

EFFECTS OF STIFFNESS ON SHORT, SEMIFLEXIBLE HOMOPOLYMER CHAINS

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Conformational and transition behavior of finite, semiflexible homopolymers is studied using an extension of the Wang–Landau algorithm. Generation of a flat distribution in the sampling parameters energy and stiffness allows for efficient investigation of transitions between various conformational phases. Of particular importance is the ability to predict behavior for a given stiffness value, where three classes of minimum energy conformations are expected: Solid-globular, rod-like and toroidal. We present first results highlighting the behavior of a single $N = 20$ length chain.

Keywords: Homopolymer; Wang–Landau; flexible; semiflexible; conformation.

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1. Introduction

Semiflexible homopolymer models represent a class of polymer chains whose local stiffness (or flexibility) depends on the angle between two bond vectors, thus affecting the persistence length of the chain. This strongly influences the conformational and thermodynamic behavior for a range of different stiffness values.¹ Variation in stiffness in semiflexible homopolymers has been studied using a number of different models and simulation techniques,^{2–9} often motivated by biological

applications, e.g. DNA and RNA are considered to be relatively stiff chains with measurable persistence length. Hence, many computational and theoretical studies utilize semiflexible homopolymer models to understand the general properties of biopolymers.

Previous work on coarse-grained semiflexible homopolymers has been focused on exploring a broad range of stiffness values for a few chain lengths in the bond-fluctuation model.^{4,5,7} In these studies, stiffness is regulated by an overall strength parameter, leading to a wide variety of conformations and transitions when varied. Three principle classes of conformations are identified: Solid-globular, rod-like and toroidal. Sub-categories of these states have also been defined, e.g. disk-like globules and racket configurations, noting these sub-categories generally fit within the bounds of the three principal classes of conformations. Although these studies have done much for the categorization of behavior in semiflexible systems, modern sampling techniques aimed at elucidating low temperature crystallization effects and providing more precise estimations of conformational boundaries have not been applied.

Recent studies of fully-flexible homopolymers have produced a complete description of thermodynamic and conformational behavior,^{10–14} illuminating crystalline structures and low temperature solid–solid transitions previously overlooked by the majority of polymer studies. Utilizing sophisticated applications of generalized ensemble techniques, these studies afford rich sampling of previously inaccessible regions of conformational space and estimation of thermodynamic quantities at nearly all temperatures. It has been shown that a near one-to-one correlation exists between crystalline states of fully-flexible homopolymers and those of classical clusters.^{15–17} Such packing considerations have yet to be fully explored in understanding low-temperature behavior in semiflexible systems. With the current knowledge of flexible-homopolymers as defined by cluster behavior, it is only natural to apply this understanding to the study of semiflexible systems.

In this study, a variant of the Wang–Landau algorithm is used to explore the dependence of thermodynamic behavior in semiflexible homopolymers as it relates to stiffness and temperature. By flattening the distribution with respect to system energy and the stiffness parameter, the resulting two-dimensional density of states can be used to analyze thermodynamic quantities, and thus the transition behavior as a function of multiple parameters. Results of these simulations are presented here, focusing on a single $N = 20$ length chain.

2. Model and Methods

A polymer chain is a linear sequence of repeating units, e.g. proteins (or peptides) consist of repeating amino acids. An effective approach for studying very general properties of polymer chains is to use coarse-grained homopolymers, where each unit in the sequence is replaced with a single spherical monomer with generalized interactions. In this study, a chain of N identical monomers is defined in continuous space, with each monomer having bonded, nonbonded and bond-angle interactions.

The Hamiltonian is given by

$$\mathcal{H} = J_L \sum_{i=1}^{N-1} U^{\text{Bond}}(l_i) + J_A \sum_{i=1}^{N-2} U^{\text{Angle}}(\theta_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N U^{\text{NB}}(r_{ij}), \quad (1)$$

where $U^{\text{Bond}}(l_i) = -0.5kR_o^2 \ln[1 - (l_i/R_o)^2]$ is a FENE^{18,19} potential ($R_o = 1.2$, $k = 2$) representing chemical bonds of length l_i between two neighboring monomers along the chain, $U^{\text{Angle}}(\theta_i) = (1 - \cos \theta_i)$ represents stiffness (or flexibility) measured by the angle θ_i between two adjacent bonds, and $U^{\text{NB}}(r_{ij}) = \epsilon[(\sigma/r_{ij})^{12} - 2(\sigma/r_{ij})^6]$ represents a nonbonded, van der Waals-like, interaction ($\epsilon = 1$, $\sigma = 2^{-1/6}$) between all nonbonded monomers separated by a distance r_{ij} .

Our choice of simulation method is the Wang–Landau algorithm, an iterative procedure for generating the density of states (algorithmic details can be found elsewhere^{20–23}). In order to study thermodynamic properties of our homopolymer model with varying stiffness, we apply two-dimensional Wang–Landau sampling in energy E and the stiffness parameter J_A . The primary output of the Wang–Landau algorithm is the density of states $g(E, J_A)$, which can in turn be used to estimate the partition function, and subsequently all thermodynamic quantities. Due to the two-dimensional nature of the simulations, thermodynamic quantities are calculated as functions of temperature T and stiffness J_A , such as average energy $\langle E(J_A, T) \rangle$ and specific heat $C_V(J_A, T)$. Resolutions for sampling quantities are $dE = 0.1$ and $dJ_A = 0.1$. Multiple density of states functions are generated from independent simulations and then averaged before calculating thermodynamic quantities.

The energy of the system is sampled using a standard move set of single monomer displacement, reptation, and end cut-join moves, while the stiffness is sampled using random shifts in J_A . The transition probability of accepting a trial move

$$p(J_{A1}, E_1 \rightarrow J_{A2}, E_2) = \min[(g(J_{A1}, E_1)/g(J_{A2}, E_2)), 1]. \quad (2)$$

This move set has been found to be efficient for small chains, but will need to be optimized for larger chains in order to handle the many unique conformations spanning a broad range of stiffness values.¹³

3. Expectations of Varying Stiffness

A schematic of the expected conformational dependence of semiflexible homopolymers on temperature T and stiffness J_A is presented in Fig. 1, where solid lines represent the boundaries between various conformations, and the axes represent general scales of J_A and T . This depiction relies heavily on a number of semiflexible homopolymer studies simulating the bond-fluctuation model,^{4,5,7} along with studies employing other models.^{3,6,9} For low temperatures and low stiffness, a solid-globular region exists. Increasing temperature for zero stiffness within the solid-globular region illuminates the behavior of fully-flexible homopolymers, where a liquid–solid and a coil-globule transition occur for finite chains. Higher-order geometries similar to the flexible case are expected to exist for a range of low J_A values within the

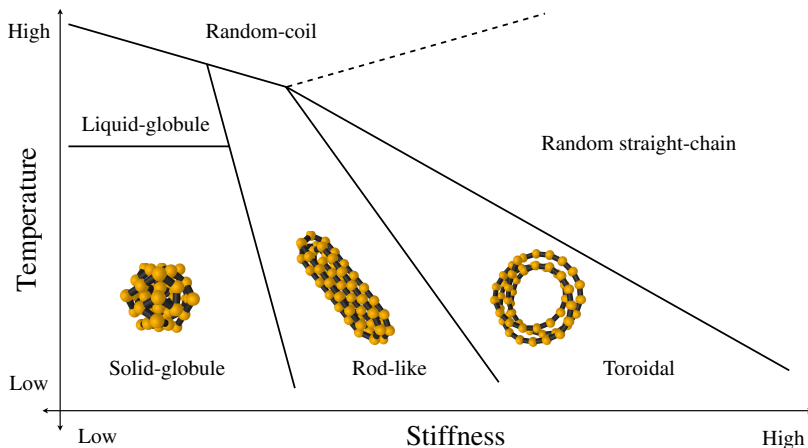


Fig. 1. (Color online) Schematic diagram of conformational behavior as it is related to stiffness J_A and temperature T in semiflexible homopolymers. Three classes of minimum energy conformations occur at low temperatures: solid-globular, rod-like and toroidal. In the case of low stiffness, behavior is similar to flexible homopolymers, which undergo liquid–solid and coil-globule transitions as temperature is increased. For higher stiffness values, liquid-globular conformations are suppressed, giving way to order–disorder transitions from rod-like to random-coil conformations. Conformations come from preliminary simulations of an $N = 55$ length chain.

solid-globular region. The liquid region lies at higher temperatures and still holds many of the same properties found in the flexible case. It is expected to disappear as stiffness increases, giving way to abrupt transformations from random coils and straight chains, to more ordered states such as rod-like and toroidal configurations. At low temperatures, both the rod-like and the toroidal regions offer highly ordered states. First-order-like transitions reveal that for stiffness values producing rod-like and toroidal structures, transitions become of the order–disorder type.⁷

Boundaries between conformational classifications are not always so well drawn, and the sub-structure within such boundaries can vary greatly for large N . The trends of most studies of semiflexible homopolymers have been to explore rod-like and toroidal conformations for larger N , where more biological relevance can be drawn. Rods and toroids are particularly abundant for long chains, with some cases of rod-like bundles folding onto themselves to create toroidal-like conformations.⁷ However, it must be stated that in finite systems, the solid-globular conformation is as important as the rod-like and toroidal conformations. Furthermore, the 20 monomer chain is not long enough to sustain toroidal conformations, and although toroids are not discussed in the following results section, toroidal conformations do exist for chain lengths slightly larger than $N = 20$.

It should be noted that these transitions are generally not phase transitions in the traditional sense due to the finite nature of this system. Recently, we have introduced a classification scheme for transitions in finite systems¹⁴ by means of a micro-canonical inflection-point analysis.^{24,25}

4. Results: Specific Heat $N = 20$

Figure 2 represents the specific heat profile $C_V/N(J_A, T)$ for an $N = 20$ length chain; $C_V/N(J_A, T)$ is color-coded using the scale to the right of the figure. Comparing C_V/N with the previous depiction in Fig. 1 shows that our results are aligned with the expectations provided by previous studies. Conformational regions are inferred by changes in color, i.e. maxima representing transition lines are indicated by the lightest color, while stable conformational regions are represented by dark colored regions. A liquid–solid transition spanning $0 \leq J_A < 4.5$ is indicated between $0.25 \leq T < 0.45$. Increasing temperature from this structure shows a liquid region, and then a random-coil region with an associated coil-globule transition at $T \approx 1.2$ (not shown for clarity of low T behavior). Both the liquid–solid and the coil-globule transitions dissipate for $J_A > 4.5$, giving way to order–disorder transitions from random straight-chain conformations to crystalline states. These order–disorder

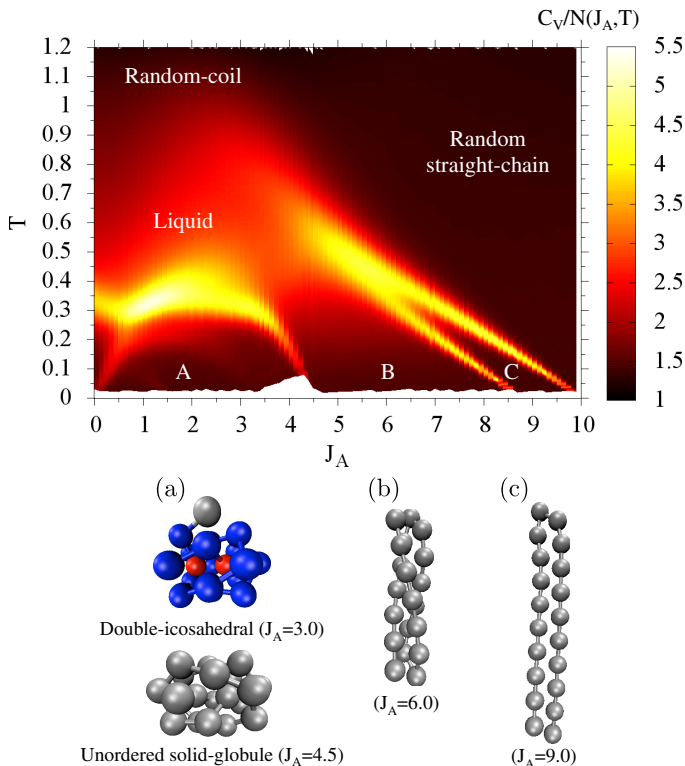


Fig. 2. (Color online) Specific heat $C_V(T, J_A)/N$ for $N = 20$ as a function of stiffness J_A and temperature T . The profile of $C_V(T, J_A)/N$ is color-coded. Bright colors (light on gray scale) are maxima representing conformational transitions, or boundaries between conformational regions. Dark colors represent stable regions of conformational behavior. Conformations are given for specific stiffness values representing a typical state in the three major minimum energy conformations: (a) solid-globular, (b) three segment rod-like and (c) two segment rod-like.

transitions are indicated by the large (light color) peaks found between $4.5 \leq J_A < 10.0$, noting that these peaks branch near $J_A \approx 6.5$. The remainder of this section will focus on crystalline states at various J_A values, and how these conformations change as T increases.

Three low-temperature conformational regions are identified within C_V/N based on minimum energy conformations, solid-globule $0 \leq J_A < 4.5$ and rod-like bundles $4.5 \leq J_A < 10.0$, where $J_A \approx 8.6$ represents the boundary between rod-like bundles of three and two segments. Toroidal conformations are not found for the $N = 20$ length, but are found in test simulations for larger sizes, e.g. $N = 30$. The solid-globule region encompasses a large part of the overall conformational behavior presented, and preliminary results show that conformations tend to exhibit icosahedral behavior found in studies of flexible homopolymers.^{10–14} We do not rule out the existence of other geometries, particularly for larger N . Within the low-temperature boundaries of the solid-globule region $0.0 \leq J_A < 4.5$ in Fig. 2, very subtle signals of sub structure can be seen in the specific heat, implying that conformational behavior may vary from only icosahedral ordering. Structural quantities designed specifically to look at crystalline order need to be employed in order to track such variation. Additionally, the liquid–solid transition is quite complicated in this region, showing two tails extending towards zero temperature between both $0.0 \leq J_A \leq 1.0$ and $3.5 \leq J_A < 4.5$, indicating possible solid–solid transitions. An equally important feature is the dissipation of the liquid–solid transition as J_A increases, giving way to an order–disorder transition from random-coils to rod-like conformations at $J_A \approx 4.5$.

The rod-like region $4.5 \leq J_A < 10.0$ at low T provides less varying conformational behavior compared to the solid-globule region. Rod-like conformations of three segments $4.5 \leq J_A < 8.6$ encompass a large portion of the conformational space with little variation within its boundaries. The rod-like conformations of two segments $8.6 \leq J_A < 10.0$ exist within the fork between random-coils and the three segment rods. This fork should span a larger portion of the stiffness values as N increases, and is also expected to include toroidal configurations. This is not to say that rod-like bundles with two segments will disappear completely, as test simulations up to $N = 30$ have shown a more complicated mix of multi-segment rods and varying toroidal conformations (unfortunately, complete thermodynamics are unavailable at this time). Of equal interest is the existence of order–disorder transitions from random-coils to rod-like conformations. For $6.5 \leq J_A \leq 8.5$, there are even two larger first-order like transitions occurring at low T when J_A is fixed.

5. Conclusions

Conformational behavior for a $N = 20$ length semiflexible homopolymer chain has been investigated as it depends on temperature and stiffness. Three classes of minimum energy conformation exist for the $N = 20$ length chain: solid-globular, rod-like

with three segments, and rod-like with two segments. Toroidal conformations do not exist for $N = 20$, but will appear for larger chain lengths.

These results represent the first steps toward studies aimed at uncovering behavior for all stiffness values in larger systems. Some challenges remain, namely optimizing our methods such that a single simulation is required to simulate properties at all stiffness values, regardless of chain length.

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