Knottedness in Ring Polymers

Kleanthes Koniaris
Department of Physics, University of Massachusetts, Amherst, Massachusetts 01003

M. Muthukumar
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003
(Received 10 December 1990)

We represent ring polymers in free space with the rod-bead model and show through unbiased computer simulations that the probability of observing a trivial self-entanglement (P) has a decreasing exponential dependence on the contour length (N) of the polymer, or that $P=\exp(-N/N_0)$. The characteristic length (N_0) varies by many orders of magnitude depending on chain flexibility and solvent quality. We also suggest that sufficiently large knots are always composite, not prime.

PACS numbers: 61.41.+e, 36.20.Ey, 36.20.Fz, 84.20.+m

Both chemists and biochemists have synthesized polymeric rings. Once a ring is formed, its topological state is uniquely defined and invariant, at least until a bond is broken. Any nondestructive manipulation—like stretching, bending, or folding—will not impact a ring's topological state. While natural (circular) DNA is unknotted, synthetic rings can exhibit very complex knotted configurations.[1,2]

A great deal of theoretical effort has been expended in the study of entangled systems, since both the dynamic and the thermodynamic properties of such systems are functions of their topological state.[3-10] The simplest system that exhibits entanglement is a single-ring polymer. More complicated polymeric systems that are of interest are a ring linked to a wire (this problem bears an interesting relation to the Aharonov-Bohm effect[10]), rings linked to each other, and networks.

A most fundamental question about self-entanglement has been posed by Delbrück:[1] How does the probability of observing self-entanglement $(1-P)$ in a ring depend on the contour length (N)? Delbrück's question has so far proven resistant to all analytical attacks, so several numerical efforts have been attempted by various researchers.[11-16]

Much of the early numerical work[11,12] was done on a lattice (instead of in free space); biased methods were used to generate ring polymers, and systems were small. Later work[14] fixed many of the aforementioned problems, where the polymers were modeled off lattice and properly formed, but computer technology at the time was not sufficient for researchers to study systems with very large sizes and good statistics. The most well received work to date seems to be that of Michels and Wiegel,[10,15] which suggests that a power law relates P to N for Gaussian chains. (A Gaussian chain has $r=0$ for the model that we describe shortly.)

In this work, we study unbiased rings in free space, which seem to be the largest analyzed to date (by almost an order of magnitude), and for the first time attempt a methodical study of the effects of the polymers's excluded volume and flexibility on knotting. We believe that a decreasing exponential relates P to N, or that $P=\exp(-N/N_0)$, where the characteristic length (N_0) can vary by several orders of magnitude depending on the flexibility of the rings.

We represent ring polymers with the free-space rod-bead model.[17] Two parameters are required to create a model instance: the contour length (N) and the bead radius (r). A ring is composed of a closed backbone of N unit bonds. At the N vertices where two bond ends abut, we imagine beads, each of radius r. If any two beads intersect, the excluded-volume condition is said to be violated, and the entire instance must be rejected. A small r represents a flexible polymer in an ideal (Θ) solvent, while a large r represents a swollen (and less flexible) polymer in a good solvent.

We produce ring-polymer model instances with the dimerization method of Chen.[14] This method is preferable to alternatives[17] for three reasons: It is unbiased, it is very efficient in terms of computer time, and it is well suited to parallel architectures.

The rings produced by dimerization each have a unique topological state, and can be characterized by a knot invariant known as the Alexander polynomial $\Delta(s)$.[18,19] Other more elaborate invariants exist, like the Jones polynomial,[20] but their complexity makes them difficult to efficiently calculate, so we follow the lead of other researchers and use $\Delta(s)$.

The Alexander polynomial is a true invariant, in that a given knot will always be represented by the same $\Delta(s)$, no matter how much we bend, fold, or stretch it. However, there are cases where aliasing exists; that is, two knots in different topological states can lamentably share the same $\Delta(s)$. For example, Fig. 1 demonstrates that $\Delta[5_1]=\Delta[10_{132}]$ and that $\Delta[8_{10}]=\Delta[(3_1)(3_1)(3_1)]$. It is particularly unfortunate that some common combinations of simple prime knots [like a granny knot, $(3_1)(3_1)$] can be mistaken for more exotic prime knots (like 8_{20}).

Given a knot, there is a simple algorithm to determine

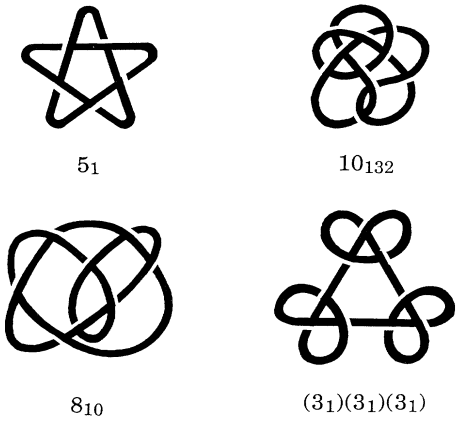

FIG. 1. Knots 5_1 and 10_{132} share the same Alexander polynomial, $\Delta(s)=s^4-s^3+s^2-s+1$, as do knots 8_{10} and $(3_1)(3_1)(3_1)$, which have $\Delta(s)=s^6-3s^5+6s^4-7s^3+6s^2-3s+1$.

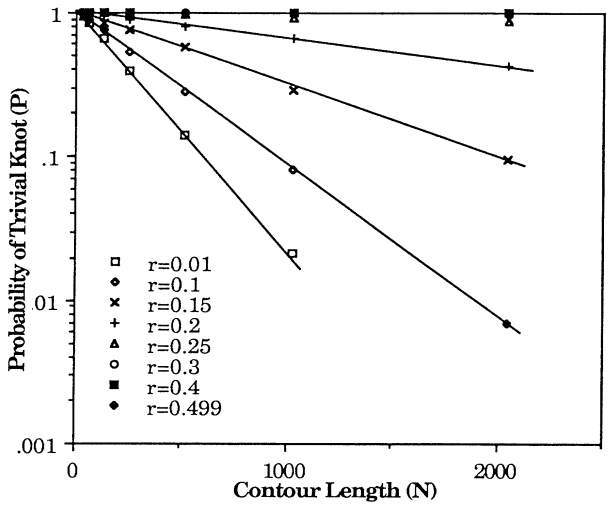

FIG. 3. A semilogarithmic plot of the probability of observing a trivial knot (P) as a function of the number of beads in a ring (N), for several values of bead radius (r).

its Alexander polynomial.[10,18,19] However, one step requires taking the determinant of an M by M matrix of polynomials, where $M+1$ is the number of bond-bond crossings observed when the knot is properly projected onto a plane. Even using Gaussian elimination to take the determinant requires time M^3, which can be prohibitive in the study of large systems; it is easy to get many hundreds or even thousands of crossings.

It is advantageous to preprocess a ring in such a way as to reduce the number of crossing $(M+1)$ that it displays when projected onto a plane. We have developed a very simple smoothing operation that properly maintains any ring's topological state while significantly reducing $M+1$; if the triangle defined by any three sequential beads is not crossed by any bond, the middle bead is removed and the two survivors are directly connected. This operation does distort the ring, but the underlying topological state is properly maintained. This operation can be done very efficiently, in time $N\ln(N)$, frequently to the point where the resulting ring has three beads left, with zero crossings. We feel that many entanglement problems are impractical unless one strives to remove detail that is irrelevant to the underlying topological features.

After smoothing a large ring, it is not efficient to immediately start the expensive Gaussian elimination. It often becomes apparent that one has a composite knot that is composed of several factors.[21] If a knot is composed of parts A and B, as in Fig. 2, $\Delta[AB]=\Delta[A]\Delta[B]$.

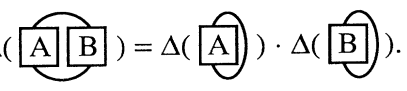

FIG. 2. If a knot can be "factored" into two parts as indicated, the $\Delta(s)$ of the entire composite knot is the product of the Alexander polynomials of the constituents.

Given that the identification time goes as M^3, "halving" the problem results in a fourfold speedup. [A second benefit is that it is sometimes possible to identify a $(3_1)(3_1)$ without concern that it might be an 8_{20}, for example.] We calculate determinants by using Gaussian elimination to solve a system of polynomials, utilizing symbolic methods.[22] It is possible to avoid symbolic computation altogether [by precompiling tables of $\Delta(s=-1)$ and $\Delta(s=-2)$ for known Alexander polynomials], but one gives up the ability of identifying new large knots.[11,21] We have indeed found knots with more than ten crossings,[21] the size of the knot table that we have used,[18] but this happens rarely.

Figure 3 is a semilogarithmic plot of the probability of observing a trivial knot (open loop), P, as a function of the number of beads, N, for various values of bead radius r. Each point represents 5000 rings. The error in P is 2%, given a 95% confidence interval. We see a linear fit, and therefore propose the empirical relation $P(N)$

TABLE I. The characteristic length (N_0) and radius-of-gyration exponent (ν_{eff}) as functions of bead radius (r).

Radius	N_0	ν_{eff}
0.01	2.6×10^2	0.51
0.1	4.0×10^2	0.54
0.15	8.7×10^2	0.57
0.2	2.4×10^3	0.59
0.25	1.5×10^4	0.60
0.3	1.1×10^5	0.60
0.4	3×10^5	0.61
0.499	8×10^5	0.61

TABLE II. The most common knots found as functions of the number (N) and radius (r) of the beads. An asterisk suggests a possible composite (nonprime) knot.

Size	r=0.01	r=0.1	r=0.15	r=0.2	r=0.25	r=0.3	r=0.4	r=1/2
32	0.1, 3.1, 4.1, 5.2, 5.1, 8.20*, 6.2	0.1, 3.1, 4.1, 5.2, 8.20*, 5.1, 6.1, 6.3....	0.1, 3.1, 4.1, 5.2, 6.2	0.1, 3.1, 8.20*, 4.1	0.1, 3.1	0.1	0.1	0.1
64	0.1, 3.1, 4.1, 5.2, 5.1, 8.20*, 8.21*, 6.1, 6.2....	0.1, 3.1, 4.1, 5.2, 5.1, 8.20*, 6.1, 8.21*....	0.1, 3.1, 4.1, 5.1, 5.2, 8.20*, 6.2....	0.1, 3.1, 4.1, 8.20*, 5.2, 6.1	0.1, 3.1	0.1	0.1	0.1
128	0.1, 3.1, 4.1, 5.2, 8.20*, 5.1, 8.21*, 6.2, 6.3, 6.1, 7.6, 8.18*, 7.5, 8.10*....	0.1,3.1, 4.1, 5.2, 8.20*, 5.1, 8.21*, 6.2, 6.1, 7.6, 6.3....	0.1, 3.1, 4.1, 8.20*, 5.2, 5.1, 6.2, 6.1, 8.21*, 7.6, 8.10*....	0.1, 3.1, 4.1, 8.20*, 5.2, 5.1, 6.2	0.1, 3.1, 4.1	0.1, 0.3	0.1	0.1
256	0.1, 3.1, 8.20*, 4.1, 5.2, 5.1, 8.21*, 6.2, 6.1, 8.18*, 8.10*, 8.11*, 6.3, 7.5, 7.7, 7.2....	0.1, 3.1, 8.20*, 4.1, 5.2, 5.1, 8.21*, 6.2, 8.10*, 6.1, 6.3, 8.18*, 10.159*, 7.5, 7.6....	0.1, 3.1, 4.1, 8.20*, 5.2, 5.1, 8.21*, 6.1, 6.2, 8.10*, 6.3, 7.5, 10.159*, 8.8*....	0.1, 3.1, 8.20*, 4.1, 5.1, 5.2, 6.1, 7.6, 7.3, 8.21*, 7.5	0.1, 3.1, 4.1	0.1, 3.1, 5.1	0.1	0.1
512	3.1, 0.1, 4.1, 8.20*, 5.2, 5.1, 8.21*, 8.10*, 6.2, 8.18*, 6.1, 7.6, 6.3, 10.65*, 7.5, 8.11*....	3.1, 0.1, 8.20*, 4.1, 5.2, 8.21*, 8.10*, 5.1, 6.2, 8.18*, 6.1, 7.6, 10.65*, 6.3, 8.11*....	0.1, 3.1, 8.20*, 4.1, 8.21*, 5.2, 5.1, 8.10*, 6.2, 8.18*, 7.6, 6.1, 6.3....	0.1, 3.1, 8.20*, 4.1, 8.21*, 5.2, 5.1, 8.10*, 6.1, 10.40*, 10.137*....	0.1, 3.1, 4.1, 8.20*	0.1, 3.1	0.1, 3.1	0.1, 3.1
1K		3.1, 8.20*, 4.1, 5.2, 0.1, 5.1, 8.10*, 8.21*, 8.18*, 6.2, 10.65*....	3.1, 0.1, 8.20*, 4.1, 8.21*, 8.10*, 5.2, 5.1, 8.18*....	0.1, 3.1, 8.20*, 4.1, 5.2, 8.21*, 5.1, 8.10*, 6.2	0.1, 3.1, 8.20*, 4.1, 5.2, 6.1....	0.1, 3.1, 4.1	0.1, 3.1 4.1	0.1,
2K		3.1, 4.1, 5.2, 5.1, 8.20*, 6.2, 6.1, 8.21*, 8.10*, 6.3, 8.18*....	3.1, 8.20*, 4.1, 0.1, 8.10*, 5.2, 8.21*, 8.18*, 5.1....	0.1, 3.1, 8.20*, 4.1, 8.10*, 8.21*, 5.2, 5.1....		0.1, 3.1, 8.20*....	0.1, 3.1	0.1, 3.1

$=\exp[-N/N_0(r)]$, where $N_0(r)$ is a characteristic size that depends on the bead radius.

Table I illustrates how the characteristic length (N_0) and the exponent ν_{eff} depend upon bead radius (r). (The radius of gyration of the polymer is proportional to $N^{\nu_{\text{eff}}}$.) We observe from Table I that N_0 is extremely sensitive to the quality of the solvent and the chain stiffness, and that the rings are far more knotted under ideal conditions ($\nu_{\text{eff}} \sim \frac{1}{2}$) than in good solutions ($\nu_{\text{eff}} \sim \frac{3}{5}$). Because the characteristic length (N_0) becomes significantly larger than the sizes of the systems that we were able to study at bead radii above 0.2, estimates of the characteristic length for large values of the radius are clearly questionable. For values of the bead radius at and below 0.2, the error in N_0 is 5%. The reader will note that Table I indicates that only the data for $r=0.2$ reach the asymptotic regime (where $\nu_{\text{eff}}=0.5889$). The chains that feature smaller or larger beads are too short to reach the limiting value of ν_{eff}, and are still in the crossover regime, from the random coil and stretched states, respectively.

In their work, Michels and Wiegel[10,15] have proposed an empirical fit $P(N)=Cm^N N^a$, where $m=0.9964$, $a=0.0088$, and $C=1.026$. Given that m is less than unity, C is close to unity, and a is so close to zero, their formula is—for all practical purposes—indistinguishable from ours, except that their value for $N_0(r=0)$ is 277. We do not find this discrepancy in N_0 to be too surprising because the rings that they studied were of $N=300$, which is only comparable to N_0, and an estimate of their N_0 is extremely sensitive to the least significant figure of m.

Table II provides the most common knots observed at various combinations of N and r. After observing hundreds of computer-generated figures, we strongly suspect that the knots marked with an asterisk in Table II are rarely prime and are in fact usually composite. If this is true, $8_{20} \rightarrow (3_1)(3_1)$, $8_{10} \rightarrow (3_1)(3_1)(3_1)$, $10_{136} \rightarrow (4_1)(3_1)$, $10_{137} \rightarrow (4_1)(4_1)$, $8_{18} \rightarrow (4_1)(3_1)(3_1)$, $8_{21} \rightarrow (4_1)(3_1)$, etc. It is possible (but expensive) to determine what fraction of these knots are in fact composite.[21] We have made a few dozen rings with 16384 beads, and each one always contained numerous trefoil (3_1) knots, leading us to conjecture that very big systems are always composite.

In summary, we conclude that the probability of observing a trivial knot in a ring polymer is an exponentially decreasing function of chain length and that the characteristic length for nontrivial rings (N_0) changes by at least 3 orders of magnitude when the solvent quality is changed, i.e., while the radius-of-gyration exponent (ν_{eff}) changes from $\frac{1}{2}$ to $\frac{3}{5}$. These conclusions are based on very large rings, created off lattice, without any statistical bias, for different solvent qualities.

This work was supported by the National Science Foundation Grant No. DMR-9008192, and the Materials Research Laboratory at the University of Massachusetts. We thank Jim Reardon and J. P. Massar of Thinking Machines Corporation for providing time on a Connection Machine 2.

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