Article

Statistical Behaviours of Semiflexible Polymer Chains Stretched in Rectangular Tubes

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Abstract: We quantitatively investigated the statistical behaviors of semiflexible polymer chains, which are simultaneously subjected to force stretching and rectangular tube confinement. Based on the wormlike chain model and Odijk deflection theory, we derived a new deflection length, by which new compact formulas are obtained for the confinement free energy and force-confinement-extension relation. These newly derived formulas have been justified by numerical solutions of an eigenvalue problem associated with the Fokker-Planck governing equation and extensive Brownian dynamics simulations based on the so-called Generalized Bead-Rod (GBR) model. We found that, comparing to the classical deflection theory, these new formulas are valid for a much extended range of the confinement-size /persistence-length ratio, and have no adjustable fitting parameters for sufficient long semiflexible chains in the whole deflection regime.

Keywords: wormlike chain model; rectangular tube confinement; slit confinement; Odijk length; stretch; GBR model; Brownian dynamics simulation

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1. Introduction

Statistical physics properties of single polymer chains can be significantly influenced or even determined by geometrical confinements and applied external forces [1–4]. A detailed understanding of the behaviors of polymers under such circumstances is still considered as an unsolved problem in polymer physics after more than half a century. However, even so, advances in the study of geometrically and potentially constraint polymers do have continuously promoted the development of many existing nanotechnologies of genomics and materials science etc. [5–7].

For polymers under confinements, the effects of constraints have usually been classified into three regimes, the weak, moderate, and strong confinements, which are distinguished in terms of the comparison between polymer's unconfined radius of gyration, R_g, and Kuhn length, a, to the typical confinement length scale. In the regime of weak confinement, Casassa [8] has discussed the free energy of ideal chains trapped in pores with different shapes based on the theory of diffusion. Then de Gennes and his coworkers [9, 10] developed the so-called blob model to describe the statistical behaviors of polymers in moderate confinements and predicted the free energy expression as

$$\frac{F}{k_B T} = N\left(\frac{a}{H}\right)^2, \ H \gg a \tag{1}$$

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where N represents the polymerization index and H the typical confinement length scale. A widely used physical model of single polymer chains is the wormlike chain (WLC) model characterized by the inextensible contour length, L, and persistence length, $p=a/2$, which was first proposed by Kratky and Porod in 1949 [11]. In the strong confinement regime, Odijk [12, 13] revealed that the free energy of confinement can be related to a deflection length scale, λ, so that statistical behaviors of the polymer at each deflection length can be in analogy with the movement of a particle in a potential field satisfied the classical limit [15, 16]. Based on this understanding, Odijk [12–14] obtained expressions of the confinement free energy, F, and average extension of the chain, $R_{||}$, in terms of λ as

$$F \approx k_{\mathrm{B}} T \frac{L}{\lambda}, \tag{2}$$

$$1-\frac{R_{||}}{L} \approx \frac{\lambda}{2p} \tag{3}$$

where $\lambda \propto p^{1/3} D^{2/3}$ [12] was suggested for the confinement of cylindrical tube with diameter D. For the confinement of a rectangular tube with height and width, H_{h} and H_{w}, the deflection length associated with the free energy calculation has been suggested as [17, 21]

$$\lambda \triangleq \frac{1}{A_{\square}} (p^{1/3} H_{\mathrm{h}}^{2/3} + p^{1/3} H_{\mathrm{w}}^{2/3}) \cdot \tag{4}$$

In contrast, this deflection length associated with the average extension was given as

$$\lambda \triangleq \alpha_{\square} (p^{1/3} H_{\mathrm{h}}^{2/3} + p^{1/3} H_{\mathrm{w}}^{2/3}) \cdot \tag{5}$$

Prefactors in Equations (4) and (5) have been determined by using various numerical techniques and theoretical derivations, such as the Monte Carlo simulations [18, 19] and eigenvalue technique associated with the Fokker-Planck equations [17, 20]. Examples of the determined prefactors are illustrated in Table 1. We can see that the prefactors, $1/A_{\square}$ and $\alpha_{\square}$, respectively determined from the free energy and extension are in almost 10 times difference in quantity.

Table 1. Prefactors of the Odijk deflection length scale

$A_{\square}$	$\alpha_{\square}$
1.1036 [17]	--
1.108 ± 0.013 [18]	--
1.1038 ± 0.0006 [19]	0.09137 ± 0.00007 [19]
1.1032 ± 0.0001 [20]	0.09143 ± 0.0001 [20]

In addition, a slit of separation H can be regarded as a rectangular tube with height, $H_{\mathrm{h}}=H$, and infinite width. Statistical properties of polymer chains confined in the slit have been extensively studied [22–27] based on Monte Carlo simulations and eigenvalue analysis. The deflection length in strong confinement regime has been confirmed to follow the Odijk scaling law

$$\lambda \sim p^{1/3} H^{2/3} . \tag{6}$$

It can be observed from Equations (4) - (6) that the deflection length for the rectangular tube mentioned above can be viewed as the combination of that for two slits with heights, H_{h} and H_{w}, respectively [17].

Beyond the Odijk regime, Chen [26] numerically calculated the confinement free energy by treating the problem of confined polymer as an eigenvalue problem. He also suggested an

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interpolating formula which can have very good agreement to that of the numerical calculations for the polymers under confinements of both strong and weak. In addition, an extended de Gennes regime [22, 28, 29] has also been identified based on the Monte Carlo simulations.

Interestingly, external forces can pose similar effects to the statistical behaviors of single polymer chains as the geometrical confinements. For a polymer chain to be stretched by a sufficiently large force, f_s, a deflection length also exists and can be expressed as [3, 30], $\lambda_f = p/\sqrt{\hat{f}}$, where $\hat{f} = f_s p/k_B T$, so that the force-extension relation can be expressed as

$$1-\frac{R_{\|}}{L} \approx \frac{1}{2\sqrt{\hat{f}}}. \tag{7}$$

Polymers in real microenvironments usually subject to both of the geometrical constraints and external forces. Wang and Gao [31] have revealed that the average extension of a strongly tube confined and force stretched polymer chain can be equivalent to that of an unconfined chain subjecting to an effective stretching force. Li and Wang [32] later confirmed that this property of equivalence is still valid for the tube confined polymers in a much extended Odijk regime. Therefore, for a semiflexible polymer chain in the deflection confinement regime, one can generally have

$$1-\frac{R_{\|}}{L} \approx \frac{1}{2\sqrt{\hat{f}+\hat{f}_c}} \tag{8}$$

where $\hat{f}_c = p^2/\lambda^2$ is the normalized effective force due to the existence of strong confinement, and λ is the deflection length scale without stretching force.

However, as we have pointed out above, the Odijk deflection lengths are very different in quantities for that determined based on the free energy and the extension calculations, respectively. Then a critical question arises. Which deflection length should be used if the polymer chain is simultaneously under both geometrical confinement and force stretching? Obviously, it is still an open question on how the Odijk length can be uniquely and precisely defined for the polymer chains confined in rectangular tubes.

In this study, for the semiflexible polymer chains confined in rectangular tubes and slits, we will derive a modified deflection length, which is expected to be valid for a more extended range than the classical Odijk deflection length. And this extended deflection length will be directly used to quantitatively formulate both of the confinement free energy and force-extension relation. Then we will perform numerical calculations based on the eigenvalue technique developed by Chen and co-works [20, 36, 37], and the Brownian dynamics simulations in terms of the Generalized Bead Rod (GBR) model [33, 34] to justify our theoretical predictions.

2. Materials and Methods

2.1. Model

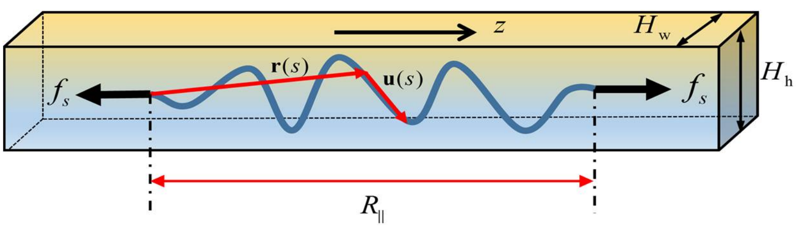

Figure 1. Schematic of a WLC confined in a tube and stretched by a force.

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We first consider a WLC confined in a rectangular tube with width, H_w, and height, H_h, as shown in Fig. 1. We assume that the tube is small so that chain's configurations with the so-called "hairpin" structures rarely exist. That means statistical behaviors of the chain fall in the deflection regime. In order to obtain a universal deflection length scale, λ, to simultaneously characterize both of the free energy and extension of the chain. In terms of the idea of de Gennes [9, 10] and Odijk [12], the chain is assumed to behave like L/λ independent free segments, aligning one by one along the tube axis, so that the conformational free energy can still be scaled as Equation (1), and the average extension can be simply the sum of that for each free segment. On the other hand, when considering the average extension of the chain, quantitative behavior of each segment should be in analogy with a free chain of effective contour length, $c_1\lambda_{\mathrm{m}}$, in which the parameter, c_1, actually reflects the influence of two artificial ends of each such segment. For a free WLC segment of contour length $c_1\lambda_{\mathrm{m}}$, projection of the position vector of one end, $\mathbf{r}(s_2)$, to the tangential vector of the other end, $\mathbf{u}(s_1)$, can be given by [35]

$$<\mathbf{r}(s_1)\cdot\mathbf{u}(s_2)>=p(1-e^{-c_1\lambda_{\mathrm{m}}/p}). \tag{9}$$

Then average extension of the whole chain, can be estimated as

$$R_{\|}=c_2\frac{L}{\lambda_{\mathrm{m}}}<\mathbf{r}(s_1)\cdot\mathbf{u}(s_2)>=c_2\frac{pL}{\lambda_{\mathrm{m}}}(1-e^{-c_1\lambda_{\mathrm{m}}/p}) \tag{10}$$

in which c_2 is introduced as an unknown dimensionless factor. Equation (10) should reproduce Equation (3) in the deflection regime, which can determine $c_1=\vartheta=8A_{\square}\alpha_{\square}$ and $c_2=1/\vartheta$, so that eventually we have

$$R_{\|}=\frac{Lp}{\vartheta\lambda_{\mathrm{m}}}\left(1-e^{-\vartheta\lambda_{\mathrm{m}}/p}\right). \tag{11}$$

For a tightly confined polymer in a channel with a rectangular cross section, Burkhardt and Yang et al. [18, 20] have derived that the confinement free energy of the polymer chain can be scaled by the average length of tube occupied by the polymer, which is the average extension of the polymer chain, as follows

$$\frac{F}{R_{\|}}=A_{\square}\frac{k_{\mathrm{B}}T}{p^{1/3}}(H_{\mathrm{h}}^{-2/3}+H_{\mathrm{w}}^{-2/3}). \tag{12}$$

Assuming that λ_{m} should satisfy both of the Equations (2), (11) and (12), one has

$$\frac{L}{\lambda_{\mathrm{m}}}k_{\mathrm{B}}T=A_{\square}\frac{k_BT}{p^{1/3}}(H_{\mathrm{h}}^{-2/3}+H_{\mathrm{w}}^{-2/3})\frac{Lp}{\vartheta\lambda_{\mathrm{m}}}\left(1-e^{-\vartheta\lambda_{\mathrm{m}}/p}\right) \tag{13}$$

or

$$\frac{\lambda_{\mathrm{m}}}{p}=-\frac{1}{\vartheta}\ln[1-\vartheta A_{\square}^{-1}(\hat{H}_{\mathrm{h}}^{-2/3}+\hat{H}_{\mathrm{w}}^{-2/3})^{-1}] \tag{14}$$

where $\hat{H}_{\mathrm{h}}\triangleq H_{\mathrm{h}}/p$ and $\hat{H}_{\mathrm{w}}\triangleq H_{\mathrm{w}}/p$. Equation (14) can be regarded as a new deflection length that fulfills both requirements for the free energy and statistics of geometrical quantities. We can see from Equation (14), as long as $\mathrm{Min}(H_{\mathrm{w}}, H_{\mathrm{h}})/p \ll 1$, low order Taylor expansion of this equation reproduce the result in Equation (4). Insertion of Equation (14) into Equation (2), we can obtain the confinement free energy as follows

$$\frac{F}{k_BT}=-\frac{\vartheta L}{p\ln[1-\vartheta A_{\square}^{-1}(\hat{H}_{\mathrm{h}}^{-2/3}+\hat{H}_{\mathrm{w}}^{-2/3})^{-1}]}. \tag{15}$$

For the extension of the chain under both confinement and stretching force as shown in Figure 1, Wang and Li [38] have suggested the force-extension relation as shown in Equation (8), which now can be rewritten as

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$$1-\frac{R_{\parallel}}{L}\approx\frac{1}{2}\frac{1}{\sqrt{\hat{f}+\vartheta^{2}\left\{\ln[1-\vartheta A_{\square}^{-1}(\hat{H}_{\mathrm{h}}^{-2/3}+\hat{H}_{\mathrm{w}}^{-2/3})^{-1}]\right\}^{-2}}}. \quad (16)$$

2.3. Numerical Verifications

2.3.1 Solutions to the Fokker-Planck Equation

In order to verify the derived free energy expression, we consider the solutions to the Fokker-Planck equation, which can be used to describe the statistical behaviors of confined polymer chains. We first introduce $q(\mathbf{r},\mathbf{u},s)$ to represent the probability that a polymer chain at arc length s has the end position vector $\mathbf{r}$ and end unit tangential vector $\mathbf{u}$. Then we can have the partition function of the chain with contour length, L, as, $Z=\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{u}q(\mathbf{r},\mathbf{u},L)$, and the Fokker-Planck equation [36]

$$\frac{\partial}{\partial s}q(\mathbf{r},\mathbf{u},s)=\left\{-\mathbf{u}\cdot\nabla_{\mathrm{r}}+\frac{1}{2p}\nabla_{\mathrm{u}}^{2}+\left[(\mathbf{u}\cdot\nabla_{\mathrm{r}})\mathbf{u}\right]\bullet\nabla_{\mathrm{u}}-\frac{1}{k_{\mathrm{B}}T}V(\mathbf{r})\right\}q(\mathbf{r},\mathbf{u},s) \quad (17)$$

where

$$V(\mathbf{r})=\begin{cases}0, & |x|<H_{\mathrm{w}}/2 \text{ and } |y|<H_{\mathrm{h}}/2\\ \infty, & |x|>H_{\mathrm{w}}/2 \text{ and } |y|>H_{\mathrm{h}}/2\end{cases} \quad (18)$$

is the potential energy per unit length due to the confinement of rectangular tube. As suggested by Chen [20, 36], solution of Equation (17) can be expanded into a series of eigenfunctions associated with negative exponential terms of eigenvalues. By noting that the chain is sufficient long and high order eigenvalues are large enough, the solution can be approximated by the ground state eigenfunction, $\Psi_0(\mathbf{r},\mathbf{u})$, and eigenvalue, μ_0, as follows.

$$q(\mathbf{r},\mathbf{u},L)\approx\exp(-\frac{\mu_0 L}{2p})\Psi_0(\mathbf{r},\mathbf{u})\cdot \quad (19)$$

Then the free energy can be written as

$$F=-k_{\mathrm{B}}T\ln Z\approx k_{\mathrm{B}}TL\frac{\mu_0}{2p}\cdot \quad (20)$$

Comparing Equation (2) and Equation (20) gives

$$\lambda=\frac{2p}{\mu_0}\cdot \quad (21)$$

Chen and his co-works [20, 36, 37] have proposed an iteration method to numerically determine the ground state eigenvalue and eigenfunction. In this study, we have adopted this method to calculate the confinement free energy. As examples, we consider polymer chains confined in slits with different heights, *H*. When using Chen's method to calculate μ_0, we have set the tolerance error as 10^{-4}. Figure 2 shows the comparison of the confinement free energy as a function of *H*/*p* obtained by numerical solutions of the ground state eigenvalue, Equation (15), and Equation (2) in terms of the classical Odijk length, respectively. It can be seen from Figure 2 that free energy based on the modified deflection length has a better agreement with the numerical results than that based on the classical one.

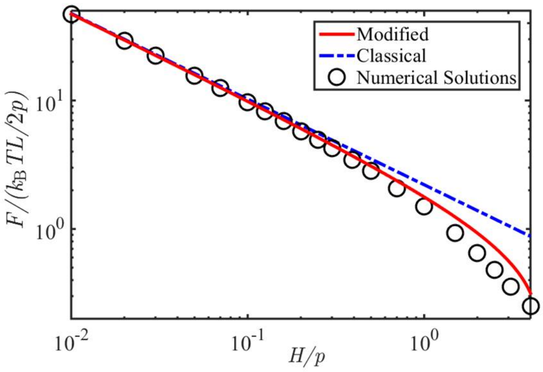


Figure 2. Normalized confinement free energy as a function of the normalized slit height, predicted based on the classical and modified deflection lengths, and the solutions of the eigenvalue problem.

2.3.2 Brownian Dynamics Simulations

We use the technique of statistical dynamics simulations to verify the derived force-extension relation on polymer chains subjected to both confinement of rectangular tubes and stretching of external forces. We perform the simulations by using our GBR model for Brownian dynamics of semiflexible polymer chains in confinements [33, 34]. This model has been successfully applied to the quantitative analysis of statistical behaviors of polymers confined on spherical surfaces [34] and in cylindrical tubes [31], and subjected to stretching forces [33]. In this GBR model, we consider the polymer chain as a discrete WLC with *N* identical virtual beads of radius, *a*, at different positions, $\mathbf{r}_k(t)=\{x_k(t), y_k(t), z_k(t)\}'$, where *k*=1, 2, …, *N*, linked by *N*-1 rods with inextensible length, *b*. The virtual beads are used to feel the hydrodynamic interactions. And angle changes of the adjacent rods are used to account the bending deformation. As long as the position vectors of all *N* beads at the *n*th time step, denoted as $\mathbf{r}_{(n)}=\{\mathbf{r}_{1,(n)}, \mathbf{r}_{2,(n)}, \ldots, \mathbf{r}_{N,(n)}\}'$, is obtained, the new position vector at the (*n*+1)th time step, $\mathbf{r}_{(n+1)}$ can be calculated from [33, 34]

$$\mathbf{r}_{(n+1)} = (\mathbf{I}-\mathbf{T}_{(n)}\mathbf{B}_{(n)})(\mathbf{r}_{(n)} + \boldsymbol{\chi}^{\text{wall}}_{(n)} + \frac{\Delta t}{k_B T}\mathbf{D}_{(n)}\mathbf{F}_{(n)} + \boldsymbol{\xi}_{(n)}) + \mathbf{T}_{(n)}\mathbf{d} \tag{22}$$

where k_B is the Boltzmann constant, *T* the absolute temperature, Δt the time step, $\delta_{nn'}$ the Kronecker delta symbol, $\mathbf{F}_{(n)}$ the collective vector of internal and external forces, $\mathbf{I}-\mathbf{T}_{(n)}\mathbf{B}_{(n)}$ a projection matrix which together with $\mathbf{T}_{(n)}\mathbf{d}$ sets the inextensible constraints, $\boldsymbol{\chi}^{\text{wall}}_{(n)}$ the penalty displacement vector for the tube/slit walls, $\mathbf{D}_{(n)}$ the translational diffusion matrix determined through hydrodynamic interactions between beads, $\boldsymbol{\xi}_{(n)}$ the vector of random force generated at each time step from a Gaussian distribution with zero mean and variance equal to

$$\left\langle \boldsymbol{\xi}_{(n)}\boldsymbol{\xi}_{(n')} \right\rangle = 2\mathbf{D}_{(n)}\Delta t\delta_{nn'}\,. \tag{23}$$

We have performed Brownian dynamics simulations for WLCs confined in square tubes, rectangular tubes and narrow slits of different sizes and subjected to various stretching forces. In all simulations, the chains are initially set in a straight configuration. Confinements and constant tensile forces are then applied during chains' relaxation. At the *n*th time step, we record the end-to-end distance along z-axis (tube axis), $z_{N,(n)}$-$z_{0,(n)}$. For each simulation, we run total 6 million time steps, so that the steady extension states can last sufficient long time (see Figure 3). For each case, average extension of the WLC is obtained by first averaging over time, and then averaging over 120 independent trajectories with different random seeds, which is then denoted as $R_{||}$. For the simulation parameters, we should note that the contour length should be larger than, at least, two times of the persistence length, and much larger than the deflection length scale, λ_m. As we are only interested in the equilibrium properties of the polymer chains, therefore specific values of bead radius and time steps are not the key factors as long as sufficient large numbers of different configurations of the polymer chain can be generated. And the bond length should be selected much smaller than the deflection length scale, λ_m, and the persistence length.

For all these Brownian dynamics simulations, we choose persistence length of the chain, p= 50 nm, viscosity of water, $\eta_0 = 1.005725\times10^{-4}\,\mathrm{Pa.s}$, and absolute temperature, $T = 293\mathrm{K}$. Figure 3 shows convergence of the simulations for the evolution of the ensemble average of the extension over 120 different trajectories, $\overline{R}_{||}$, for slit and sqaure tube confined WLCs under stretching. It can be seen from Figure 3 that the equilibrium state can last sufficient long time to gurantee the effectiveness of time averaging.

Figures 4 - 6 show the comparison of Brownian dynamics simulation results and corresponding theoretical predictions based on the classical Odijk length in Equation (8) and the present new deflection length in Equation (16), for the normalized average extension of the WLCs stretched by different forces and confined in square tubes, rectangular tubes and slits of different sizes, respectively. Simulation parameters on bead radius, a, bond length, b, time step, Δt, and contour length, L, are listed in Tables 2 - 4 for different chains in different confinements .

Table 2 Simulation parameters for the confinement of square tubes

Confinement size H/p	Bead radius a	Bond length b	Time step Δt	Contour length L
0.2	1.85 nm	4 nm	10 ps	120 nm
0.3	1.85 nm	4 nm	10 ps	120 nm
0.4	1.85 nm	4 nm	20 ps	600 nm
0.6	1.85 nm	4 nm	20ps	600 nm

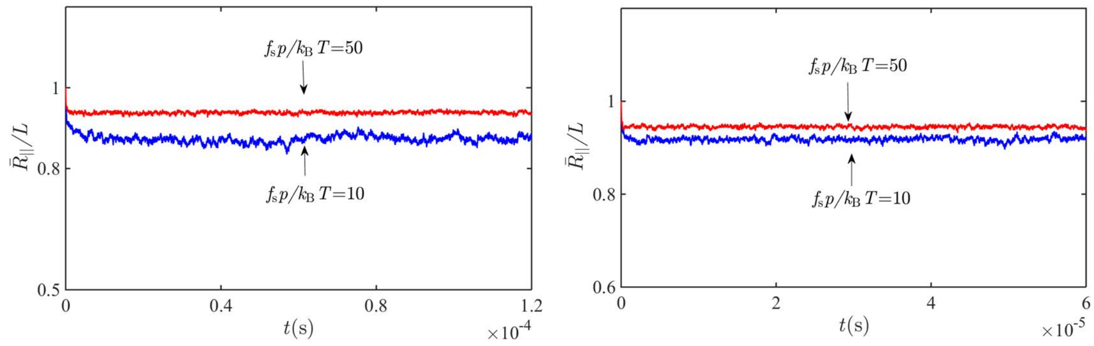
Table 3 Simulation parameters for the confinement of rectangular tubes

Confinement size $H_x/p, H_y/\mathrm{p}$	Bead radius a	Bond length b	Time step Δt	Contour length L
0.2, 0.3	2 nm	5 nm	20 ps	300 nm
0.3, 0.4	1.85 nm	4 nm	20 ps	200 nm
0.3, 0.6	1.85 nm	4 nm	20 ps	200 nm
0.4, 0.6	2 nm	5 nm	20ps	300 nm

Table 4 Simulation parameters for the confinement of slits

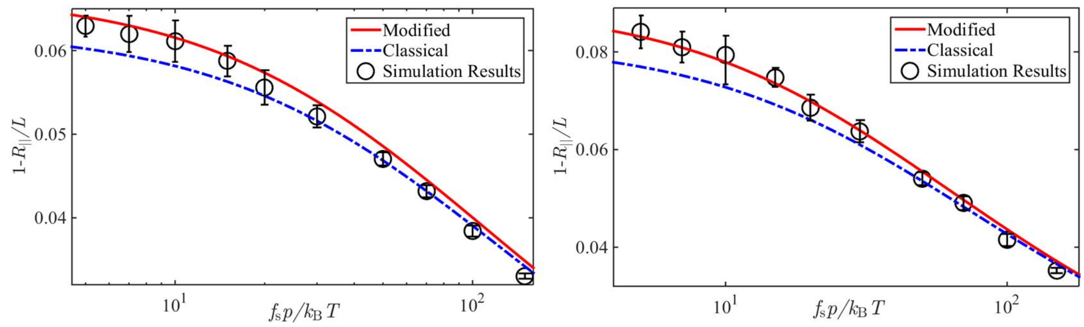
Confinement size H/p	Bead radius a	Bond length b	Time step Δt	Contour length L/p
0.2	2 nm	5 nm	15 ps	200 nm
0.3	2 nm	5 nm	20 ps	150 nm
0.4	1.85 nm	4 nm	25 ps	400 nm
0.6	1.85 nm	4 nm	20ps	400 nm

It can be seen from Figures 4 - 6 that results based on the newly derived formula on the average extension of the confined WLC agree with the simulation results very well, and that based on the classical Odijk length shows apparent discrepancy with the simulation results when the tube diameter becomes large and stretching force is small.

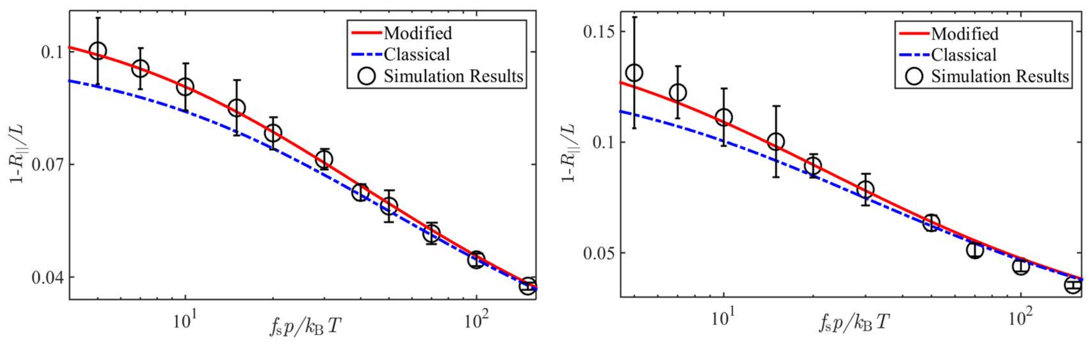


(**a**) $H_h/p = 0.3, H_w/p = \infty$ (**b**) $H_w/p = H_h/p = 0.3$

Figure 3. Evolution of the extension for slit and tube confined WLCs under stretching. (**a**) Slit, $H_h/p = 0.3, H_w/p = \infty$. (**b**) Square tube, $H_w/p = H_h/p = 0.3$.

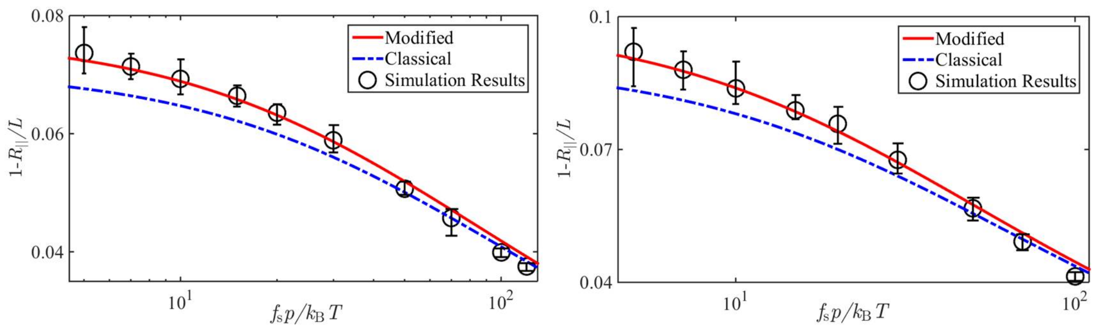


(**a**) $H_w/p = H_h/p = 0.2$ (**b**) $H_w/p = H_h/p = 0.3$



(**c**) $H_w/p = H_h/p = 0.4$ (**d**) $H_w/p = H_h/p = 0.6$

Figure 4. Comparison of Brownian dynamics simulations and theoretical predictions on the relative average extension of the WLC under stretching forces and confinements of square tubes of sizes (**a**) $H_w/p = H_h/p = 0.2$, (**b**) $H_w/p = H_h/p = 0.3$, (**c**) $H_w/p = H_h/p = 0.4$, and (**d**) $H_w/p = H_h/p = 0.6$.



(a) $H_w/p = 0.2, H_h/p = 0.3$ (b) $H_w/p = 0.3,\ H_h/p = 0.4$

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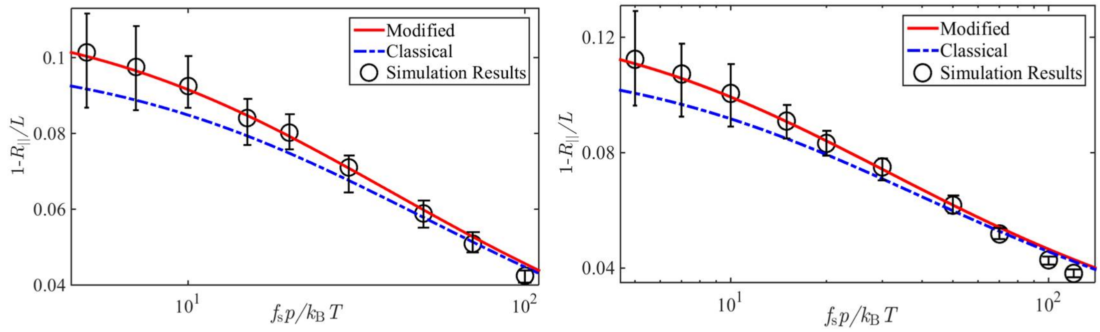
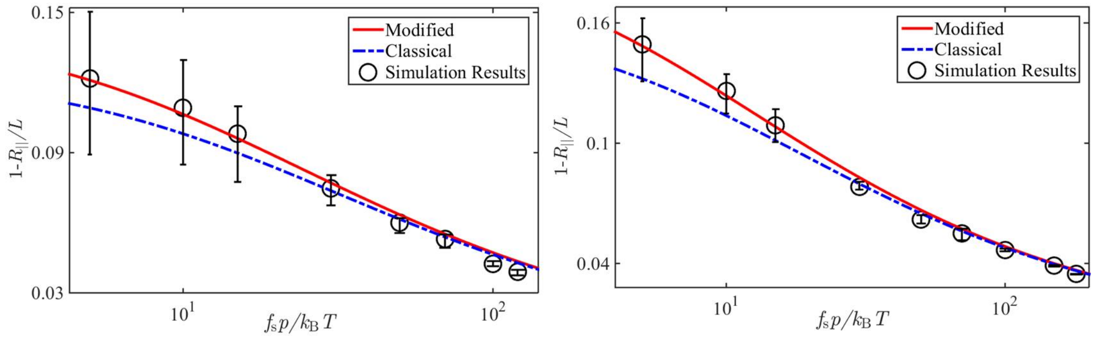
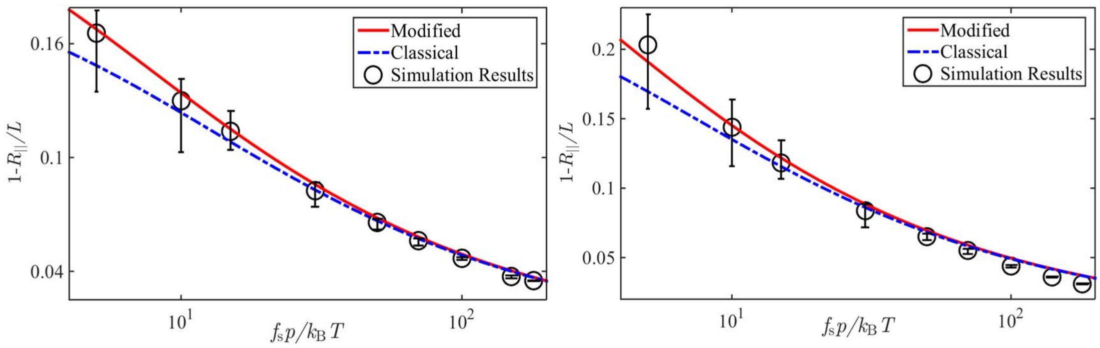


(c) $H_w/p = 0.3, H_h/p = 0.6$ (d) $H_w/p = 0.4, H_h/p = 0.6$

Figure 5. Comparison of Brownian dynamics simulations and theoretical predictions on the relative average extension of the WLC under stretching forces and confinements of rectangular tubes with sizes (**a**) $H_w/p = 0.2, H_h/p = 0.3$, (**b**) $H_w/p = 0.3$, $H_h/p = 0.4$, (**c**) $H_w/p = 0.3, H_h/p = 0.6$, and (**d**) $H_w/p = 0.4, H_h/p = 0.6$.



(**a**) $H_h/p = 0.2, H_w/p = \infty$ (**b**) $H_h/p = 0.3$, $H_w/p = \infty$



(**c**) $H_h/p = 0.4, H_w/p = \infty$ (**d**) $H_h/p = 0.6, H_w/p = \infty$

Figure 6. Comparison of Brownian dynamics simulations and theoretical predictions on the relative average extension of the WLC under stretching forces and confinements of slits with sizes (**a**) $H_h/p = 0.2, H_w/p = \infty$, (**b**) $H_h/p = 0.3$, $H_w/p = \infty$, (**c**) $H_h/p = 0.4, H_w/p = \infty$, and (**d**) $H_h/p = 0.6, H_w/p = \infty$.

4. Discussions

Based on the WLC theory and existing results on statistical properties of strongly confined semiflexible polymers, we have theoretically and numerically studied the confinement free energy and force-confinement-extension relations of semiflexible polymer chains under stretching and confinements of rectangular tubes in the deflection regime. We derived a modified deflection length without any adjustable parameters, which is valid for quantitative formulations of both of the free energy and geometrical extension. By using this deflection length scale, we have obtained compact formulas on the confinement free energy and force-extension relation without any fitting parameters. Numerical analysis based on the eigenvalue problem of the governing Fokker-Planck equations and the GBR Brownian dynamics simulations have justified these theoretical predictions to be valid for a much more extended range of the confinement/persistence length ratio than that based on the classical deflection length.

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Author Contributions: J.W. and K.L. conceived and designed the study; K.L. performed the simulations; J.W. and K.L. analyzed the data; J.W. contributed reagents/materials/analysis tools; J.W. and K.L. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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