technique, and assuming for SAPs with fixed knot type $k$ the scaling (2), evidence is found [11] that

$$\mu_k = \mu_\emptyset, \qquad \alpha_k = \alpha_\emptyset + \pi_k, \tag{4}$$

where $\pi_k$ is the number of prime components in the knot decomposition of $k$ (see also [13]). It is interesting to notice that results similar to (4) have been obtained also for off-lattice models of rings such as the bead–rod models [19], suggesting that the scaling behaviour (2) with (4) is a universal property of loops in free space with a given knot type $k$. Relations in (4) are consistent with recent findings showing that prime knots in swollen rings are weakly localized, i.e. have an average 'length' $\langle l \rangle \sim N^t$ with an exponent $0 < t < 1$, which has been estimated in [20]–[22] as $t \simeq 0.7$. Indeed weak localization of prime knots implies that, in the limit $N \to \infty$, each prime component behaves essentially as a decorating vertex fluctuating along an unknotted ring. This additional configurational degree of freedom brings a factor $N$ in front of $Z_\emptyset$ for each prime component and, in the general case of a knot $k$ made by $\pi_k$ prime components, one may guess:

$$Z_k(N) \simeq N^{\pi_k} Z_\emptyset(N). \tag{5}$$

Although the above simple argument furnishes a plausible explanation of relations (4), it is too crude to fully characterize the entropy of a knotted ring in the large $N$ limit.



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For example, the amplitude $A_k$ is still undetermined and there is no trace of the type of prime knots that contribute to $Z_k(N)$. In fact, by regarding prime knots as point-like objects, we are neglecting the effective entropic cost that the system has to pay in order to tie them into unknotted loops. This entropic cost would decrease the $Z_k(N)$ in (5) by a factor, say $C_k$, giving the more precise expression

$$Z_k(N) \simeq \frac{A_\emptyset}{C_k} \mu_\emptyset^N N^{\alpha_\emptyset - 2 + \pi_k}. \tag{6}$$

It is interesting to notice that, if $C_k$ is related to an entropic cost to tie a given knot, its value should depend on the knot type $k$ and not only on the number of its prime components. If this is the case, equation (6) would furnish a more fundamental description of the large $N$ behaviour of the entropy of a knot since it would distinguish the type of knot of the polygon. This description should depend also on topological invariants of $k$ other than $\pi_k$.

It is important to stress that a numerical check of the validity of (6) and, in particular, a numerical estimate of $C_k$ as a function of $k$, is a quite hard task to perform because it requires good statistics of polygon configurations with very large values of $N$. This is particularly crucial for SAPs on discrete lattices, for which a reasonable amount of knotted configurations can be sampled only for $N \geq N_0 \sim 10^5$. This is probably the reason why no attempts have been made so far to look in more detail at the asymptotic form (6). In this paper we explore this issue by sampling polygons on the cubic lattice with $N$ up to 200 000. Unlike previous Monte Carlo simulations, where the sampling was performed in the fixed knot ensemble using the BFACF [17, 18] algorithm, we decided to sample in the free topology ensemble by using the very efficient two-point pivot algorithm [23] and subsequently to partition the sampled configurations according to their topology.

In section 2 we describe the algorithm that we use to sample knotted SAPs and the procedure designed to detect knots out of configurations that, for large values of $N$, turn out to be highly intricate. As a first outcome of this investigation we will give a sharper estimate both of the difference $\alpha - \alpha_\emptyset$ and of the ratio $A_\emptyset / A$. This will establish a more detailed relation between the subclass of unknotted rings and the full class of rings with unrestricted topology. In section 3 we test the validity of (6) and estimate $C_k$ as a function of $k$. This is the main result of the paper: it will be first established for the simplest case of prime knots and later generalized to composite knots. Section 3.3 also includes further conjectures on the connective constants of SAP ensembles with restricted topology. Section 4 is devoted to a discussion and conclusions.

## 2. Model, Monte Carlo method and knot detection procedure

To model polymer rings with excluded volume interaction we consider $N$-step SAPs on the cubic lattice, i.e. self-avoiding walks with the two extremities separated by one lattice unit. These polygons are sampled in free space by using the two-point pivot moves, a fixed-$N$ algorithm that has been proved to be ergodic in the class of all polygons and shown to be very efficient in sampling uncorrelated configurations [23]. With this procedure we generate configurations with $N$ up to 200 000. As an example, in figure 1 we plot a configuration with $N = 50\,000$, together with a closer view of part of it.

Since the pivot moves can change the knot type of polygons, the topology of each configuration must be detected by means of some topological invariant. This is indeed the

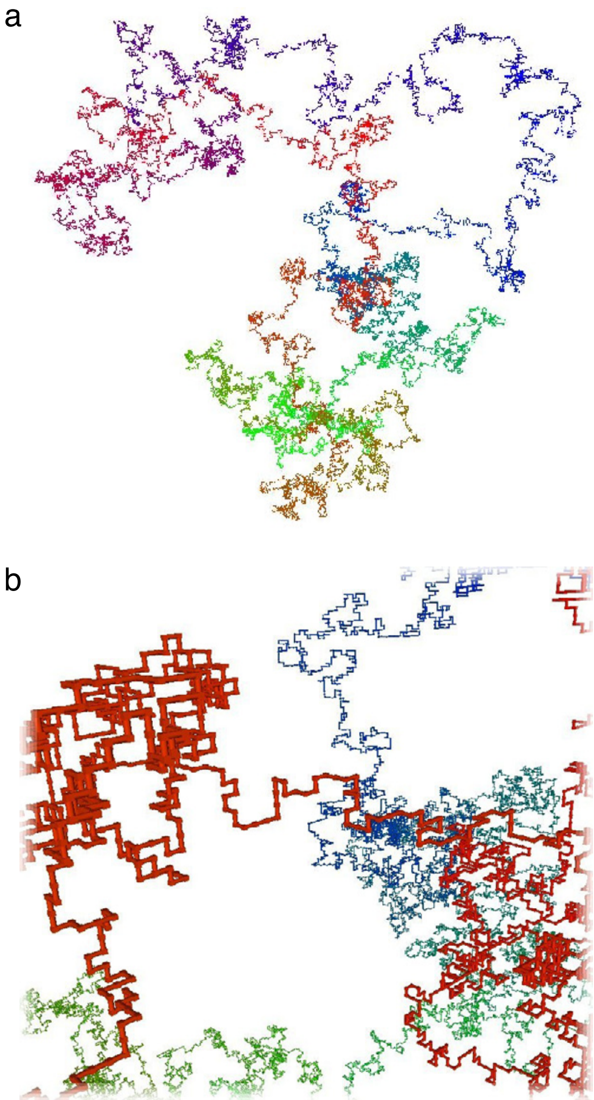


**Figure 1.** Equilibrium configuration of SAP on the cubic lattice with $N = 50\,000$ steps (above) and a detail of its central part (below).

most problematic part of the whole investigation since, even in good solvent conditions, very long polygons may assume an intricate spatial arrangement. This 'geometrical' entanglement gives rise, in general, to knot projections with a very large number of unessential crossings (from the topological point of view) that severely hinder the knot detection algorithm based on the calculation of polynomial invariants [4].

To circumvent this difficulty, we simplify each sampled configuration before performing its planar projection. This is achieved by applying to the polygon a smoothing algorithm that progressively reduces the length of the chain while keeping its knot type unaltered (for a similar procedure, see [24]–[26]). This procedure is based on the $N$-varying BFACF algorithm [17, 18] and has the nice feature of being ergodic within each knot type. We set a sufficiently small step fugacity (i.e. the parameter conjugate to $N$), such that the algorithm induces a rapid reduction in the number of steps of the polygon.

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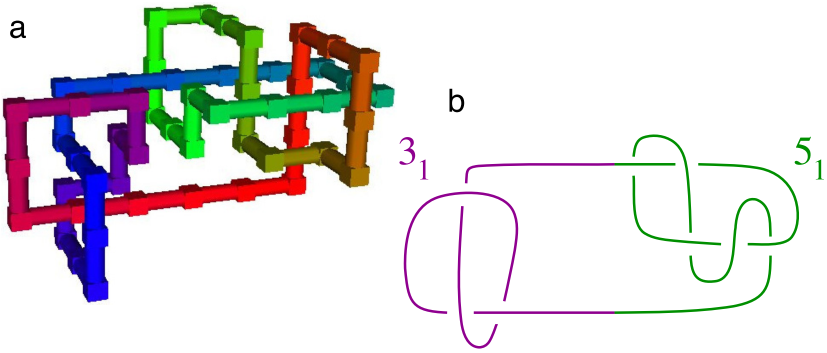


**Figure 2.** By applying the step-reduction algorithm that preserves the topology, the configuration of figure 1 is simplified to one with $N = 82$ steps (left). A further simplification of the Dowker code allows one to identify the knot as the composite $3_1\#5_1$ knot, whose minimal diagram representation is shown on the right.

This simplification technique can dramatically reduce the number of crossings encountered in an arbitrary projection. An example of how efficient this simplification procedure can be is shown in figure 1, where a configuration of initially $N = 50\,000$ steps is shrunk down to the $N = 82$ steps configuration of figure 2. A further reduction is achieved by performing 500 projections and choosing the projection with the minimal number of crossings. The resulting knot diagram is encoded in terms of the Dowker code [27]. A further simplification of the Dowker code based on Reidemeister-like moves is performed. Finally, a factorization of the Dowker code is attempted. This procedure, whenever successful, splits composite knots into their prime components. From each component of the original Dowker code we extract, by using KNOTFIND [28], the knot type of the original configuration (see figure 2 for the example given in figure 1). In this way we have been able to distinguish composite knots with up to 5 prime components, and with each component having crossing number up to 11 [25, 26]. The unbiased sampling with unconstrained topology allows us to estimate the probability $P_k \equiv Z_k/Z$ of occurrence of a given knot type $k$ and to estimate its configurational entropy with respect to unknotted polygons, i.e. the ratio $Z_k/Z_\emptyset$. Since the statistics of unknotted polygons will be used extensively as a reference, it is convenient to start by performing a good estimate of $Z_\emptyset(N)$. This can be achieved by looking at the scaling of the unknotting probability (3) as $N$ increases.

In figure 3 we plot $\ln P_\emptyset$ as a function of $N$. The two lines correspond to two different fits of the data. To estimate the difference $\alpha - \alpha_\emptyset$ we first perform a nonlinear fitting (dashed line) of the form $a - N/N_0 + b \ln N$. This yields $\alpha - \alpha_\emptyset = b = -3 \times 10^{-5} \approx 0$, supporting the conjecture $\alpha = \alpha_\emptyset$. If we now assume $\alpha_\emptyset = \alpha$ we can perform a linear fit (solid line) $a - N/N_0$. This gives $N_0 = 210\,400 \pm 1300$ and $a = 0.003(2)$. The estimate of $a$ strongly suggests that within error bars $A_\emptyset = A$. This last result is quite interesting since it strengthens the relation between the statistics of unknotted SAPs and the one of all SAPs, not only at the level of the entropic exponents, but also at the level of amplitudes. Clearly the main difference relies on the entropies per monomer $\mu$ and $\mu_\emptyset$. However, the difference $\mu - \mu_\emptyset \simeq \mu/N_0$ is very small: with the most recent and precise estimate



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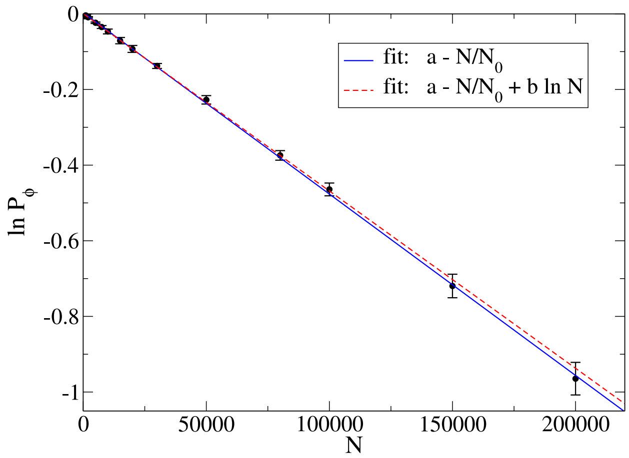


**Figure 3.** Decay of the probability of unknotted configurations (log scale) with the chain length. Fits are also shown.

$\mu = 4.684\,044 \pm 0.000\,011$ by Slade *et al* [29], we estimate $\mu - \mu_\emptyset = 0.000\,022(2)$ (that is twice the statistical error for $\mu$) and thus $\mu_\emptyset = 4.684\,022 \pm 0.000\,013$.

## 3. The entropic cost of a knot

### 3.1. Prime knots

To estimate the entropic cost $C_k$ for polygons with fixed knot type $k$, we compute the ratios $Z_k(N)/Z_\emptyset(N)$. Indeed, by assuming the scaling form (6) we expect $Z_k(N)/Z_\emptyset(N) \simeq N^{\pi_k}/C_k$. Let us consider first knotted SAPs where $k$ is a prime knot. Figure 4 shows the $N$-behaviour (in log–log scale) of the ratio $Z_k(N)/Z_\emptyset(N)$ for prime knots up to 6-crossings. As expected from (6), no exponential behaviour is observed and the scaling $\sim N/C_k$ is confirmed (note that $\pi_k = 1$ since we are considering prime knots), with a $C_k$ whose value increases as the knot complexity increases. The estimates of $\alpha_k - \alpha_\emptyset$, reported in table 1 in the second column, are all consistent with the relation $\alpha_k - \alpha_\emptyset = 1$. The estimates of $C_k$ are reported in the third column of table 1. The most striking feature to notice is the simple relation observed between the value of $C_k$ and the knot type $k$. Indeed, from column 4, it turns out that, to a good approximation, the entropy cost necessary to host a prime knot $k$ goes like

$$C_k \simeq \mu_\emptyset^{\ell_k/3} \tag{7}$$

where $\ell_k$ (see last column of table 1) is the minimal length required to tie a knot $k$ on the cubic lattice [30]. Thus, the entropic cost $C_k$ is intimately related to a 'microscopic' property of the knot $k$, that is, the length of its 'ideal' representation [31, 32] on the cubic lattice [30].

It is tempting to interpret $V_k = \ell_k/3$ as an equivalent number of monomers 'lost' by the polygon in order to form the knot. For example, the partition function of a trefoil, $Z_{3_1}$, would be described by the exponential factor $\mu_\emptyset^{N-V_{3_1}}$ with $V_{3_1} = 8$. In other words, a $N$-step polygon with a $3_1$ knot has the same configurational entropy (in the limit of large $N$) as an unknotted polygon with $N - 8$ steps endowed with a sliding decorating vertex

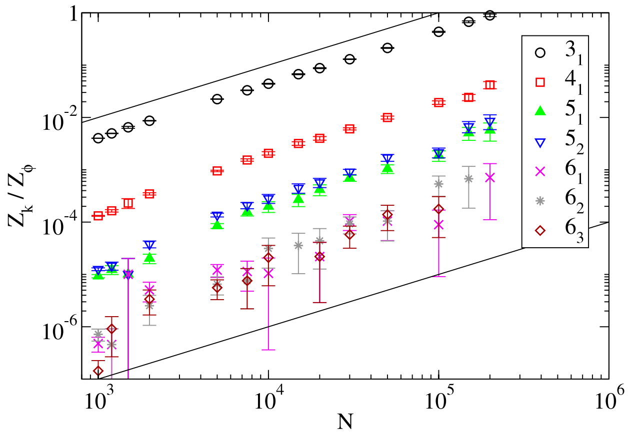


**Figure 4.** Partition function of the simplest prime knots divided by that of the unknot (log–log scale versus $N$). Straight lines are a guide to the eye, scaling $\sim N$.

**Table 1.** Estimates of the difference $\alpha_k - \alpha_\emptyset$ (second column) and of the entropic cost $C_k$ (third column) for the simplest prime knots. The last two columns suggest a linear relation between the logarithm of $C_k$ and the minimal length $\ell_k$ of a knot on the cubic lattice ($\ell_k$ taken from [30]).

| Knot | $\alpha_k - \alpha_\emptyset$ | $C_k$ | $V_k = \log_{\mu_\emptyset} C_k$ | $\ell_k$ |
|---|---|---|---|---|
| $3_1$ | 1.002(7) | $227\,800 \pm 1400$ | 7.989(4) | 24 |
| $4_1$ | 0.96(3) | $5.04(15) \times 10^6$ | 9.995(20) | 30 |
| $5_1$ | 1.13(6) | $4.48(35) \times 10^7$ | 11.41(5) | 34 |
| $5_2$ | 1.10(8) | $3.19(25) \times 10^7$ | 11.19(5) | 36 |
| $6_1$ | 1.23(25) | $60(24) \times 10^7$ | 13.1(2) | 40 |
| $6_2$ | 1.22(13) | $38(12) \times 10^7$ | 12.8(2) | 40 |
| $6_3$ | 1.08(22) | $61(19) \times 10^7$ | 13.1(2) | 40 |

(the knot). These findings suggest that it is sufficient to know the length $\ell_k$ of a given prime knot in its ideal lattice representation in order to make an accurate prediction of its frequency along a swollen ring.

The factor of 1/3 is quite intriguing and we have no explanation for that so far. Clearly it will be important to test further this value by looking at more complicated knots. This would require a much larger statistics and consequently much larger values of $N$. Another interesting issue would be to see if the relation is model dependent, for example by looking at polygons embedded on different lattices.

### 3.2. Composite knots

We now extend the analysis of $C_k$ to composite knots, namely knots made by connecting prime component knots (such as the $3_1\#5_1$ in figure 2). In the most general case we may assume $k$ to be composed by the prime knots $k_1, k_2, \ldots, k_m$, each appearing respectively $\pi_1$, $\pi_2$ and $\pi_m$ times. The number $\pi_i$ represents somehow the degree of degeneracy of the prime knot $k_i$ in the composite knot $k$. For the composite knot $k$ the entropic cost $C_k$



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could, in principle, depend on the set $\{k_i\}$ in a quite complicated way. However, if we still assume that each prime knot localizes along the chain in the large $N$ limit, regardless of the presence of other knot components, we can make the working hypothesis that the cost of a composite knot $k_1\#k_2$ factorizes as $C_{k_1\#k_2} = C_{k_1} \times C_{k_2}$ (for $k_1 \neq k_2$). This suggests the conjecture that, in the $N \to \infty$ limit,

$$Z_k(N) \simeq Z_\emptyset(N) \left[ \frac{1}{(\pi_1)!} \left( \frac{N}{C_{k_1}} \right)^{\pi_1} \cdots \frac{1}{(\pi_m)!} \left( \frac{N}{C_{k_m}} \right)^{\pi_m} \right]. \tag{8}$$

The presence of the factorial terms $1/(\pi_i)!$ can be explained as follows: first, if two knots $k_\mathrm{A}$ and $k_\mathrm{B}$ are different and 'positioned' respectively at $n_\mathrm{A} \in [1, \approx N]$ and $n_\mathrm{B} \in [1, \approx N]$, the counting of all pairs $(n_\mathrm{A}, n_\mathrm{B})$ yields $\approx N^2$ independent configurations. If instead $k_\mathrm{A} = k_\mathrm{B}$, a given configuration $(n_\mathrm{A}, n_\mathrm{B})$ is indistinguishable from $(n_\mathrm{B}, n_\mathrm{A})$, hence there is an overcounting, which can be easily removed, in this case by dividing the full counting $N^2$ by two. In general, within each group of $\pi_i$ identical knots, the overcounting is removed by dividing $N^{\pi_i}$ by the number of possible permutations of $\pi_i$ objects, i.e. $(\pi_i)!$.

With these notations, the full cost of a composite knot is then

$$C_k = \prod_i \pi_i!\, C_{k_i}^{\pi_i}. \tag{9}$$

Equations (8) and (9) suggests that, if we knew the entropic cost $C_{k_i}$ necessary to tie each prime component $k_i$, the number of configurations $Z_k(N)$ of the composite knot $k$ could be easily deduced, in the large $N$ limit, by looking at the partition function $Z_\emptyset(N)$ of unknotted polygons of the same length.

We first check equation (8) for composite knots including only copies of the trefoil knot, for which we have good statistics up to four prime components. From equation (8) we expect the following relation to hold:

$$\begin{aligned} &Z_{3_1}/Z_\emptyset \simeq N/C_{3_1} \\ &Z_{3_1\#3_1}/Z_\emptyset \times 2 \simeq (N/C_{3_1})^2 \\ &Z_{3_1\#3_1\#3_1}/Z_\emptyset \times 3! \simeq (N/C_{3_1})^3 \\ &Z_{3_1\#3_1\#3_1\#3_1}/Z_\emptyset \times 4! \simeq (N/C_{3_1})^4. \end{aligned} \tag{10}$$

In figure 5 we show these ratios times the suitable factorials, in log–log scale as a function of $N$. The four straight lines are power-law fits whose exponents agree within error bars with equations (10). Moreover, as expected, all fits cross each other at a single point $(C_{3_1}, 1)$ with abscissa $C_{3_1} \approx 227\,000$. Hence the starting assumption that the total entropic cost to tie a composite knot of $\pi_i$ prime knots simply factorizes (see equation (9)) is crisply verified, at least for trefoil knots. Note that, by extrapolating the data of figure 5 to larger values of $N$, for $N > C_{3_1}$ it is entropically more convenient to tie composite knots made by trefoils than forming unknotted polygons.

The statistics collected for multiple copies of the next simplest knots, like the $4_1$, is not sufficient to repeat the analysis of equation (10). We can however look at equation (8) in the case in which other prime knots are present, in addition to multiple $3_1$'s. In particular in figure 6 we plot $Z_{4_1}/Z_\emptyset$, $Z_{3_1\#4_1}/Z_{3_1}$, and $Z_{3_1\#3_1\#4_1}/Z_{3_1\#3_1}$. As expected, all ratios are consistent with the presence of the term $N/C_{4_1}$ in the scaling, with $C_{4_1} \simeq 5 \times 10^6$. This result extends to components of different knot type the hypothesis of entropic independence between prime components in the statistics of polygons with a composite knot type $k$.

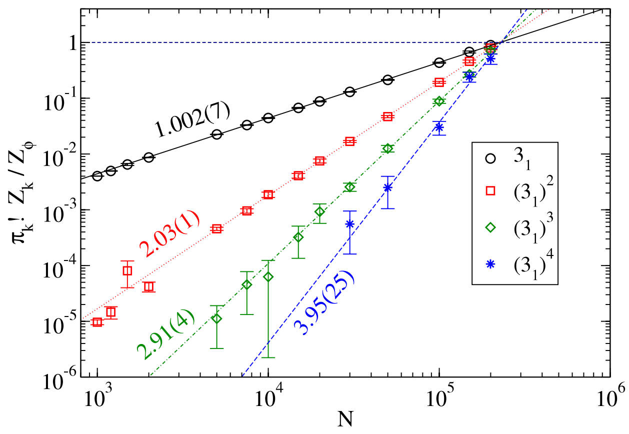


**Figure 5.** Partition function of knots involving copies of $3_1$ divided by that of the unknot and multiplied by the factorial of the number of $3_1$ components, in log–log scale as a function of the chain length. Oblique straight lines are power-law fits (exponents are shown close to them). The horizontal line crosses the other ones at $(C_{3_1}, 1)$.

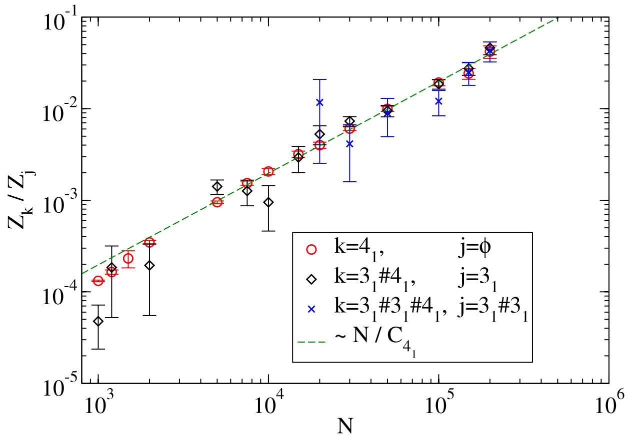


**Figure 6.** Partition function of knots including a prime component $4_1$ divided by that of the same knots without the $4_1$, in log–log scale versus $N$. The straight line is a guide to the eye, scaling $\sim N$.

### 3.3. On the connective constant of a class of composite knots

So far the only results available on the limiting entropy of knotted polygons are the rigorous inequality $\mu_\emptyset < \mu$ and the conjectured identity $\mu_\emptyset = \mu_k$, where $\mu_k$ refers to the connective constant of the subset of polygons having a given knot type $k$. The essential difference between $\mu$ and $\mu_\emptyset$ or $\mu_k$ is that in the first case the sum over all topologies is taken into account while for $\mu_\emptyset$ and $\mu_k$ the topology is kept fixed.

By exploiting equation (8) it is tempting to interpolate between the extreme cases $\mu$ and $\mu_k$ by looking at the statistics of particular subsets of polygons in which an infinite (although partial) sum over topologies is considered.

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Suppose for example we consider the set of all polygons that can have an arbitrary number of trefoil components tight in:

$$Z_{(3_1\#)^\infty}(N) = Z_{3_1}(N) + Z_{3_1\#3_1}(N) + Z_{3_1\#3_1\#3_1}(N) + \cdots. \tag{11}$$

In the limit of large $N$, using equation (8), we get

$$Z_{(3_1\#)^\infty}(N) \simeq \sum_{n=0}^{\infty} Z_\emptyset(N)\frac{1}{n_k!}\left(\frac{N}{C_{3_1}}\right)^n \simeq Z_\emptyset(N)\mathrm{e}^{N/C_{3_1}}.$$

By rewriting the exponential factor as $(\mu_\emptyset \mathrm{e}^{1/C_{3_1}})^N = (\mu \mathrm{e}^{-1/N_0+1/C_{3_1}})^N = (\mu_{(3_1\#)^\infty})^N$, since $C_{3_1} > N_0$, we get $\mu > \mu_{(3_1\#)^\infty} > \mu_\emptyset$. It is interesting to notice that, if we apply the same argument to the set of composite knots made only by $4_1$ knots, since $C_{4_1} > C_{3_1} > N_0$, we will get $\mu_{(3_1\#)^\infty} > \mu_{(4_1\#)^\infty} > \mu_\emptyset$. In general we would expect that given two prime knots $k'$ and $k''$ with $C_{k''} > C_{k'}$

$$\mu_{(k'\#)^\infty} > \mu_{(k''\#)^\infty} > \mu_\emptyset. \tag{12}$$

This can be explained by arguing that each prime knot, being localized, brings the same entropic gain $\sim N$ to the partition function, but the simplest ones require less entropic cost to be formed. On the other hand the statistics of topologically unconstrained polygons are, in the large $N$ limit, dominated by extremely complex composite knots made by an arbitrary number of different prime components. It is then interesting to look at more complex subsets of polygons whose topology is characterized by an arbitrary number of $3_1$'s and $4_1$'s. Clearly $Z_{(3_1\#)^\infty,(4_1\#)^\infty}(N) > Z_{(3_1\#)^\infty}(N) + Z_{(4_1\#)^\infty}(N)$ and by applying the same argument we obtain $\mu_{(3_1\#)^\infty,(4_1\#)^\infty} = \mu_\emptyset \mathrm{e}^{1/C_{3_1}+1/C_{4_1}}$. Hence, in general, we should expect a sequence of the kind

$$\begin{aligned}\mu_\emptyset = \mu_{3_1} = \mu_{4_1} = \cdots < \cdots < \mu_{(5_1\#)^\infty} < \mu_{(4_1\#)^\infty} < \mu_{(3_1\#)^\infty} < \\ < \mu_{(3_1\#)^\infty,(4_1\#)^\infty} < \mu_{(3_1\#)^\infty,(4_1\#)^\infty,(5_1\#)^\infty} < \cdots < \\ < \mu. \end{aligned} \tag{13}$$

## 4. Conclusions

By sampling polygons with $N$ up to 200 000 we have been able to get accurate estimates of the large $N$ behaviour of the configurational entropy of SAPs with a fixed knot type $k$. We have corroborated the belief that in good solvent conditions, and in the large $N$ limit, prime knots are localized within small regions that slide independently along the unknotted part of the polygon. The existence of each prime component $k$ requires an entropic cost $C_k$ whose dependence on $k$ turns out to be relatively simple and intriguingly related to the minimal knot length $\ell_k$, i.e. the minimal number of steps necessary to build a knot of type $k$ on the cubic lattice. The above findings allow one to write down a general formula for the partition function of arbitrary complex composite knots and to conjecture a sequence of inequalities relating the connective constants of polygons with different topologies, including families of composite knots. In the future it would be nice to explore more broadly the asymptotic relation (8), and in particular to test the robustness of the relation $\log C_k \propto \ell_k$ with respect to different polymer models. In particular, it would be interesting to test it in the case of off-lattice polymers, where $\ell_k$ should be replaced by the length of the knot in its ideal representation [31, 32]. Finally we hope that, inspired by the results presented above, the set of conjectured inequalities in (13) could be put on a rigorous basis by following new approaches to the problem.

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