Macromolecules **2000,** *33,* 3447−3452

Elasticity of Comb Copolymer Cylindrical Brushes

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Received June 28, 1999; Revised Manuscript Received February 23, 2000

ABSTRACT: An analysis of the cylindical brush of an isolated comb copolymer molecule consisting of a semiflexible backbone and flexible side chains is presented. Using the Alexander−de Gennes approximation, we calculate the free energy of both straight and bent cylindrical brush and the brush persistence length λ, and show that λ scales as a function of the side chain length M as $\lambda \propto M^2$. The discrepancy between the asymptotic scaling behavior and recent computer simulation results is also discussed.

I. Introduction

It is well-known that comb copolymers with densely grafted side chains in a good solvent can adopt a worm-like cylindrical brush configuration, in which the side chains are stretched in the direction normal to the backbone owing to the excluded volume interaction. The theory of polymer brushes, including cylindrical brushes and polymers grafted to convex surfaces, received a lot of attention recently.[1−17] However, less attention has been given to the bending elasticity of the brushes. Moreover, seemingly large discrepancies exist between the different theoretical approaches[8,9] and computer simulations[14,16] on bending elasticity of cylindrical brushes. Generally, the volume interaction between the side chains results in stiffening of the cylindrical brush described by the persistence length λ. There are two different predictions for the dependence of this persistence length on the length M of the side chains. According to Birshtein and co-workers,[8] the persistence length is proportional to diameter of the brush D ($D \propto M^{3/4}$), $\lambda/D \sim 1$, a result that seems to be supported by computer simulations.[14,16] However, using scaling arguments, Fredrickson clearly showed[9] that the osmotic energy increases on bending, which results in the following asymptotic behavior: $\lambda/D \propto M^{9/8}$. The validity of this equation implies that solutions of comb copolymer brushes can form liquid crystalline phases. Furthermore, as shown recently theoretically and by computer simulations, the persistence length of cylindrical brushes with rodlike side chains of length L increases as $\lambda \propto L^2$.[16,17]

In the present paper we analyze the bending elasticity of cylindrical brushes with flexible side chains using a self-consistent field approach. One of our objectives is to understand the discrepancy between the scaling prediction and recent computer simulation results. We will define the persistence length in the usual way through an increase of the free energy of the brush upon bending. If the cylindrical brush of contour length L^* homogeneously bends with a radius of curvature R, the free energy connected with this bend is given by

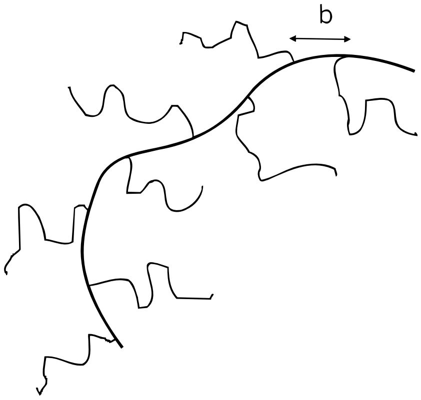

Figure 1. Model of comb copolymer chain studied in the present paper.

$$\Delta F = \frac{\lambda L^*}{2R^2} \tag{1}$$

II. Free Energy of a Straight Cylindrical Brush

To model the system, we consider a semiflexible backbone of contour length L^* and persistence length λ_0, grafted with flexible side chains consisting of M beads with excluded volume v, which are connected by springs with spring constant $\kappa = 3k_BT/a^2$, Figure 1. The free energy of interaction between the beads will be approximated by the second-virial approximation and is given by $f(c) = 0.5vc^2$, where c is the concentration of beads. We assume that the distance between two consecutive grafting points is b, $b < \lambda_0$. Obviously, the cylindrical brush regime appeares when the Flory radius of the side chain, $R_F \simeq a(v/a^3)^{1/5} M^{3/5}$, exceeds b:$b \ll a(v/a^3)^{1/5} M^{3/5}$.

First we will consider a straight cylindrical brush. The free energy per length b of the backbone in the cylindrical brush regime coincides with the free energy of the side chain and can in the most general form be written

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10.1021/ma991031l CCC: $19.00

as[18]

$$F = b \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\infty} r\, \mathrm{d}r \Big(- g(r, \varphi) \ln Z_M (r, \varphi|\mu) - \mu(r, \varphi)\, c(r, \varphi) + g(r, \varphi) \ln g(r, \varphi) + \frac{v}{2} c^2(r, \varphi)\Big) \quad (2)$$

Here we use polar coodinates (r, φ) in the cross section (further on we will also use Cartesian coordinates (x, y) so that $x = r \cos \varphi$, $y = r \sin \varphi$). In eq 2 we introduced the following functions: $g(r, \varphi)$ is the distribution function of the free chain end normalized as $b \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\infty} r\, \mathrm{d}r\, g(r, \varphi) = 1$, $c(r, \varphi)$ is the concentration profile, $\mu(r, \varphi)$ is the chemical potential of a chain segment, and $Z_M(r, \varphi|\mu)$ is the statistical sum of the chain with the free end position fixed at the point (r, φ) in the external field $\mu(r, \varphi)$. The first two terms in eq 2 represent the conformational free energy of the chain, the third term is the translational entropy of the free end, and the last term corresponds to the interaction. Together with eq 2 the self-consistency condition

$$\delta F/\delta c = 0 \quad (3)$$

should be fulfilled. This connects the concentration with the chemical potential: $\mu(r, \varphi) = vc(r, \varphi)$.

The functions $g(r, \varphi)$, $c(r, \varphi)$, and $\mu(r, \varphi)$ have to be determined by minimization of the free energy. Symmetry implies that they do not depend on φ. Note that owing to eq 3 we can consider the free energy as a function of the chemical potential and the free end distribution function. In that case, the minimum of the free energy as a function of the concentration actually implies a maximum as a function of the chemical potential due to the conjugation between the concentration and the chemical potential.

The statistical sum of a chain of $m + 1$ segments is related to that of a chain of m segments by the following well-known recursive relation[18]

$$Z_{m+1}(\mathbf{r}) = \int \mathrm{d}\mathbf{r}_1\, \rho(\mathbf{r} - \mathbf{r}_1)\, Z_m(\mathbf{r}_1) e^{-\mu(\mathbf{r})}, \quad \rho(\mathbf{r}) = \left(\frac{3}{2\pi a^2}\right)^{3/2} \exp\left(-\frac{3\mathbf{r}^2}{2a^2}\right) \quad (4)$$

which can be written in the differential form as

$$\frac{\partial Z_m(r, \varphi)}{\partial m} = \frac{a^2}{6}\left(\frac{\partial^2 Z_m(r, \varphi)}{\partial r^2} + \frac{1}{r}\frac{\partial Z_m(r, \varphi)}{\partial r} + \frac{1}{r^2}\frac{\partial^2 Zm(r, \varphi)}{2\varphi^2}\right) - \mu(r) Z_m(r, \varphi) \quad (5)$$

The statistical sum $Z_m(r, \varphi)$ does not depend on φ and can be expressed in terms of the chemical potential $\mu(r)$ if we consider the chain conformations as trajectories of classical particles moving in the external field $\mu(r)$. The transition from the Schrödinger type eq 5 to the corresponding equation of motion of a classical particle is well-known as a transition between wave and classical mechanics.[19,20] Using this analogy and writing the statistical sum in the form

$$Z_m(r) = Z_0(m, r) \exp (-mE - S(r)) \quad (6)$$

where the amplitude $Z_0(m, r)$ depends only slightly on m, r, we get the following equation for the function $S(r)$

$$\frac{a^2}{6}\left(\frac{\partial S(r)}{\partial r}\right)^2 \simeq \mu(r) - E \quad (7)$$

or

$$S(r) \simeq \frac{\sqrt{6}}{a} \int_0^r \mathrm{d}r_1 \sqrt{\mu(r_1) - E} \quad (8)$$

where the parameter E is equivalent to the energy of the particle. In eq 7 we also use the fact that $r \gg b$. Note that the function $S(r)$ coincides with the action in classical mechanics for a particle having the mass $3/a^2$. The linear momentum is $p = \partial S/\partial r$; therefore, the chain trajectory equation is given by[19,20]

$$\frac{\mathrm{d}r(m)}{\mathrm{d}m} = \frac{a^2}{3}\frac{\partial S(r)}{\partial r} = \frac{a\sqrt{6}}{3}\sqrt{\mu(r) - E} \quad (9)$$

and the initial condition is $r(0) = 0$. Generally, the parameter E depends on the position $r^* = r(M)$ of the free end, $E = E(r^*)$. The free energy of the chain can be found from eq 2 using eqs 6 and 8

$$F = 2\pi b \int_0^{\infty} r^*\, \mathrm{d}r^*\, g(r^*) \left(ME(r^*) + \frac{\sqrt{6}}{a}\int_0^{r^*} \mathrm{d}r \sqrt{\mu(r) - E(r)}\right) + 2\pi b \int_0^{\infty} r\, \mathrm{d}r \left(g(r) \ln g(r) - \mu(r)\, c(r) + \frac{v}{2} c^2(r)\right) \quad (10)$$

On the basis of the free energy 10 and eliminating the translational entropy term, we arrive at the well-known equations for a cylindrical brush.[4-6] Indeed minimization of this free energy over $g(r^*)$ and $\mu(r)$ results in the following equations

$$ME(r^*) + \frac{\sqrt{6}}{a}\int_0^{r^*} \mathrm{d}r \sqrt{\mu(r) - E(r^*)} = M\Lambda \quad (11)$$

$$\frac{\sqrt{6}}{2a}\int_r^{\infty} \frac{r^* g(r^*)\, \mathrm{d}r^*}{\sqrt{\mu(r) - E(r^*)}} = rc(r) \quad (12)$$

which together with eq 3s and 9, rewritten in the form

$$\frac{\sqrt{6}}{2a}\int_0^{r^*} \frac{\mathrm{d}r}{\sqrt{\mu(r) - E(r^*)}} = M \quad (13)$$

give the full system of equations for the unknown functions $c(r)$, $E(r)$, $g(r)$, and $\mu(r)$. The Lagrange multiplier Λ is determined from the normalization condition for the free end distribution function. After differentiation of eq 11 with respect to r^* and using eq 9, we find that

$$\frac{\mathrm{d}r(m)}{\mathrm{d}m}\Big|_{m=M} = \frac{a\sqrt{6}}{3}\sqrt{\mu(r^*) - E(r^*)} = 0 \quad (14)$$

or $E(r^*) = \mu(r^*)$, i.e, the velocity $\mathrm{d}r(m)/\mathrm{d}m$ vanishes at the free chain end.

Equations 12−14 have been considered in refs 5 and 6 for melt and marginal solvent, and, as has been shown, the free chain ends cannot penetrate close to the cylinder axis and are distributed in a zone $D^* < r < D$. In ref 6 it was shown that in a marginal solvent $D \simeq 0.65a(v/a^2b)^{1/4}M^{3/4}$, $D^*/D = 4/3\pi$, and the free energy is

$F \simeq 1.13(Mv/a^2b)^{1/2}$ (note, in our case the parameter a^2 is three times larger than that used in ref 6).

The translational entropy term complicates the equations; however, we can analyze the situation qualitatively. The boundary condition at the free end can be found from the equation $(\mathrm{d}/\mathrm{d}r^*)[\delta F/\delta g(r^*)] = 0$

$$\frac{\mathrm{d}r(m)}{\mathrm{d}m}\Big|_{m=M} = -\frac{a^2}{3}\frac{\partial}{\partial r^*}\ln g(r^*) \qquad (15)$$

It is natural to assume that the distribution function has a bell-like shape and thus has a maximum value at some distance h. As follows from eq 15, the velocity at the free end is not zero and is positive for $r^* < h$ and negative for $r^* > h$. A negative velocity implies that the chain trajectory attains the maximum distance $r_{\max}$ for some intermediate value $m = m^* < M$, $r_{\max} = r(m^*) > r^*$. At that point the velocity is zero, $\mathrm{d}r(m)/\mathrm{d}m|_{m=m^*} = 0$, and for $m > m^*$ the particle moves in the opposite direction inside the brush so that the trajectory equation is given by eq 8 but with a negative value of the square root. Mathematically it implies that in equation of motion 9 we transform from the positive to the negative branch of the double-valued function $\mathrm{d}S/\mathrm{d}r$. The trajectory that finishes at the point $r^* > h$ is always straight. We will not consider here the effect of the translational entropy on the free end distribution function and the free end distribution zone, leaving these questions for later.

Now, we simplify the calculations assuming that $E = E_0 =$ const. The free ends distribution function in this case is given by $g(r) = (1/2\pi)\delta(r - D^*)$. Obviously, in this way we return to the Alexander–de Gennes approximation. Accordingly, the free energy is given by

$$F = ME_0 + \frac{\sqrt{6}}{a}\int_0^{D^*}\mathrm{d}r\,\sqrt{\mu_0(r) - E_0} + 2\pi b\int_0^{D^*} r\,\mathrm{d}r\left(-\mu_0(r)c_0(r) + \frac{v}{2}c_0^2(r)\right) \qquad (16)$$

The system of equations for the functions $c_0(r)$, $\mu_0(r)$, and E_0 follows from eqs 3, 12, 13

$$\mu_0(r) = vc_0(r) \qquad (17)$$

$$\frac{1}{\sqrt{\mu_0(r) - E_0}} = \frac{4\pi bar}{\sqrt{6}v}\mu_0(r) \qquad (18)$$

$$\frac{\sqrt{6}}{2a}\int_0^{D^*}\frac{\mathrm{d}r}{\sqrt{\mu_0(r) - E_0}} = M \qquad (19)$$

The chemical potential inside the brush can be found from eq 18 and is in a good approximation given by

$$\mu_0(w) = E_0 + \left(\frac{\sqrt{6}v}{4\pi abD^*w}\right)^{2/3} \qquad (20)$$

where $w = r/D^*$. This equation gives the correct asymptotic behavior both for $w \to 0$ and $w \gg 1$. E_0 follows from the normalization condition $2\pi b\int_0^{D^*} c_0(r)\,r\,\mathrm{d}r = M$

$$E_0 = \frac{Mv}{\pi bD^{*2}} - \frac{3}{2}\left(\frac{\sqrt{6}v}{4\pi abD^*}\right)^{2/3} \qquad (21)$$

and the radius of the brush D^* can be found after minimization of the free energy eq 16

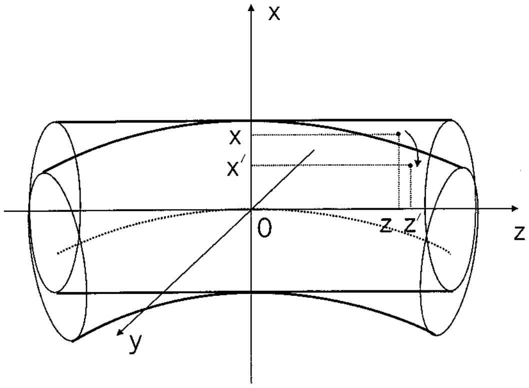

Figure 2. Illustration of the brush deformation. The point with coordinates $(x, y = 0, z)$ transforms into the point $(x', y = 0, z')$.

$$D^* \simeq 0.46a\left(\frac{v}{a^2b}\right)^{1/4}M^{3/4} \qquad (22)$$

(note, for $b \simeq R_F$, $D^* \simeq R_F$). Hence, the final result for the energy E_0 and the chemical potential is

$$E_0 \simeq 0.67\left(\frac{v}{a^2bM}\right)^{1/2},\quad \mu_0(w) \simeq E_0\left(1 + \frac{1}{3}\left(\frac{4}{w}\right)^{2/3}\right) \qquad (23)$$

and the free energy is given by

$$F \simeq 1.098\left(\frac{vM}{a^2b}\right)^{1/2} \qquad (24)$$

These results qualitatively coincide with those that have been obtained in refs 5 and 6. Moreover, the difference between the free energy eq 24 and the free energy obtained in ref 6 is very small and is about 3%.

III. Free Energy of Bent Brush

In this section we generalize the above approach to calculate the free energy of a bent brush. A similar problem, the distortion of a molten plane polymer brush, has been analyzed in ref 7 on the basis of an analogy with an almost equivalent electrostatic problem.[4] However, this approach essentially involves the incompressibility of the molten layer and cannot be applied in our case.

Let us consider the bending with radius of curvature R. Upon bending, any point (x, y, z) of the brush, where z is the coordinate along the cylinder axis and (x, y) are the coordinates in the cross section, transforms into a point (x', y', z'), Figure 2, so that

$$x' = x + u_x,\quad u_x = -\frac{z^2}{2R} \qquad (25)$$

$$y' = y$$

$$z' = z + u_z,\quad u_z = \frac{xz}{R}$$

Here we assume that the bending occurs in the (x, z) plane. Now let us transform to the coordinate system Z', which is connected with the bent cylinder. The coordinate z in this system is directed along the bent cylinder axis, and two other coordinates (r, φ) are polar coordinates in the cross section of the bent cylinder.

Note, the bent cylinder can also be considered as part of a torus. In the coordinate system Z'

$$x' = (r \cos \varphi + R) \cos(z/R) - R \qquad (26)$$

$$y' = r \sin \varphi$$

$$z' = (r \cos \varphi + R) \sin(z/R)$$

Bending transforms the free end distribution function, the concentration and the chemical potential as follows: $g'(x', y', z') \equiv g^*(r, \varphi)$, $c'(x', y'\ z') \equiv c^*(r, \varphi)$, and $\mu'(x', y', z') \equiv \mu^*(r, \phi)$, and they do not depend on z. The volume element $\mathrm{d}x'\mathrm{d}y'\mathrm{d}z' = (1 + r \cos \varphi/R)\ r\ \mathrm{d}r\mathrm{d}\varphi\mathrm{d}z$. Therefore, on bending the free energy is given by

$$F' = \frac{\lambda_0 b}{2R^2} + \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\infty} r\ \mathrm{d}r \left(1 + \frac{r \cos \varphi}{R}\right) \left(-g^*(r, \varphi) \ln Z'_M (r, \varphi|\mu^*) + g^*(r, \varphi) \ln g^*(r, \varphi) - \mu^*(r, \varphi)\ c^*(r, \varphi) + \frac{v}{2} c^{*2}(r, \varphi)\right) \qquad (27)$$

The first term in this equation corresponds to the bending energy of the backbone. The statistical sum $Z'_m(r, \varphi)$ can be found after transformation of eq 5 using eq 26

$$\frac{\partial Z'_m(r, \varphi)}{\partial m} = \frac{a^2}{6}\left(\frac{\partial^2 Z'_m(r, \varphi)}{\partial r^2} + \frac{1}{r}\frac{\partial Z'_m(r, \varphi)}{\partial r} + \frac{1}{r^2}\frac{\partial Z'_m(r, \varphi)}{\partial \varphi^2} + \frac{\cos \varphi}{R}\frac{\partial Z'_m(r, \varphi)}{\partial r} - \frac{\sin \varphi}{rR}\frac{\partial Z'_m(r, \varphi)}{\partial \varphi}\right) - \mu^*(r, \varphi)\ Z'_m(r, \varphi) \qquad (28)$$

The statistical sum can be written again in the form of eq 6, where the function $S = S(r, \varphi|\varphi_0)$ approximately satisfies

$$\frac{a^2}{6}\left[\left(\frac{\partial S(r, \varphi|\varphi_0)}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial \mathrm{S}(r, \varphi|\varphi_0)}{\partial \varphi}\right)^2\right] \simeq \mu^*(r, \varphi) - E(\varphi_0) \qquad (29)$$

Here we retain only the leading terms, which give the dominant contribution to the asymptotic behavior for large M. Generally, the energy $E = E(\varphi_0)$ depends on the azimuth of the free end φ_0. For small bending the chemical potential $\mu^*(r, \varphi)$ should be close to its value for the straight brush and depend only weakly on φ. Therefore, the gradient $\partial\mu^*(r, \varphi)/\partial\varphi$ is small, and we can use the gradient expansion for a calculation of the function $S(r, \varphi)$ from eq 29. In first order

$$S(r, \varphi|\varphi_0) \simeq \frac{\sqrt{6}}{a}\int_0^r \mathrm{d}r_1 \sqrt{\mu^*(r_1, \varphi) - E(\varphi_0)} \qquad (30)$$

The chain trajectory equations are

$$\frac{\mathrm{d}r(m)}{\mathrm{d}m} = \frac{a^2}{3}\frac{\partial S(r, \varphi)}{\partial r}; \quad \frac{\mathrm{d}\varphi(m)}{\mathrm{d}m} = \frac{a^2}{3r^2}\frac{\partial S(r, \varphi)}{\partial \varphi} \qquad (31)$$

In order to simplify the further analysis, we neglect the surface distortion upon bending and assume that the free end distribution function is given by $g^*(r, \varphi) = (1/2\pi)\psi(\varphi)\delta(r - D)$, where $\psi(\varphi)$ can be found from the self-consistency equation $\psi(\varphi) = Ac^*(D, \varphi)$, and the normalization constant A follows from equation $(1/2\pi) \int \psi(\varphi)(1 + D \cos \varphi/R)\mathrm{d}\varphi = 1$. The free energy eq 27 can be written as

$$F' = \frac{1}{2\pi}\int_0^{2\pi} \psi(\varphi)\ \mathrm{d}\varphi \left(1 + \frac{\mathrm{D} \cos \varphi}{R}\right)\left[ME(\varphi) + \frac{\sqrt{6}}{a}\int_0^D \mathrm{d}r \sqrt{\mu^*(r, \varphi) - E(\varphi)}\right] - \frac{b}{2v}\int_0^{2\pi} \mathrm{d}\varphi \times \int_0^D r\ \mathrm{d}r \left(1 + \frac{r \cos \varphi}{R}\right)\mu^{*2}(r, \varphi) + \frac{\lambda_0 b}{2R^2} \qquad (32)$$

where we used the self-consistency equation $\mu^*(r, \varphi) = vc^*(r, \varphi)$. The chemical potential $\mu^*(r, \varphi)$ and energy $E(\varphi)$ can be found from equation $\delta F'/\delta\mu = 0$ and eqs 30 and 31 for the chain trajectory

$$\left(1 + \frac{D \cos \varphi}{R}\right)\frac{\psi(\varphi)}{\sqrt{\mu^*(r, \varphi) - E(\varphi)}} = \frac{4\pi bar}{\sqrt{6}v}\left(1 + \frac{\mathrm{r} \cos \varphi}{R}\right)\mu^*(r, \varphi) \qquad (33)$$

$$\frac{\sqrt{6}}{2a}\int_0^D \frac{\mathrm{d}r}{\sqrt{\mu^*(r, \varphi) - E(\varphi)}} = M \qquad (34)$$

The brush diameter follows from minimization of the free energy eq 32 with respect to D. The solution of this system of equations can be found using a perturbation scheme, so that

$$\mu^*(r, \varphi) = \mu_0(r) + \delta\mu(r, \varphi), \quad E(\varphi) = E_0 + \delta E(\varphi), \quad \psi(\varphi) = 1 + \delta\psi(\varphi) \qquad (35)$$

where $\mu_0(r)$ and E_0 are given by their equilibrium values, eq 23. Omitting the details of the calculation, we only give the results. In the first approximation the diameter of the bent brush coincides with its value for the straight brush, $D = D^*$. The corrections to the chemical potential, the energy E, and free end distribution function are

$$\delta\mu(w, \varphi) \simeq (0.1w^{-2/3} - 0.67w - 0.56w^{1/3} - 0.39)\frac{E_0 D^*}{R} \cos \varphi \qquad (36)$$

$$\delta E(\varphi) \simeq -1.16\frac{E_0 D^*}{R} \cos \varphi \qquad (37)$$

$$\delta\psi(\varphi) \simeq -0.82\frac{E_0 D^*}{R} \cos \varphi \qquad (38)$$

Here E_0 and D^* are given by eqs 22 and 23.

The fact that after bending the chemical potential depends on the azimuth angle implies that the chain trajectories are not straight lines any more. The corresponding trajectory equation $\varphi = \varphi(w)$ follows from eq 31

$$\frac{\mathrm{d}\varphi(w)}{\mathrm{d}w} = \frac{1}{w^2}\frac{(\partial S(w, \varphi)/\partial\varphi)}{(\partial S(w, \varphi)/\partial w)} \qquad (39)$$

This equation can be solved numerically, and the behavior of the chain trajectories is schematically shown in Figure 3. If we move along the trajectory, starting at some point A with coordinates $w = 1$, $\varphi = \varphi_0$ (see Figure

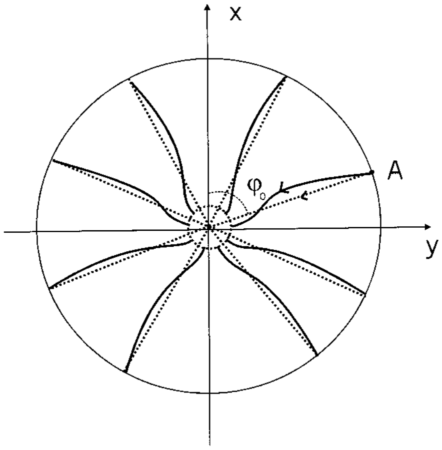

Figure 3. Chain trajectories before (dotted lines) and after (solid lines) bending.

3), the solution of eq 39 for $w \gg b/D^*$ is given by

$$\varphi(w) \simeq \varphi_0 + 0.18(1.13w^{5/3} + 2.27w + 2.93w^{2/5} - \ln w - 6.33) \sin \varphi_0 \frac{D^*}{R} \quad (40)$$

The distortion of the chain trajectories is compensated by the φ dependence of the osmotic pressure and results in an increase of the free energy.

The free energy per segment of length b can be easily calculated using the above results

$$F' = F + \frac{\lambda_0 b}{2R^2} + 0.29\,\frac{D^{*3}\,E_0^{1/2}}{aR^2} \quad (41)$$

and the persistence length of the brush is given by

$$\lambda = \lambda_0 + 0.58\,\frac{D^{*3}\,E_0^{1/2}}{ab} \simeq \lambda_0 + 0.047\,\frac{vM^2}{b^2} \quad (42)$$

The second term is connected with the side chains and scales with the length of the side chain as $\lambda \propto M^2$. This result is very close to what has been predicted by Fredrickson[9] using a scaling approach. Another limiting case corresponds to $b \simeq R_F$ when $\lambda \sim a(v/a^3)^{3/5}\,M^{4/5}$.

IV. Concluding Remarks

In the present paper we considered the bending elasticity of a comb copolymer cylindrical brush based on a self-consistent field approach and calculated the persistence length. We found that upon bending with radius of curvature R the side chain trajectories become distorted and the free energy increases with an amount $\Delta F(R) \simeq 0.023vM^2/(bR^2)$ per side chain. The persistence length increases with the side chain length M as $\lambda \simeq 0.047vM^2/b^2$, whereas the ratio of the persistence length and the brush radius scales as $\lambda/D^* \propto M^{5/4}$. This is in qualitative agreement with the scaling results $\lambda \propto M^{15/8}$ and $\lambda/D^* \propto M^{9/8}$.[8]

An important motivation for our present study was the seeming discrepancy between the latter scaling prediction and recent computer simulation results.[14-16] In the computer simulation studies, the persistence length λ^* is determined through the correlation function $\langle \cos \theta(s) \rangle = \exp(-s/\lambda^*)$, where $\theta(s)$ is the angle between two backbone chain segments separated by a distance s along the backbone. The simulations show that $\lambda^*/D^* \simeq 6$, independent of M for side chain lengths up to $M = 80$.[16] (Note, here D^* refers to the radius rather than the diameter used in ref 16.) In order to find a possible explanation for this observation, we will estimate the bending energy per side chain (or per section of length b of the brush), $\Delta F(R)$, when the brush is bent with a radius of curvature $R \simeq D^*$. Obviously, the bending of the brush is connected with the distortion of the side chain trajectories. The characteristic fluctuation energy per side chain is of the order of k_BT; therefore, in order for our asymptotic formulas to be correct, the energy of bending with a radius of curvature $R \simeq D^*$ should be much larger than k_BT, $\Delta F(D^*) \gg 1(k_BT)$. Let us estimate the corresponding value of the free energy for $M = 80$ using the same parameters as in ref 16, namely, $b = 1.74a$ and the excluded volume $v = 4\pi a^3/3$. After substitution of these values in the equation for ΔF, we find that $\Delta F \simeq 1.5(k_BT)$. This value does not satisfy the strong inequality, and, therefore, asymptotic behavior has not yet been attained for $M = 80$. Of course, since our formulas are based on the Alexander−de Gennes model together with the second-virial approximation, the numerical values of the free energy and the persistence length of the system considered in ref 16 might be slightly different.

A comparison between the present calculations and the calculations for comb copolymer cylindrical brushes with rigid rod side chains[16,17] indicate that for a fixed side chain length the stiffness of the cylindrical brush increases with increasing stiffness of the side chains. This is also confirmed by our most recent computer simulations devoted to semiflexible side chains.[21] Experiments indicate a high stiffness of real cylindrical brushes,[22-25] and we believe that this is directly related to the semiflexible nature of the side chains.

Acknowledgment. This research was supported by the Organization for Scientific Research of the Netherlands (NWO).

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MA991031L