

Confinement free energy of semiflexible polymers

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Using a novel scheme to compute the chemical potential of semiflexible polymers, we have measured the confinement free energy of a wormlike chain in a tube. We compare our result for the dependence of the free energy on the chain length, the persistence length and the diameter of the cylinder with the corresponding theoretical predictions based on the scaling theory of Odijk and the fluctuation theory of Helfrich. Our simulation data agree well with the exponents of the theoretically predicted power laws. We find evidence that, for long wavelengths, the mode damping assumption underlying Helfrich's theory is valid.

1. Introduction

The wormlike chain, proposed by Kratky and Porod in 1949 [1], is an idealized model for a semiflexible polymer. Wormlike chains have been tested extensively for dilute solutions [2,3] and they proved to explain very well the equilibrium properties, like the light scattering, small-angle X-ray and neutron scattering data and the transport and dynamical properties, like sedimentation coefficient and the intrinsic and dynamic viscosity. During the past decade, this model has been used to model [4–8] liquid crystals, gels and semiflexible polymers in confined geometries.

A key quantity in the theoretical description of confined wormlike chains is the change in free energy associated with this confinement. In ref. [4], Odijk has reviewed some of the theories that can be used to estimate the confinement free energy of a wormlike chain [5–10]. Although at first sight, the theories due to Khokhlov and Semenov [7,8], Helfrich [6,9,10] and Odijk [4,5] seem rather

different, they all lead to similar predictions for the confinement free energy. Nevertheless, many of the basic concepts in the theory of wormlike chains have never been tested directly and it would be interesting to test some of these assumptions in the theoretical description of the wormlike chains by computer simulations. However, numerical simulations of wormlike chains are difficult with the existing Monte Carlo schemes.

In this paper we report a novel computational approach to this problem based on the configurational-bias Monte Carlo method [11]. In section 2, we will briefly discuss the scaling theory of Odijk [4,5] and Helfrich's theory, based on a rather ad hoc assumption, for a semiflexible polymer in a tube. In section 3, our choice of simulation technique is explained and the results are discussed in section 4. The computational scheme is discussed in detail in the appendix.

2. Theory of semiflexible polymers

In what follows, we use the notation of Odijk [4,5]. We consider an infinitely thin polymer with contour length L and persistence length P and $L \gg P$. The bending free energy of this polymer can be written as follows:

$$F_b = \frac{1}{2} C \int_0^L ds \left[\left(\frac{d^2 r_x}{ds^2} \right)^2 + \left(\frac{d^2 r_y}{ds^2} \right)^2 \right], \quad (1)$$

where we decompose the displacements of the polymer into two independent directions, r_x and r_y . The persistence length P is related to the bending elastic modulus C ,

$$P = \frac{C}{k_B T}. \quad (2)$$

To compute the confinement free energy of a stiff chain in a long cylindrical pore of diameter D , Odijk [4,5] has introduced a very useful concept, namely the deflection length. This length scale λ corresponds to the average distance between successive deflection points of the chain in the pore. In ref. [4] it is shown that the theories of refs. [5–8] all yield qualitatively the same expression for the confinement free energy ΔF_c ,

$$\frac{\Delta F_c}{k_B T} \sim \frac{L}{\lambda}. \quad (3)$$

Eq. (3) can be made plausible by a scaling argument [4,5]. An extensive

quantity like the free energy must scale like $k_B T$ times the chain length divided by the only other relevant length scale. As the chain loses its angular correlations through these deflections, this relevant length scale is no longer the persistence length P , but the deflection length λ . Thus we arrive at eq. (3). For the deflection length of a stiff chain in a long cylindrical pore of diameter D , the following expression can be derived [5,12]:

$$\lambda \sim P^{1/3} D^{2/3}. \quad (4)$$

Inserting eq. (4) in eq. (3), we obtain

$$\frac{\Delta F_c}{k_B T} = c \frac{L}{P^{1/3} D^{2/3}} \quad (5)$$

for $P \gg \lambda$ and where c is a dimensionless prefactor.

Helfrich's line of reasoning is quite different and is based on the so-called undulation force [6] due to the confinement of the polymer. If we introduce a Fourier expansion of the displacements of the polymer:

$$r_j = \sum_{q=-\infty}^{\infty} a_{j,q} e^{iqs}, \quad j = x, y, \quad (6)$$

the mean-square amplitudes $\langle a_q^2 \rangle_{\text{free}}$ for one direction for a free polymer can be deduced from eq. (1) and the equipartition theorem,

$$\frac{1}{2} CLq^4 \langle a_q^2 \rangle_{\text{free}} = \frac{1}{2} k_B T. \quad (7)$$

If we now put the polymer in a tube the fluctuations of the polymer will be partly suppressed. Helfrich [6] assumes that all Fourier modes will be suppressed by the same amount,

$$\frac{1}{\langle a_q^2 \rangle_{\text{restr}}} = \frac{1}{\langle a_q^2 \rangle_{\text{free}}} + \tau, \quad (8)$$

where the subscript restr refers to the restricted polymer. The mean-square displacement of the confined polymer for one direction can be calculated from

$$\langle r^2 \rangle = \sum_{q=-\infty}^{\infty} \langle a_q^2 \rangle_{\text{restr}}. \quad (9)$$

On the other hand the mean square displacement must be of the order of the square of the diameter of the tube,

$$\langle r^2 \rangle = \mu D^2. \quad (10)$$

Eliminating $\langle r^2 \rangle$ between eqs. (9) and (10) and using eq. (8) will lead to

$$\frac{\tau}{L} = \frac{1}{4\mu^{4/3} D^{8/3} P^{1/3}}. \quad (11)$$

The confinement free energy can now be calculated with the help of a plausible expression for the associated change in free energy of a single mode ΔF_q [9] and by integration over all q modes and the two independent directions,

$$\frac{\Delta F_c}{k_B T} = -\frac{L}{2\pi} \int_{-\infty}^{\infty} \log R(q) dq, \quad (12)$$

with

$$R(q) = \frac{\langle a_q^2 \rangle_{\text{restr}}}{\langle a_q^2 \rangle_{\text{free}}}. \quad (13)$$

This leads again to eq. (5) for the confinement free energy. It is interesting to note that, unlike the scaling approach, Helfrich's theory leads to a prediction for the prefactor $c = \mu^{-1/3}$. Eq. (12) shows that the ratio of the mean square amplitudes for the confined chain and the free polymer is directly correlated to the confinement free energy and it is therefore interesting to investigate this quantity in more detail. Using eqs. (7) and (8), we can rewrite this quantity as follows:

$$R(q)_{\text{Helfrich}} = \frac{q^4}{q^4 + \tilde{q}^4}, \quad (14)$$

with

$$\tilde{q} = \left(\frac{\tau}{PL} \right)^{1/4} = \frac{1}{4^{1/4} \mu^{1/3} D^{2/3} P^{1/3}} \quad (15)$$

and we see that \tilde{q} scales with the reciprocal of the deflection length λ with a prefactor

$$c_1 = 2^{-1/2} \mu^{-1/3}. \quad (16)$$

We see that in this specific case, $R(q)$ is a universal function of q/\tilde{q} or $q\lambda$ as predicted on general grounds by Odijk [13]. The aim of the simulations

reported below is twofold. First, we test the scaling relations of the confinement free energy and we compute the prefactor. In the second place, we want to test Helfrich's assumption concerning the suppression of the Fourier modes of the polymer conformations and we want to investigate the scaling behaviour of these Fourier spectra by testing if $R(q)$ is indeed a universal function of q/\tilde{q} .

3. Simulation method

Our aim is to compute the increase of free energy of a semiflexible chain, due to the confinement imposed by the tube. The confinement free energy can be expressed in terms of the partition function of the confined chain and of the ideal chain, Z and Z^{id} respectively,

$$\Delta F_c = -k_B T \log\left(\frac{Z}{Z^{\text{id}}}\right). \quad (17)$$

The ideal chain is our reference state, i.e. a chain that is not confined in a cylinder. The ideal chain will have an internal potential energy that is equal to the sum of the bending energies of the individual joints. The bending energy for a joint between segments $i-1$ and i of a polymer with conformation Γ_w is

$$u_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} = C'(\theta_{\hat{w}_{i-1}\hat{w}_i})^2, \quad (18)$$

where $\theta_{\hat{w}_{i-1}\hat{w}_i}$ is the angle between the unit vectors \hat{w}_{i-1} and \hat{w}_i that specify respectively the orientations of the segments $i-1$ and i . If we compare eq. (18) with the expressions for the bending energy per unit length of a continuous, semiflexible polymer (eq. (1)), we get

$$C' = \frac{C}{2l}, \quad (19)$$

where l is the segment length. In what follows, we shall choose l to be our unit of length.

Monte Carlo simulations can be used to measure ensemble averages like $\langle A \rangle$, but cannot be used to compute the partition function directly. Thus, it is impossible to compute the confinement free energy by computing the partition function of the confined chain and of the ideal chain separately. Special techniques are required to compute free energies. Fortunately, the ratio of the two partition functions in eq. (17) can be rewritten as an ensemble average, similar to the so-called "particle-insertion method" of Widom [14]. The expression for the confinement free energy then becomes

$$\Delta F_c = -k_B T \log \left(\frac{\int \prod_{i=1}^L d\hat{w}_i \exp \left[-\beta \sum_{i=1}^L (u_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} + u_{\hat{w}_i}^{\text{wall}}) \right]}{\int \prod_{i=1}^L d\hat{w}_i \exp \left[-\beta \sum_{i=1}^L u_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} \right]} \right)$$

$$= -k_B T \log \left\langle \exp \left(-\beta \sum_{i=1}^L u_{\hat{w}_i}^{\text{wall}} \right) \right\rangle. \quad (20)$$

A naive way to simulate a wormlike chain would be to generate a very large number of completely random conformations of the freely jointed chain and compute the Boltzmann weight of the resulting conformation (fig. 1a). The problem with this approach is that the overwhelming majority of randomly generated conformations correspond to wormlike chains with a very high

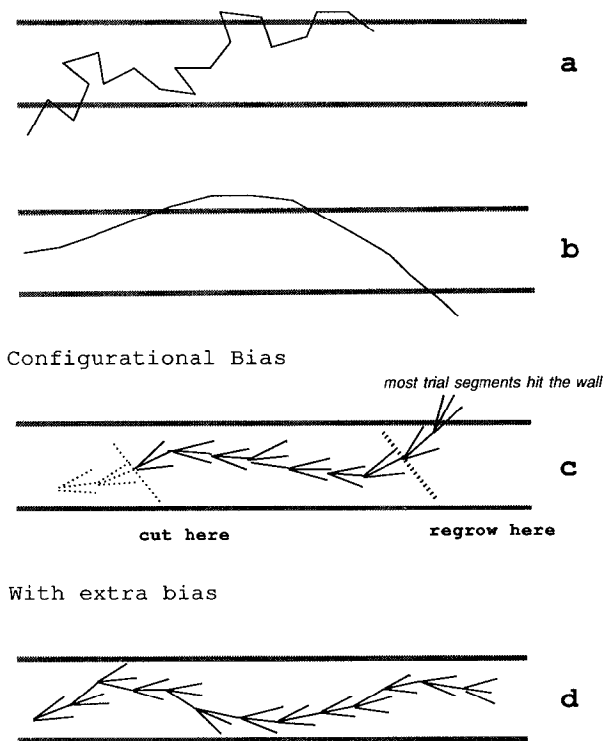


Fig. 1. Possible schemes to generate conformations of a wormlike chain. (a) Generating random conformations of a freely jointed chain. (b) Generating subsequent segments according to a probability distribution given by the intramolecular bending energy. (c) Configurational bias: generate several trial segments following scheme *b* and select one trial segment that has no overlap with the tube. (d) As in *c*, but with an additional bias that forces the chain to approach the tube wall approximately tangentially.

internal energy and probably with a very high external energy (and therefore a very small Boltzmann weight). Hence the statistical accuracy of this sampling scheme will be poor.

To alleviate the problem of high internal energies, we could sample the internal angles in the chain in such a way that the probability of finding a given angle is given by the internal Boltzmann weight (Fig. 1b). For every conformation thus generated, we compute the Boltzmann factor that corresponds to the interaction of the polymer with the hard wall of the cylinder. Thus, overlap of the polymer with the wall will give a Boltzmann factor equal to zero and no overlap will give one for the Boltzmann factor. With the average of these Boltzmann factors we can compute the confinement free energy.

This second approach is obviously superior to the first scheme. However, in many practical situations it will still yield poor statistics, because most ideal chain conformations will still not correspond to energetically favourable situations for the confined chain, as most chains will have overlap with the tube. Hence the Boltzmann weights will, again, be zero for the majority of conformations and the statistical accuracy will not be very good.

The problem with both schemes described above, is that neither allows us to focus on those conformations that should contribute most to Z , namely the ones for which both the internal and external potential energy are not much larger than a few $k_B T$ per degree of freedom. As the external energy is either zero for no overlap or infinity for overlap of the polymer with the hard wall, only non-overlapping conformations will contribute to Z . It would clearly be desirable to *bias* the sampling towards such favourable conformations.

One solution to this problem is to use the “configurational-bias Monte Carlo” sampling scheme for continuously deformable molecules [11,15]. In this scheme, the construction of chain conformations proceeds segment by segment. To add a segment, we generate a fixed number of trial segments, calculate for each trial segment the Boltzmann factor associated with the interaction with the wall and select the new segment with a probability proportional to that Boltzmann factor. Thus we will never choose a segment that has overlap with the tube, as this probability is equal to zero (fig. 1c). If we have grown a whole polymer, we cut the chain at a random position, regrow part of the chain at one or the other end and accept the new conformation with a certain probability, that is given in the appendix and is based on the condition of detailed balance. The advantage of this scheme is that we can rapidly generate, large conformational changes and a conformation that hits the wall will immediately be rejected.

Nevertheless, the problem remains that when the polymer is grown or regrown, there is still a large probability that the polymer will encounter the wall under a large angle, as the width of the orientational distribution of the

polymer after ℓ steps is equal to $\ell \langle \theta^2 \rangle$ with $\langle \theta^2 \rangle$ the width of the orientational distribution after one step. Because the trial segments are generated according to the internal Boltzmann factors, all trial segments will probably hit the wall and no trial segment will make such a large turn, that the polymer can go from the wall, or if it does, it will do so in a conformation with a high internal energy and therefore a small statistical weight. As a consequence, the statistical accuracy of this sampling scheme will be poor. We therefore introduced an extra bias into our computational scheme and the polymer will now be guided smoothly to and from the wall of the cylinder (fig. 1d). The trial segments will now not be generated according to the Boltzmann factors of the internal energy, but distributed around a new unit vector \hat{v} , that denotes the “bias” direction for the new segment. This vector \hat{v} depends on the radial distance of the segment to the axis of the cylinder and on the orientation of the $(i-1)$ th segment. Of course, in our Monte Carlo sampling we should correct for this bias. In the appendix this computational scheme is described in detail.

4. Results and discussion

As it is our aim to test the dependence of the confinement free energy of wormlike chains on the parameters characterising the chain and the confining tube, simulations were carried out on chains with lengths between 10 and 700 segments and with persistence lengths of 15 to 60 segments in tubes with diameters of 0.3 to 1.0. The parameters characterising the various simulations that we have performed have been collected in table I. Fig. 2 shows a plot of the confinement free energy per segment versus the number of segments of the

Table I

Parameters characterising the simulations of a polymer in a tube. The table shows the values for the length of the polymer L , for the persistence length P and for the diameter of the cylinder used in our simulations. The first column refers to the number of the figure. If one single value is shown in the table, we kept that parameter fixed at that value, otherwise the range is shown, wherein the value of that parameter is varied.

Fig.	L	D	P
2	10–700	0.80	60.00
3	500	0.30–1.00	60.00
4	500	0.60	15.00–60.00
5	512	0.60	60.00
6	512	0.60	60.00
7	512	0.40–1.00	60.00
8	512	0.60	20.00–60.00

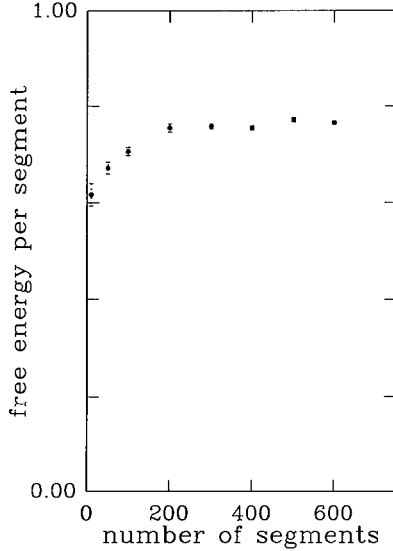


Fig. 2. A plot of the confinement free energy per segment of a polymer of length $L = 500$ and persistence length $P = 60$ in a tube with diameter $D = 0.80$, versus the number of segments of the polymer.

polymer. In order to estimate the statistical error of the confinement free energy, 40 independent simulations were performed. In each simulation we regrew the polymer 100 times. The confinement free energy per segment is found to approach a constant value for $L \gg P$, as expected, because the total free energy of the chain is an extensive quantity. In what follows, we shall always discuss simulations of wormlike chains with $L \gg P$.

The dependence of the free energy on the diameter of the cylinder and on the persistence length is shown respectively in figs. 3 and 4. The free energy is found to scale with the diameter of the cylinder as $\Delta F_c \sim D^a$, where $a = -0.66 \pm 0.07$ and with the persistence length P as $\Delta F_c/k_B T \sim P^b$, where $b = -0.31 \pm 0.05$. This should be compared with the value $a = -\frac{2}{3}$ and $b = -\frac{1}{3}$ predicted by the theory of refs. [4–8]. Thus our data are consistent with the scaling relations theoretically predicted.

Let us next consider if we can gain a better physical understanding of the scaling behaviour of the confinement free energy. Clearly, the physical origin of the confinement free energy is the suppression of chain fluctuations. Specifically Helfrich's theory is based on the argument that the scaling behaviour is a result of the *constant* suppressions of all Fourier modes of the chain fluctuations. Our simulations allow us to test this prediction in detail. In fig. 5 the difference of $1/\langle a_q^2 \rangle$ between the confined wormlike chain and the free polymer is shown as a function of q . For small q the difference appears to

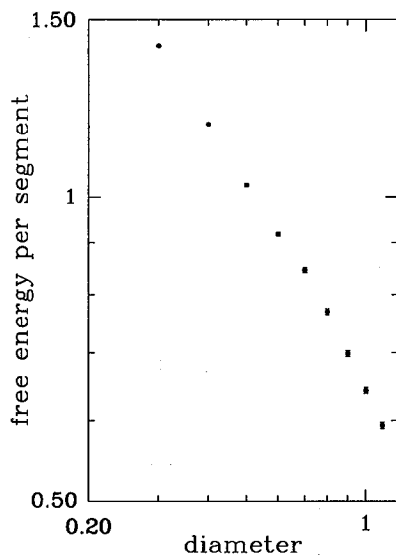


Fig. 3. A plot of the confinement free energy per segment of a polymer of length $L = 500$ and persistence length $P = 60$ in a tube, versus the diameter D of the tube.

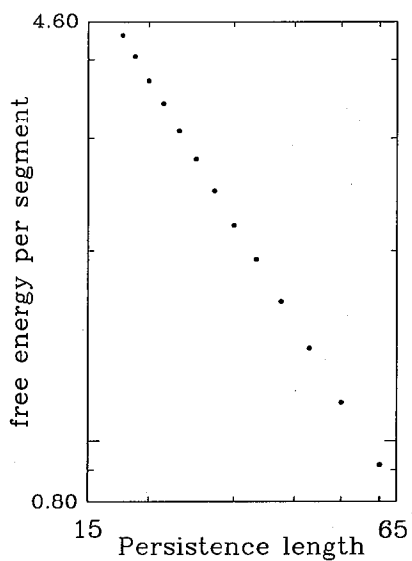


Fig. 4. A plot of the confinement free energy per segment of a polymer of length $L = 500$ in a tube with diameter $D = 0.60$, versus the persistence length P of the polymer.

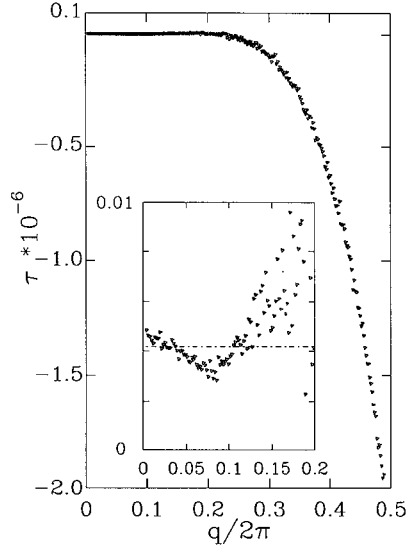


Fig. 5. A plot of $\tau = 1/\langle a_q^2 \rangle_{\text{restr}} - 1/\langle a_q^2 \rangle_{\text{free}}$ of a polymer with length $L = 512$ and persistence length $P = 60$ in a tube with diameter $D = 0.60$ as a function of q . The inset shows a magnification of the low- q region, where the dash-dot line (— · —) denotes the value of τ based on Helfrich's theory (for details see text).

be constant in agreement with eq. (8). However, we also observe, somewhat surprisingly, that the high- q Fourier modes of the confined chain are *enhanced* with respect to the free chain. For a confined continuous wormlike chain one can show that $R(q) \leq 1$ (ref. [16]). It therefore seems likely that the enhancement of the high- q modes we observe is caused by the rather small values for the diameter D used in the simulations. In any event, as we shall argue below, the confinement free energy is completely dominated by the low- q chain fluctuations that are suppressed rather than enhanced. If we magnify the plot of $1/\langle a_q^2 \rangle$ versus q in the low- q region, also shown in fig. 5, we see that the suppression of the Fourier modes varies by some 20% for $0 \leq q \leq 0.13$. This variation is not accounted for by the Helfrich theory. We expect that the fact that the suppression of the low- q Fourier modes is not completely constant, will affect the quantitative prediction of the Helfrich theory, but not the scaling behaviour.

Let us now test Helfrich's prediction for the amplitude of the low- q Fourier modes, i.e. τ in eq. (11). In order to compute τ , we must know the mean-square displacement of a polymer in a tube. (μ in eq. (10)). Helfrich gives the estimate $\mu = 1/24$. However, we can "measure" μ in our simulations. We find $\mu = 0.073 \pm 0.001$. If we insert this value of μ in eq. (11), we find that $\tau = 4.18 \pm 0.08 \times 10^3$. As can be seen from the magnified part of fig. 5, this

value of τ is indeed within the range found in our simulations. We note that if, in contrast, we would have used Helfrich's estimate $\mu = 1/24$, we would have seriously overestimated the value of τ (viz. $\tau = 8.84 \times 10^3$).

Helfrich's theory also gives a prediction for the prefactor in eq. (5), namely $c = \mu^{-1/3}$. In figs. 2 and 3 the prefactor is $c = 2.46 \pm 0.07$. With $\mu = 0.073 \pm 0.001$, we find $c = 2.39 \pm 0.01$. The actual value for c agrees within the statistical error with this value and turns out to be slightly lower than the value, obtained by using the value $\mu = 1/24$.

In order to investigate the scaling behaviour of the suppressions of these Fourier spectra, we compute the ratio $R(q)$ of the mean square amplitudes of the restricted chain and the free polymer for several values for the diameter of the tube and the persistence length. An example of the q -dependence of $R(q)$ is shown in fig. 6. As before we see the strong suppression of low- q Fourier modes of the chain fluctuations and an enhancement of the high- q modes. Odijk predicts that $R(q)$ becomes a universal function of q/\tilde{q} [13] and according to Helfrich $R(q)$ has the following functional form: $R(q)_{\text{Helfrich}} = q^4 / (q^4 + \tilde{q}^4)$ (eq. (14)). Below, we shall test this form of $R(q)$. First, we simply assume that R is an, as yet unspecified, universal function of q/\tilde{q} . We can then measure the dependence of \tilde{q} on D and P in the following way. We determine the value of q for which $R(q)$ has a given value. As R is a universal function of q/\tilde{q} , a fixed value of R corresponds to a fixed value of q/\tilde{q} , say x . If we now measure how this specific value of q depends on D and P , we immediately

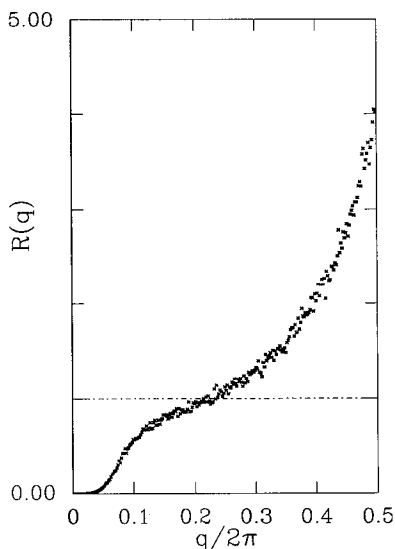


Fig. 6. A plot of the ratio of the mean-square amplitudes of the confined and the free chain as a function of q , with $D = 0.60$ and $P = 60$.

determine the dependence of $\tilde{q} = q/x$ on D and P . Following this procedure, we found that \tilde{q} scales with the diameter of the cylinder as $\tilde{q} \sim D^{a_1}$, where $a_1 = -0.69 \pm 0.06$ and with the persistence length P as $\tilde{q} \sim P^{b_1}$, where $b_1 = -0.37 \pm 0.04$. This should be compared with the value $a_1 = -\frac{2}{3}$ and $b_1 = -\frac{1}{3}$ predicted by Helfrich's theory [6,9,10].

In order to determine the prefactor c_1 in eq. (16), we have fitted our Fourier spectra with the function $R(q) = q^4/(q^4 + \tilde{q}^4)$, where $\tilde{q} = c_1/D^{2/3}P^{1/3}$. If we plot $R(q)$ versus q/\tilde{q} , we should expect that this curve is the same for all D and P . However, figs. 7 and 8 (magnification of fig. 7) show that this is only valid for $q/\tilde{q} \leq 0.15$. We find the best fits using $c_1 = 1.75 \pm 0.01$, which should be compared with the value $c_1 = 1.69 \pm 0.01$ using the value for $\mu = 0.073 \pm 0.001$ that follows from the simulations. The value for the prefactor, obtained by using $\mu = 1/24$ yields an overestimate for c_1 . In order to show the accuracy of our fits and the agreement with Helfrich's assumption, we show $R(q)/R_{\text{Helfrich}}(q)$ versus q/\tilde{q} in fig. 9. We find that, depending on P and D , this ratio may deviate some 30% from the value 1, for $q/\tilde{q} \leq 0.3$. Like the observed enhancement rather than suppression for the high- q modes it seems likely that the deviation from scaling behaviour for the high- q modes is also caused by the rather small values for the tube diameter D used in the simulations. Some support for this assumption can be obtained from the representation in the data in fig. 7, where it appears that the enhancement decreases with increasing D .

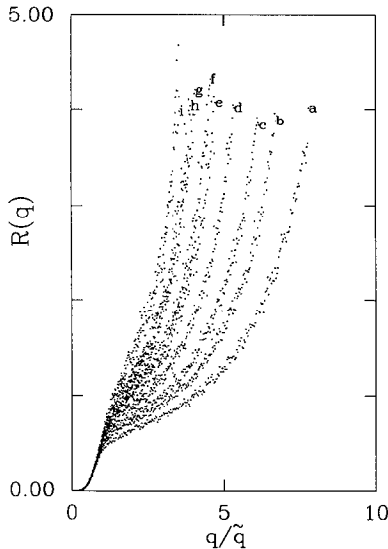


Fig. 7. A plot of the ratio of the mean-square amplitudes of the confined and the free chain as a function of q/\tilde{q} with the following values for respectively D and P : (a) 1.00, 60; (b) 0.80, 60; (c) 0.70, 60; (d) 0.60, 60; (e) 0.50, 60; (f) 0.60, 40; (g) 0.60, 30; (h) 0.40, 60; (i) 0.60, 20.

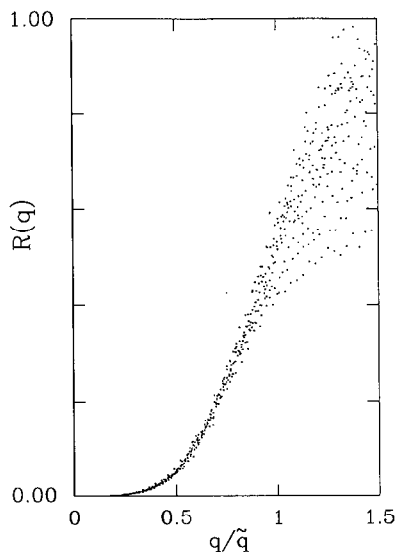


Fig. 8. A plot of the ratio of the mean-square amplitudes of the confined and the free chain as a function of q/\tilde{q} (magnification of fig. 7).

In summary, our simulations of the excess free energy of a wormlike chain confined in a tube appear to be in quantitative agreement with the scaling behaviour predicted by the theories of Helfrich, Khokhlov and Semenov and Odijk [4–8]. In addition, we find that the theory of Helfrich yields a prediction both for the absolute confinement free energy and the suppression of the long

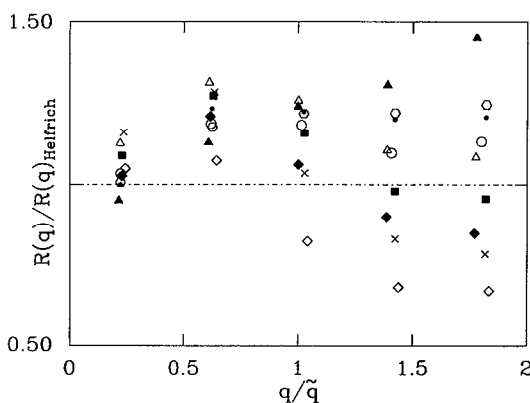


Fig. 9. A plot of the ratio of the mean-square amplitudes of the confined and the free chain divided by the ratio predicted by Helfrich as a function of q/\tilde{q} with the following values for respectively D and P , open diamond: 1.00, 60; cross: 0.80, 60; solid diamond: 0.70, 60; solid square: 0.60, 60; open triangle: 0.50, 60; open circle: 0.60, 40; open hexagon: 0.60, 30; dot: 0.40, 60; solid triangle: 0.60, 20.

wavelength modes, that is in good, but not perfect, agreement with our simulations.

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Appendix

To compute the confinement free energy of a wormlike chain in a tube, we apply the following “recipe” to construct a conformation of a chain of L segments. The construction of chain conformations proceeds segment by segment. Let us consider the addition of one such segment. To be specific, let us assume that we have already grown $i - 1$ segments, and that we are trying to add segment i . This is done as follows:

1. Generate a fixed number (say k) trial segments. The orientations of the trial segments are distributed according to the internal Boltzmann weight $P_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}} = \exp[-\beta u_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}}]$ associated with the internal bending energy times a weight function,

$$g_j = \frac{P_{\hat{v}\hat{w}_j}}{P_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}}}, \quad (21)$$

with

$$P_{\hat{v}\hat{w}_j} = \frac{1}{B} \exp[-\beta C(r_{xy}) (\theta_{\hat{v}\hat{w}_j})^2], \quad (22)$$

where r_{xy} is the radial distance of the previous segment to the axis of the tube and where $\theta_{\hat{v}\hat{w}_j}$ is the angle between the unit vectors \hat{w}_j and \hat{v} that denote respectively the orientation of the j th trial segment and the bias orientation, as yet unspecified, for the i th segment. The unit vector \hat{v} depends on the unit vector that specifies the orientation of the previous segment \hat{w}_{i-1} and on the radial distance of the previous segment to the axis of the cylinder. The normalisation constant B is equal to $\int d\hat{w} P_{\hat{v}\hat{w}}$. The bending constant $C(r_{xy})$ is

also dependent on the radial distance of the previous segment to the axis of the cylinder,

$$C(r_{xy}) = \frac{C}{1 - (2r_{xy}/D)^2}.$$

For the bias direction, we took the following boundary conditions:

$$\hat{\mathbf{v}}(\hat{\mathbf{w}}_{i-1}, r_{xy}) = \begin{cases} \hat{\mathbf{e}}_z & \text{if } r_{xy} = D/2, \\ \hat{\mathbf{e}}_z & \text{if } \hat{\mathbf{w}}_{i-1} \cdot \hat{\mathbf{e}}_z = 0, \\ \hat{\mathbf{w}}_{i-1} & \text{if } r_{xy} = 0, \end{cases} \quad (23)$$

with $\hat{\mathbf{e}}_z$ along the axis of the cylinder. An equation for the bias direction of segments i that satisfies these conditions is

$$\hat{\mathbf{v}}(\hat{\mathbf{w}}_{i-1}, r_{xy}) = \frac{\mathbf{v}(\hat{\mathbf{w}}_{i-1}, r_{xy})}{|\mathbf{v}(\hat{\mathbf{w}}_{i-1}, r_{xy})|}, \quad (24)$$

where $\mathbf{v}(\hat{\mathbf{w}}_{i-1}, r_{xy})$ is equal to

$$\mathbf{v}(\hat{\mathbf{w}}_{i-1}, r_{xy}) = (\frac{1}{2}D - r_{xy})(\hat{\mathbf{w}}_{i-1} \cdot \hat{\mathbf{e}}_z)\hat{\mathbf{w}}_{i-1} + r_{xy}(1 - \hat{\mathbf{w}}_{i-1} \cdot \hat{\mathbf{e}}_z)\hat{\mathbf{e}}_z. \quad (25)$$

We denote the different trial segment by indices $1, 2, \dots, k$. Now the probability to generate a given subset $\{\hat{\mathbf{w}}\}_i$ of k trial segments with orientations $\hat{\mathbf{w}}_1$ through $\hat{\mathbf{w}}_k$ is equal to

$$P_{\{\hat{\mathbf{w}}\}_i} = \frac{1}{B^k} \prod_{j=1}^k d\hat{\mathbf{w}}_j P_{\hat{\mathbf{w}}_{i-1}\hat{\mathbf{w}}_j}^{\text{id}} g_j = \frac{1}{B^k} \prod_{j=1}^k d\hat{\mathbf{w}}_j P_{\hat{\mathbf{v}}\hat{\mathbf{w}}_j}. \quad (26)$$

2. For all k trial segments, we compute the ‘‘external’’ Boltzmann factor $\exp(-\beta u_{\hat{\mathbf{w}}_j}^{\text{wall}})$, where $u_{\hat{\mathbf{w}}_j}^{\text{wall}}$ is the potential energy of the j th trial segment of the polymer with conformation $\Gamma_{\mathbf{w}}$ due to interaction with the wall of the cylinder.

3. Select one of the trial segments, say $\hat{\mathbf{w}}_i$, with a probability

$$P_{\hat{\mathbf{w}}_i}^{\text{wall}} = \frac{\exp(-\beta u_{\hat{\mathbf{w}}_i}^{\text{wall}})}{Z_{\{\hat{\mathbf{w}}\}_i}}, \quad (27)$$

where we have defined

$$Z_{\{\hat{\mathbf{w}}\}_i} \equiv \sum_{j=1}^k \exp(-\beta u_{\hat{\mathbf{w}}_j}^{\text{wall}}).$$

The subscript $\{\hat{w}\}_i$ means that \hat{w}_i is one of the segments of the subset, so $\hat{w}_i \in \{\hat{w}\}$.

4. Add this segment as segment i to the chain and store the corresponding partial ‘‘Rosenbluth weight’’ [11]:

$$\omega_i = Z_{\{\hat{w}\}_i} / k \quad (28)$$

and the weight-factor g_i (Eq. (21)).

The desired ratio Z/Z^{id} is then equal to the average value (over many trial chains) of the product of the partial Rosenbluth weight times the reciprocal partial weight factor divided by the average value of the product of the reciprocal partial weight factors:

$$\frac{Z}{Z^{\text{id}}} = \frac{\left\langle \prod_{i=1}^L \omega_i \cdot g_i^{-1} \right\rangle_g}{\left\langle \prod_{i=1}^L g_i^{-1} \right\rangle_g} = \left\langle \prod_{i=1}^L \omega_i \right\rangle, \quad (29)$$

where the angular brackets with the subscript g denote and average over the sampling distribution $P_{\hat{w}_j}$ and not the distribution $P_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}}$. This is similar to the Umbrella Sampling [17], where the desired average will be obtained by a biased sampling. The advantage of this scheme is that step 3 biases the sampling towards energetically favourable conformations.

However, it still remains to be shown that eq. (29) is, in fact, correct. To this end let us consider the probability with which we generate a given chain conformation. This probability is the product of a number of factors. Let us first consider these factors for one segment, and then later extend the result to the complete chain.

We wish to compute the average of ω_i , over all possible sets of trial segments and all possible choices of the segment. To this end, we must sum over all \hat{w}_i in a set and integrate over all orientations $\prod_{j=1}^k d\hat{w}_j$ to get all possible sets of trial segments,

$$\langle \omega_i \rangle = \frac{\langle \omega_i \cdot g_i^{-1} \rangle_g}{\langle g_i^{-1} \rangle_g} = \frac{\int P_{\{\hat{w}\}_i} \sum_{i=1}^k P_{\hat{w}_i}^{\text{wall}} \omega_i \cdot g_i^{-1}}{\int P_{\{\hat{w}\}_i} g_i^{-1}}. \quad (30)$$

In the numerator the summation over the external Boltzmann factors $Z_{\{\hat{w}\}_i}$ in the probability to select a trial segment ($P_{\hat{w}_i}^{\text{wall}}$) will cancel the summation in the

Rosenbluth factor ω_i ,

$$\langle \omega_i \rangle = \left(\int \prod_{j=1}^k d\hat{w}_j P_{\hat{w}_j} \sum_{i=1}^k \frac{\exp(-\beta u_{\hat{w}_i}^{\text{wall}})}{k} g_i^{-1} \right) \left(\int \prod_{j=1}^k d\hat{w}_j P_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}} \right)^{-1}. \quad (31)$$

As the labeling of the trial segments in eq. (31) is arbitrary, all k terms yield the same contribution. We now arrive at

$$\begin{aligned} \langle \omega_i \rangle &= k \int d\hat{w}_i \left(P_{\hat{w}_i} \frac{P_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} \exp(-\beta u_{\hat{w}_i}^{\text{wall}})}{P_{\hat{w}_i}} \frac{1}{k} \right) \\ &\times \left(\int \prod_{j=1, j \neq i}^{k-1} d\hat{w}_j P_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}} \right) \left(\int \prod_{j=1, j \neq i}^{k-1} d\hat{w}_j P_{\hat{w}_{i-1}\hat{w}_j}^{\text{id}} \int d\hat{w}_i P_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} \right)^{-1}. \end{aligned}$$

The integrals over the $k-1$ orientations in the numerator will cancel the $k-1$ integrals in the denominator. Thus the final equation is

$$\langle \omega_i \rangle = \frac{\int d\hat{w}_i \exp[-\beta(u_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} + u_{\hat{w}_i}^{\text{wall}})]}{\int d\hat{w}_i \exp(-\beta u_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}})} = \frac{Z_i}{Z_i^{\text{id}}}. \quad (32)$$

The subscript in eq. (32) denotes that this expression holds for the i th segment. The extension to a polymer of L segments is similar. Note that with this scheme Z_i/Z_i^{id} is equal to one, when the cylinder is taken away, so when $u_{\hat{w}_i}^{\text{wall}} = 0$. It is not necessary to sample over a large distribution; the correct answer is immediately obtained.

For the configurational bias method, we used the detailed balance condition [11] in the Metropolis form,

$$\text{acc}(a|b) = \min\left(1, \frac{P_a/\exp(-\beta U_a)}{P_b/\exp(-\beta U_b)}\right), \quad (33)$$

where P_a and P_b are respectively the probabilities that the chain is in conformation a and b . If we now impose the ‘‘super-detailed’’ balance condition, we have to consider the probability of generating a new chain via one particular choice of trial directions $\{\hat{w}\}_i$ and of choosing a set of trial directions $\{\hat{w}'\}_i$ from all possible sets that contains the old configuration. The probability of generating a new chain of L segments via the set $\{\hat{w}\}_i$ and of choosing the set $\{\hat{w}'\}_i$ will now be equal to the probability to generate the old set of trial directions $\{\hat{w}'\}_i$ excluding the old orientation (denoted by $P_{\{\text{rest}'\}_i}$, where $\{\text{rest}'\}$ denotes the set of $k-1$ orientations of $\{\hat{w}'\}_i$ excluding the old

orientation) times the probability to generate a new set of trial directions $\{\hat{w}\}_i$ that contains the new orientation (i.e. $P_{\{\hat{w}\}_i}$) times the probability to select this new orientation (i.e. $\exp(-\beta u_{b_i}^{\text{wall}})/Z_{\{\hat{w}\}_i}$),

$$P_b = \prod_{i=1}^L P_{\{\hat{w}\}_i} P_{\{\text{rest}'\}_i} \frac{\exp(-\beta u_{b_i}^{\text{wall}})}{Z_{\{\hat{w}\}_i}}, \quad (34)$$

where $P_{\{\hat{w}\}_i}$ will be given by eq. (26). $U_b = \sum_{i=1}^L u_{b_i}^{\text{id}} + u_{b_i}^{\text{wall}}$ and the Rosenbluth factor is equal to

$$\mathcal{W}_b = \prod_{i=1}^L \frac{Z_{\{\hat{w}\}_i}}{k}. \quad (35)$$

We now arrive at

$$\frac{P_b}{\exp(-\beta U_b)} = \prod_{i=1}^L \left(\frac{P_{\{\text{rest}'\}_i} P_{\hat{w}_i}^{\text{id}} P_{\{\text{rest}'\}_i}}{B P_{\hat{w}_{i-1}\hat{w}_i}^{\text{id}} k \mathcal{W}_b} \right). \quad (36)$$

Substitution of eq. (36) in eq. (33) gives

$$\text{acc}(a|b) = \min(1, \mathcal{W}_b G_b^{-1} / \mathcal{W}_a G_a^{-1}), \quad (37)$$

with

$$G_b = \prod_{i=1}^L g_{b_i}. \quad (38)$$

In words, the configurational bias Monte Carlo (CBMC) scheme works as follows:

1. Generate a trial conformation by using the Rosenbluth scheme (i.e. eq. (34)) to regrow the entire molecule, or part thereof.
2. Compute the Rosenbluth weights times the weight functions,

$$\mathcal{W}_{\text{old}} G_{\text{old}}^{-1} \quad \text{and} \quad \mathcal{W}_{\text{trial}} G_{\text{trial}}^{-1},$$

of the trial conformation and of the old conformation.

3. Accept the trial move with a probability

$$\min(1, \mathcal{W}_{\text{trial}} G_{\text{trial}}^{-1} / \mathcal{W}_{\text{old}} G_{\text{old}}^{-1}).$$

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