Nonequilibrium Relaxation Times in Polymer Knot Groups

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Flexible polymer knots with strict topological constraint of no segment crossing are studied by Monte Carlo simulations. The nonequilibrium relaxation time of an equilibrated polymer knot cut at one point to relax to a linear chain is measured. Prime knots up to 20 essential crossings from the groups $(3_1, 5_1, 7_1, \ldots)$, $(4_1, 6_1, 8_1, \ldots)$ and $(5_2, 7_2, 9_2, \ldots)$, $(6_2, 8_2, 10_2, \ldots)$ are studied. The nonequilibrium relaxation time for knots within a group are found to increase stepwise linearly with the number of essential crossings of the original knot. Our results suggest an equally spaced topological interaction energy spectrum for knots in the same group and thus provide a quantitative description of topological interactions.

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The fact that segments are forbidden to cross in a knot gives rise to strong topological interactions which is manifested by the various topological invariants that catagorize the knot. These invariants, such as the number of essential crossings, unknotting number, topological writhe number, bridge number, polynomial invariants, etc. [1,2], will persist their values/forms no matter how the knot is deformed, but without cutting it. The conventional nomenclature of a knot is denoted by C_K where C is the number of essential crossings, i.e., the minimum number of crossings in any planar projection of the knot (see Fig. 1), and K is just a label to distinguish topologically different knots. C is a fairly weak topological invariant and can have an exponentially large degeneracy when C is large. Advances had been made in classifying knots and topological invariants [3–5]. More sophisticated topological invariants such as Alexander and Jones polynomials and Vassiliev invariant can distinguish knots much better, but there is still no one-to-one correspondence for more complex knots.

Although the desire to connect knot theory and physics dated back to Lord Kelvin who imagined different atoms as distinct knots embedded in ether, there was limited progress until recent decades due to the breakthrough of Jones polynomials. Some advances in the connections between knot theory and physics can be seen in knotlike structures in quantum and classical field theories recently [6,7]. Even then, the connection tends to be mathematical and abstract. Furthermore, due to the advances in recent experimental techniques in chemical and biological systems which can manipulate naturally occurring knotted DNA [8–11] as well as artificially tying up a knot molecule [12], there is a real urge for some fundamental understanding of the physical properties of knots. Topological constraints dictate the physical and geometrical properties of the knot [13–19]. Such topological interactions give rise to the entanglement effects which govern the dynamics in polymeric systems [20]. Topological interactions in knots are easy to picture but hard to quantify, and yet they are robust and have good memories. On the other hand, there have been various studies on the energy of physical knots [21–24], but the precise form of a satisfactory energy function that can describe all the physical properties of a knot molecule accurately or distinguish different knots is still lacking. This is largely due to the absence of a suitable quantitative description of the topological interactions among the segments in a physical knot. Topological interactions in a knot can be intuitively thought of as the free energy difference of a polymer constrained to a particular

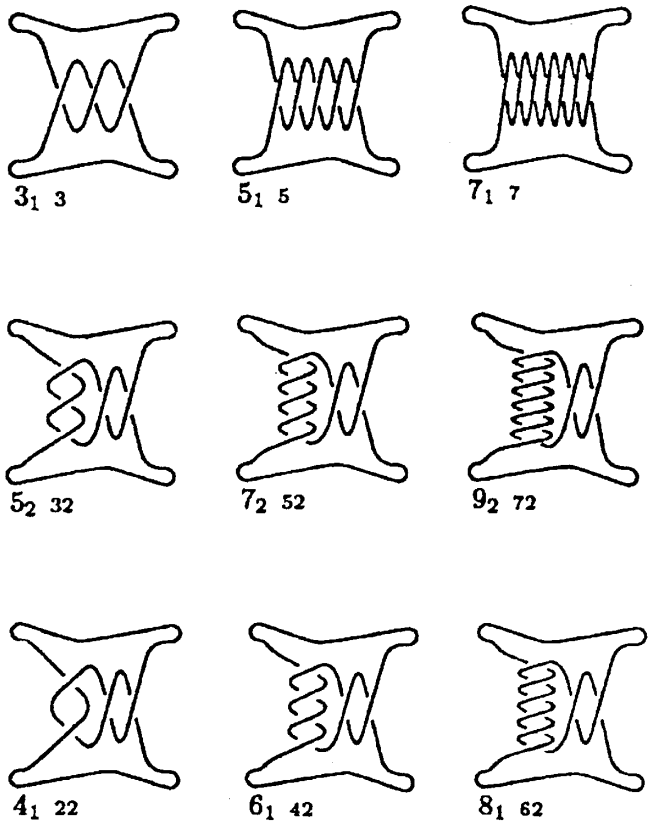

FIG. 1. Knot diagrams for the $(3_1, 5_1, \ldots)$, $(4_1, 6_1, \ldots)$, and $(5_2, 7_2, \ldots)$ groups. The Conway notations of the knots are also shown.

knot type relative to some reference state, such as a free linear polymer. Such a topological free energy difference is entropic in nature since the number of possible configurations of the chain constrained to a knot is much less than that of a linear free chain.

To probe the nature of topological interactions in a knot, one should look for the physical quantities that can best manifest the pure topological interactions. In our previous work [25], we demonstrated that prime knots can be categorized into groups according to their nonequilibrium relaxation times obtained by cutting the knots. However, the interactions in the knot using the bead-spring model in our previous approach [25] consist of topological as well as other energies such as spring energies of the bonds and attraction between monomers, and hence masking the probe for pure topological interactions.

In this Letter, we aim to study knots with only topological constraint but without other extra interaction energies such as attractions among monomers and solvent and consider knotted flexible polymers. Using the bond-fluctuation model for polymer chain [26], various knotted ring polymers with 180 effective monomers up to $C = 20$ under good solvent conditions are studied by dynamic Monte Carlo simulations. There are only two basic interactions in our model: the first are the hardcore excluded volume effects between the monomers which can be thought of as a knot having a finite cross-section thickness; the second is the prohibition of any segment crossing in the course of the dynamics and hence entanglement effects are taken care of automatically. It is clear that the latter interaction is of a strong topological nature which would guarantee that the initial knot will remain the same type unless a segment is cut. The equilibrium average contour lengths of these prime knots are the same as the equilibrium average of the corresponding linear free chain (of the same number of monomers) within 0.8%, indicating that the knots are far away from the tight knot limit [23]. The well-equilibrated knot is then cut at a randomly selected segment at $t = 0$ and allowed to relax to the free linear conformation. In our simulations, the cut polymer knot is allowed to relax for a long period of time until it eventually reaches a state that is physically indistinguishable from a free linear chain at equilibrium. Figure 2 shows the snapshots of a 20_1 knot that is well equilibrated (top), then one segment is cut at $t = 0$ and allowed to relax to the final state of a free linear chain (bottom).

The cut knot is considered to be "untied" when all of its physical properties, such as characteristic size, contour length, average crossing number, average writhe, bond lengths, autocorrelation time, and flexibility, etc. have approached the same equilibrium values as the linear chain of the same length under the same condition. It should be noted that here "untying" does not literally mean that all the chain segments are untangled, just like an ordinary free long linear polymer, it is possible to have some portion of its segments entangled during the course of its dynamical movements. The average number of crossings projected

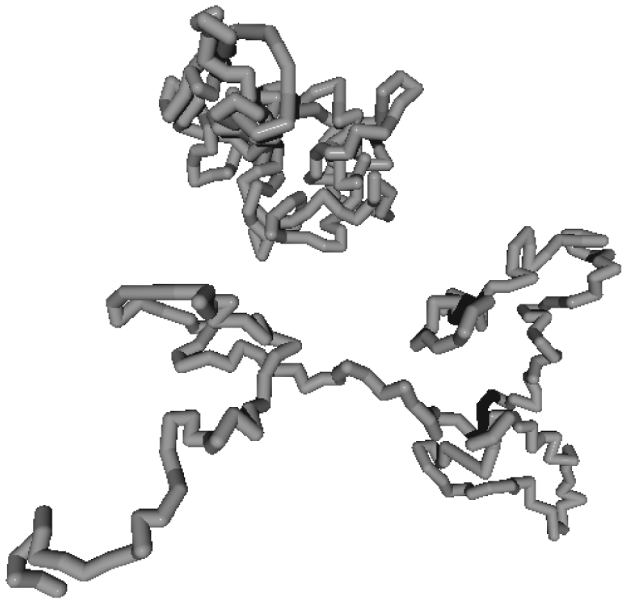

FIG. 2. Snapshots of the equilibrium configuration of a 20_1 knot (top) and the final configuration of the cut knot after 1.25×10^6 Monte Carlo steps (MCS) per monomer.

in all directions, X, gives a good indication of untying the knot. The average projected crossings is calculated as [11] $X = \frac{1}{4\pi} \int_0^L \int_0^L |\frac{(\vec{r}-\vec{r}') \cdot d\vec{r} \times d\vec{r}'}{|\vec{r}-\vec{r}'|^3}|$ where the double line integral is over the polymer and L is its contour length. The radius of gyration R_g, which characterizes the size of the polymer, is also carefully monitored. Figure 3 displays the relaxation of the radii of gyration and average crossing numbers of the trefoil and 6_2 knots; they approach their corresponding values of a free linear chain of the same length. The overbar denotes averages over different realizations (typically ~4000 to 5000) of the relaxation processes. By untying the knot, one can get information on the topological state of the original knot. In the course of relaxation, the topological information of the original knot is lost and the characteristic relaxation time measures its rate. The equilibrium ensemble averages of the radius of gyration of the uncut knot and that of a free linear chain of the same length, denoted by $\langle R_g \rangle$ and $\langle R_g \rangle_{\text{linear}}$, respectively, are also measured independently. The characteristic nonequilibrium relaxation time is extracted from the data of $\overline{R_g(t)}$ as the time needed for $\langle R_g \rangle_{\text{linear}} - \overline{R_g(t)}$ to decay to $1/e \simeq 0.368$ of its initial value ($= \langle R_g \rangle_{\text{linear}} - \langle R_g \rangle$). Loosely speaking, τ is the typical time scale needed to untie the cut knot by random Brownian motion. The variation of τ versus C is highly nonmonotonic, although naively one would imagine that it would take a longer time to untie the knot with more crossings. Some knots such as 7_1, have a longer τ than other knots having more crossings (such as 8_1, 8_2, 9_2, 10_1, 11_2, and 12_1). This indicates that the particular knot type is very important in determining τ. Knots on the first three groups in Table I have also been observed to follow the same group in the bead-spring model in our previous study (only up to $C = 9$ and $N = 60$) [25]. Here with a different polymer model and

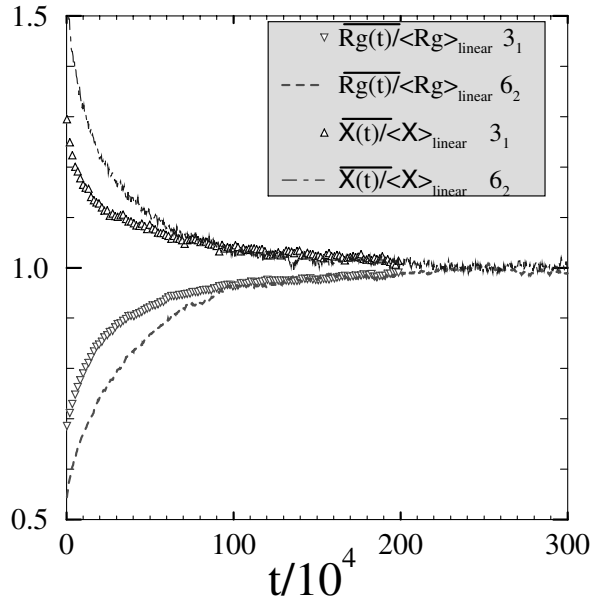

FIG. 3. Average relaxations of the radius of gyration $\overline{R_g(t)}$ and mean crossing number $\overline{X(t)}$ of the 3_1 and 6_2 knots cut at $t = 0$. $\langle\cdots\rangle_{\text{linear}}$ denotes the independently measured equilibrium ensemble average of the corresponding a free linear chain. Time is in units of MCS/monomer.

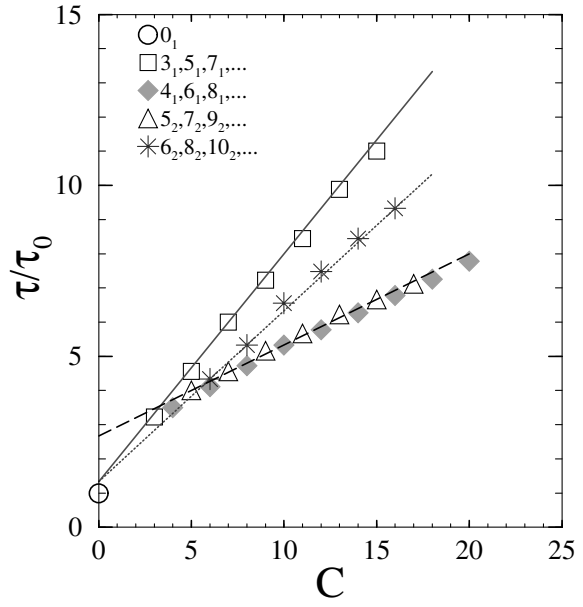

FIG. 4. Monte Carlo simulation data for the nonequilibrium relaxation time of the radius of gyration of the knot vs C. Each knotted polymer consists of 180 monomers. Uncertainties are about the size of the symbols. τ is measured in units τ_0 and $\tau_0 \simeq 9 \times 10^4$ MCS/monomer.

with more different knot types with higher C, such a classification is also observed for knots for one more group as shown in Fig. 4 and Table I. Careful inspection reveals that the Alexander polynomials [1,2] of the knots in each group have the same parametrization in terms of C as listed in Table I. These groups are known as "homologous families" to knot theorists. Such a parametrization has the same origin as the physical classification we observed: both are due to the fundamental similarity in the topology of knots in the same group. Our observation indicates that conventional labeling of knots can further be parametrized naturally into groups in a way that has a direct physical meaning in terms of the topological interactions in a knot. Also the variations of τ with C are appreciably stronger for the $(3_1, 5_1, \ldots)$ and $(6_2, 8_2, \ldots)$ groups than the twist knot groups, this may have some relation to the fact that the degree of the polynomial invariants of the former two groups increase with C, while for the other two twist knot groups their $\Delta(s)$'s are always of degree 2. The parametrized form of the Alexander polynomials of the latter two groups are similar (but not the same) and their variations of τ with C are close to each other as shown in Fig. 4. However, the variation of τ with C of the odd twist knot groups is systematically slightly larger than that of the even twist knot group. The similarity in topological interactions in a group is also supported by the observation that the Conway notations [1,2] of the knots are parametrized in the same way within a group (see Table I).

The most remarkable fact in the present study is that τ increases linearly with C for all the four groups, as shown in Fig. 4. On the contrary, for knots with nonpure topological interactions a nonlinear (but monotonic within a group) variation of τ with C was observed in the bead-spring model [25], which is due to the presence of other energies among monomers and the fact that the chain length is relatively short (the knots with high C are somewhat

TABLE I. Table for the different knot groups in this paper with their Alexander polynomials $\Delta(s)$, Conway notations, and the empirical formulas for the mean writhe number and scaled nonequilibirum relaxation times. τ_0 is the relaxation time of the trivial knot.

Knot group	$\Delta(s)$	Conway notation	$\langle Wr\rangle$	τ/τ_0
$(2, C)$ torus knots $(3_1, 5_1, 7_1, \ldots)$	$(1 + s^C)/(1 + s)$	C	$\frac{10}{7}C - \frac{6}{7}$	$\frac{2}{3}C + \frac{4}{3}$
Even twist knots $(4_1, 6_1, 8_1, \ldots)$	$\frac{C}{2} - 1 - (C - 1)s + (\frac{C}{2} - 1)s^2$	$(C - 2)\,(2)$	$\frac{4}{7}C - \frac{16}{7}$	$\frac{4}{15}C + \frac{8}{3}$
Odd twist knots $(5_2, 7_2, 9_2, \ldots)$	$\frac{C-1}{2} - (C - 2)s + \frac{C-1}{2}s^2$	$(C - 2)\,(2)$	$\frac{4}{7}C - \frac{16}{7}$	$\frac{4}{15}C + \frac{8}{3}$
$(6_2, 8_2, 10_2, \ldots)$	$-1 + 3s(\frac{1+s^{C-3}}{1+s}) - s^{C-2}$	$(C - 3)\,(1)\,(2)$	$\frac{10}{7}C - \frac{40}{7}$	$\frac{1}{2}C + \frac{4}{3}$

tight in [25]). The fact that classification into homologous groups was still observed in the bead-spring model in [25] suggests that the interactions inside the knots were predominately topological; however, with the presence of other energies the quantitative relaxation behavior becomes nonlinear with C.

It is worth noting that many equilibrium physical properties such as equilibrium size, mean crossing number, and autocorrelation decay time, etc. [25,27], show a much less prominent difference for uncut knots with the same C but belong to different group, although current experimental techniques in sedimentation and gel electrophoretic migration [28,29] can detect these differences. By cutting the knot and releasing the strong topological constraint, such a knot group classification emerges naturally and clearly. One can imagine that by cutting the knot and relaxing to the linear free chain, the chain releases some sort of free energy which we call "topological free energy" $\mathcal{F}$, since its dominant contribution comes from topological interactions. If the knot is somewhat tight [23,24] or some other interactions are present [25], then $\mathcal{F}$ would have significant contributions other than topological interactions. In the present case, since all the polymer knots are not tight and there is no other energy scale present in our model, $\mathcal{F}$ is purely topological. $\mathcal{F}$ is dissipated by Brownian type motions in some characteristic time scale τ with a certain rate, thus $\mathcal{F} = \text{Rate} \times \tau$. Since the knots in our simulations are far from the tight knot limit and the monomer concentration is in the dilute regime, the rate of dissipation is the same for all the knot types. Furthermore, as shown in Fig. 4, τ varies linearly with C remarkably well within a group, for all the groups we studied. Hence one has $\mathcal{F} = A_g C + B_g$, where A_g and B_g are constants within a group. The topological energy spectrum has equal spacing of A_g for knots within a group. One can imagine the topoisomerase enzyme supplies a *"topolon"* of energy in changing the knot type by increasing two crossings in a knotted DNA molecule. The equally spaced spectrum implies that tying two more crossings within the same knot group increases the "topological interaction energy" by one step on average, regardless of the number of crossings the knot already has. The quantized linear increment of the mean writhe number $\langle Wr \rangle$, of knots with C within a knot group has also been observed for ideal [17,18] and flexible [27] uncut knots at equilibrium. $\langle Wr \rangle$ is the average of all projected signed crossings and presumably reflects some topological details of the knot. Our results of an equally spaced topological energy spectrum could provide a plausible picture for the observed quantumlike behavior of $\langle Wr \rangle$ in knots and links. Motivated by the observation that $\langle Wr \rangle$ can be quite well represented by the linear empirical expressions [17,18,27,] displayed in the 4th column in Table I, we attempt to summarize the linear behavior of τ as follows. If one scales the nonequilibrium relaxation times of the knots by that of the trivial knot τ_0, the stepwise increase of τ with C can be quite well approximated by the suggestive linear relations with C as shown in the 5th column in Table I. Although we have no explanation for the rational coefficients in the linear relation, they are quite close to the best fit values. For example, for the torus group, the best fitted linear relation is $(0.66 \pm 0.02)C + (1.33 \pm 0.08)$. We hope our results can stimulate further theoretical understanding of topological interactions in knots.

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