Critical Exponents for Random Knots

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The size of a zero-thickness (no excluded volume) nonphantom polymer ring is shown to scale with chain length N in the same way as the size of the excluded-volume (self-avoiding) linear polymer, that is, as N^{ν}, where $\nu \approx 0.588$. The consequences of this fact are examined, including the sizes of trivial and nontrivial knots.

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Knots have entertained physicists and mathematicians for one and a half centuries, since Thomson [1]. In a more specific context, knotted polymers and DNA have remained at the center of attention for over three decades [2–4]. Nevertheless, many simple basic questions remain unanswered. For instance, the most fundamental physical property of any macromolecule—its size $R(N)$ (e.g., mean-squared gyration radius), which scales with chain length N and depends on the solvent conditions—is not understood for knotted polymers. It is worth emphasizing that mere ends closure does not affect scaling of $R(N)$, but reduces it only by a factor ($\sqrt{2}$ for Gaussian chain). It has been conjectured theoretically [5] that quenched topology may have a much more serious effect and alter the scaling of polymer size. Some evidence supporting this conjecture came recently from simulations [6].

Our goal in this paper is to address on the scaling level the following problem, whose formulation is elementary: Given the polymer ring of a quenched topology, we want to estimate its average size. Consider the simplest ring polymer with no excluded volume, consisting of some N freely joined straight segments, length l each [7]. Assume that every spatial shape, or conformation, of this polymer is just as likely as any other. In mathematical language, our "polymer" is simply a closed broken line embedded in $3D$. With probability 1, this object does not have self-intersections, and, therefore, represents a knot, trivial (topologically equivalent to a circle) or nontrivial. It was proved as early as in 1988 [8] that the probability of a trivial knot configuration decays exponentially with N:

$$p_{\mathrm{tk}}(N) \simeq \exp(-N/N_0), \qquad (1)$$

where the subscript tk stands for "trivial knot" and a constant N_0 is a characteristic length. Similar exponential dependence on N, albeit perhaps with a different value of N_0, holds also for other models, such as a smooth wormlike ring object of the length Nl with effective segment l [9], the system of straight segments with Gaussian distributed random lengths [10], etc. Mathematical prediction (1) has been beautifully confirmed in computer simulation [11], yielding $N_0 \simeq 340 \pm 4$ for one particular model.

One of the important consequences of the result (1) is that we cannot use the continuous model (the Wiener trajectory), since it corresponds to the limit $N \to \infty$, $l \to 0$, $Nl^2 = \text{const}$, because in this limit *all* conformations (apart from the fraction of measure zero) are heavily knotted, or trivial knot probability is exactly zero.

While rigorous proof of the result (1) is not simple, it can be readily understood on a hand-waiving level. Indeed, consider our polymer as a sequence of N/g blobs, with g segments in each blob. The probability of trivial topology for each blob is $p_{\mathrm{tk}}(g)$, and formula (1) is equivalent to saying that $p_{\mathrm{tk}}(N) = [p_{\mathrm{tk}}(g)]^{N/g}$, which means that topological constraints between blobs are negligible compared to those between segments inside each blob. The temptation is then to conclude that the *vast majority of knots occur on small length scales.* Care should be exercised, however, while using this jargon in this context: Indeed, while the blob may be much smaller than the entire polymer $g \ll N$, the argument above holds only if it is large compared to N_0 ($g \gg N_0$), which itself is numerically large.

The exponentially small probability of a trivial knot (1) immediately explains why topological constraints *can* significantly alter the polymer size. Indeed, $lN^{1/2}$ is the size averaged over *all* conformations, while the size of a trivial knot is an average over an exponentially small *subset* of conformations. When relatively compact complex knots are removed, the remaining average increases. In order to bring this idea to a quantitative level, a couple of further preliminary arguments will be handy.

To begin with, consider an auxiliary problem of two ring polymers, with N segments each. They form a link, trivial (nonconcatenated) or nontrivial. If rings overlap, i.e., the distance between their centers of mass is smaller than their sizes, the probability that the link is trivial vanishes, $p_{\mathrm{tl}}(N) \to 0$, when $N \to \infty$. While the exact expressions for $p_{\mathrm{tl}}(N)$ are not known, it should be qualitatively similar to the trivial knot probability (1), and we assume that the corresponding characteristic chain length N_1 is of the order of N_0 [see also Eq. (7) below].

In speaking about the trivial link probability, one has to make the distinction between a link made by two rings, each of which may be an arbitrary knot, and a link made by two trivially knotted rings. Since the former probability is higher, and goes to 0 for large N, the latter, which we use below, goes to zero as well.

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Since trivial link topology is highly unlikely for overlapping rings, the untangled ring polymers effectively present excluded volume for each other, even if there is no bare excluded volume for monomers. Simple scaling argument suggests that the excluded volume can be estimated as

$$v_{\mathrm{excl}}(N) \simeq R^3(N)[1 - p_{\mathrm{tl}}(N)], \quad (2)$$

where $R(N)$ is the (properly averaged) size of one ring. The concept of "topological excluded volume" was introduced in one of the first works on computer simulation of knots and links [12]. It can be easily understood in terms of an exactly solved model [13,14] in which one polymer is a ring and the other is a straight line. It has recently been rigorously proven [15] that the excluded volume scales as $R^3(N)$ in $N \to \infty$ limit for two rings if their Gaussian linking number remains zero, even though this condition does not guarantee the untangled topology. As regards Eq. (2), it is actually almost trivially correct. Indeed, $1 - p_{\mathrm{tl}}(N)$ is the probability for two phantom rings to be tangled, i.e., to adopt a conformation prohibited for real (nonphantom) untangled rings [16].

We are now prepared to directly attack the question of the size $R_{\mathrm{tk}}(N)$ of a trivial knot without excluded volume. Let us color two different pieces of our N-segment ring, both containing some g ($1 \ll g \ll N$) monomers (segments). Since neither of the pieces has open ends, they present uncrossable objects for one another. Therefore, the arguments above apply and suggest that these two pieces exclude for each other some volume which is of the order of $v_{\mathrm{excl}}(g)$. While this identification of the pieces of a ring chain with separate small rings may be doubtful for small g, we expect it to become increasingly accurate with increasing g, especially when g becomes greater than N_0. In that case, $p_{\mathrm{tl}}(g)$ is negligible, and we end up with $v_{\mathrm{excl}}(g) \simeq R^3(g)$ for $g > N_0$, which immediately implies that the chain of g blobs belongs to the universality class of self-avoiding walks, and thus

$$R_{\mathrm{tk}}(N) \simeq R(g)\,(N/g)^{\nu}, \quad \text{where } \nu \approx 0.588 \approx \tfrac{3}{5}. \quad (3)$$

We expect this to hold at $g > N_0$, while at smaller scales the effect of topological constraints is only marginal. Thus, we assume $R(g) \simeq lg^{1/2}$ for g up to about N_0 and apply the above result (3) choosing $g \sim N_0$:

$$R_{\mathrm{tk}}(N) \simeq \begin{cases} lN^{1/2} & \text{if } N < N_0 \\ lN_0^{-\nu+1/2}N^{\nu} & \text{if } N \gg N_0 \end{cases}. \quad (4)$$

Thus, chain size in the case of trivial knot topology is controlled by the standard excluded volume exponent close to $\frac{3}{5}$. This confirms the conjecture made by J. des Cloizeaux as early as in 1981 [5]. We see also that this "swollen" regime comes only for really long chains, because N_0 is numerically large [11]. Furthermore, while in terms of parameters the crossover to the swollen asymptotic is controlled by N_0, there are grounds to expect that this asymptotic actually develops at N around a few times N_0 [which we expressed with the $\gg$ sign in formula (4)]. On the other hand, although topological constraints lead to swelling only when N is really large, the prefactor in the second line of formula (4) is of order unity: $N_0^{-\nu+1/2} \approx 340^{-0.088} \approx 0.6$.

The result Eq. (4) is also in good agreement with the recent work [6]. It reports simulation data for the ring polymer which preserves the topology of a trivial knot, but does not have any width (excluded volume). The average size of this polymer has been measured for a series of lengths $N = 2^n$, ranging from 32 to 2048 monomers. The sizes of N-mers were found to follow Gaussian statistics, $N^{0.5}$, for small N ($n = 5, 6, 7$), then the dependence was slowly getting sharper, and finally the ratio of the sizes of 2048- and 1024-mers was close to $2^{0.58}$.

Consider now some nontrivial knot, still without any excluded volume. This can be addressed using the so-called "tube inflation" or "ideal knot" approach. This idea has been proposed in several contexts, in the aspect addressing knot entropy it was suggested in [17]. Recently, an entire book [18] was devoted to the subject. In particular, the present author's contribution in this book addressed the size of an arbitrary knot. However, the result (4) was not established at the time; instead, the size of an arbitrary knot was estimated under the assumption that the size of a trivial knot scales as N^{μ} with an unknown exponent μ. We can now directly use the results of the author's work in [18], simply substituting $\mu = \nu$ there. To make the present work self-contained, we repeat the argument briefly.

When polymer is a knotted ring, fluctuations of each segment are restricted by the neighboring segments. Following the standard trick of the reptation theory [19], we replace these constraints by an effective tube confining the entire polymer. The difficult part of the problem is that, unlike the usual case of a melt [19], the tube shape for the swollen single chain fluctuates very strongly, and we have to find a reasonable approximation for it. To this end, we argue that there are two possibilities to achieve maximal entropy, corresponding to "uniform" and "phase segregated" [20] structures. Let us explain the meaning and examine both possibilities one by one.

We call the structure uniform when the freedom of transverse fluctuations is about the same everywhere along the polymer. That corresponds to finding the maximal diameter D for which the tube of the length L can be knotted into the given knot without self-penetration. The shape of this "maximally inflated" tube, or the shape of its central axis line, is called "ideal representation of a knot." It is characteristic of the topology, and so is this tube "axis ratio" $p = L/D$.

Thus, we replace the real topological constraints with the confinement within the tube whose aspect ratio p is that characteristic for the given knot topology. The tube is closed, and the polymer makes exactly one turn within the tube. We assume further that the polymer is not knotted inside the tube [21]. These two conditions together guarantee that the polymer has exactly the desirable topology. We can now determine the overall size of the polymer in space, R, using the following Flory-style argument: When R increases, the polymer loses entropy because it gets stretched along the tube axis; when R decreases, the polymer loses entropy because it gets squeezed perpendicular to the tube axis. Thus, the equilibrium size R can be conjectured to balance these two entropic factors. To implement this idea, we choose D and L such that $LD^2 \sim R^3$ and, since $L/D = p$, that means $L \simeq Rp^{2/3}$, $D \simeq Rp^{-1/3}$. We further recall that the unknotted polymer behaves just as an excluded volume one on large scales. That allows us to employ the standard scaling arguments [22] to estimate the relevant entropy. Specifically, transverse compression and longitudinal stretching in the tube are associated with, respectively, concentration blobs and Pincus tension blobs:

$$S \simeq -\left(\frac{L}{N^{\nu}}\right)^{1/(1-\nu)} - \left(\frac{N^{3\nu}}{LD^2}\right)^{1/(3\nu-1)}. \quad (5)$$

Provided the above expressions for L and D, this entropy has a maximum with respect to R at $R \sim lN^{\nu}p^{-\nu+1/3}$, and we identify it as the average size of the knot. This result applies as long as each of the aforementioned blobs remains larger than N_0 monomers. Equivalently, the equilibrium tube diameter D should be greater than lN_0^{ν}, yielding $N > pN_0$. For smaller blobs, Gaussian statistics should be valid, which means physically that we can consider a phantom [16] polymer confined within the tube. This case has been already examined in [17]. Collecting everything together, we obtain

$$R_k(N) \simeq \begin{cases} lN^{1/2}p_k^{-1/6} & \text{if } N < p_k N_0 \\ lN_0^{-\nu+1/2}N^{\nu}p_k^{-\nu+1/3} & \text{if } N > p_k N_0 \end{cases}, \quad (6)$$

where we have included the subscript in p_k to emphasize that this parameter is taken for the given knot k.

Thus, in terms of N dependence in the limit of very large N, every knot acts as an effective excluded volume, making the exponent equal to $\nu \approx 0.588$. However, more complex knots, with larger p, are significantly less expanded than trivial or simple knots. Furthermore, for complex knots the onset of swollen behavior is pushed to the range of really long chains. These results are consistent with numerical observation [11,23] suggesting that the probability of any particular knot, and not only the trivial one, decays exponentially at large N (1), with the characteristic length N_0 independent of the knot type. Qualitatively, one can say that increasing N for the polymer with any given topology eventually leads to the situation when the polymer is dominated by very long strings in which knot restriction is not felt at all, and thus it should become in this sense equivalent to the trivial knot.

Another way to look at Eq. (6) is from the point of view of p dependence. For the very long chain, with $N \gg N_0$, topological "memory" acts as an excluded volume for relatively simple knots, with $p < N/N_0$, for which R obeys the last line of Eq. (6). With increasing knot complexity, the system crosses over to the other regime, described by the upper line in Eq. (6). Note that at the crossover the chain size is about $R \sim lN^{1/3}N_0^{1/6}$. In terms of N dependence, this is already a collapsed chain, although there is an extra "swelling" factor $N_0^{1/6} \approx 2.6$.

Note also that the maximal value of entropy (5) is about $S \sim -p$: the knot creates about one constraint per polymer length which is about tube diameter.

As we mentioned, there is an alternative way to maximize entropy, which we call "phase segregated." To explain what we mean by that, consider first a prime knot. It may be entropically favorable to tighten this knot as much as possible, losing virtually all the freedom for segments involved in the tight knot, but gaining maximal entropy for the rest of the chain which then fluctuates as a free unknotted loop. For the composite knot, this picture must be slightly modified: We still imagine a long free unknotted loop with several little knots—prime components of the original composite knot—independently tightened in different places on the loop. To estimate roughly the entropy of such a knot segregated state, we can use again formula (5), applying it twice (or several times for a composite knot): for the tightened part, where p is roughly equal to that of the original knot, and for the unknotted loop part, where p is of order 1. The chain lengths for these two are about p and $N - p$, respectively. Since equilibrium entropy is linear in p, this simplest estimate yields that the phase segregated state is about as favorable entropically as the uniform one. A more sophisticated approach may be needed to decide which of them is more stable. It is also likely that the answer is sensitive to the details of local chain geometry (e.g., freely joined vs wormlike segments, and the like). For one particular model, the segregated state with tightened knot was observed in recent simulation work [24].

Although the qualitative statement that $p_{t1}(N)$ is practically zero for long rings is sufficient for the main stream of arguments in this paper, to estimate $p_{t1}(N)$ is itself an interesting problem. The simple estimate is obtained in the following way. Consider two strongly overlapping rings. Since we are counting probabilities over all possible configurations of rings, regardless of their knots, the statistics is Gaussian, and there should be about $\sqrt{N}$ contacts between the rings. As long as N is not very large, each contact can be thought of as being capable of providing up to one (positive or negative) unit of linking. Therefore, there are about $\sqrt{N}$ different linking states, with the probability of order $1/\sqrt{N}$ for each of them, including the untangled one. When N gets really very large, the situation becomes more complicated, because each of the $\sqrt{N}$ "contacts" is itself a large crowd of segments, which can realize a variety of linking arrangements. Since entanglements in different contact regions do not commute to each other in this regime [25], there appears exponential diversity of different types of links. Adjusting prefactors for continuity, we arrive at

$$p_{\text{tl}}(N) \sim \begin{cases} \sqrt{N_1/N} & \text{if } N < N_1 \\ \exp[1 - \sqrt{N/N_1}\,] & \text{if } N > N_1 \end{cases}, \qquad (7)$$

where subscript "tl" stays for the trivial link, N_1 is the characteristic length. The first line of this formula is in a very good agreement with the simulation data [25] where links of the lengths up to 500 were examined. This is consistent with our conjecture that N_1 is of the order of N_0. It would be interesting to simulate longer chains, as we expect the N dependence to crossover to exponential in the range of several hundred segments.

So far we have been considering a thin polymer with no excluded volume effect. What happens if volume interactions are presented? It is fairly obvious that the scaling exponent at very large N remains equal ν. The crossover to this regime occurs when N exceeds *both* $p_k N_0$ (6) for the given knot k and $(l/d)^2$ for the chain diameter d [7]. More detailed analysis, including cases of good and poor solvent, can be easily performed on the Flory theory level, combining the entropy (5) with the volume interactions term. This sheds light on the long-standing puzzle of extreme sensitivity of the knotting probability to the excluded volume [26]. As in the usual Flory theory for linear chains, as soon as entropy (5) is written with correlations taken into account, the volume interactions part should be written accordingly (e.g., proportional to the density to the power $\approx$2.25 instead of 2; see [22,27] for details).

To conclude, it is worth making it absolutely clear that this Letter deals with isolated loops, or loops in a very dilute solution *only.* In a melt or concentrated solution of unconcatenated rings, each ring is contracted [28]; this situation remains under close scrutiny [29].

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