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Polymer-Based Accurate Positioning: An Exact Worm-like-Chain Study

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ABSTRACT: Precise positioning of molecular objects from one location to another is important for nanomanipulation and is also involved in molecular motors. Here, we study single-polymer-based positioning on the basis of the exact solution to the realistic three-dimensional worm-like-chain (WLC) model. The results suggest the possibility of a surprisingly accurate flyfishing-like positioning in which tilting one end of a flexible short polymer enables positioning of the other diffusing end to a distant location within an error of ~ 1 nm. This offers a new mechanism for designing molecular positioning devices. The flyfishing effect (and reverse process) likely plays a role in biological molecular motors and may be used to improve speed of artificial counterparts. To facilitate these applications, a new force-extension formula is obtained from the exact WLC solution. This formula has an improved accuracy over the widely used Marko-Siggia formula for stretched polymers and is valid for compressed polymers too. The new formula is useful in analysis of single-molecule



stretching experiments and in estimating intramolecular forces of molecular motors, especially those involving both stretched and compressed polymer components.

1. INTRODUCTION

Precise positioning of molecular objects by rationally designed molecular devices¹⁻⁴ is emerging as a new method for nanomanipulation. Notably, a recent study¹ by Funke and Dietz finds that position resolution near Bohr radius (~ 0.04 nm) is feasible using a DNA origami device. The conventional tools like atomic force microscopy (AFM), optical or magnetic tweezers, and scanning tunneling microscopy are all intrusive methods as they involve microscale tips or beads. The molecular device-based method is nonintrusive and has found applications in calibrating AFM,³ engineering nanocavity emission,⁴ and delivering of molecules.² The positioning devices reported to date are all rather rigid structures made of multiple molecular components or even bigger DNA origami. This paper reports an exact worm-like-chain (WLC) study suggesting the possibility of fairly accurate remote positioning (within 1 nm resolution) by a single short and rather soft polymer.

Besides, soft oligomer-based molecular relay from one location to another is used by track-walking bipedal molecular motors from biology^{5,6} and nanotechnology.⁷⁻¹⁰ From the perspective of first passage time,^{11–14} a better positioning accuracy results in a higher rate for site-specific binding and hence a higher speed for a motor. Intramolecular force of the relaying oligomer is important for uphill processes within a motor or in a crowded environment. On the basis of the exact WLC study, we also obtain an empirical formula for the

intramolecular force of a polymer versus its end-to-end distance that applies to stretched as well as compressed polymers. This formula is not available before but is important for studying molecular motors¹⁵⁻¹⁷ that involve stretched and compressed states of the same polymer component.

2. RESULTS AND DISCUSSION

2.1. Single-Polymer "Flyfishing" by a Local Alignment at One End. A prominent example of polymer-based positioning is found in a bipedal biological motor called kinesin, which is capable of hand-over-hand walking toward the plus end of a linear cytoskeletal track (microtubule). When this motor has one leg bound to the track and the other leg diffusing, fuel binding to the track-bound leg triggers a zippering-like alignment⁵ of the interleg soft peptide linker at this leg toward the track's plus end. This zippering effect throws forward the diffusing leg at the linker's other end toward the next binding site for the walker's hand-over-hand walking. Such a polymer "zippering" had been suggested⁵ to provide a forward bias for kinesin's leg binding. Whether this polymer effect really contributes to directionality of a chemical motor like kinesin is questioned¹⁸ later, but the effect certainly improves¹⁹ speed and

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Figure 1. Mechanics of a worm-like-chain polymer with its one end located at the origin (x = 0, y = 0, z = 0) and the other end diffusing to reach a location on the *z* axis. The probability distribution of the free end along the *z* axis, Q(z) = Q(0, 0, z), and the free energy F(z) = F(0, 0, z), the intrachain force f(z) = F'(z) derived are shown. The results are for two scenarios: the end at the origin either has free orientation or is aligned at a fixed angle θ with respect to the *z* direction. The polymer has a contour length $l_c = 10$ nm and a persistence length $l_p = 4$ nm.

power output of motors like kinesin. In this paper, we study the zippering-like effect not for directional rectification in a motor but as a potentially general mechanism of polymer-based positioning of a molecular agent (e.g., the diffusing leg of kinesin biped) at one end of the polymer by controlling the position and orientation of the other end. This study will be focused on the positioning accuracy for its importance for molecular position/ delivery in wider applications beyond molecular motors. The

positioning accuracy also affects the leg binding rate and thereby speed of bipedal motors like kinesin.

The polymer-based positioning is a fine interplay among the conformational entropy and bending energy of the polymer. Therefore, we prefer for this study a general and rigorous polymer theory that counts the conformational entropy and bending energy accurately and allows the study of positioning mechanisms in a generic, conceptually clear way. Such a general framework will be particularly useful in providing guidelines for



Figure 2. Most probable end location and the fwhm probability vs the angle of alignment at the other end for the polymer of Figure 1. The results (symbols) are extracted from the Q(z) = Q(0, 0, z) distributions in Figure 1.



Figure 3. Dependence of the end probability, free energy and intrachain force on persistence length for WLC polymers as for Figure 1 for the alignment angle $\theta = 0$. The polymers have the same contour length $l_c = 10$ nm but different persistence length (l_p) . The exact solutions are shown by symbols with the lines to guide eyes.

developing molecular positioning devices from scratch. Previous theoretical studies of device/motor-relevant polymer effects focus on specific molecular systems^{14,20–27} (mostly biological motors and associated peptide systems) or are based on approximate solution of polymer mechanics.^{28–30} A good candidate for developing the general framework is the WLC model for semiflexible polymers. On the one hand, the exact solutions to the WLC model from the path integral scheme^{31,32} and the green function scheme^{33–38} become available recently to allow a precise counting of the conformational entropy, which remains difficult for other methods like atomic simulations. The

new solutions are already applied to study polymer brush^{36,38} and diblock copolymer melt.³⁷ On the other hand, the WLC model has only two parameters: contour length as a measure of the maximum stretch of a polymer and persistence length as a measure of the polymer's bending rigidity. Both parameters can be extracted by fitting experimental data, potentially making the WLC model a realistic working model for any polymeric building blocks of molecular devices.

In this study, we extend the method in refs 31 and 34 for solving the WLC model in two dimensions to three dimensions (see the Methods section) and then apply the exact solution to



Figure 4. Most probable end location and the fwhm probability vs persistence length for WLC polymers. The results for the scenarios of the end at the origin having free orientation or being aligned parallel to the *z* axis ($\theta = 0$) are shown. The polymers have the same contour length ($l_c = 10$ nm) but different persistence length (l_p). The results (symbols) are extracted from the Q(z) distributions as in Figure 1. In the left panel, a fitting is also shown for the results for one scenario (the nonlinear part for $l_p > 2.5$ nm is fitted by a polynomial function for spline interpolation, and the part for lower l_p is fitted by a linear line).

study the zippering-like polymer-based positioning. Figure 1 presents the probability distribution of one free end of a threedimensional WLC polymer when the other end is located at the origin of the *z* axis and has different orientations for its tangent: the end at the origin either has free orientation or is aligned toward an angle $\theta = 90$, 45, 0° with reference to the positive *z* direction to mimic the zippering effect (following a treatment of Spakowitz and Wang in ref 34). For the free orientation and the vertical orientation ($\theta = 90^\circ$), the free end has two symmetric most probable positions at a positive and a negative *z* value. When the fixed end is tilted from 90 to 45° and further 0°, the probability peak at negative *z* values virtually vanishes but the peak at the positive *z* value rises.

Distinct patterns are observed by examining the extent of accuracy by which aligning the end can position the other free end to a certain location. First, the full width at half maximum (fwhm) of the probability peaks becomes as small as ~ 2 nm for the zero-degree alignment (Figure 2). This suggests the possibility of positioning the free end to the most probable location (z_c) within an error of ~1 nm for a polymer with a contour length of 10 nm. Second, such a precise site-selective positioning may occur for rather flexible polymers with $l_p/l_c =$ 0.3–0.4, not necessarily require a rigid molecular rod $(l_p/l_c > 1)$. Indeed, the probability for locations around z_c peaks at intermediate values of persistence length (l_p) for a certain contour length (l_c) (Figure 3). In addition, the fwhm becomes largely flat when l_p/l_c changes from 0.3 to 1 (Figure 4). Hence, a flexible polymer of $l_p/l_c \approx 0.3-0.4$ already accesses the regime of precise positioning. Third, the precise positioning can be modulated by adjusting the end alignment and polymer rigidity. Changing the end alignment from 90° to 0° shrinks the fwhm of the probability peaks monotonically (Figure 2) and hence improves the positioning accuracy. The most probable location of positioning (z_c) may be modulated too by the alignment (Figure 2) or by changing the polymer rigidity (Figure 4), which may be done by adjusting the solution conditions like ion concentrations, pH values, temperature, and so forth.

Hence, aligning a flexible polymer of $l_p/l_c = 0.3-0.4$ and $l_c = 10$ nm at one end positions the other free end to a most probable position of $z_c \approx 8$ nm within an error of ~ 1 nm along the path parallel to the alignment. Such a surprisingly precise positioning to a unique, remote location (relative to the length of the polymer) is achieved by controlling the flexible polymer at one end, essentially resembling the art of flyfishing but at molecular level. The speed of a bipedal nanomotor is largely decided by the position-selective binding of its legs, which is in turn affected by

the mechanics of the interleg polymer linker. Fine-tuning a nanomotor into the regime of molecular "flyfishing" may improve the motor's speed by accelerating forward binding of its legs: from the free or vertical orientation to zero-degree orientation, the fwhm drops by a factor of ~ 2 (Figure 2) and two most probable positions merge into one. This amounts to a drop of a factor of ~ 4 for the search volume of a diffusing leg at the linker's free end. A rough estimation for the first passage time^{11–14} suggests more than twofold increase in the leg's forward binding rate by the flyfishing. The single-polymer flyfishing likely plays a role in biological nanomotors. This is consistent with the observation of zippering in biomotor kinesin, which is the smallest bipedal motor found in biology but has a rather high speed³⁹ of a few micrometers per second.

2.2. Reverse Detachment by Intrachain Force and a New Force-Extension Formula. If the polymer's free end is captured at the most probable location, for example, via a binding agent there or equivalently an attractive binding potential, the polymer's both ends are bound and the polymer enters the state with the lowest free energy and the lowest intrachain force (Figure 1, bottom panels). When the orientation control at the previously fixed end is removed, both ends remain to be fixed in location but become free for orientation. Then, the polymer enters a state with elevated free energy and higher intrapolymer force (Figure 1, top panels). Similar intrachain forces occur in the interleg linkers of bipedal biomotors in a two-leg bound state on their tracks and have been suggested to be a cause 24,40,41 for leg dissociation in biomotors (i.e., reverse process of the flyfishing-enabled leg binding). The leg dissociation induced purely by an intrachain force in the interleg polymer linker has also been successfully implemented in artificial DNA bipedal nanomotor¹⁵⁻¹⁷ not only for a stretched linker but also for a compressed one. However, the widely used force-extension formula for polymers, including the Marko–Siggia formula and later improvements,⁴² apply only to stretched polymers which have an end-to-end distance larger than the thermodynamically most probable extension. To facilitate molecular motor studies, we use the exact solution to three-dimension WLC polymers to produce an empirical forceextension formula that is conveniently usable for both stretched and compressed polymers.

The intrachain force of a polymer depends on the end-to-end distance as well as the polymer's persistence length and contour length. We obtain an analytical formula capturing these dependencies by fitting the force-extension results from the exact WLC solution for $0 \le z < l_c$



Figure 5. New approximate formula for the force–extension relation of WLC polymers. The force–extension relation from the exact solutions in three dimensions for a $l_c = 10$ nm polymer in comparison with the predictions by the new formula (eq 1) and the Marko–Siggia formula are shown. Both ends of the polymer have free orientation.

$$\frac{f(z)}{k_{\rm B}T} = \frac{\beta}{l_{\rm c}} \left[\frac{z}{l_{\rm c}} + \frac{1}{4(1 - z/l_{\rm c})^2} - \frac{1}{4} e^{(5.1/\beta^{0.3}) \times (z/l_{\rm c})} \right] + \frac{1}{l_{\rm c}} \frac{1}{e^{0.94\beta}} \left[52.4 \times \left(\frac{z}{l_{\rm c}}\right)^2 - 35.8 \right] \times \left[1 - e^{(10/\beta) \times (z/l_{\rm c})} \right]$$
(1)

This new formula recovers the empirical Marko–Siggia formula, ${}^{43}\frac{f(z)}{k_{\rm B}T} = \frac{\beta}{l_{\rm c}} \left(\frac{z}{l_{\rm c}} + \frac{1}{4(1-z/l_{\rm c})^2} - \frac{1}{4}\right)$, at the limit $\beta = l_{\rm c}/l_{\rm p}$ $\rightarrow \infty$, which corresponds to soft or long polymers. At this limit, the second term of eq 1 vanishes and the first term decays to the Marko–Siggia formula. For short chains with small β values, namely, rod-like polymers near the other limit $\beta = l_{\rm c}/l_{\rm p} \rightarrow 0$, the

new formula captures the exact WLC solution better than the Marko–Siggia formula for stretched polymers (Figure 5, positive values for the intrachain force) and also captures the exact WLC solution for compressed polymers (Figure 5, negative values for intrachain force). At the limit $\beta = l_c/l_p \rightarrow 0$, the first term of eq 1 vanishes as it is proportional to β . This implies a dropping importance of the entropy effect for increasingly more rigid polymers, as the entropy effect is reflected in the Marko–Siggia formula. The second term,

n a m e ly,
$$\frac{1}{l_c e^{0.94\beta}} \left[52.4 \times \left(\frac{z}{l_c}\right)^2 - 35.8 \right] \times [1 - e^{(10/\beta) \times (z/l_c)}],$$

yields a force that changes its sign when the end-to-end extension drops beyond a threshold (approximately $z/l_c \approx 0.83$). This is a typical behavior for rigid rods under a compressing or stretching force. As can be seen clearly in Figure 5, the rod-like behavior and the entropy-dominated behavior are both captured by the exact WLC result as well as by eq 1.

Being valid for both long and short polymers, the new forceextension formula of eq 1 is useful not only for nanomotor studies but also for interpreting single-molecule mechanical experiments, which had motivated Marko-Siggia formula. The formula applies not only to stretched polymers but also to compressed polymers that have an end-to-end distance smaller than the most probable extension.

For a polymer of a certain contour length, changing its end-toend distance and persistence length switches the polymer between the stretched and compressed regimes, resulting in different directions and magnitudes of the intrachain force. Quantitative details of these patterns from the exact solution are well captured by the new formula (Figures 5, and 3, lowest panels). The new force—extension formula (eq 1) also yields the most probable end-to-end distance, which occurs at zero intrachain force and matches the exact WLC result (Figure 4, left panel).

3. CONCLUSIONS

In summary, a precise, flyfishing-like control is possible in which tilting one end of a flexible polymer enables positioning of the other diffusing end to a remote location within an error of ~ 1 nm. The location and accuracy of this single-polymer flyfishing can be modulated by adjusting the tilting angle and the chain rigidity. The single-polymer flyfishing likely plays a role in biological nanomotors and might be used in artificial nanomotors (for speed improvement) and in molecular devices for precise positioning of molecular objects. To facilitate these applications, a new force-extension formula is obtained from the exact solution to the realistic three-dimensional WLC model. The new formula has an improved accuracy over the widely used Marko-Siggia formula for stretched polymers, and also is valid for compressed polymers. Thus, the new force-extension formula is useful in analysis of single-molecule stretching experiments and in estimating the intramolecular force of molecular motors, especially those involving both stretched and compressed polymer components.

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4. METHODS

The simplest model for describing semiflexible polymers without self-avoidance is the so-called WLC model.⁴⁴ In this model, the polymer is modeled as a continuous curve-a configuration *C*—that can be specified by a *d*-dimensional (d > d)1) curve x(s) ($0 \le s \le l_c$), with *s* the arc-length parameterization of the curve and l_c is the contour length of the polymer. The unit tangent vector to the chain at s is denoted as t(s) = dx(s)/ds(1) $t(s)|^2 = t(s) \cdot t(s) = 1$, and the curvature of the polymer at s is given by $\kappa(s) = |dt(s)/ds|$. For the simplicity of notations, we suppose that one end of the polymer is tethered to the origin, that is, x(0) = 0, and the other end $x(l_c) = r$ is tagged. As the polymer configuration changes with thermal agitation, the location r of its tagged end fluctuates. The quantity we want to compute is Q(r), which is the probability distribution for the location r of the tagged end, and the free energy F(r) which is defined as the change in Q(r) if the tagged end is pulled from r to r + dr. Thus, Q(r) is directly related to the force-extension relation of the polymer, that is, intrachain force f(r).

4.1. Probability Distribution Q(r). Different analytical, asymptotic, and numerical methods have been proposed in the literature^{31,34} for solving the WLC model. Here, we extend the method for solving the WLC model for a two-dimensional case³¹ to a full three-dimensional case. For a given three-dimensional curve C: x(s) ($0 \le s \le l_c$) of a polymer, we have $r = \int_0^{l_c} t(s) ds$ and the bending energy of the polymer is $E(C) = A/2 \int_0^{l_c} |dt(s)/ds|^2 ds$ with A the bending modulus. To compute Q(r), we need to sum over all polymer configurations C which end at r, with a Boltzmann weight or the partition function according to the Boltzmann's law

$$Z = \sum_{C} e^{-E(C)/k_{\rm B}T}$$
⁽²⁾

where $k_{\rm B}$ is the Boltzmann constant and *T* is temperature. This is a standard counting problem in statistical mechanics and can be naturally addressed in the language of path integration by considering the Brownian motion in the space of the tangent vectors t(s) ($0 \le s \le l_c$). The advantage of this approach is that the tangent vectors form a unit sphere and thus the problem reduces to studying Brownian motion on the unit sphere, which can be handled by the standard operator techniques familiar from quantum mechanics.

Denote $t_A = t(0)$ and $t_B = t(l_c)$ as the two unit tangent vectors at the two ends of the configuration *C*, respectively, of the polymer, and let $l_p = A/k_BT$ be the persistence length of the polymer and denote the dimensionless parameter $\beta = l_c/l_p$. Then, Q(r) with t_A and t_B two given unit vectors for the configuration *C* can be expressed by the path integral representation^{31,34}

$$Q(\vec{r}) = N \int_{\vec{t}_{A}}^{\vec{t}_{B}} D[\vec{t}(s)] e^{-(l_{p}/2) \int_{0}^{l_{c}} |d\vec{t}(s)/ds|^{2} ds}$$
$$\times \delta^{3} \left(\vec{r} - \int_{0}^{l_{c}} \vec{t}(s) ds\right), \quad \vec{r} \in \mathbb{R}^{3}$$
(3)

where $\delta^3()$ is the Dirac function in three dimensions and *N* is a normalization constant such that all polymer configurations *C* which end at *r* with different t_A and t_B are counted. We remark here that Q(r) = 0 when $|r| > l_c$. To find Q(r), we define its generating function $\tilde{P}(k)$ through the Laplace transform

$$\tilde{P}(\vec{k}) = \frac{1}{N} \int_{\mathbb{R}^3} d\vec{r} \ e^{\vec{k} \cdot \vec{r}/l_p} Q(\vec{r}), \qquad \vec{k} \in C^3$$
(4)

From eqs 3, 4 and the inverse Laplace transform, using the change of variable $k = -iu/\beta$ with $i = \sqrt{-1}$, we get

$$Q(\vec{r}) = \frac{N}{(2\pi l_c)^3} \int_{\mathbb{R}^3} \tilde{P}(-i\vec{u}/\beta) e^{i\vec{u}\cdot\vec{r}/l_c} d\vec{u}, \qquad \vec{r} \in \mathbb{R}^3$$
(5)

Plugging eqs 3 into 4 and using the change of variable $s = il_p \tau$ and denoting $\tilde{t}(\tau) = t(s) = t(il_p \tau)$, we obtain

$$\tilde{P}(\vec{k}) = \int_{\vec{t}_{A}}^{\vec{t}_{B}} D[\vec{t}(\tau)] e^{i \int_{0}^{-i\beta} [(d\vec{t}(\tau)/d\tau)^{2}/2 + \vec{k} \cdot \vec{t}(\tau)] d\tau}$$
(6)

In this equation, if τ and $(d\tilde{t}/d\tau)^2/2 + k\cdot\tilde{t}$ are viewed as time and Lagrangian, respectively, then it can be interpreted as the path integral representation for the kernel of a quantum particle on the unit sphere at inverse temperature β . Thus, we can express $\tilde{P}(k)$ for $k = (k_1, k_2, k_3)^T \in C^3$ as the quantum amplitude to go from an initial tangent vector state t_B to the final tangent vector state t_A in the imaginary time with length β in the presence of an external potential $-k_1 \sin \theta \cos \varphi - k_2 \sin \theta \sin \varphi$ $- k_3 \cos \theta$ with (θ, φ) the spherical coordinates of the unit sphere. Therefore, eq 6 can be written as a "vacuum persistence amplitude"

$$\tilde{P}(\vec{k}) = \langle g_{A} | e^{-i(-i\beta)H_{\vec{k}}} | g_{B} \rangle = \langle g_{A} | e^{-\beta H_{\vec{k}}} | g_{B} \rangle$$
(7)

where

$$H_{\bar{k}} = -\frac{1}{2}\nabla^2 - k_1 \sin \theta \cos \phi - k_2 \sin \theta \sin \phi - k_3 \cos \theta$$

:= $H_0 - k_1 H_1 - k_2 H_2 - k_3 H_3$ (8)

is the corresponding Hamiltonian with

$$H_0 = -\frac{1}{2}\nabla^2, \qquad H_1 = \sin\theta\cos\phi$$
$$H_2 = \sin\theta\sin\phi, \quad H_3 = \cos\theta \qquad (9)$$

In addition, $g_A := g_A(\theta, \varphi)$, $g_B := g_B(\theta, \varphi)$ are the distribution functions of the unit vectors t_A and t_B over the unit sphere, respectively.

Let $Y_l^m := Y_l^m(\theta, \varphi)$ $(l \ge 0 \text{ and } |m| \le l)$ be the standard spherical harmonic functions, then we have

$$\tilde{P}(\vec{k}) = \sum_{l,l'=0}^{\infty} \sum_{m,m'=-l}^{l} \langle g_{A} | Y_{l'}^{m'} \rangle \langle Y_{l'}^{m'} | e^{-\beta H_{k}^{-}} | Y_{l}^{m} \rangle \langle Y_{l}^{m} | g_{B} \rangle$$

$$\approx \sum_{l,l'=0}^{L} \sum_{m,m'=-l}^{l} \langle g_{A} | Y_{l'}^{m'} \rangle \langle Y_{l'}^{m'} | e^{-\beta H_{k}^{-}} | Y_{l}^{m} \rangle \langle Y_{l}^{m} | g_{B} \rangle$$

$$\coloneqq U^{T} e^{-\beta G} V \qquad (10)$$

where *L* is an integer chosen numerically for the truncation, *U* and *V* are two column vectors with components $\langle g_A | Y_l^m \rangle :=$ $\int_0^{\pi} \int_0^{2\pi} g_A(\theta, \varphi) Y_l^m(\theta, \varphi) \sin \theta \, d\varphi \, d\theta \, (|m| \le l \text{ and } 0 \le l \le L)$ and $\langle Y_l^m | g_A \rangle \, (|m| \le l \text{ and } 0 \le l \le L)$, respectively. Here, for example, if the end A of the polymer is aligned at a fixed unit direction, that is, $t_A = (\sin \theta_A \cos \varphi_A \sin \theta_A \sin \varphi_A \cos \theta_A)$ with θ_A and φ_A two fixed angles, then $g_A(\theta, \varphi) = \delta(\cos \theta - \cos \theta_A)\delta(\varphi - \varphi_A)$; if the end B of the polymer is free, that is, t_B is uniformly distributed on **ACS Omega**



Figure 6. Probability distribution Q(x, y, z) at different *y* planes for the diffusing end of a WLC polymer with its other end fixed at the origin of the *x*, *y*, *z* axes and aligned in parallel to the *z* axis. The polymer is characterized by different values of $\beta = l_c/l_p$. The *x*, *y*, *z* values shown in the figure are in unit of l_c .

the sphere, then $g_{\rm B}(\theta, \varphi) = 1/4\pi$. *G* is a matrix with entries $\langle Y_{l'}^{m'}|$ $H_k|Y_l^m\rangle = \langle Y_{l'}^{m'}|H_0|Y_l^m\rangle - k_1\langle Y_{l'}^{m'}|H_1|Y_l^m\rangle - k_2\langle Y_{l'}^{m'}|H_2|Y_l^m\rangle - k_3\langle Y_{l''}^{m'}|H_3|Y_l^m\rangle$ (|m|, $|m'| \leq l$ and $0 \leq l$, $l' \leq L$). By using the properties of the standard spherical harmonic Y_l^m , we can find for |m|, $|m'| \leq l$ and l, $l' \geq 0$ that

$$\langle Y_{l'}^{m'}|H_0|Y_l^m\rangle = \begin{cases} l(l+1)/2, & l=l' \& m'=m\\ 0, & \text{otherwise} \end{cases}$$

$$\langle Y_{l'}^{m'}|H_{l}|Y_{l}^{m}\rangle = \begin{cases} 1/\sqrt{6}\,, & l=m=0\&\,l'=m'=1\\ \sqrt{\frac{(l+m+2)(l+m+1)}{4(2l+1)(2l+3)}}\,, & l'=l+1\&\,m'=m+1\&\,l'\geq 1\\ -\sqrt{\frac{(l-m)(l-m-1)}{4(2l-1)(2l+1)}}\,, & l'=l-1\&\,m'=m+1\&\,l\geq 1\\ -\sqrt{\frac{(l-m+2)(l-m+1)}{4(2l+1)(2l+3)}}\,, & l'=l+1\&\,m'=m-1\&\,l'\geq 1\\ \sqrt{\frac{(l+m)(l+m-1)}{4(2l-1)(2l+1)}}\,, & l'=l-1\&\,m'=m-1\&\,l\geq 1\\ 0, & \text{otherwise} \end{cases}$$

$$\langle Y_{l'}^{m'} | H_2 | Y_l^m \rangle = \begin{cases} -i/\sqrt{6}, & l = m = 0 \& l' = m' = 1 \\ -i\sqrt{\frac{(l+m+2)(l+m+1)}{4(2l+1)(2l+3)}}, & l' = l+1 \& m' = m+1 \& l' \ge 1 \\ i\sqrt{\frac{(l-m)(l-m-1)}{4(2l-1)(2l+1)}}, & l' = l-1 \& m' = m+1 \& l \ge 1 \\ -i\sqrt{\frac{(l-m+2)(l-m+1)}{4(2l+1)(2l+3)}}, & l' = l+1 \& m' = m-1 \& l' \ge 1 \\ i\sqrt{\frac{(l+m)(l+m-1)}{4(2l-1)(2l+1)}}, & l' = l-1 \& m' = m-1 \& l \ge 1 \\ 0, & \text{otherwise} \end{cases}$$

$$\langle Y_{l'}^{m'} | H_{3} | Y_{l}^{m} \rangle = \begin{cases} 1/\sqrt{3} , & l = m = m' = 0 \& l' = 1 \\ \sqrt{\frac{(l+1+m)(l+1-m)}{(2l+1)(2l+3)}} , & l' = l+1 \& m' = m \& l' \ge 1 \\ \sqrt{\frac{(l-m)(l+m)}{(2l-1)(2l+1)}} , & l' = l-1 \& m' = m \& l \ge 1 \\ 0, & \text{otherwise} \end{cases}$$

In practical computations, we choose the integer L large enough such that the truncation error in eq 10 can be negligible and choose the distribution functions $g_A(\theta, \varphi)$ and $g_B(\theta, \varphi)$ for the two unit vectors t_A and t_B , respectively, based on the assumption of the chain, for example, both end free or one end free, the other end fixed, and so forth. Then, we can compute the matrix G and the two vectors U and L in eq 10. Then, the matrix exponential $e^{-\beta G}$ is computed numerically via the Páde approximation and $\tilde{P}(k)$ can be evaluated by matrix multiplication. Finally, Q(r) is obtained from P(k) through eqs 4 and 5. To check the method and our code as well as to compare it with existing results, we consider a WLC polymer with one end located at the origin and aligned toward the z direction, that is, t_A = $(0, 0, 1)^T$ and the other end free. After we compute Q(r), we display the distribution in the x-z plane for different y values (Figure 6). The results agree very well with those obtained in ref 34 by a different method.

4.2. Free Energy F(r) and Intrachain Force f(r). On the basis of the probability distribution function Q(r), we can derive the thermodynamic quantities such as the free energy F(r) and the intrachain force f(r). In fact, the free energy of the ensemble F(r) can be computed as

$$F(\vec{r}) = -k_{\rm B}T \ln Q(\vec{r}), \qquad |\vec{r}| < l_c \tag{11}$$

To keep the free end staying at the position r, a force must be applied, that is, intrachain force f(r) which can be computed as

$$\overline{f}(\overline{r}) = \nabla F(\overline{r}), \qquad |\overline{r}| < l_{c}$$
(12)

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Notes

The authors declare no competing financial interest.

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