Knots are Generic Stable Phases in Semiflexible Polymers

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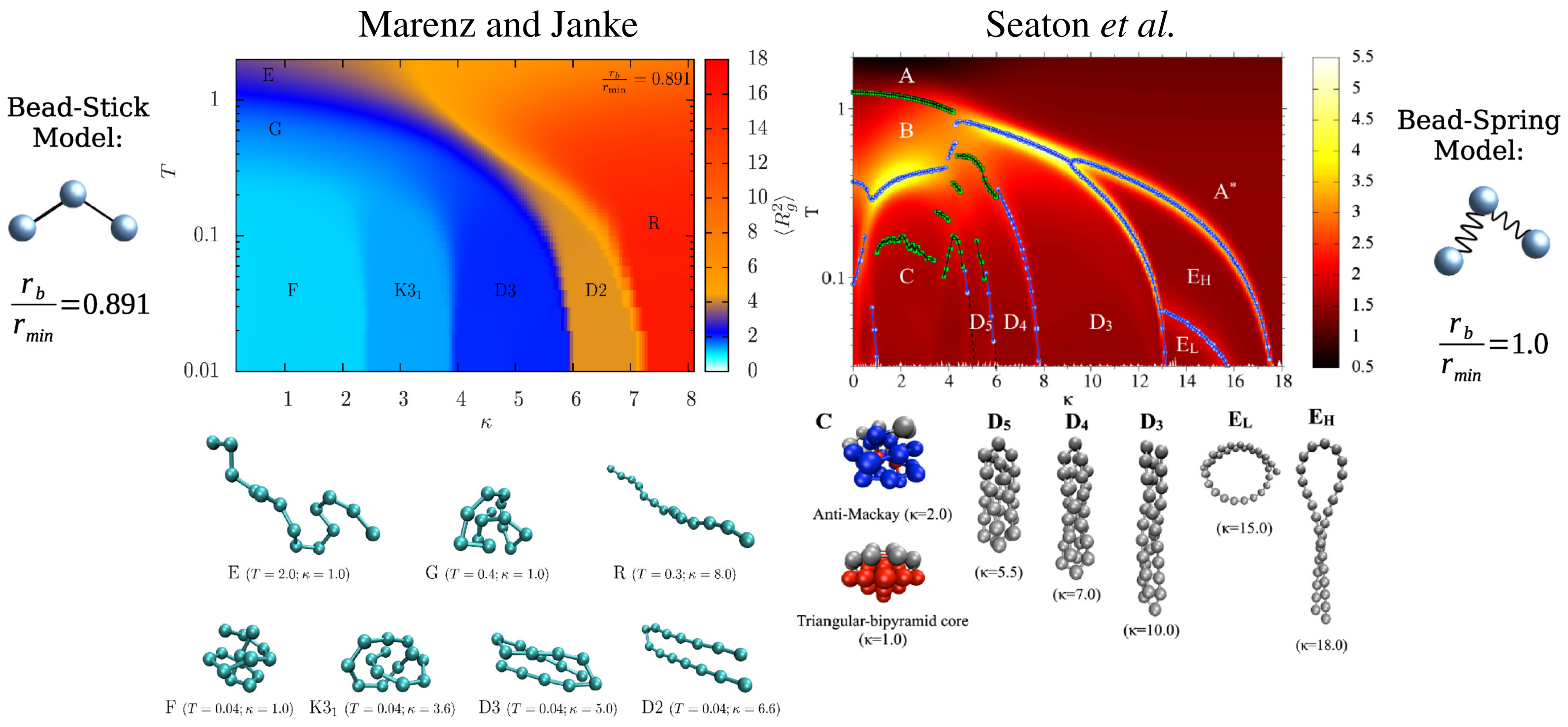
Abstract

While investigations of knots in polymers have lured scientists for decades, the existence of phases characterized by a stable knot of specific type has attracted attention only recently. In this work, we treat two popular models that encompass the complete spectrum of real polymers (flexible to stiff) via extensive replica exchange Monte Carlo simulations, and show that the existence of stable knots in the phase diagram depends only on the ratio r_b/r_{min}, where r_b is the equilibrium bond length and r_{min} is the distance for the strongest nonbonded contacts in an attractive Lennard-Jones (LJ) potential. Our results provide evidence that irrespective of the specific model, bead-stick or bead-spring, if the ratio r_b/r_{min} is outside a small window around unity then one always encounters for semiflexible polymers stable knotted phases at low temperatures.

Introduction

In a previous work [1] from our group, it was reported that along with the various typical conformations, one observes knots as one of the stable phases for a bead-stick semiflexible polymer. This is in contrast to a similar work using a bead-spring polymer by Seaton *et al.* [2], where the presence of knots was not mentioned.



Questions

⇒ Are knots specific to bead-stick polymers ?

⇒ Else, did Seaton *et al.* simply not search for knots ?

⇒ Do the existence of knots in a polymer depend only on the ratio r_b/r_{min} ?

Models

We consider two semiflexible polymer models: (i) bead-stick and (ii) bead-spring. Monomers are considered to be spherical beads with diameter σ, and the nonbonded interaction energy is given as

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

is the standard LJ potential with a minimum at $r_{\mathrm{min}} = 2^{1/6}\sigma$. In the bead-stick model the bonds are rigid with fixed length r_b. In the bead-spring model the bond energy is given by the standard finitely extensible non-linear elastic (FENE) potential

$$E_{\mathrm{FENE}} = -\frac{K}{2}R^2 \sum_{i=1}^{N-1} \ln\left[1 - \left(\frac{r_{ii+1} - r_b}{R}\right)^2\right], \quad (2)$$

where r_b is the equilibrium bond distance, and we set $R = 0.3$ and $K = 40$.
In both models the bending energy penalty is given by

$$E_{\mathrm{bend}} = \kappa \sum_{i=1}^{N-2} (1 - \cos\theta_i), \quad (3)$$

where θ_i is the angle between consecutive bonds and κ is the bending stiffness of the polymer. We perform simulations of both models for a range of r_b/r_{min} values.

Simulation Details and Analyses

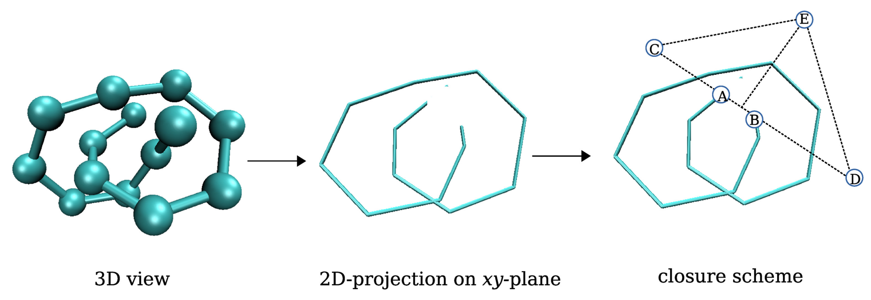
We use the two-dimensional replica exchange (2D-RE) simulations [1, 3] by splitting the system Hamiltonian as

$$H = E_0 + \kappa E_1, \quad (4)$$

where E_0 is the base energy defined in Eq. (1) and (if any) in Eq. (2), and E_1 is the energy per κ in Eq. (3). In the simulation parameter space (T, κ), the exchange probability is given as $p(\mu \leftrightarrow \nu) = \min[1, \exp(\Delta\beta\Delta E_0 + \Delta(\beta\kappa)\Delta E_1)]$, where $\beta = 1/k_{\mathrm{B}}T$. The 2D version of the weighted histogram analysis method [4] is used for generating appropriate canonical estimates.

Knot Identification in Polymer

First, a closure scheme is applied on the open polymer as following:



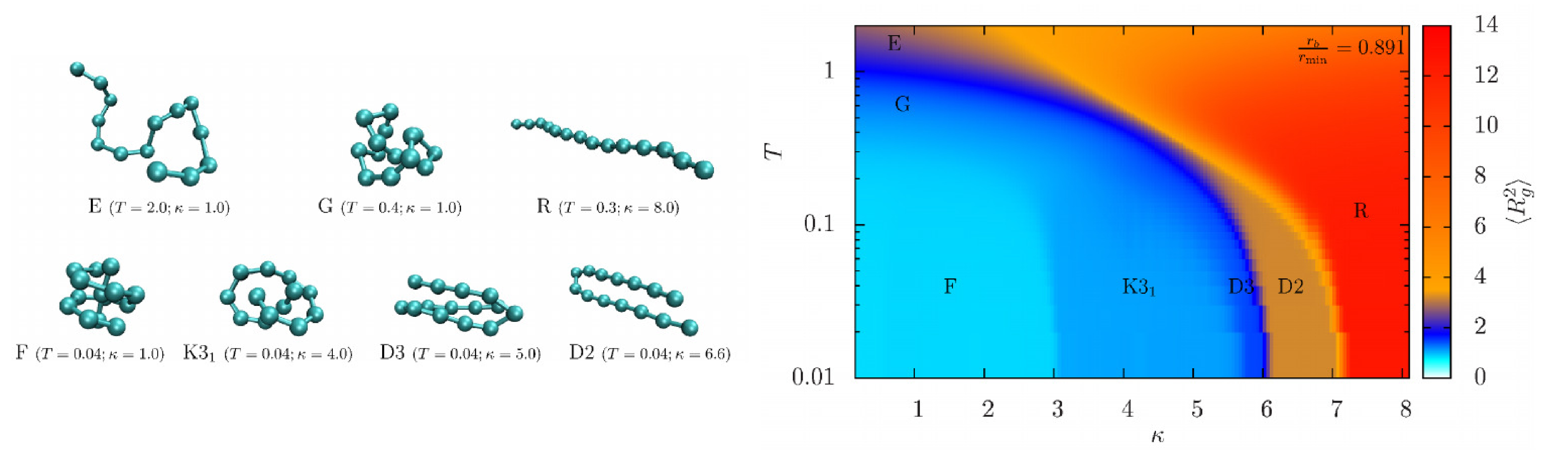
Then, knots are identified using a variant [5] of the corresponding Alexander polynomial $\Delta(t)$ as

$$\Delta_p(t) = |\Delta(t) \times \Delta(1/t)|, \quad (5)$$

evaluated at $t = -1.1$. This defines the invariant knot parameter $D \equiv \Delta_p(-1.1)$.

Results [6]

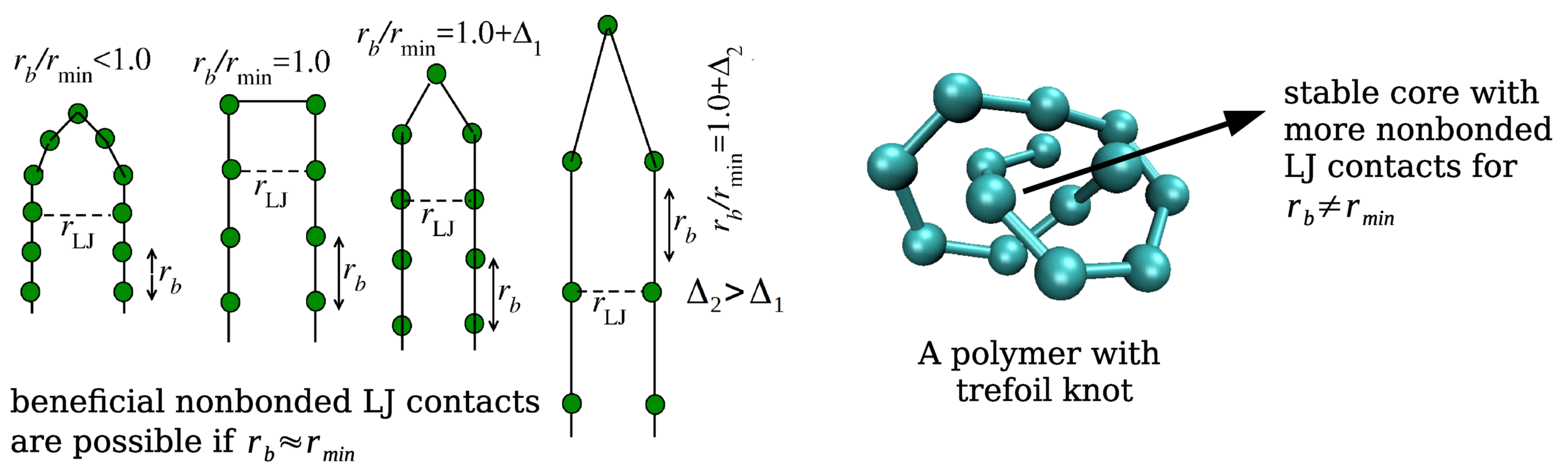
Bead-spring polymer of length $N = 14$ with $r_b/r_{\mathrm{min}} = 0.891$



⟹ Stable knots do exist for bead-spring polymer as well. For $N = 14$, they are trefoil knots (3_1).

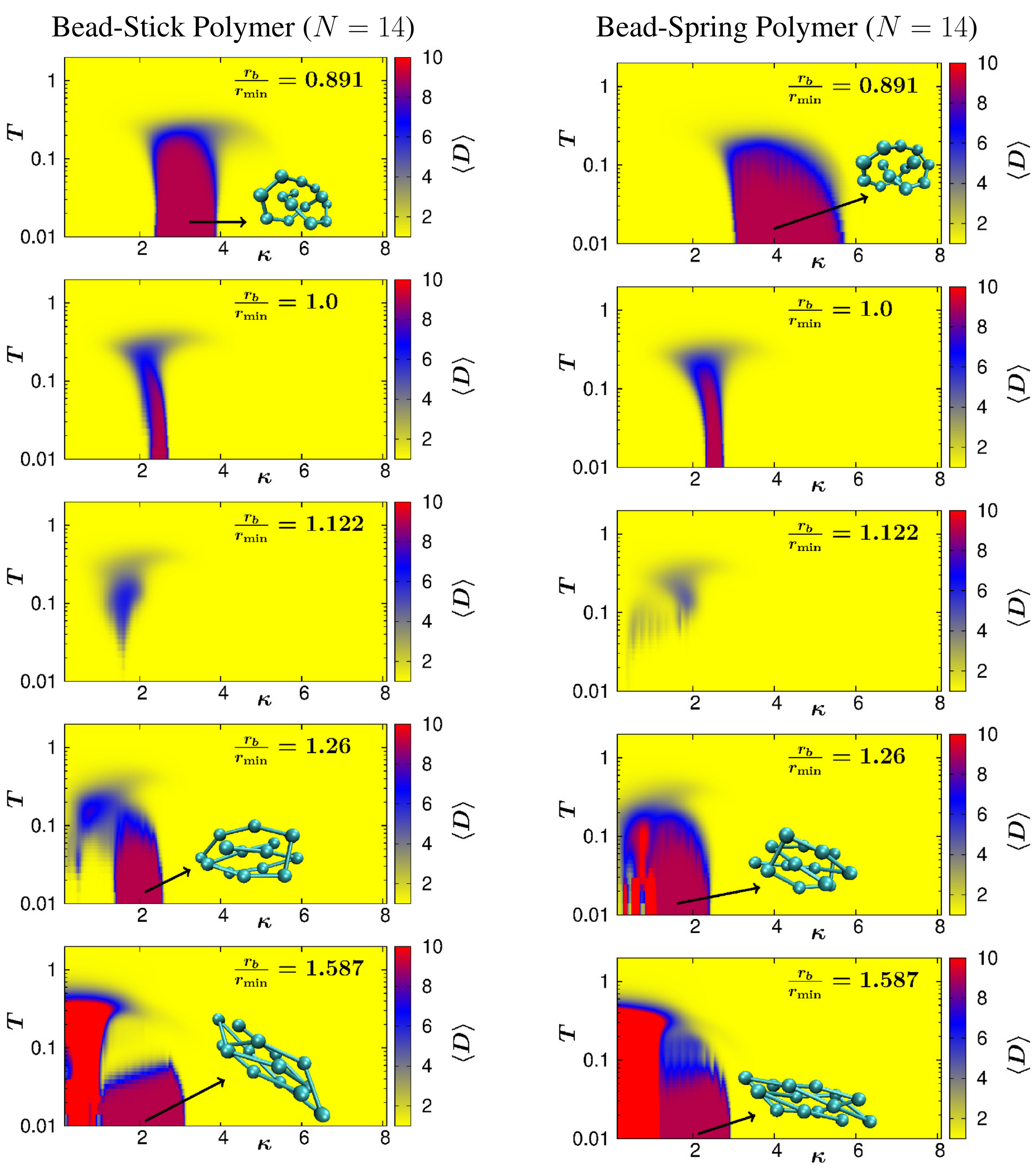
⟹ Possibly, then the ratio r_b/r_{min} is the key to stable knots.

Stability of bent vs knotted conformation



Speculation: Knots are more likely to be stable conformations for semiflexible polymers, if $r_b \neq r_{\mathrm{min}}$.

Existence of knots for varying r_b/r_{min} ($\langle D \rangle = 9.05463 \triangleq 3_1$ knot)



- Indeed knots do exist for both models if $r_b \neq r_{\mathrm{min}}$.
- So, Seaton *et al.* would not have observed knots simply because for their model $r_b = r_{\mathrm{min}}$.
- This fact has been verified from simulation results of our bead-spring model with parameters analogous to their model.

Conclusions

♠ We have investigated the existence of knotted phases in semiflexible polymers via 2D-RE simulations of a bead stick and a bead spring model.

♠ From simple qualitative arguments, we understood that if the ratio r_b/r_{min} is not close to unity, then one always observes stable knots in semiflexible polymers, irrespective of the model. Our simulation results support this.

♠ From this point of view, it would also be worth exploring the sequence dependent formation of knotted structures in semiflexible heteropolymer, a paradigm for proteins.

References

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