Knots as Topological Order Parameter for Semi-Flexible Polymers

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Using a combination of the replica-exchange Monte Carlo algorithm and the multicanonical method, we investigate the influence of bending stiffness on the conformational phases of a bead-stick homopolymer model and present the pseudo-phase diagram for the complete range of semi-flexible polymers, from flexible to stiff. Although a simple model, we observe a rich variety of conformational phases, reminiscent of conformations observed for synthetic polymers or biopolymers. Changing the internal bending stiffness, the model exhibits different pseudo phases like bent, hairpin or toroidal. In particular, we find thermodynamically stable knots and transitions into these knotted phases with a clear phase coexistence, but almost no change in the mean total energy.

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Since the first simulation of knotted polymers in 1975 [1], the occurrence and behavior of knots in polymers has been studied in various contexts. Scanning through protein databases has revealed that several proteins form knots [2–4]. In particular, Virnau et al. [5] have reviewed the whole Protein Data Bank (http://www.pdb.org [6]) and identified 36 different proteins forming simple knots, none of which features more than five crossings – somehow evolution tries to avoid knotted proteins [7]. On the other hand, flexible polymers form much more complicated knots, which occur by chance in the swollen [8–10] and in the collapsed phase [10, 11]. Essential for the existence of these two phases is the excluded volume and attraction of the monomers. Already lattice polymer simulations [12, 13] show that models integrating self-avoidance and attraction exhibit a swollen, a globular, and a frozen phase. In this work we go a step ahead and investigate the knottedness of semi-flexible bead-stick polymers. There exists already some works concerning the more complex phase space of polymer models that incorporate bending stiffness [14]. The most comprehensive study uses a model for semi-flexible polymers of bead-spring type with finitely extensible nonlinear elastic (FENE) bonds [15]. By varying the bending stiffness, these models are able to mimic a large class of polymers, exhibiting, for instance, bent, hairpin or toroidal conformations.

Nevertheless, none of the former work considered the knottedness of the polymer over the full bending stiffness range, which we will discuss in this Letter. By measuring the knot type we found pseudo phases with thermodynamically stable knotted polymers. The knot type will be shown to be an ideal topological order parameter to identify the knotting transition and, moreover, the behavior at the transition from an unknotted to a knotted pseudo phase turns out to be surprisingly different from all other pseudo-phase transitions of the bead-stick polymer in that it does not fit into the common classification scheme of first- and second-order phase transitions.

To model a coarse-grained polymer with an adjustable stiffness, we use a modified version of the bead-stick model of Refs. [16–18], which neglects the hydrophobicity of the monomers. The model then consists of \( N \) identical monomers connected by bonds with length one. Non-adjacent monomers interact via the Lennard-Jones potential

\[
E_{\text{LJ}} = 4\epsilon \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right],
\]

where \( r_{ij} \) is the distance between two monomers. The parameters \( \epsilon \) and \( \sigma \) are set to one for the rest of this work, i.e., energies are measured in units of \( \epsilon \) and lengths in units of \( \sigma \). The stiffness is modeled through the cosine potential adopted from the well-known discretized worm-like chain model [19] and defined by

\[
E_{\text{bend}} = \sum_{i=1}^{N-2} (1 - \cos \theta_i),
\]

where \( \theta_i \) represents the angle between adjacent bonds. The complete Hamiltonian is then given by

\[
E = E_{\text{LJ}} + \kappa E_{\text{bend}},
\]

where \( \kappa \) parametrizes the strength of the bending term compared to the Lennard-Jones potential.

Topological barriers between the knotted phases forced us to apply relatively complex Monte Carlo algorithms in order to obtain reliable results. To simulate the system in the complete \((T, \kappa)\)-plane, we used two complementary Monte Carlo algorithms. The first is a combination of the parallel multicanonical method [20, 21] and a one-dimensional replica exchange [22] in the \( \kappa \) direction (PMUCA+RE). The second is a two-dimensional version of the replica-exchange method (2D-RE), which simulates the system in \( T \) and \( \kappa \) directions in parallel. By means of a two-dimensional weighted histogram analysis algorithm [23], we are able to calculate the canonical mean values for every point in the \((T, \kappa)\)-plane within the simulated parameter ranges. To generate well equilibrated results it was necessary to apply quite intricate bridge-end and double-bridging moves that respect the fixed bond-length constraint, besides the common crankshaft, spherical-rotation and pivot moves. The results of both methods, PMUCA+RE and 2D-RE, are in good agreement with each other.
To identify the knotted phases, we measured the knot type of the polymer, which turns out to be an ideal order parameter. In principle, the knot type, denoted by $C_n$, defines which smooth closed curves can be transformed into each other by applying multiple Reidemeister moves.

Practically, this means two knots are not of the same type if one of them cannot be deformed into the other without cutting and rejoining the curve. The integer number $C$ counts the minimal number of crossings for any projection on a plane and the subscript $n$ distinguishes topologically different knots with the same number of crossings. A detailed exposition of mathematical knot theory can be found in Ref. [25]. Of course, an open polymer cannot satisfy the mathematical definition of a knot, unless the termini are closed virtually. In this work we applied a closure which is inspired by tying a real knot. Both termini are connected by a straight line, which is enlarged in both directions to a point far outside the polymer. These new termini are then connected through a point which lies on a line perpendicular to the connecting line of the termini and which is also located far away from the center of mass of the polymer. We have tested our results with different other closures and obtained almost identical results. To calculate $C_n$, we employed a technique described in Ref. [26], which is based on a...
The blue regime, $\Delta_p(-1.1)$ clearly signals the pseudo-phase transition and goes from 1 (unknotted polymer) to 9.0546 (3 knot) only in the case of a transition into a stable knot. As expected, the 28mer (and even more the 42mer [27]) exhibits a richer phase diagram with more complicated knot types, see Fig. 1(b). However, the qualitative behavior at the phase boundaries turned out to be very similar so that we will focus in the following on the 14mer.

The knotting transitions from one structured state to another (e.g., $K_{31} \leftrightarrow D3$) are quite interesting. At first glance, one could assume that they behave first-order-like, similar to other solid-solid-like transitions at low temperatures. However, the microcanonical analysis indicates a second-order-like behavior by a peak in $d\beta_{\text{micro}}(E)/dE$ which is smaller than zero (not shown here). Likewise, the canonical probability distribution $p(E)$ does not exhibit a double-peak structure, see Fig. 3(a). On the other hand, the two-dimensional energy distribution $p(E_{\text{LJ}}, E_{\text{bend}})$ points to a phase coexistence. In Fig. 3(b) one can clearly identify two separate peaks, one corresponding to the knotted phase and the other to the unknotted phase. Surprisingly, both phases have almost identical mean total energy $\langle E \rangle$ at the coexistence point, and there is almost no signal in the total energy and heat capacity at the transition, see Fig. 4. We thus observe no latent heat where the polymer undergoes the transition into the knotted phase. Rather, the Lennard-Jones energy $E_{\text{LJ}}$ and the bending energy $E_{\text{bend}}$ are transformed into each other [28].

This behavior changes if the polymer enters the knotted phase from an unstructured conformation. For example, staying on the transition line between $K_{31} \leftrightarrow D3$ for $N = 14$ and going to higher temperatures, the two peaks in $p(E_{\text{LJ}}, E_{\text{bend}})$ start to merge until they form a single peak at the transition between $AC \leftrightarrow K_{31}$, where the phase coexistence vanishes. This behavior is similar for all other observed knotting transitions.

The reason for the missing knotted phases in Ref. [15] is not rooted in this intricate behavior with “concealed” signals, however, but may rather lie in the choice of the bond length $r_b$ and the minimum of the Lennard-Jones potential $r_{\text{min}}$ which are identical in [15] but different by a factor of 1.22 in this work. We have tested a few parametrizations of bead-spring models and always observed thermodynamically stable knots except for the special parametrizations used in [15]. The observation that the polymer minimizes its total energy in bent conformations by maximizing the number of monomers located in the Lennard-Jones minima of other monomers suggests the following conjecture: if $r_b \approx r_{\text{min}}$ and the bonds are flexible enough, bent conformations are energetically so strongly favored that knotted states become unlikely.

In conclusion, we have investigated the complete stiffness dependent behavior of a semi-flexible bead-stick ho-
FIG. 3. (color online) Energy probability distribution of a 14mer at a point where $\Delta p(-1.1)$ suggests a knotting transition ($\kappa = 3.9$ and $T = 0.0483$). Plot (a) shows the one-dimensional probability distribution $p(E)$. In (b) the energy is split into the two sub-energies, which leads to a double peak in the two-dimensional probability distribution $p(E_{\text{LJ}}, E_{\text{bend}})$. The left peak corresponds to the knotted state K3, and the right one to the bent state D3. The one-dimensional probability distribution is exactly the projection of $p(E_{\text{LJ}}, E_{\text{bend}})$ along the line connecting the two peaks, thus the phase coexistence is perfectly hidden in $p(E)$.

FIG. 4. (color online) Energy $\langle E \rangle$ and heat capacity $C_v$ of a 14mer at $T = 0.0483$ over the complete range of investigated $\kappa$ values. At both knotting transitions, $\kappa = 2.7 : F2 \leftrightarrow K3_1$ and $\kappa = 3.9 : K3_1 \leftrightarrow D3$, there is nearly no shift in the energy and therefore no signal in the heat capacity that is larger than the statistical error.
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