

Numerical Simulation of the Distribution Function and Free Energy of a Single Wormlike Polymer Confined between Hard Walls

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Abstract We focus on the distribution and free energy of a wormlike polymer confined between two parallel hard walls. The variation in the distribution and free energy of the wormlike chain as the spacing between the walls decreases (or as the total contour length of the wormlike chain increases or as the persistence length of the chain increases) is simulated. The main reason for these changes is a degradation of the long wormlike chain into a Gaussian long chain under weak confinement.

Keywords Wormlike polymer; Free energy; Weak confinement

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INTRODUCTION

In both synthetic and natural systems, in practical applications, polymer chains are always limited to different restricted areas, such as chromatography, nanocomposite applications, colloidal stabilization, polymer adhesion, protein folding,^[1] materials science, and life sciences. The properties of a polymer chain in a restricted region are significantly different from those in a free region. Therefore, the analysis of a polymer chain in a restricted region is of great significance.

For the theoretical analysis of polymer chains in restricted areas, there are two special cases, namely, the “blob” theory of de Gennes^[2] in weak confinement and the “deflection” theory of Odijk^[3] in strong confinement. De Gennes believes that in the case of weak confinement, where the confining size of a system is much larger than the persistence length of a chain, the polymer chain will form a series of contiguous self-avoiding random “blobs”. The diameters of these “blobs” are equal to the constraint size of the confinement region. Odijk believes that in strong confinement, where the confining size of a system is much smaller than the persistence length of a chain, the polymer chain will form a chain of connected “small hard bars” that deviate from the confining direction. Chen^[4–6] used the eigenvalue method to theoretically analyze the structure of a long wormlike chain between parallel hard walls and numerically analyzed the variation in the free energy of the wormlike chain using the difference method. In

strong and weak confinement limits, the free energy of a long wormlike chain can be scaled to the confining size, which proves the above theory.

When a wormlike chain is confined in two parallel walls, the following theoretical conclusions are drawn: when the distance between the parallel walls is much larger than the persistence length of the polymer chain, the polymer chain is almost free and distributes freely between the walls; Cordeiro^[7] used variational theory to find that the polymer chain is gradually compressed until it reaches a minimum as the distance between the walls decreases, while the size of the polymer chain gradually increases when the distance between the walls decreases again. Since the mean square radius of gyration of the polymer chain can be directly measured and can directly reflect the average size of the polymer chain, Tang^[8] found that the radius of gyration of ssDNA increases with a decrease in tube diameter when ssDNA is confined in a very small tube. Tang’s experimental observation is consistent with the foregoing conclusions. Chen^[4] presented the simulation results about a wormlike chain in a square tube and a circular tube with confinement but reported little on the case that a wormlike chain is confined in two parallel walls separated by a distance H despite he mentioned it in the article. Here we investigate this case in detail with strictly convergent numerical scheme to compute the propagator equation.

We focus on a wormlike chain confined between two parallel walls. With a gradually decreasing distance between the walls, the variation in the distribution function and free energy of the wormlike chain are carefully studied. On this basis, to form a complete system, an analysis of the distribution function and free energy of a wormlike chain with different total contour lengths and different persistence lengths in the

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restricted area are performed in this article. On the one hand, a numerical verification of the existing theory regarding distribution is carried out. On the other hand, we analyze the change in the free energy, which has not yet been studied.

THEORETICAL ANALYSIS

The wormlike chain model describes the configuration of a semiflexible polymer chain by a continuum space curve.^[9] Any point on the curve represents the position of a segment of the wormlike chain, denoted by s ; the range of s is $[0, N]$, where N is the degree of polymerization. To simplify the calculation, we normalize s such that $s = s/N$, then $s \in [0, 1]$. The spatial position of the s segment is denoted by $\mathbf{r}(s)$. The unit tangent vector of the curve at the s segment $\mathbf{u}(s)$ indicates the orientation direction of the segment. We define the propagator $q(\mathbf{r}, \mathbf{u}, s)$ to be a probability density that indicates the s -terminal end appearing at the spatial point specified by $\mathbf{r}(s)$ and points in the direction called $\mathbf{u}(s)$.

The partition function is a concept regarding the sum of states. Given the initial state $q(\mathbf{r}, \mathbf{u}, 0) = 1$, the partition function of the wormlike chain is $Q = \int d\mathbf{r} d\mathbf{u} q(\mathbf{r}, \mathbf{u}, 1)$. The monomer density reflects the distribution of the wormlike chain, and its expression is

$$\rho(\mathbf{r}, \mathbf{u}) = Q^{-1} \int_0^1 ds q(\mathbf{r}, \mathbf{u}, s) q(\mathbf{r}, -\mathbf{u}, 1-s)$$

where the monomer density satisfies $\int d\mathbf{r} d\mathbf{u} \rho(\mathbf{r}, \mathbf{u}) = 1$. In addition, the free energy is $\beta F = -\ln Q$, where $\beta = 1/k_B T$. As a result, as long as the propagator $q(\mathbf{r}, \mathbf{u}, s)$ is found, the distribution and free energy of the wormlike chain can be obtained.

The propagator satisfies the following-modified diffusive equation (MDE):

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{u}, s) = -L \mathbf{u} \cdot \nabla_{\mathbf{r}} q(\mathbf{r}, \mathbf{u}, s) + \frac{L}{2\lambda} \nabla_{\mathbf{u}}^2 q(\mathbf{r}, \mathbf{u}, s) \quad (1)$$

where L is the total contour length of the wormlike chain and λ indicates the persistence length. The orientations of the segments within the persistence length are related. When $L \gg \lambda$, almost all segments are free in orientation and the polymer chain is flexible; when $L \ll \lambda$, the orientations of almost all segments are related, and the polymer chain is rigid.

We add a variant^[10] into Eq. (1) to deepen our understanding of the second term on the right side of Eq. (1).

If $\mathbf{u}$ is related to $\mathbf{r}$, i.e., $\mathbf{u}$ is a function of $\mathbf{r}$, we establish a curvilinear coordinate system for $\mathbf{u}$. Let $\mathbf{e}_i$ be the base vector of the curvilinear coordinate; then, $\mathbf{e}_i$ is a function of $\mathbf{r}$. Let $\mathbf{u} = \sum \mathbf{u}_i \mathbf{e}_i$; then, the derivative of $\mathbf{u}$ with respect to $\mathbf{r}$ is denoted by

$$\nabla_{\mathbf{r}} \mathbf{u} = \sum \mathbf{u}_i \nabla_{\mathbf{r}} \mathbf{e}_i$$

According to the chain rule, we obtain

$$\nabla_{\mathbf{r}} q(\mathbf{r}, \mathbf{u}, s) = \nabla_{\mathbf{r}} q(\mathbf{r}, \mathbf{u}, s)|_{\mathbf{u}} + \nabla_{\mathbf{r}} \mathbf{u} \cdot \nabla_{\mathbf{u}} q(\mathbf{r}, \mathbf{u}, s)$$

Therefore, we can rewrite the MDE as

$$\frac{\partial}{\partial s} q(\mathbf{r}, \mathbf{u}, s) = \left(\frac{L}{2\lambda} \nabla_{\mathbf{u}}^2 - L \mathbf{u} \cdot \nabla_{\mathbf{r}} + L[(\mathbf{u} \cdot \nabla_{\mathbf{r}}) \mathbf{u}] \cdot \nabla_{\mathbf{u}} \right) q(\mathbf{r}, \mathbf{u}, s) \quad (2)$$

Concerning the behavior of a wormlike chain on curved surfaces, the orientation of the wormlike chain is related to the spatial position. Generally, a curve coordinate system is established, and Eq. (2) is used as the basic model. In addition, in a Cartesian coordinate system, the base vectors are regard-

less of the position of the wormlike chain. Therefore, the third term on the right side of Eq. (2) disappears.

Three length scales, including the total contour length, persistence length, and plate spacing, affect the conformation and free energy of a wormlike chain according to the restricted system.

Next, we introduce an effective energy scaling law within an asymptotic limit. The exponent in the energy law is a general constant and independent of the model used and the geometry of the actual experimental constraints. The coefficients in the energy law, e.g., $A_{||}$, depend on the constrained geometry and the statistical physics model used for the semiflexible chain. The value of the coefficients can be calculated using various numerical methods.^[4]

Strong Confinement

The situation in which the persistent length of the wormlike chain is far greater than the distance H between the two walls, i.e., $\lambda \gg H$, is called strong confinement. Odijk^[3,11] found that the restricted free energy of a wormlike chain satisfies a scaling law. The polymer chain will extend parallel to the restraining wall in strong confinement. When the wormlike chain is a long chain, i.e., $L \gg \lambda \gg H$, the free energy of the system is mainly caused by a loss of entropy, satisfying the asymptotic scaling law:

$$\beta F = \frac{L}{\lambda} \left[A_{||} \left(\frac{\lambda}{H} \right)^{2/3} + \dots \right] \quad (3)$$

Weak Confinement

Contrary to the situation of strong confinement, when the persistent length of the wormlike chain is much smaller than the constraint length, i.e., $\lambda \ll H$, it can be shown that^[4] the entire system is in a Gaussian state, and almost all segments of the polymer rotate freely within the confining area. Generally, the restricted free energy follows the Gaussian-de Gennes scaling law:^[2]

$$\beta F = \frac{L}{\lambda} \left[A_{||} \left(\frac{\lambda}{H} \right)^2 + \dots \right] \quad (4)$$

Medium Confinement

In the case of two extreme constraints (strong confinement $\lambda \gg H$ and weak confinement $\lambda \ll H$), the physical properties of a wormlike chain follow the energy laws described in the previous two sections. Here, we focus on the situation between the two extreme constraints. The Monte Carlo method^[12] and the eigenvalue method^[6] are used to numerically verify that the aforementioned asymptotic energy laws are connected by smooth curves in the middle situation.

For the polymer restriction problem, the long chain limit of $L \gg \lambda$ will simplify the theoretical calculation of the limiting free energy. This is because, physically, for very long polymers, the physical properties of two separate segments are highly irrelevant.

Consider $L \gg \lambda$.

Consider the eigenvalue problem:

$$-f_m \psi_m(\mathbf{r}, \mathbf{u}) = H \psi_m(\mathbf{r}, \mathbf{u}) \quad (5)$$

where $H = -2\lambda \mathbf{u} \cdot \nabla_{\mathbf{r}} + \nabla_{\mathbf{u}}^2 + 2\lambda[(\mathbf{u} \cdot \nabla_{\mathbf{r}}) \mathbf{u}] \cdot \nabla_{\mathbf{u}}$.

The eigenvalues are solved: $0 < f_0 < f_1 \leq f_2 \leq f_3 \leq \dots$.

Therefore, the solution to the MDE (2) is

$$q(\mathbf{r}, \mathbf{u}, s) = \sum_m \exp(-f_m L s / 2\lambda) \psi_m(\mathbf{r}, \mathbf{u}) \quad (6)$$

Then, the partition function is

$$Q = \int d\mathbf{r} d\mathbf{u} q(\mathbf{r}, \mathbf{u}, 1) = \sum_m \exp\left(-\frac{f_m L}{2\lambda}\right) \int d\mathbf{r} d\mathbf{u} \psi_m(\mathbf{r}, \mathbf{u}) \quad (7)$$

When $L \gg \lambda$, the first item in Q plays a decisive role. The behavior of the wormlike chain is determined by the main eigenvalue. Let $C_m = \int d\mathbf{r} d\mathbf{u} \psi_m(\mathbf{r}, \mathbf{u})$, $N = L/2\lambda$; then,

$$Q = \exp(-f_0 N) (C_0 + C_1 \exp(-(f_1 - f_0)N) + \dots) \quad (8)$$

Therefore,

$$Q = \exp\left(-\frac{f_0 L}{2\lambda}\right) \int d\mathbf{r} d\mathbf{u} \psi_0(\mathbf{r}, \mathbf{u}) \quad (9)$$

The free energy of the single wormlike chain becomes

$$\beta F = \frac{f_0 L}{2\lambda} - \ln \left[\int d\mathbf{r} d\mathbf{u} \psi_0(\mathbf{r}, \mathbf{u}) \right] \neq \frac{f_0 L}{2\lambda} \quad (10)$$

MODEL

For a wormlike chain confined between two parallel walls spaced apart by H , as shown in Fig. 1, we establish an x - y - z Cartesian coordinate system.

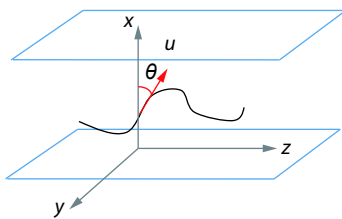


Fig. 1 A wormlike chain confined between two parallel hard walls.

Write $\mathbf{u}$ in spherical coordinates, that is

$$\mathbf{u} = \cos\theta \hat{x} + \sin\theta \cos\varphi \hat{y} + \sin\theta \sin\varphi \hat{z}$$

where $\theta \in [0, \pi]$, $\varphi \in [0, 2\pi]$. Due to the translational symmetry in both the y - and z -axes and the rotational symmetry of the propagator $q(\mathbf{r}, \mathbf{u}, s)$ about the x -axis, q is only related to x , θ , and s . $q(\mathbf{r}, \mathbf{u}, s)$ can be simplified as $q(x, \theta, s)$. This simplifies Eq. (2) into a three-variable equation.

To simplify Eq. (2), we plug the gradient operator in spherical coordinates which is

$$\nabla_{\mathbf{r}} = \mathbf{e}_r \cdot \frac{\partial}{\partial r} + \mathbf{e}_\theta \cdot \frac{1}{r} \frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \cdot \frac{1}{r \sin\theta} \frac{\partial}{\partial \varphi}$$

and the two-step operator on the unit sphere, which is

$$\nabla_{\mathbf{u}}^2 = \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2}$$

back into Eq. (2). In addition, the third term on the right side of Eq. (2) vanishes as it is a Cartesian coordinate system. We perform a scalable transformation of x but continue to use the same variable x , that is $x = x/H$. As a result, we obtain

$$\frac{\partial q(x, \theta, s)}{\partial s} = \left(-\frac{L}{H} \cos\theta \frac{\partial}{\partial x} + \frac{L}{2\lambda} \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \right) q(x, \theta, s) \quad (11)$$

where $x \in [0, 1]$.

Below, we discuss the boundary conditions. The boundary conditions for the polymer chain in a restricted area are usually such that the external potential is zero in the restricted area and infinite at the boundary. For a Gaussian chain, the boundary condition is very simple with the form $q_{GS}|_{\text{Hard Wall}} = 0$. However, a wormlike chain has a more complicated

boundary condition for the orientation.

When the terminal end of a segment appears at the boundary of a restricted area, that is, the surface of the hard wall, its orientation can only be towards the interior of the hard wall. In other words, to be in a confined area, the terminal $\mathbf{u}$ vector of the wormlike chain and the wall surface normal $\mathbf{n}$ vector follow $\mathbf{u} \cdot \mathbf{n} < 0$. On the other hand, the whole chain is inside the hard wall when $\mathbf{u} \cdot \mathbf{n} \geq 0$ (see Fig. 2). Hence, we obtain the external potential

$$U = \begin{cases} 0, & \mathbf{u} \cdot \mathbf{n} < 0 \\ +\infty, & \text{otherwise} \end{cases} \quad (12)$$

The boundary condition of wormlike chains can be expressed by

$$q|_{\text{Hard wall}} = 0, \quad \text{when } \mathbf{u} \cdot \mathbf{n} \geq 0 \quad (13)$$

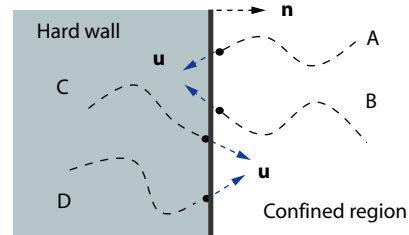


Fig. 2 Illustration of a wormlike chain with a terminal end located at the surface of the hard wall. $\mathbf{n}$ is the normal of the surface of the wall.

Specifically, the boundary condition for the x -direction corresponding to Eq. (11) is

$$q(0, \theta, s) = 0, \quad \text{if } \theta \in [0, \pi/2) \quad \text{and} \quad s \neq 0 \quad (14)$$

$$q(1, \theta, s) = 0, \quad \text{if } \theta \in (\pi/2, \pi] \quad \text{and} \quad s \neq 0 \quad (15)$$

The propagator $q(x, \theta, s)$ is axisymmetric about the x -axis and, as a result, axisymmetric with respect to $\theta = 0$, and $\theta = \pi$. Thus, the boundary condition for the θ -direction is the Neumann boundary condition

$$\frac{\partial}{\partial \theta} q(x, 0, s) = 0, \quad \frac{\partial}{\partial \theta} q(x, \pi, s) = 0 \quad (16)$$

Let the initial condition be

$$q(x, \theta, 0) = 1 \quad (17)$$

Next, the main work involves a numerical solution of the MDE Eq. (11) with the boundary conditions (14), (15), (16), and the initial boundary condition (17).

NUMERICAL SCHEMES

To improve the accuracy, the second-order operator splitting is used to split the right-hand side terms of Eq. (11) into two operators. Then, we obtain a partial differential equation for x and a partial differential equation for θ .

$$O_1 q(x, \theta, s) = -\frac{L}{H} \cos\theta \frac{\partial}{\partial x} q(x, \theta, s) \quad (18)$$

$$O_2 q(x, \theta, s) = \frac{L}{2\lambda} \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} q(x, \theta, s) \right) \quad (19)$$

$$q(x, \theta, s+h) = e^{\frac{h}{2} O_1} e^{h O_2} e^{\frac{h}{2} O_1} q(x, \theta, s) \quad (20)$$

For operator O_1 , the boundary conditions (14) and (15) in the x direction only represent half the information, as shown in Fig. 3. Therefore, we use the upwind scheme for discretiza-

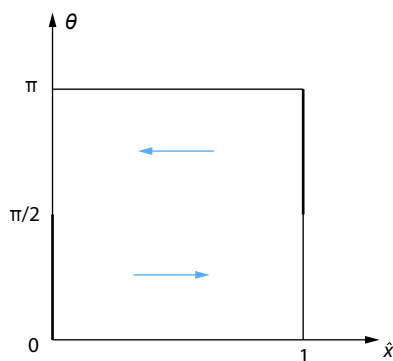


Fig. 3 The line segment where $x = 0$ and $x = 1$ represent the boundary in x direction. The half segment which is thickened represents $q(x, \theta, s) = 0$, and the value of $q(x, \theta, s) = 0$ in other half is unknown.

tion.

According to the upwind scheme, when $\theta_k \in (0, \pi/2)$, we use the backward difference scheme; when $\theta_k \in (\pi/2, \pi)$, we use the forward difference scheme. Finally, the operator O_1 can be discretized as follow.

When $\theta \in [0, \pi/2]$,

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = -\frac{L}{H} \cos \theta_k \frac{q_{j,k}^{n+1} - q_{j-1,k}^{n+1}}{\Delta x} \quad (21)$$

and when $\theta \in (\pi/2, \pi]$,

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = -\frac{L}{H} \cos \theta_k \frac{q_{j+1,k}^{n+1} - q_{j,k}^{n+1}}{\Delta x} \quad (22)$$

Due to the symmetry, the central difference scheme is used to discretize the operator O_2 . The Neumann boundary condition in the θ direction (16) is handled by constructing a virtual point to extend symmetrically. In particular, when θ tends to the boundary point, the original partial differential equation can be simplified as shown below to avoid zero appearing in the denominator.

When $\theta \rightarrow 0$ and $\frac{\cos \theta}{\sin \theta} \frac{dq}{d\theta} < \infty$, we have

$$\lim_{\theta \rightarrow 0} \frac{\cos \theta}{\sin \theta} \frac{dq}{d\theta} = \lim_{\theta \rightarrow 0} \frac{\frac{dq}{d\theta}}{\frac{\theta}{\theta}} = \lim_{\theta \rightarrow 0} \frac{d^2 q}{d\theta^2}$$

Thus, when $\theta \rightarrow 0$,

$$\begin{aligned} \lim_{\theta \rightarrow 0} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} q \right) \right) &= \lim_{\theta \rightarrow 0} \left(\frac{\cos \theta}{\sin \theta} \frac{dq}{d\theta} + \frac{d^2 q}{d\theta^2} \right) \\ &= \lim_{\theta \rightarrow 0} \left(2 \frac{d^2 q}{d\theta^2} \right) \end{aligned}$$

Substituting the expression above into the operator O_2 , we obtain

$$O_2 q(x, \theta; s) = \frac{L}{\lambda} \frac{d^2}{d\theta^2} q(x, \theta; s) \quad (\theta \rightarrow 0) \quad (23)$$

Similarly,

$$O_2 q(x, \theta; s) = \frac{L}{\lambda} \frac{d^2}{d\theta^2} q(x, \theta; s) \quad (\theta \rightarrow \pi) \quad (24)$$

In the end, according to the center difference scheme, the operator O_2 can be discretized as follows.

When $\theta \in (0, \pi)$,

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = \frac{L}{2\lambda} \frac{1}{\sin \theta_k} \frac{1}{\Delta \theta} \left(\sin \theta_{k+\frac{1}{2}} \frac{q_{j,k+1}^{n+1} - q_{j,k}^{n+1}}{\Delta \theta} - \sin \theta_{k-\frac{1}{2}} \frac{q_{j,k}^{n+1} - q_{j,k-1}^{n+1}}{\Delta \theta} \right)$$

When $\theta = 0, \pi$:

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = \frac{L}{\lambda} \frac{q_{j,k+1}^{n+1} - 2q_{j,k}^{n+1} + q_{j,k-1}^{n+1}}{\Delta \theta^2} \quad (25)$$

Eliminating the constructed virtual point in the boundary conditions,

when $\theta = 0$,

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = \frac{L}{\lambda} \frac{2q_{j,k+1}^{n+1} - 2q_{j,k}^{n+1}}{\Delta \theta^2} \quad (26)$$

and when $\theta = \pi$,

$$\frac{q_{j,k}^{n+1} - q_{j,k}^n}{\Delta s} = \frac{L}{\lambda} \frac{-2q_{j,k}^{n+1} + 2q_{j,k-1}^{n+1}}{\Delta \theta^2} \quad (27)$$

NUMERICAL RESULTS

Selecting different parameters to solve the numerical schemes (21), (22), (25), (26), and (27), we then obtain numerical solutions of the propagator, from which the monomer density and free energy of the wormlike chain can be determined. Since the monomer density is a function of x and θ for visual analysis, we define

$$\hat{\rho}(x) = \int d\theta \rho(x, \theta) / \int dx d\theta \rho(x, \theta) \quad (28)$$

$$\hat{\rho}(\theta) = \int dx \rho(x, \theta) / \int dx d\theta \rho(x, \theta) \quad (29)$$

In Eq. (11) there are three parameters L , λ , and H and the solution of Eq. (11) will depend on the ratios of L/H and L/λ . From the viewpoint of mathematics, we hope to investigate the whole scene, so we compute three cases by changing one with the other two parameters fixed.

Next, we choose different values of L , λ , and H to calculate the monomer density and free energy. We fix two of the three parameters and change the third one; then, we draw pictures of $\hat{\rho}(x)$, $\hat{\rho}(\theta)$, and βF to observe the changes in the monomer density and free energy. Finally, a system will hopefully be formed.

Fix L and λ and Decrease H

Now we fix $L = 100$, $\lambda = 2$ and take $H = 2^{10}, 2^9, \dots, 2^{-6}, 2^{-7}$ to study the process of a long wormlike chain confined between two parallel hard walls that are constantly approaching.

As shown in Figs. 4 and 5, when H decreases, the density in the middle of the parallel wall increases first and then decreases. This phenomenon conforms to the distribution theory introduced in the introduction. Below we conduct a detailed analysis.

When the wall spacing H is large, the wormlike chain is almost freely distributed between the parallel walls, and thus the densities of a single chain at different positions are equal to each other except for the positions near the walls.

When we reduce the value of H , owing to the principle of

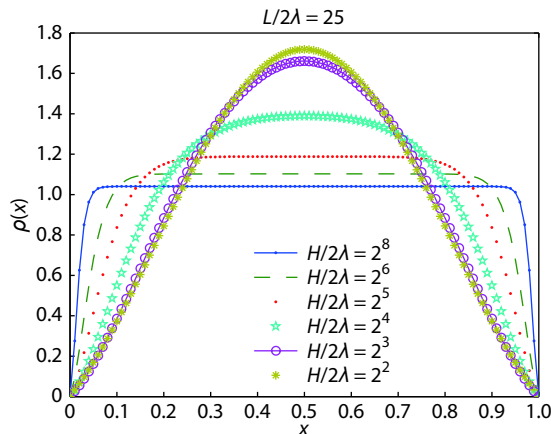


Fig. 4 The profile of the normalized segment density with respect to x when $L/2\lambda = 25$. Stage 1.

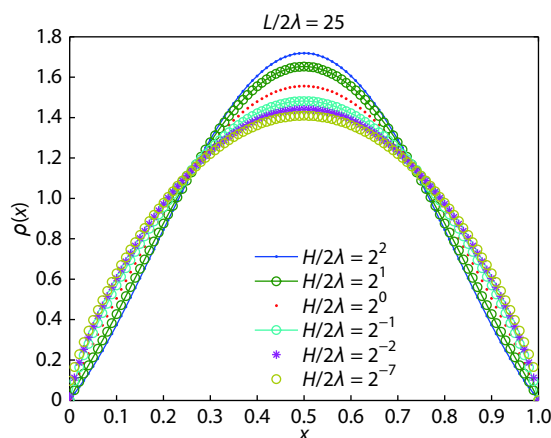


Fig. 5 The profile of the normalized segment density with respect to x when $L/2\lambda = 25$. Stage 2.

increasing entropy, the wormlike chain will appear more in the middle between the parallel walls after being restricted by the wall. Therefore, the monomer density of the wormlike chain in the middle is larger than that of the other positions. As one continues to decrease H , the wormlike chain is compressed and keeps moving closer to the center, and thus the monomer density in the middle increases. When the value of H is approximately 4, which is $H \sim \sqrt{2L\lambda}$, the behavior of the chain is mainly Gaussian. At this stage, the size of the chain has a minimum value, corresponding to the situation where the monomer density in the middle is the largest (see the yellow line in Fig. 4 and the blue line in Fig. 5).

After the chain size reaches the minimum H again, the monomer density in the middle decreases. At this time, the chain begins to exhibit wormlike chain behavior. The size of the wormlike chain increases. When H is extremely small, the distribution of the chain is similar to a series of small hard rods that are connected to each other with a direction that deviates from the restricted direction. The rigidity of the chain slowly decreases the size and monomer density in the middle with decreasing H .

Fig. 6 shows that the orientation of the wormlike chain is constantly approaching the direction parallel to the surface of

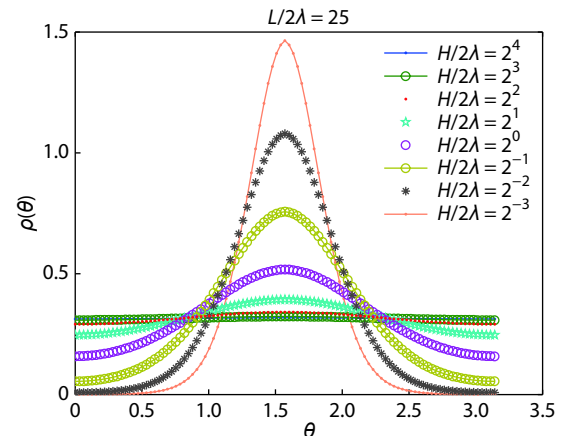


Fig. 6 The profile of the normalized segment density with respect to θ with $L/2\lambda = 25$.

hard walls, with the greatest probability of orientation parallel to the walls.

When the wall spacing H is large, the densities of all values of θ are equal, indicating that the wormlike chain is freely oriented between the parallel walls. The orientation parallel to the hard walls is not affected by the walls, while the other orientations are affected. As H decreases, the probability of an orientation parallel to the walls slowly increases, while the probability of other orientations gradually decreases. That is, the value of θ keeps getting closer to $\pi/2$, and the orientation of the wormlike chain keeps moving closer to the direction parallel to the walls.

However, due to the rigidity of the wormlike chain, when the value of H is very small, and the values of θ near $\pi/2$ are dominant, the orientation of the wormlike chain is not only parallel to the walls, but also at a small angle to the walls.

The free energy of a single wormlike chain confined between hard walls is indicated in Fig. 7. As H increases, the free energy decreases and the decreasing speed is slow at first,

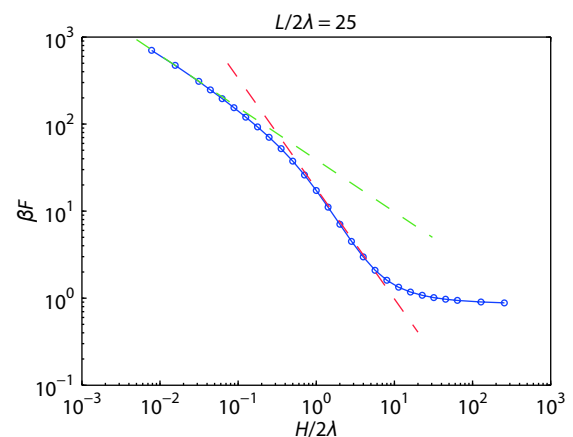


Fig. 7 The profile of the free energy with respect to $H/2\lambda$ with $L/2\lambda = 25$. In fact, the free energy has negative values. To clearly observe the changes in the free energy, we translate the free energy and use a double logarithmic scale. The green line represents the strong confinement asymptotic power law. The orange line represents the Gaussian asymptotic power law.

then fast and finally slow until it is almost constant.

The changes in the free energy have the following stages, among which stages 3 to 5 correspond to the analysis results of Chen:^[6]

Stage 1: When H is extremely large, equivalent to an unrestricted situation, the wormlike chain is almost completely free, and the free energy is almost constant.

Stage 2: When H slowly decreases, the wormlike chain begins to be compressed. Since H is still relatively large at this time, most segments are free. Due to the large H , the change in the free energy is slow, and the number of possible forms of the chain decreases slowly, which leads to a slow increasing of free energy.

Stage 3: When H decreases to satisfy the formula $H \sim \sqrt{2L\lambda}$, this stage is called weak confinement. The entire system degenerates into a Gaussian chain model in the restricted area. The free energy obeys a Gaussian asymptotic power law and increases linearly with decreasing H . For the flexibility of the Gaussian chain, it changes greatly by the limit of the hard walls, and the free energy increases rapidly.

Stage 4: When H continues to decrease, the influence of excluded volume between the segments gradually increases. As a result, the free energy decreases more slowly than that in stage 3 but faster than that in stage 5.

Stage 5: When H is extremely small, the two walls are very close and the walls have a great effect on the wormlike chain, which is called strong confinement. At this point, the free energy obeys the strong confinement asymptotic power law and decreases linearly as H decreases. In addition, the speed of decrease is lower than that in stage 3. Due to the obvious rigidity of the wormlike chain, the chain changes little, and the free energy increases slowly.

Fix λ and H and Increase L

Now we fix $\lambda = 2$, $H = 4$ and take $L = 2^{-7}, 2^{-6}, \dots, 2^9, 2^{10}$ to study the situation of a wormlike chain with different total contour lengths confined between two parallel hard walls.

It is observed that the changes in the wormlike chain shown in Figs. 8–10 are similar to those in the former section. When the value of L increases, the number of segments increases, and the restriction on the chain increases as a result (similar to the increase in the restriction on the chain caused

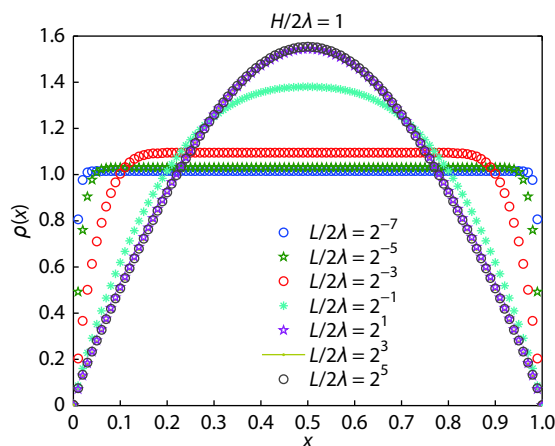


Fig. 8 The profile of the normalized segment density with respect to x when $H/2\lambda = 1$. Stage 1.

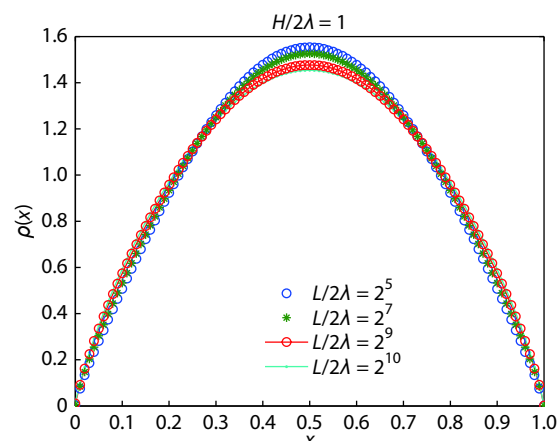


Fig. 9 The profile of the normalized segment density with respect to x when $H/2\lambda = 1$. Stage 2.

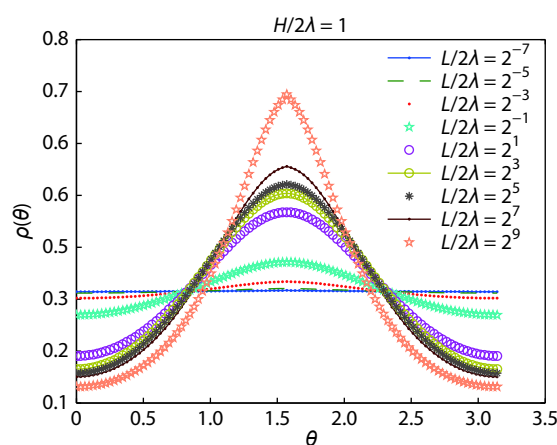


Fig. 10 The profile of the normalized segment density with respect to θ with $H/2\lambda = 1$.

by a decrease in H). The density in the middle of the parallel walls first increases and then decreases. Meanwhile, the orientation of the wormlike chain is most likely parallel to the walls.

Fig. 11 shows that the free energy changes from being almost constant to increasing as $L/2\lambda$ increases. When $L \gg \lambda$, the free energy is proportional to $L/2\lambda$, which is consistent with Chen's analysis.^[6]

When L is extremely small, the chain is hardly limited by the walls. Thus, the free energy is almost unchanged. As L slowly increases, the chain begins to be constrained by the walls. Since we have $H \gg L$ at this time, the limitations of the walls are small, which leads to a small increase in the free energy. When the chain becomes an ideal Gaussian chain, that is, when L satisfies $H \sim \sqrt{2L\lambda}$ and $L \gg \lambda$ (the system is reduced to a Gaussian chain model under weak confinement) or only $L \gg \lambda$, chain flexibility has the same effect on the free energy. Thus, the free energy per unit chain length is the same. Therefore, the free energy is proportional to L , which is proportional to $L/2\lambda$ (see in the latter part of Fig. 11). Because of the flexibility of the chain and the increasing limitations of the walls, the wormlike chain changes quickly and the free energy increases faster than in the previous stage.

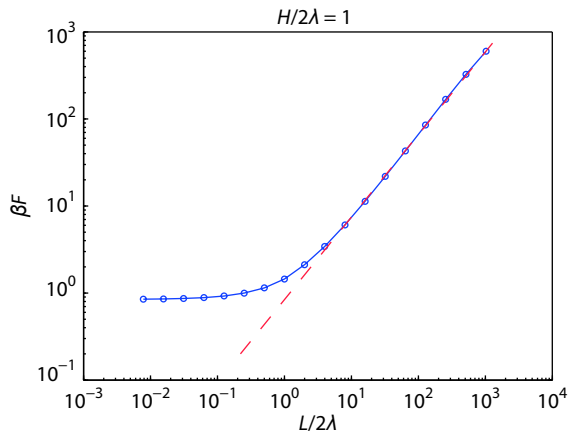


Fig. 11 The profile of the free energy with respect to $L/2\lambda$ with $H/2\lambda = 1$. We make an overall translation of the free energy and take double logarithmic scales. The orange line represents the proportional relationship.

Fix L and H and Increase λ

Here, we fix $L = 4$ and $H = 2$, and take $\lambda = 2^{-10}, 2^{-9}, \dots, 2^9, 2^{10}$ to study the situation of a wormlike chain with different persistence lengths confined between two parallel hard walls.

It is seen from Figs. 12–14 that increasing λ , decreasing H and increasing L cause the same changes in the distribution and orientation of the wormlike chain. For this reason, we no longer need to analyze in detail.

Fig. 15 reveals that the free energy increases with λ and the increase is slow at first, then gets faster, and finally slows down until it is almost constant. The entire change in the free energy and the causes of the change are similar to those in the former section.

When λ is extremely small, we have $H \gg \lambda$, and the chain is subject to very small restrictions. As the stiffness increases slowly, the free energy of the entire chain increases slowly. When λ increases to a certain extent (satisfying $H \sim \sqrt{2L\lambda}$ and $L \gg \lambda$), the model becomes a Gaussian chain model. Due to the flexibility of the chain, the morphology changes rapidly after compression, and the free energy increases sharply. Continuing to increase λ until $L \sim \lambda$, the chain exhibits worm-

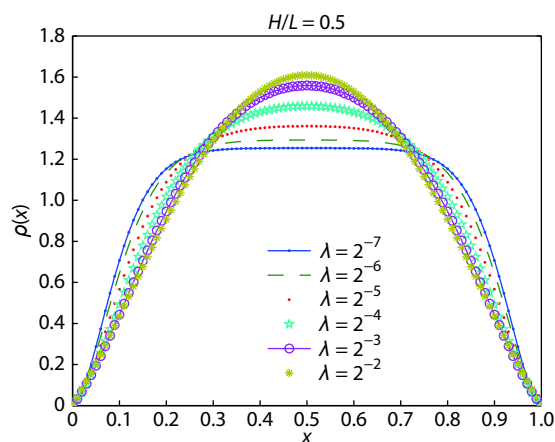


Fig. 12 The profile of the normalized segment density with respect to x when $H/L = 0.5$. Stage 1.

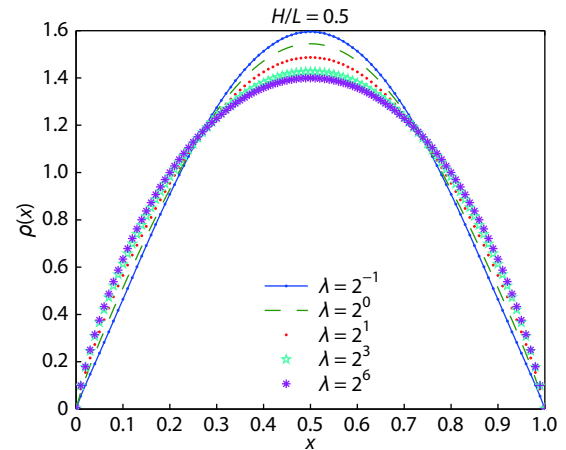


Fig. 13 The profile of the normalized segment density with respect to x when $H/L = 0.5$. Stage 2.

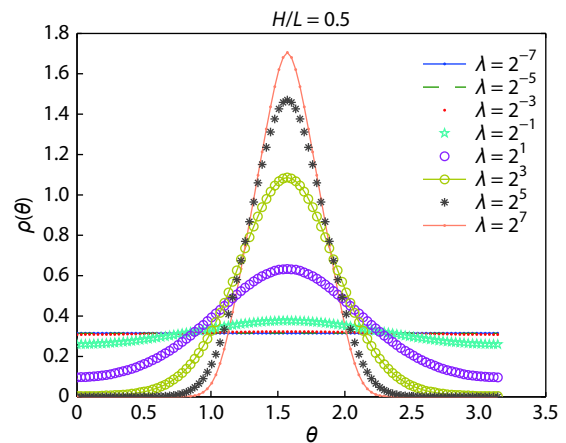


Fig. 14 The profile of the normalized segment density with respect to θ when $H/L = 0.5$.

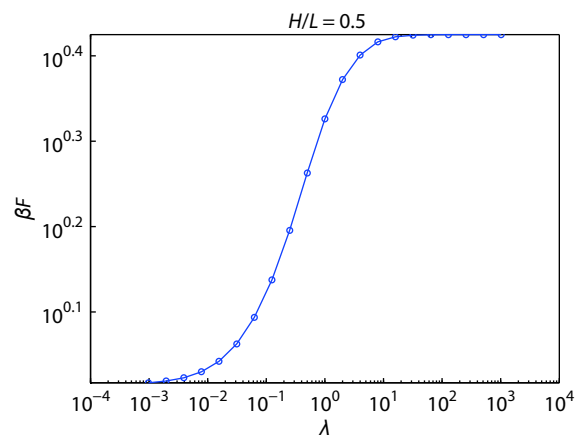


Fig. 15 The profile of the free energy with respect to λ with $H/L = 0.5$. We make an overall translation of the free energy and take double logarithmic scales. $H/L = 0.5$.

like chain behavior. At this time, the speed at which the free energy increases declines due to the rigidity. When λ is particularly large, that is, $L \ll \lambda$, the chain can hardly change shape in the restricted area. In such a case, the wormlike chain has

the smallest degree of freedom and the largest free energy. At this stage, the free energy is basically unchanged and corresponds to the maximum value. Correspondingly, we present the results shown in Fig. 13 as $\lambda = 2^6$ and shown in Fig. 14 as $\lambda = 2^7$, which corresponds to the case of the rigid rod under confinement.

CONCLUSIONS

Now we summarize the distribution of the wormlike chain. As the distance between the two hard walls gradually decreases (or as the total contour length of the wormlike chain gradually increases or as the persistence length gradually increases), the size of the wormlike chain continuously decreases and then gradually increases after reaching a minimum value. The speed of the increase is high at first and then declines. The orientation of the wormlike chain constantly approaches the direction parallel to the surface of the hard walls, with the greatest probability of orientation parallel to the walls.

The free energy of the wormlike chain has been analyzed by three situations as stated in the previous section. For a long wormlike chain, the free energy decreases as the distance between the walls increases. The decreasing speed is low at first, then gets larger, and finally becomes low until it is almost constant. There are two special cases at this time. In strong confinement, the free energy obeys the strong confinement asymptotic power law; in weak confinement, the wormlike chain exhibits Gaussian chain behavior and the free energy obeys a Gaussian asymptotic power law. This conclusion is consistent with the analysis of Chen.^[6] For a wormlike chain, the free energy changes from almost constant to increasing as the total contour length increases. When $L \gg \lambda$, the free energy is proportional to $L/2\lambda$, which is consistent with Chen's analysis.^[4] In addition, the free energy increases with L and the increasing is slow at first, then fast, and finally slow until it is almost constant. The causes of these changes in free energy are similar. The stage in which the free energy increases faster corresponds to the stage in which the restricted system exhibits Gaussian chain behavior.

The most important theoretical result is that the long wormlike chain can be described by a Gaussian long chain

under weak confinement.

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