physics

MDPI

Article

Scaling Conjecture Regarding the Number of Unknots among Polygons of $N \gg 1$ Edges

Alexander Y. Grosberg

Center for Soft Matter Research, Department of Physics, New York University, 726 Broadway, New York, NY 10003, USA; ayg1@nyu.edu

Abstract: The conjecture is made based on a plausible, but not rigorous argument, suggesting that the unknot probability for a randomly generated self-avoiding polygon of $N \gg 1$ edges has only logarithmic, and not power law corrections to the known leading exponential law: $P_{\text{unknot}}(N) \sim \exp[-N/N_0 + o(\ln N)]$ with N_0 being referred to as the random knotting length. This conjecture is consistent with the numerical result of 2010 by Baiesi, Orlandini, and Stella.

Keywords: polymers; knots; unknot probability

check for updates

Citation: Grosberg, A.Y. Scaling Conjecture Regarding the Number of Unknots among Polygons of $N \gg 1$ Edges. *Physics* **2021**, *3*, 664–668. https://doi.org/10.3390/physics3030039

Received: 22 June 2021
Accepted: 30 July 2021
Published: 12 August 2021

1. Introduction and Problem Formulation

Randomly generated self-avoiding polygons represent an interesting object for mathematical physics, for several reasons. First, such polygons can serve as a zeroth approximation model for ring polymers. Different realizations, or members of the ensemble, of random polygons mimic different spatial arrangements of polymers, sampled via thermal fluctuations; importantly, ring polymers are currently the subject a great deal of interest, as evidenced, for example, by recent papers [1–5]. Despite this multitude of studies, the fundamentals of the statistical mechanics of topologically constrained polymers remain insufficiently understood. Second, random polygons—especially those comprised of the edges of a lattice, e.g., a cubic lattice—allow for concise mathematical formulation of the problems of interest, which, for an off-lattice model, is difficult even to formulate, let alone solve. Of course, this situation is by no means unique; other problems are also frequently more easily addressed using lattice models. Specifically, here, the problem in question is that of the knot entropy; see [6] for a general discussion. Indeed, this quantity is easy to define for the lattice polygon. Let $\Omega_{\text{unknot}}(N)$ be the total number of distinct rooted, i.e., with one point fixed, polygons with N edges, which are topologically equivalent to the trivial knot (an unknot or a circle). Since lattice polygons are considered, $\Omega_{\text{unknot}}(N)$ is a well-defined finite number. By definition, then, $\ln \Omega_{\text{unknot}}(N)$ is the entropy of an unknot.

Let us emphasize that this paper deals only with loops made by the closing of one single line, like letter O, not like letter θ or sign ∞, etc.; the loop may be embedded in various ways in three dimensions, forming an unknot or knots of different topologies, but the loop itself remains a simple O, albeit a "lattice O".

The number of unknots must be compared with the total number of distinct rooted polygons of N edges in three-dimensional space; let us call it $\Omega_{\text{loop}}(N)$. Then, $\ln \Omega_{\text{loop}}(N)$ is the entropy of the full ensemble of loops of all knot types. In terms of these quantities, the probability of finding an unknot among the randomly (and uniformly) generated polygons is:

$$P_{\text{unknot}}(N) = \Omega_{\text{unknot}}(N)/\Omega_{\text{loop}}(N)\,. \tag{1}$$

Clearly, $\ln P_{\text{unknot}}$ represents the corresponding change of entropy. Under the conditions of thermodynamic equilibrium, $\ln P_{\text{unknot}}$ is related to the minimal amount of mechanical work, needed to untie all the knots.

Some statements are rigorously established about these quantities; see review [7] and references therein. In particular, it is known that there exists a limit,

$$\lim_{N\to\infty} \frac{\ln P_{\text{unknot}}(N)}{N} = -\frac{1}{N_0} \,. \tag{2}$$

In other words,

$$P_{\text{unknot}}(N)|_{N\gg 1} \simeq \text{const} \cdot \exp[-N/N_0] \,. \tag{3}$$

The quantity N_0 is sometimes referred to as the random knotting length: for $N < N_0$, most polymers are unknots, while, for $N > N_0$, unknots are exceedingly rare. The exponential behavior of unknotting probability (3) is also proven for random off-lattice polygons and established numerically for a number of other models [7], albeit with very different values of N_0, ranging from a few hundred to a few million. Remarkably, no analytical method is known to find this quantity for any model.

The subject of the present note is the question—how does P_{unknot} approach its exponential asymptotic? In other words, how does the difference, $\ln P_{\text{unknot}}(N)/N + 1/N_0$ (note that $\ln P_{\text{unknot}}(N) < 0$), behave at large N, or how does this difference tend towards zero? The question is about the tail of probability $P_{\text{unknot}}(N)$ and whether it is similar to other subtle probability distributions known in various branches of physics; see, e.g., [8].

2. Developing the Argument

Let us start with $\Omega_{\text{linear}}(N)$—the number of distinct self-avoiding "open polygons" of N edges in three-dimensional space starting from, i.e., rooted in the origin (the open polygon is simply a broken line, with non-connected ends). This quantity was carefully studied in the theory of self-avoiding walks (see, e.g., [9], as a classical source), and it is known to behave as

$$\Omega_{\text{linear}}(N)|_{N\gg 1} \simeq \text{const} \cdot z^N \cdot N^{\gamma-1} \,, \tag{4}$$

where γ is a critical exponent which is universal, unlike the growth constant z, which is not universal. Therefore, z depends, for example, on the lattice type, while γ does not. The numerical value of γ was studied with great attention both analytically by renormalization group and ε-expansion [10], and by high-precision Monte Carlo [11,12]: the result was $\gamma \approx 1.16$.

Based on the knowledge of $\Omega_{\text{linear}}(N)$, one can deduce the estimate of $\Omega_{\text{loop}}(N)$. This deduction is known [9], and, here, for the purpose of subsequent generalization, let us repeat the derivation using the scaling argument, originally due to Khokhlov [13] and later developed by Duplantier [14]. This argument views transformation from a linear chain to a loop as a chemical reaction between chain ends. The argument suggests that the probability of two ends of a linear chain, meeting together in space, is of the same order as the conditional probability of the ends of two separate chains meeting in space, conditioned on the fact that these two chains share the same volume $R^3 \sim N^{3\nu}$. Here, $\nu \approx 0.588$ is a usual "metric" or Flory critical exponent, while R is the mean squared average gyration radius of the chain of length N. This argument yields the following estimate for $\Omega_{\text{loop}}(N)$:

$$\frac{\Omega_{\text{loop}}(N)}{\Omega_{\text{linear}}(N)} \sim \frac{\Omega_{\text{linear}}(2N)}{[\Omega_{\text{linear}}(N)] \times [R^3 \Omega_{\text{linear}}(N)]} \,. \tag{5}$$

This relation can also be explained in a different way. Equation (5) represents the statement that two different probabilities are of the same order, i.e., they scale with the same power of N. The left-hand side of Equation (5) is the probability that a randomly chosen linear chain of N monomers can be closed due to two ends being next to each other by pure chance. The right-hand side of Equation (5) estimates the probability, dealing with two linear chains of the same length N being co-localized in the same volume $\sim R^3$; for these two chains, the right-hand side of Equation (5) indicates the probability that the end of one of the chains is found next to the end of the other. Indeed, the numerator of

the right-hand side of Equation (5) represents the number of states of one linear chain of combined length $2N$ that is the same as two separate chains with the ends of these chains forced to be next to each other. The first factor in the denominator is the number of states for one half-chain, while the second factor is enhanced by a factor R^3 as soon as the second chain can be rooted in any place within volume R^3 around the root of the first chain (the monomer size is taken to be unity). Assembling all this together, one arrives at:

$$\Omega_{\text{loop}}(N)\Big|_{N\gg 1} \simeq \text{const} \cdot z^N \cdot N^{-3\nu} \,. \tag{6}$$

This result also follows straight from Equations (1.10) and (1.11) of Ref. [14], and is known for self-avoiding polymers, as stated in textbooks, see, e.g., [9]. The most important property of the result (6) is that it does not involve the index γ, which cancels away from the "chemical equilibrium" condition (5). This cancellation of γ has an important physical interpretation: γ describes the situation around chain ends, as monomers close to the ends find themselves in a different kind of environment compared to internal monomers close to the middle of the chain. Since the loop does not have any ends, there is no effect to be described by γ.

The estimate (6) is accurate in terms of the power, so we can rewrite it as:

$$\Omega_{\text{loop}}(N)\Big|_{N\gg 1} \simeq \text{const} \cdot e^{N\ln z - 3\nu \ln N + o(\ln N)} \,. \tag{7}$$

Thus, corrections in the exponential are much smaller than $\ln N$.

The next step in building the argument is yet another mathematically proven statement [7] that the number of N-step self-avoiding unknots, $\Omega_{\text{unknot}}(N)$, behaves such that there exists a limit,

$$\lim_{N\to\infty} \frac{\ln \Omega_{\text{unknot}}(N)}{N} = z_0 < z \,, \tag{8}$$

or

$$\Omega_{\text{unknot}}(N)|_{N\gg 1} \simeq z_0^{N+o(N)} \,. \tag{9}$$

At the same time, there is a scaling prediction [15], supported by a significant amount of numerical evidence [16–18], suggesting that a trivial knot loop, in terms of its overall size (e.g., gyration radius), is controlled by the same index $\nu \approx 0.588$, which describes the self-avoiding walks. Although there is a counter-argument pointing to the limited depth of analogy between trivial knots and self-avoiding loops [19], one can try to take this analogy one step further and conjecture that the number of unknots has the same scaling as the number of self-avoiding loops (6), but with a modified growth constant:

$$\begin{aligned} \Omega_{\text{unknot}}(N)|_{N\gg 1} &\simeq \text{const} \cdot z_0^N \cdot N^{-3\nu} \\ &\simeq \text{const} \cdot e^{N\ln z_0 - 3\nu \ln N + o(\ln N)} \,. \end{aligned} \tag{10}$$

In other words, the above argument yields the conjecture that the cancellation of the index γ, as in Equation (5), occurs for knot-avoiding loops—just as it is proven to do for self-avoiding loops. From physics point of view, this is justified by the fact that γ is supposed to characterize chain ends, while an unknot has no ends. Since this is a non-rigorous conjecture, it is important to stress where the argument may have limitations. In this regard, cancellation of the index γ is the most essential point where the conjecture is justified only by a physical argument and not by mathematics.

Another important point is also that the power ν needs to be of the same value in both relation (6) and relation (10). If this conjecture is correct, then the probability of unknot, $P_{\text{unknot}}(N) = \Omega_{\text{unknot}}(N)/\Omega_{\text{loop}}(N)$, is predicted to have the following asymptotic behavior:

$$P_{\text{unknot}}(N)|_{N\gg 1} \simeq \text{const} \cdot e^{N(\ln z_0 - \ln z) + o(\ln N)} \,. \tag{11}$$

To reiterate, the non-rigorous conjecture, found here, is, first, motivated by the analogy between knots-avoiding and self-avoiding—both described by the same metric exponent ν, and, second, by the fact that there is no index γ or its analogs since there are no ends in the loop.

3. Concluding Remarks

Equation (11) represents the result of the present paper. Of course, this equaion indicates that the random knotting chain length can be expressed as $1/N_0 = \ln(z/z_0)$. However, this is not a significant result because the growth constant z_0 (or even z) are not simple quantities to compute theoretically or to measure experimentally; essentially, z_0 and N_0 contain the same information. The real non-trivial statement is that there is $o(\ln N)$ instead of $o(N)$ in the exponential. In other words, the conjecture suggests that there is no power-law correction factor to the main exponential trend in unknot probability. The correction, of course, exists, but it is at most logarithmic. This can be contrasted with the fact that the probabilities of various non-trivial knots are routinely fitted to expressions like $N^{\mu}\exp(-N/N_0)$ (with N_0 as for trivial knots); see, e.g., [20–22]. In these terms, the result of the present paper is that for the trivial knots, $\mu = 0$ exactly.

The questions of critical exponents, related to the entropy of random polygons, were examined numerically, in quite some detail in the series of studies by the Italian group of E. Orlandini and co-authors [21–23]. In particular, Ref. [23] presented the most accurate study to date of (in the present notation) the exponent μ and it was found that, within the numerical accuracy of the Monte Carlo simulations made there, the result for an unknot was so small that it was not distinguishable from $\mu = 0$. In this sense, the result of the present study can be viewed as a confirmation or rather an explanation of the numerical observation made about a decade ago.

Does this result have practical implications beyond mathematical curiosity? In general, random knots are a fact of life in case of a DNA plasmid and a number of other biological contexts; see, e.g., [24]. Historically, in the first study [25] on random polymer topology, the main surprise was to observe that the probability of non-trivial knots, i.e., $1 - P_{\text{unknot}}(N)$, although still rather small at the tested range of N values, is, nevertheless, an increasing function of N. In this sense, the main observation is that for long polymers, $P_{\text{unknot}}(N)$ is small. This is, of course, consistent with the statement of the mathematical theorem (2), except the latter deals with the mathematical limit of $N \to \infty$, while, in practice, the exponential dependence of $P_{\text{unknot}}(N)$ on the chain length, N, seems to be consistent with observations, even at modest values of N being certainly smaller than random knotting length N_0; see, e.g., [26]. In this sense, the statement of the absence of power law corrections, made in the present paper, may have quite some practical implications.

Funding: The work of AYG was partially supported by the MRSEC Program of the National Science Foundation under Award Number DMR-1420073. This work was performed at the Aspen Center for Physics, which is supported by National Science Foundation Grant Number PHY-1607611.

Acknowledgments: The author acknowledges the fruitful atmosphere of the Aspen Center for Physics where this work was conceived and performed.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Smrek, J.; Chubak, I.; Likos, C.N.; Kremer, K. Active topological glass. *Nat. Commun.* **2020**, *11*, 26–36. [CrossRef]
2. O'Connor, T.C.; Ge, T.; Rubinstein, M.; Grest, G.S. Topological linking drives anomalous thickening of ring polymers in weak extensional flows. *Phys. Rev. Lett.* **2020**, *124*, 027801. [CrossRef]
3. Kruteva, M.; Allgaier, J.; Monkenbusch, M.; Porcar, L.; Richter, D. Self-similar polymer ring conformations based on elementary loops: A direct observation by SANS. *ACS Macro Lett.* **2020**, *9*, 507–511. [CrossRef]
4. Liebetreu, M.; Likos, C.N. Shear-induced stack orientation and breakup in cluster glasses of ring polymers. *ACS Appl. Polym. Mater.* **2020**, *2*, 3505–3517. [CrossRef]

5. Parisi, D.; Costanzo, S.; Jeong, Y.; Ahn, J.; Chang, T.; Vlassopoulos, D.; Halverson, J.D.; Kremer, K.; Ge, T.; Rubinstein, M.; Grest, G.S.; Srinin, W.; Grosberg, A.Y. Nonlinear shear rheology of entangled polymer rings. *Macromolecules* **2021**, *54*, 2811–2827. [CrossRef]
6. Grosberg, A.Y.; Nechaev, S.K. Polymer topology. *Adv. Polym. Sci.* **1993**, *106*, 1–30.
7. Orlandini, E.; Whittington, S.G. Statistical topology of closed curves: Some applications in polymer physics. *Rev. Mod. Phys.* **2007**, *79*, 611–642. [CrossRef]
8. Tribelsky, M.I.; Grosberg, A.Y. Laser heating of a transparent medium containing random absorbing inhomogeneities. *Sov. Phys. JETP* **1976**, *41*, 524–526.
9. De Gennes, P.G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, USA, 1979.
10. Le Guillou, J.C.; Zinn-Justin, J. Accurate critical exponents from field theory. *J. Phys.* **1989**, *50*, 1365–1370. doi: 10.1051/jphyslet:01985004604013700. [CrossRef]
11. Caracciolo, S.; Causo, M.S.; Pelissetto, A. High-precision determination of the critical exponent γ for self-avoiding walks. *Phys. Rev. E* **1998**, *57*, R1215–R1218. [CrossRef]
12. Clisby, N. Scale-free Monte Carlo method for calculating the critical exponent γ of self-avoiding walks. *J. Phys. A Math. Theor.* **2017**, *50*, 264003. [CrossRef]
13. Khokhlov, A.R. Influence of excluded volume effect on the rates of chemically controlled polymer-polymer reactions. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 633–636. [CrossRef]
14. Duplantier, B. Statistical mechanics of polymer networks of any topology. *J. Stat. Phys.* **1989**, *54*, 581–680. [CrossRef]
15. Grosberg, A.Y. Critical exponents for random knots. *Phys. Rev. Lett.* **2000**, *85*, 3858 – 3861. [CrossRef] [PubMed]
16. Dobay, A.; Dubochet, J.; Millett, K.; Sottas, P.E.; Stasiak, A. Scaling behavior of random knots. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 5611–5615. [CrossRef] [PubMed]
17. Matsuda, H.; Yao, A.; Tsukahara, H.; Deguchi, T.; Furuta, K.; Inami, T. Average size of random polygons with fixed knot topology. *Phys. Rev. E* **2003**, *68*, 011102. [CrossRef] [PubMed]
18. Moore, N.T.; Lua, R.C.; Grosberg, A.Y. Topologically driven swelling of a polymer loop. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 13431–13435. [CrossRef]
19. Moore, N.T.; Grosberg, A.Y. Limits of analogy between self-avoidance and topology-driven swelling of polymer loops. *Phys. Rev. E* **2005**, *72*, 061803. [CrossRef]
20. Deguchi, T.; Uehara, E. Statistical and dynamical properties of topological polymers with graphs and ring polymers with knots. *Polymers* **2017**, *9*, 252. [CrossRef]
21. Orlandini, E.; Tesi, M.; Janse van Rensburg, E.; Whittington, S. Entropic exponents of lattice polygons with specified knot type. *J. Phys. Math. Gen.* **1996**, *29*, L299–L303. [CrossRef]
22. Orlandini, E.; Tesi, M.; Janse van Rensburg, E.; Whittington, S.G. Asymptotics of knotted lattice polygons. *J. Phys. A Math. Gen.* **1998**. *31*, 5953–5967. [CrossRef]
23. Baiesi, M.; Orlandini, E.; Stella, A.L. The entropic cost to tie a knot. *J. Stat. Mech. Theory Exp.* **2010**, *2010*, P06012. [CrossRef]
24. Vologodskii, A.V. *Biophysics of DNA*; Cambridge University Press: Cambridge, UK, 2015. [CrossRef]
25. Frank-Kamenetskii, M.D.; Lukashin, A.V.; Vologodskii, A.V. Statistical mechanics and topology of polymer chains. *Nature* **1975**, *258*, 398–402. [CrossRef] [PubMed]
26. Plesa, C.; Verschueren, D.; Pud, S.; van der Torre, J.; Ruitenberg, J.W.; Witteveen, M.J.; Jonsson, M.P.; Grosberg, A.Y.; Rabin, Y.; Dekker, C. Direct observation of DNA knots using solid state nanopore. *Nat. Nanotechnol.* **2016**, *11*, 1093–1097. [CrossRef] [PubMed]