Collapse of Randomly Linked Polymers

In a recent Letter, Bryngelson and Thirumalai (BT) [1] consider an ideal (i.e., non-self-interacting) polymer in which M randomly chosen pairs of monomers are constrained to be in close proximity. The unconstrained chain of N monomers is expanded, with a typical radius scaling as $R \propto \sqrt{N}$. By comparing variational estimates to the free energies of expanded and collapsed states, BT argue that increasing the number of (uncorrelated) links causes the polymer to collapse into a localized state in which R is independent of N. From Eq. (10) in Ref. [1] it follows that for a generic set of constraints, where the distance (along the backbone) between linked monomers is of the order N, a constraint density $A/\ln N$ creates a collapsed state for sufficiently large A.

Here, we demonstrate that the polymer remains expanded unless $M \sim N$. We derive an exact lower bound to the squared end-to-end distance, $r^2 > N/M$, which proves that, contrary to the conclusion of BT, uncorrelated links do not cause the polymer to collapse. Numerical simulations are also performed by exploiting an analogy to random resistor networks [2]: r^2 equals the resistance of a chain of uniform resistivity in which randomly chosen pairs of points are connected by shorts of zero resistance. Elimination of series and parallel resistors reduces the problem to a network of, at most, M nodes. Extensive simulations show that $r^2 \approx 1.5N/M$.

The lower bound for r^2 is obtained by noting that M links break the polymer into $2M + 1$ segments. r^2 is certainly larger than the sum of the end-to-end distances of the two extremal segments. (The resistance of the network is larger than its two end pieces.) In the limit of large M, the length of each segment is independently taken from an exponential distribution with mean size $N/(2M + 1)$. We choose parameters such that a segment of length s has $r(s)^2 = s$, i.e., the corresponding chain has unit resistivity. The contributions of the two end segments thus add up to $2N/(2M + 1) \approx N/M$.

Therefore, for large M, we have $r^2 > N/M$. This bound ensures the absence of a localized state for vanishing density M/N. The model of BT includes soft constraints, which corresponds to replacing the shorts in our model by finite resistors; such modification increases the total resistance and makes the inequality even stronger.

Simple scaling suggests that in the continuum limit $N \gg 1$, $r^2(M, \lambda N) = \lambda r^2(M, N)$, and hence $r^2 = f(M)N$. We confirmed this scaling numerically for several values of N. Figure 1 depicts (on a logarithmic scale) r^2/N, as a function of M, for $N = 2560$. Every point on this figure represents an average over 1600 configurations of random links. The numerical results gradually converge to a slope of -1, as depicted by the solid line. A least squares fit to *all* points of the figure produces a slope 0.97, and the curve cannot be fitted as $\ln M/M$. In fact, we conclude that $r^2 \approx 1.5N/M$, with a prefactor that is surprisingly close to the value of 1 which appears in our simple lower bound. Details of the numerical algorithm, as well as a discussion of implications for self-avoiding polymers appear in a companion paper [3].

After completion of this work, we became aware of a work by Solf and Vilgis [4]. Although they consider more general polymer networks, their results also agree with the above findings.

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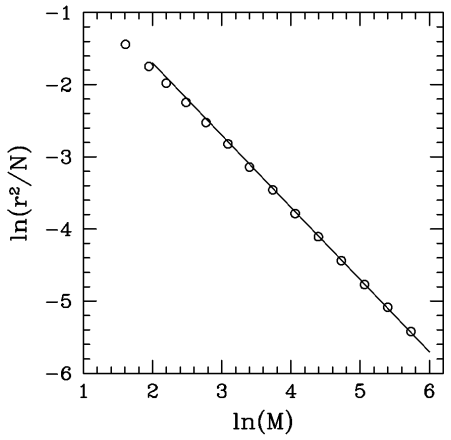

FIG. 1. Logarithmic plot of the scaled squared end-to-end distance as a function of the number of links M. Each point is an average over 1600 randomly linked chains. The solid line represents $r^2/N = 1.5/M$.

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