

Free Energy of a Wormlike Polymer Chain Confined in a Slit: Crossover between Two Scaling Regimes

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Received April 18, 2006; Revised Manuscript Received August 14, 2006

ABSTRACT: We consider a wormlike polymer confined between two flat surfaces separated by a distance W . Using a wormlike chain formalism that couples the orientational and positional degrees of freedom, for a wormlike chain much longer than the persistence length ℓ_p , we calculate the free energy per segment as a function of W and compare it with the two scaling behaviors valid in the large and small W/ℓ_p limits.

I. Introduction

Theoretical understanding of a polymer confined in a restricted space, either between parallel plates or inside a cylindrical or spherical pore, is a topic that has generated much interest because of its relevance in practical systems.^{1,2} The competing length scales, in the problem of a confined flexible polymer chain without excluded volume interactions, are the radius of gyration R_0 and the typical confinement length scale W . The pioneering work of Casassa and Tagami,³ as well as the later work of de Gennes,⁴ yielded the well-known scaling behavior of the free energy

$$F \propto k_B T (R_0/W)^2 \quad (1)$$

which is valid in the parameter regime $a \ll W \ll R_0$, a being the Kuhn length of the polymer. Here, k_B is the Boltzmann constant and T the temperature of the system.

A wormlike polymer is characterized by the persistence length ℓ_p ,^{5–7} which, based on the definition of the end-to-end distance, can be related to the Kuhn length a by the relationship $\ell_p = a/2$ in the long polymer limit.^{5,8} In a strong cylindrical-confinement problem where the diameter W of the cross section of the cylinder is less than a , $W \ll a \ll R_0$, Odijk showed that the scaling behavior of the free energy can be written as^{9,10}

$$F \propto k_B T \frac{L}{\ell_p} \left(\frac{a}{W}\right)^{2/3} \propto k_B T R_0^2 / (a^4 W^2)^{1/3} \quad (2)$$

where L is the total length of the polymer and we have used $R_0^2 \propto L \ell_p$ for the last part of the above equation. In this expression, the persistence length ℓ_p directly enters, in contrast with eq 1. Equation 2 has also been analytically deduced for a wormlike polymer in a cylindrical¹¹ tube with a soft confinement potential and rectangular¹² tube with a hard boundary condition. Recent computer simulations have also explored the validity of the Odijk scaling relationship in this regime of parameter space for a wormlike chain in a tube.^{13–15} As well, the associated concept of deflection length can be used to guide our understanding of the Brownian dynamics of such a system.¹⁶

The scaling properties of a confined wormlike chain with excluded volume interactions in the strong-confinement limit have recently been discussed in association with DNA confinement.¹⁷

Equally important is the topic of wormlike chains confined between two plates (see Figure 1).¹⁸ For confinement of a wormlike polymer in a narrow rectangular tube, Burkhardt has shown that the free energy is the sum of two contributions, each having the same form in eq 2 but with W replaced by the length of one of the two sides of the rectangle.¹² This result can be generalized to the system of strong confinement of a wormlike polymer in a narrow slit, as will be briefly discussed in section IV. Recently, actin molecules confined between walls have been experimentally studied.^{19–21} The wall-to-wall separation, for example, is as small as 1 μm , an order lower than the persistence length.¹⁹ Hendricks and co-workers have conducted molecular dynamics simulations to examine a wormlike polymer chain confined between plates to understand the angular correlation function in such a system.²²

In this paper, we examine the free energy of a wormlike chain confined between two hard walls with varying size of the width-to-Kuhn-length ratio, W/a . We first examine an analytic solution for a wormlike chain in the large width regime, recovering eq 1 (section III). The free energy in the crossover regime between the two limits in eqs 1 and 2 is then numerically calculated and discussed in section V.

II. Statistical Weight for a Wormlike Chain in External Field

In the Saito–Takahashi–Yunoki (STY) treatment,⁵ the configuration of a polymer is described by a continuous space curve $\mathbf{r}(t)$, for which the statistical weight depends on the local curvature variation and an external potential

$$P \propto \exp \left[- \int_0^{L/a} dt \left\{ \frac{1}{4} \left| \frac{d\mathbf{u}(t)}{dt} \right|^2 + \beta V[\mathbf{r}(t), \mathbf{u}(t)] \right\} \right] \quad (3)$$

where $\mathbf{u}(t)$ is the unit vector $\mathbf{u}(t) \equiv (1/a) d\mathbf{r}(t)/dt$, $\beta = 1/k_B T$, and $V(\mathbf{r}, \mathbf{u})$, a function of both \mathbf{r} and \mathbf{u} , is the external potential energy acting on a unit segment. For a polymer confined between hard walls, $V(\mathbf{r}, \mathbf{u}) = 0$ in the region between the walls

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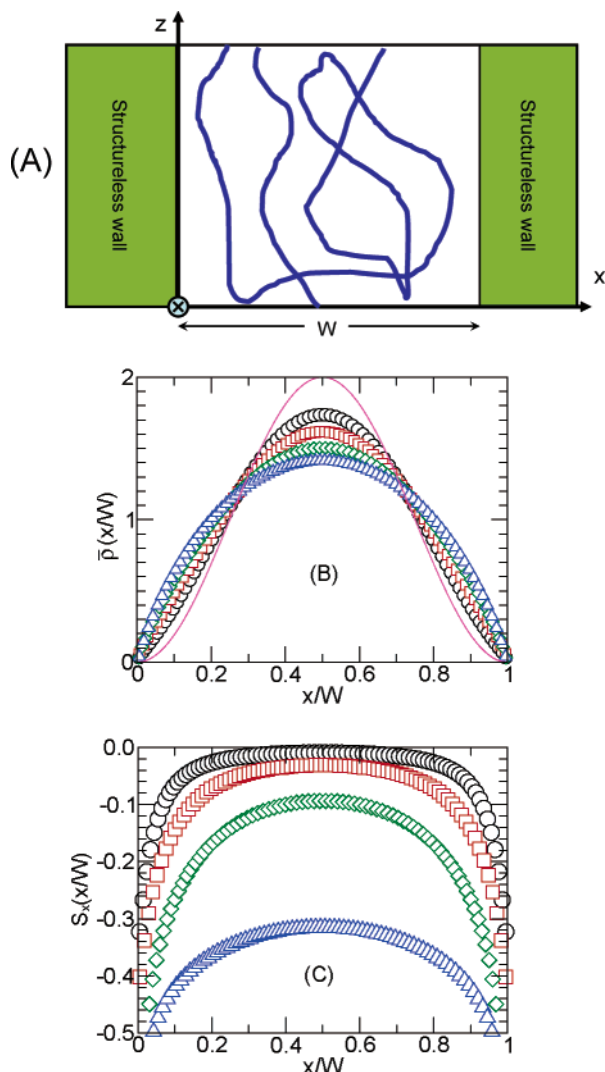


Figure 1. (A) Schematic diagram of a wormlike chain confined between two parallel walls and the coordinate system used, (B) the normalized segment density profile, and (C) the orientational order parameter profile. The two hard walls, located at $x = 0$ and $x = W$, are assumed to be without any features and sterically confine a wormlike chain. The solid curve in (B) represents the limit of $W \gg a$ and can be obtained exactly. Circles, squares, diamonds, and triangles represent the profiles obtained numerically for $W/a = 4, 2, 1,$ and 0.25 , respectively.

and is infinite outside this region. The variables \mathbf{r} and \mathbf{u} in the probability function can be treated as independent variables, after incorporating both the constraints $\mathbf{u}^2 = 1$ and $\mathbf{u}(t) \equiv (1/a)d\mathbf{r}(t)/dt$.²³ Hereafter we explicitly use the equivalent Kuhn length, a

$$a \equiv 2l_p \quad (4)$$

instead of l_p in order to make a direct comparison with the properties of a flexible chain.

We consider the conditional probability, $\Psi(\mathbf{r}, \mathbf{u}; t)$, that a polymer portion of length t has an end located at \mathbf{r} and whose tangent vector points in the direction \mathbf{u} . One can show that $\Psi(\mathbf{r}, \mathbf{u}; t)$ satisfies the partial differential equation⁶

$$-\frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{u}; t) = -[\nabla_{\mathbf{u}}^2 - a\mathbf{u} \cdot \nabla_{\mathbf{r}} - \beta V(\mathbf{r}, \mathbf{u})] \Psi(\mathbf{r}, \mathbf{u}; t) \quad (5)$$

with the “initial” condition

$$\Psi(\mathbf{r}, \mathbf{u}; 0) = 1 \quad (6)$$

The average segmental distribution function over the entire chain, i.e., the probability for finding a segment of the polymer to be located at \mathbf{r} and with a tangent vector pointing in direction \mathbf{u} , can be written as

$$\rho(\mathbf{r}, \mathbf{u}) = \frac{\int_0^{L/a} dt \Psi(\mathbf{r}, \mathbf{u}; t) \Psi(\mathbf{r}, -\mathbf{u}; L/a - t)}{\int d\mathbf{r} d\mathbf{u} \Psi(\mathbf{r}, \mathbf{u}; L/a)} \quad (7)$$

In the rest of this paper, we are only concerned about long wormlike chains where the radius of gyration of the chain, R_0 , is much greater than both l_p and W . Within this parameter regime, the ground-state solution for the operator in the square brackets of eq 5 is the dominating function contributing to the free energy and segmental density distribution. Adopting the coordinate system in Figure 1A, we need to obtain the ground-state solution to the eigenproblem

$$\beta\mu \Psi(x, \mathbf{u}) = -\left[\nabla_{\mathbf{u}}^2 - a u_x \frac{\partial}{\partial x} - \beta V(x, \mathbf{u})\right] \Psi(x, \mathbf{u}) \quad (8)$$

where u_x is the projection of the \mathbf{u} vector onto the x axis. The ground-state eigenvalue can be identified with $\beta\mu$, where μ is the segmental chemical potential. After obtaining the ground-state eigenfunction $\Psi_0(x, \mathbf{u})$ and eigenvalue $\beta\mu$, we have asymptotically for large t

$$\Psi(\mathbf{r}, \mathbf{u}; t) \approx \Psi_0(x, \mathbf{u}) \exp(-\beta\mu t) \quad (9)$$

Considering the relationship between ρ and Ψ in eq 7, we have

$$\rho(x, \mathbf{u}) \propto \Psi_0(x, \mathbf{u}) \Psi_0(x, -\mathbf{u}) \quad (10)$$

Note the physical meaning of the product on the right-hand side of eq 10: two polymer portions with terminal ends located at x are needed to form a nonterminal segment at x . The appearance of the opposite signs of the two \mathbf{u} vectors on the right-hand side of eq 10 is the indication that for a nonterminal segment to point along \mathbf{u} the two connected terminal segments must have terminal ends with one pointing along \mathbf{u} and the other $-\mathbf{u}$. A closely related problem to the current system is the adsorption of a wormlike chain at a flat surface with a varying potential well depth and width; for this problem, similar theoretical approaches have been taken recently.^{24–26} The negative sign in front of the second \mathbf{u} vector can only be omitted for systems containing a reversal symmetry in \mathbf{u} , such as in the case of studying the bulk properties of a nematic phase.^{10,27,28}

III. Recovery of the Flexible-Chain Results for $W \gg a$

One of the most important features of the above formalism for $\Psi_0(x, \mathbf{u})$ is that for a “wide” confinement gap, $W \gg a$, it recovers the well-known formalism for a flexible-chain confined in a slit. We start by noting that the only relevant orientational variable is $u_x \equiv \mathbf{u} \cdot \hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is a unit vector along the x axis.

Expanding $\Psi_0(x, u_x)$ in terms of Legendre functions $P_l(u_x)$, we write

$$\Psi_0(x, u_x) = \sum_{l=0}^{\infty} \Phi_l(x) P_l(u_x) \quad (11)$$

for $0 \leq x \leq W$, where, at this stage, $\Phi_l(x)$'s ($l = 0, 1, 2, \dots$) are undetermined functions of x . The substitution of this expression

into eq 8 allows us to identify the coupled differential equations that $\Phi_l(x)$ must satisfy. For $l = 0$, we have

$$\beta\mu\Phi_0(x) = \frac{1}{3} \frac{a}{W} \frac{d}{d\bar{x}} \Phi_1(x) \quad (12)$$

where

$$\bar{x} \equiv x/W \quad (13)$$

For $l = 1, 2, 3, \dots$, we have

$$\beta\mu\Phi_l(x) = l(l+1)\Phi_l(x) + \frac{l}{2l-1} \frac{a}{W} \frac{d}{d\bar{x}} \Phi_{l-1}(x) + \frac{l+1}{2l+3} \frac{a}{W} \frac{d}{d\bar{x}} \Phi_{l+1}(x) \quad (14)$$

A comparison between the first and the second terms on the right-hand side reveals that for any l the l th order function, $\Phi_l(x)$, has order of magnitude $(a/W)^l$ for small a/W . In addition, according to eq 12, the eigenvalue $\beta\mu$ has order of magnitude $(a/W)^2$, which agrees with eq 1.

More specifically, for $l = 1$ we have

$$-\beta\mu\Phi_1(x) = -2\Phi_1(x) - \frac{a}{W} \frac{d}{d\bar{x}} \Phi_0(x) - \frac{2}{5} \frac{a}{W} \frac{d}{d\bar{x}} \Phi_2(x) \quad (15)$$

where the left-hand side and the last term on the right-hand side are of order $(a/W)^3$. Dropping these terms because they are 2 orders of a/W smaller than other terms in eq 15, we have

$$\Phi_1(x) = -\frac{1}{2} \frac{a}{W} \frac{d}{d\bar{x}} \Phi_0(x) + \mathcal{O}\left(\frac{a}{W}\right)^3 \quad (16)$$

Combining eqs 12 and 16, for the region $0 \leq x \leq W$, we arrive at

$$-\beta\mu\Phi_0(x) = \left[\frac{1}{6} \left(\frac{a}{W}\right)^2 \frac{d^2}{d\bar{x}^2} \right] \Phi_0(x) + \mathcal{O}\left(\frac{a}{W}\right)^4 \quad (17)$$

which for small (a/W) is identical to the eigenproblem in same space region for a confined flexible chain.⁷ The solution to this eigenproblem leads to

$$\beta\mu = (\pi^2/6)(a/W)^2 \quad (18)$$

and a normalized density

$$\bar{\rho}(x) = \rho(x) \left[\int_0^1 \rho(x) d(x/W) \right]^{-1} = 2 \sin^2(\pi x/W) \quad (19)$$

This density function is plotted as the solid curve in Figure 1B. The free energy for a confined flexible polymer can then be written as

$$F = \mu L/a \propto k_B T (\sqrt{La}/W)^2 \propto k_B T (R_0/W)^2 \quad (20)$$

where $R_0 = \sqrt{La}$ is the root mean square end-to-end distance.^{3,7}

It is known that most physical properties of a wormlike chain (obeying eq 3) recover those of a flexible chain (obeying the Edwards weight⁷) in the limit of $L \gg a$; we see here no exception for the current system, as long as the persistence length is much smaller than the slit width $l_p \ll W$. Because $\Phi_l(x) \propto (a/W)^l$, there is no significant orientational ordering in the system, as expected for a flexible chain. In addition, for $W \lesssim a$ systems, the estimation $\Phi_l(x) \propto (a/W)^l$ is an indication of

the necessity of including more terms on the right-hand side of eq 11 in a calculation.

The mathematical problem in this section is analogous to the one-velocity-group-transport approximation in neutron transport theory.²⁹ A similar discussion of the recursion relation in eq 14 for recovering the Gaussian limit, but in a different context not involving the width W , has been previously described by Schmid and Müller.³⁰ Morse and Fredrickson also discussed this briefly for the interface problem of a polymer mixture.³¹ The Legendre-function expansion for the current problem has been used in related systems³² and is a simpler version of an expansion based on spherical harmonics.³³⁻³⁵

IV. The Case of $W \ll a$

The other important limit is strong confinement where $W \ll a$. Burkhardt has shown that the solution of the partial differential equation, eq 8, can be rewritten in an integral form where further analysis requires numerical computation.¹² His derivation was for a narrow rectangular tube where two directions along the sides of the rectangle can be treated separately. On the basis of his treatment for one of the two directions, his result suggests that, for a wormlike chain confined by parallel plates where $W \ll a$, the same Odijk scaling

$$\beta\mu = A(a/W)^{2/3}, \quad W/a \ll 1 \quad (21)$$

is valid. Using a rather than l_p as the basic unit length, we can relate A to Burkhardt's A_0 by $A = 2^{1/3}A_0$. Taking his estimate¹² of $A_0 = 1.1036$, we have

$$A = 1.3905 \quad (22)$$

which will be verified by our numerical data in the next section.

V. The Case of $W \sim a$

We now return to the general case of $W \sim a$ where we must solve the full eq 8. Experimental studies are most likely to be performed in this regime. For example, the crossover of the two scaling limits was tested experimentally by observing confined DNA molecules in a tube.³⁶

To represent the potential well for the coordinate system described in Figure 1, we might be tempted to write the external potential energy $V(x, u_x) = V_w(x, u_x)$, where

$$\beta V_w(x, u_x) = \begin{cases} 0 & 0 < x < W \\ \infty & x < 0 \text{ or } x > W \end{cases} \quad (23)$$

with $V_w(0, u_x) = V_w(W, u_x) = \infty$. This potential energy, however, does not reflect the actual physics within a distance of approximately a from the walls. Consider a polymer that has its terminal end located at $x = 0^+$. The terminal segment that points in the negative x -direction is not directly influenced by the hard-wall steric interaction; hence V_w is zero. On the other hand, a polymer terminal segment that points in the positive x -direction is subject to the hard-wall steric interaction; hence $V_w = \infty$. This implies that $V_w(0, u_x)$ has a strong orientational dependence, and this must be treated carefully:

$$\beta V_w(0, u_x) = \begin{cases} 0 & u_x < 0 \\ v_\infty & u_x \geq 0 \end{cases} \quad (24)$$

where $v_\infty \equiv \infty$. According to the same rationale, we write

$$\beta V_w(W, u_x) = \begin{cases} 0 & u_x > 0 \\ v_\infty & u_x \leq 0 \end{cases} \quad (25)$$

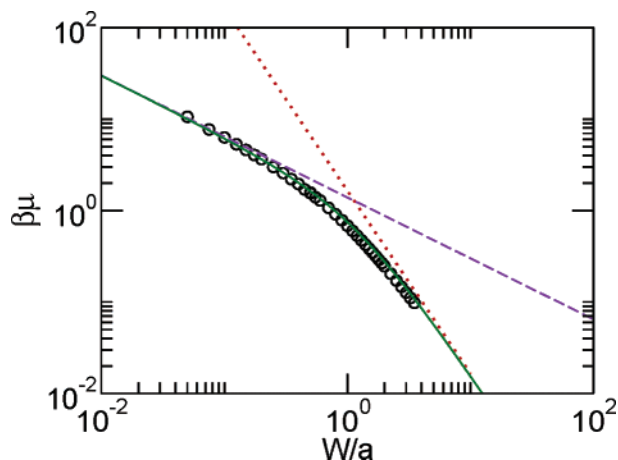


Figure 2. Numerical solution of the confinement free energy per segment μ in reduced form, $\mu/k_B T$, as a function of the well width to effective Kuhn length ratio, W/a , for a wormlike chain, shown in circles. The dotted line represents the asymptotic scaling behavior $\mu/k_B T = (\pi^2/6)(a/W)^2$, consistent with that determined based on a model for flexible chains. The dashed line represents the asymptotic scaling behavior $\mu/k_B T = 1.3905(a/W)^{2/3}$, consistent with the scaling theory for the strong confinement case. The solid curve is an empirical formula (eq 27) that interpolates between these two asymptotic limits.

Note that this set of boundary conditions has been used previously for treating related systems.^{12,34}

To proceed further, we have developed a numerical scheme to handle the coupled equation set in eqs 12 and 14 where the region $[0, 1]$ for \bar{x} is divided into N_x slabs. A numerical representation of the functions $\Phi_l(x)$ at the nodes dividing the slabs was considered, for $l = 0, 1, 2, \dots, n$; all functions beyond $l = n$ have been neglected in the computation. The boundary conditions in eqs 24 and 25 were also expanded in a Legendre series, where, instead of ∞ , we used a finite but large v_∞ in the actual calculation:

$$\beta V_w(x, u_x) = \sum_{l=0}^{\infty} v_l(x) P_l(u_x) \quad (26)$$

where $v_l(0)$ as well as $v_l(W)$ can be obtained from eqs 24 and 25 by the Legendre transformation.

The right-hand side of eq 8 was then expanded in Legendre functions based on the expansions for $V_w(x, u_x)$ and $\Psi_0(x, u_x)$ in eqs 11 and 26. The coupling term, $\beta V_w(x, u_x)\Psi_0(x, u_x)$ in eq 8, was expressed by a single summation of the Legendre functions, with the coefficients dependent on $\Phi_l(x)$ and constants defined by the integration of three Legendre functions. The operator in the square brackets of eq 8 could then be represented by a tridiagonal block matrix of dimension $M \times M$, where $M = (n + 1) \times N_x$. The lowest eigenvalue $\beta\mu$ of this matrix was found computationally. In carrying out the numerical calculation, we used $n = 16$, $v_\infty = 50$, and $N_x = 120$.

Figure 2 shows the numerical results (circles) for $\beta\mu$ as a function of W/a in a double-logarithmic plot. The errors of the data points are approximately represented by the size of the circles. Although our main interest is in the crossover regime, $W \sim a$, our results in the large W/a regime approach the dotted line in the figure, which represents the large W/a limit $\beta\mu = \pi^2/6(a/W)^2 + \mathcal{O}(a/W)$ in eq 18. In addition, in the small W/a regime, the numerical results for $\beta\mu$ approach the Odijk scaling, represented by a slope of $-2/3$ in a double-logarithmic plot. The crossover between these two asymptotic scaling behaviors can be seen to occur near $W/a \approx 1$. A preliminary result of our

numerical results was reported recently,³⁵ but with inadequate data to clearly demonstrate the Odijk limit.

Our numerical solution can be well represented by an empirical expression

$$\beta\mu = \frac{(\pi^2/6)(a/W)^2}{[C_2(a/W)^2 + C_1(a/W) + 1]^{2/3}} \quad (27)$$

where the coefficient C_2 in the denominator has been fixed to match the value in eq 22 in the $W/a \ll 1$ limit, $C_2 = 1.2865$. The numerical value of the coefficient C_1 was obtained by a least-squares fit to the numerical data in Figure 2, $C_1 = 0.9920$. The solid curve in Figure 2 represents this formula. Using this expression, we can finally write down a crossover expression for the free energy of a wormlike chain confined in slit

$$F = \frac{k_B T (\pi^2/6) (R_0/W)^2}{[1.2865(a/W)^2 + 0.9920(a/W) + 1]^{2/3}} \quad (28)$$

The normalized segment density

$$\bar{\rho}(\bar{x}) = \frac{\int d\mathbf{u} \rho(\bar{x}, \mathbf{u})}{\int d(x/W) d\mathbf{u} \rho(\bar{x}, \mathbf{u})} \quad (29)$$

and order parameter profiles

$$S_x(\bar{x}) = \frac{\int d\mathbf{u} P_2(u_x) \rho(\bar{x}, \mathbf{u})}{\int d\mathbf{u} \rho(\bar{x}, \mathbf{u})} \quad (30)$$

are plotted in Figure 1B,C for several values of W/a . The illustration demonstrates that as W/a is decreased from a rather large value (circles where $W/a = 4$) to a small value (crosses where $W/a = 0.25$), $\bar{\rho}(x)$ deviates from the universal form predicted for flexible chains [the result given in eq 19 (solid curve)] and starts to show a W/a -dependent behavior. For small W/a , instead of occupying the central region between the walls to maximize the entropy, the polymer segments are forced toward the near-wall regions by the smaller separations. As a consequence, polymer segments near the walls develop significant orientational ordering, lying parallel to the walls—a value $-1/2$ for S_x implies that the segments are perfectly parallel to the surface of the wall.

VI. Summary

In summary, the free energy of confined wormlike polymer chains was studied based on a wormlike-chain model. We have numerically calculated the free energy as a function of the confinement width, W , in the crossover regime between two limits: the large W/a limit where a flexible-chain model can be applied and the small W/a limit where the strong confinement gives rise to a different scaling behavior.

Acknowledgment. We thank NSERC for financial support and SHARCNET for computation time.

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MA060871E