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Polymer Adsorption on Curved Surfaces: Finite Chain Length Corrections

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ABSTRACT: The structural properties of polymers adsorbed onto a surface have been widely investigated using self-consistent mean-field theories. Recently, analytical mean-field theories have been applied to study polymer adsorption on curved surfaces but all in the context of the ground state dominance approximation in which the polymer chain length (N) is essentially infinite. Using an expression for the free energy by Semenov, we determine leading order (in $1/N$) corrections due to the finiteness of the polymer chain length on surface tension, spontaneous curvature, and rigidity constants.

1. Introduction

The influence of polymer adsorption onto surfaces has been a topic that has attracted much attention for several decades. This is not only because it has great practical interest but also because it serves as a testing ground of theoretical models for confined polymer systems.[1−3] Recently, investigations have been dedicated to study the interplay between colloidal particles and polymers.[4−9] In these systems, the *curvature* of the surface of the colloidal particle becomes a factor, and work has focused on the situation where either the colloidal particle is much larger or much smaller than the polymer coil.[4,5] When the radius of curvature is large, it is reasonable to expand the free energy for polymer adsorption in curvature. Helfrich supplied the general form of the surface free energy expanded to second order in the curvature:[10]

$$F_{\mathrm{H}} = \int \mathrm{d}A \left[\sigma - \frac{2k}{R_0}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) + \frac{k}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)^2 + \bar{k}\frac{1}{R_1 R_2}\right] \tag{1.1}$$

where R_1 and R_2 are the local radii of curvature. Apart from the surface tension, σ, one can identify three parameters in the Helfrich free energy that describe the physical properties of the curved interface: the spontaneous curvature $1/R_0$, the bending rigidity constant k, and the Gaussian rigidity $\bar{k}$.

A great deal of attention has turned to the determination of the value of these curvature parameters in complex systems, both theoretically and experimentally. For surfaces interacting with polymers, the curvature parameters were calculated by a number of groups.[3,7−9,11−15] In the work by Eisenriegler and others,[3,7−9] the polymer density is assumed to be zero at the surface of the colloidal particle so that a depletion layer exists around each particle. For surfaces with *enhanced* polymer adsorption, calculations[12,14,15] were performed in the context of the ground state dominance approximation[1,16,17] in which the polymer chain length is essentially infinite. In the present work, we use recent extensions to ground state dominance to determine corrections to the curvature parameters due to the finite length of the polymer chain. Such a calculation is of interest since the polymer chain length is an important parameter in experiments and computer simulations[18] thus providing a more stringent testing of theoretical models. Moreover, it was expected,[2,19] and later verified,[20−24] that in certain situations, the “tails” of the polymer chain become important, leading to *qualitatively* different behavior. An example is the repulsion between two planar walls when the separation is on the order of the polymer’s radius of gyration.[22] In the ground state dominance model the radius of gyration is infinite and the interaction between plates is attractive for all separations.[22,25]

The first extension of the ground state dominance model was proposed by Semenov, Bonet-Avalos, Johner, and Joanny.[20] They took the presence of tails into account by including a *second* order parameter related to the end segment density. Good agreement was obtained for the loop and tail distribution of adsorbed polymer when the theoretical predictions are compared with lattice self-consistent mean-field calculations.[21] The two-order parameter model was later extended to also take into account the presence of free (nonadsorbed) polymer away from the surface.[21,23,24] Subsequently, Semenov showed that the two-order parameter model may be cast into a free energy formalism of a single order parameter[23] in which the Euler−Lagrange equations are the Edwards equations, just as de Gennes had previously done in the context of the ground state dominance approximation.[1] In this article, we use the expression for the free energy by Semenov[23] to determine the polymer length corrections to the curvature parameters.

The outline of the paper is as follows: In the next section we review the description of finite chain length corrections to polymer adsorption on a planar wall in the two-order parameter model. We show how from the two-order parameter model a *single* order parameter model, to which we refer to as the Semenov model, is constructed to describe leading order corrections in $1/N$ to ground state dominance. In section 3, the single order parameter model is applied to the study of curved surfaces. Explicit expressions for the surface tension and curvature parameters are given. We end with a discussion of results.

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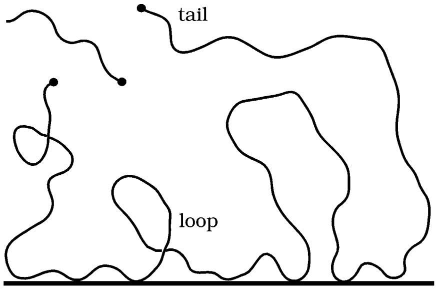

Figure 1. Sketch of a polymer chain adsorbed to a planar, solid surface located at $z = 0$. The polymer chain consists of a series of "loops", with both ends adsorbed to the substrate, and with two "tails", having one end free.

2. Semenov Model for Adsorption onto a Planar Surface

Before addressing the properties of curved surfaces, we discuss finite chain length corrections to the structure and tension of polymer adsorption onto a *planar* surface. We then generalize the description to polymer adsorption onto curved surfaces.

The situation under consideration is that of a polymer chain adsorbed onto a planar wall located at $z = 0$ (see Figure 1). The calculations presented here are performed in the context of self-consistent mean-field theory whereby a *single* polymer chain is considered with the effect of the other polymers taken into account by the presence of an external field proportional to the local segment density.[16] Furthermore, the interaction of the polymer with the wall is taken into account through an infinitely short-ranged (attractive) interaction potential.[1]

Before taking the finite length of the polymer chain into account, we remind ourselves of the de Gennes–Lifshitz description[1,17] for polymer adsorption of an *infinite* chain, the so-called *ground state dominance approximation*. The free energy is a functional of the polymer segment density $\phi(z)$[1]

$$\frac{F[\phi]}{Ak_{\rm B}T} = \int_0^\infty {\rm d}z \left[\frac{a^2}{24}\frac{\phi'(z)^2}{\phi(z)} + \frac{v}{2}[\phi(z) - \phi_{\rm b}]^2\right] - \frac{1}{d}\frac{a^2}{6}\phi_{\rm w} \tag{2.1}$$

where $k_{\rm B}$ is Boltzmann's constant, T is the temperature, A the surface area, and a is the polymer segment length. The subscripts b and w refer to the value of the polymer segment density in the bulk, $\phi_{\rm b} \equiv \lim_{z\to\infty} \phi(z)$, and at the wall, $\phi_{\rm w} \equiv \phi(0)$, respectively. The first term is the Lifshitz expression for the chain entropy,[17] the second term gives the mean-field interaction between polymer segments in a good solvent (v is the *excluded volume* parameter), and the last term accounts for the polymer interaction with the surface[1] (d is the *extrapolation length*; its inverse measures the interaction strength with the surface).

The above free energy is the *excess* or *surface* free energy since it is constructed such that when the polymer segment density becomes equal to the bulk segment density, $\phi(z) \to \phi_{\rm b}$, the integrand reduces to zero. The result is that the surface tension is equal to the above free energy per area when evaluated at its minimum, i.e., when the "optimum" segment density profile, determined by the Euler–Lagrange equation, is inserted into it.[26]

Rather than the segment concentration, it is convenient to consider the free energy as a functional of $\psi(z) \equiv \phi(z)^{1/2}$

$$\frac{F[\psi]}{Ak_{\rm B}T} = \int_0^\infty {\rm d}z \left[\frac{a^2}{6}\psi'(z)^2 + \frac{v}{2}[\psi(z)^2 - \phi_{\rm b}]^2\right] - \frac{1}{d}\frac{a^2}{6}\psi_{\rm w}{}^2 \tag{2.2}$$

where $\psi_w \equiv \psi(0)$. Minimization of the above free energy gives the following Euler–Lagrange equation for $\psi(z)$ with the following boundary condition:

$$\frac{a^2}{6}\psi''(z) = v\,[\psi(z)^2 - \phi_{\rm b}]\,\psi(z)$$

$$\psi'_{\rm w} = -\frac{1}{d}\psi_{\rm w} \tag{2.3}$$

The Euler–Lagrange equation can be recognized as the Edwards equation for an infinitely long polymer chain.[1,16]

The expression for the free energy in eq 2.2 has been the starting point of many density functional treatments of polymer solutions.[1,2] Owing to the nature of the ground state dominance approximation, this treatment is, however, limited to infinitely long chains. Recent investigations[20–24] have therefore been addressed to include finite length corrections to the ground state dominance model.

To account for the finiteness of the polymer chain length, a second-order parameter, $\varphi(z)$, was introduced[20] connected to the description of chain *ends*. To understand better the physical origin of this term, consider a polymer chain with at least one segment touching the surface. Such a chain consists of a series of "loops" with a "tail" on both sides[2] (see Figure 1). The segment density of adsorbed chains, $\phi(z)$ is then a sum of two terms; $\phi_\ell(z) = \psi(z)^2$ connected to the loop segment density and $\phi_t(z) = \psi(z)\,\varphi(z)$ connected to the tail segment density:

$$\phi(z) = \phi_\ell(z) + \phi_t(z) = \psi(z)^2 + \psi(z)\,\varphi(z) \tag{2.4}$$

This description is restricted to polymer chains that have one or more segments touching the surface. As a consequence, since the polymer chains are finite, $\lim_{z\to\infty} \phi(z) = 0$. The segment density $\phi(z)$ therefore does not describe the polymers in the bulk region.

The density of *chain ends*, $\phi_{\rm e}(z)$, is proportional to a single $\psi(z)$:[20]

$$\phi_{\rm e}(z) = B\,\psi(z) \tag{2.5}$$

The value of the proportionality constant B is obtained by a normalization onto the number of end segments. To show this in more detail, we denote Γ as the total adsorption of chains having one or more segments touching the wall:

$$\Gamma \equiv \int_0^\infty {\rm d}z\,[\psi(z)^2 + \psi(z)\,\varphi(z)] \tag{2.6}$$

The proportionality constant B is then determined by the fact that every adsorbed chain has *two* ends so that the fraction of end-segments therefore is $2/N$, with N the total number of segments:[20]

$$\int_0^\infty \mathrm{d}z\; B\, \psi(z) = \frac{2}{N}\,\Gamma = \frac{2}{N}\int_0^\infty \mathrm{d}z\; [\psi(z)^2 + \psi(z)\,\varphi(z)] \tag{2.7}$$

The profiles of the two order parameters, $\psi(z)$ and $\varphi(z)$, are determined by the following set of Edwards-like equations:[20]

$$\frac{a^2}{6}\,\psi''(z) = v\,[\psi(z)^2 + \psi(z)\varphi(z) + \epsilon_0 - \phi_b]\psi(z)$$
$$\frac{a^2}{6}\,\varphi''(z) = v\,[\psi(z)^2 + \psi(z)\varphi(z) + \epsilon_0 - \phi_b]\varphi(z) - B \tag{2.8}$$

As boundary conditions at the surface, we have

$$\psi'_{\mathrm{w}} = -\frac{1}{d}\,\psi_{\mathrm{w}}, \quad \varphi_{\mathrm{w}} = 0 \tag{2.9}$$

The latter condition follows from the interpretation of $\psi(z)\varphi(z)$ as the tail segment density distribution, that is zero at the surface by definition. As boundary conditions far away from the surface, we have

$$\lim_{z\to\infty} \psi(z) = 0, \quad \lim_{z\to\infty} \varphi(z) = \frac{B}{v\,(\epsilon_0 - \phi_b)} \tag{2.10}$$

The following functional is derived as a first integral of the two differential equations in eq 2.8 identified as the free energy:

$$\frac{F}{Ak_BT} = \int_0^\infty \mathrm{d}z \left[\frac{a^2}{6}(\psi')^2 + \frac{a^2}{6}\psi'\varphi' + \frac{v}{2}[\psi^2 + \psi\varphi - \phi_b]^2 - B\psi + \epsilon_0(\psi^2 + \psi\varphi)\right] - \frac{1}{d}\frac{a^2}{6}{\psi_{\mathrm{w}}}^2 \tag{2.11}$$

(For notational brevity we suppress the z dependence of ψ, and φ in the free energy.)

The parameter ϵ_0, which appears in the differential equations for $\psi(z)$ and $\varphi(z)$, may be interpreted as the chemical potential (in units of k_BT) of the attached polymers. Its value is determined by a balance of the chemical potential of the polymers at the surface with the chemical potential of bulk polymer. It is derived in refs 20 and 21 that ϵ_0 is approximately given by

$$\epsilon_0 \simeq \frac{1}{N}\ln\left(\frac{\Gamma^2}{\phi_b\,[\int_0^\infty \mathrm{d}z\;\psi(z)]^2}\right) \tag{2.12}$$

Combining the above expression for ϵ_0 with eq 2.7, we can rewrite the normalization condition for B as

$$B \simeq \frac{2}{N}\,{\phi_b}^{1/2}\mathrm{e}^{\epsilon_0(N/2)} \tag{2.13}$$

This model is the two-order parameter model which has been shown to be in agreement with numerical solutions of the self-consistent field equations.[21] One disadvantage of the two-order parameter model is the rather artificial distinction made between chains that have one or more segments touching the wall and free polymer chains, leading to the presence of $\epsilon_0 \neq 0$. Furthermore, the above formalism to determine the segment density profiles and free energy does not correspond to a *free energy functional formalism* in which the differential equations determining $\psi(z)$ and $\varphi(z)$ are the Euler–Lagrange equations to the free energy in eq 2.11. The reason is that a minimization of F would not necessarily lead to the boundary condition $\varphi(0) = 0$, and more importantly, B and ϵ_0 are not constants in the minimization but are themselves functionals of $\psi(z)$ and $\varphi(z)$ (eqs 2.7 and 2.12).

To circumvent these difficulties, we now turn to the derivation of what we term the *Semenov model*.[23] In this model, no explicit distinction between adsorbed chains and free chains is made, leading to a *single* order parameter describing the total segment density, $\phi(z)$. As a first step we consider again the free energy given by eq 2.11

$$\frac{F}{Ak_BT} = \int_0^\infty \mathrm{d}z \left[\frac{a^2}{6}(\psi')^2 + \frac{a^2}{6}\psi'\,\varphi' + \frac{v}{2}[\psi^2 + \psi\,\varphi]^2 - B\psi\right] - \frac{1}{d}\frac{a^2}{6}{\psi_{\mathrm{w}}}^2 \tag{2.14}$$

Since adsorbed and free chains are now treated equally, we have taken $\epsilon_0 = 0$. Furthermore, we have set $\phi_b = 0$, for the time being, and deal with the inclusion of bulk polymer below.

Next, since the combination $\psi(z)\,\varphi(z)$ is related to the tail segment density, whose contribution to the total segment density profile is of order $1/N$, we can conclude that $\varphi(z)$ describes effects that are of order $1/N$, i.e. $\varphi(z) = \mathcal{O}(1/N)$. With $\phi(z) = \psi(z)^2 + \psi(z)\,\varphi(z)$, the total segment density, we can therefore write in an expansion in $1/N$:

$$\frac{\phi'(z)^2}{4\,\phi(z)} = \psi'(z)^2 + \psi'(z)\,\varphi'(z) + \mathcal{O}\left(\frac{1}{N^2}\right)$$
$$\phi(z)^{1/2} = \psi(z) + \mathcal{O}\left(\frac{1}{N}\right) \tag{2.15}$$

Inserting this into the free energy in eq 2.14, we have

$$\frac{F}{Ak_BT} = \int_0^\infty \mathrm{d}z \left[\frac{a^2}{24}\frac{(\phi')^2}{\phi} + \frac{v}{2}\phi^2 - B\,\phi^{1/2}\right] - \frac{1}{d}\frac{a^2}{6}\phi_{\mathrm{w}} \tag{2.16}$$

with corrections of $\mathcal{O}(1/N^2)$. Next, we insert the explicit formula for B given in eq 2.13, with $\epsilon_0 = 0$, into the free energy. We are then left with the following free energy functional:

$$\frac{F[\phi]}{Ak_BT} = \int_0^\infty \mathrm{d}z \left[\frac{a^2}{24}\frac{(\phi')^2}{\phi} + G(\phi)\right] - \frac{1}{d}\frac{a^2}{6}\phi_{\mathrm{w}} \tag{2.17}$$

where

$$G(\phi) = \frac{v}{2}\phi^2 - \frac{2}{N}{\phi_b}^{1/2}\phi^{1/2} \tag{2.18}$$

To impose a certain value of the bulk polymer density, we introduce the bulk chemical potential in $G(\phi)$:

$$G(\phi) = \frac{v}{2}\phi^2 - \frac{2}{N}{\phi_b}^{1/2}\phi^{1/2} - \mu\,\phi \tag{2.19}$$

The value of the bulk chemical potential, μ, is chosen such that the bulk density, as given by the *minimum* of $G(\phi)$, is equal to a certain ϕ_b:

$$G'(\phi_b) = v\phi_b - \frac{1}{N} - \mu = 0 \Rightarrow \mu = v\phi_b - \frac{1}{N} \quad (2.20)$$

As expected, the chemical potential is lowered by reducing the chain length. As a final step, we subtract from $G(\phi)$ the asymptotic bulk free energy $G(\phi_b)$ in order for the above free energy to be the surface free energy. Our final expression for $G(\phi)$ then reads as follows:

$$G(\phi) = \frac{v}{2}(\phi - \phi_b)^2 + \frac{1}{N}(\phi^{1/2} - {\phi_b}^{1/2})^2 \quad (2.21)$$

One notices that the above form of $G(\phi)$ reduces to that in *ground state dominance* (see eq 2.1) in the limit $N \to \infty$, as it should.

Even though we started from an expression for the free energy in eq 2.11, which we stressed is not the free energy functional, we have now constructed a free energy functional in eq 2.17. It is a functional of $\phi(z)$, that is now the *total* segment density profile in which no reference to "loops" or "tails" is explicitly made. Its form was first proposed by Semenov,[23] who also determined the *next* order contribution and showed it to be of $\mathcal{O}(1/N^{3/2})$. Semenov[23] points out that this approach agrees with the two-order parameter model (to $\mathcal{O}(1/N)$), even though this agreement has to be interpreted somewhat loosely since a direct comparison is difficult to make owing to the difference in the treatment of bulk polymer.

It is convenient to rescale all densities by ϕ_b and all lengths by the bulk correlation length $\xi_b \equiv a/\sqrt{3v\phi_b}$:

$$x \equiv z/\xi_b, \quad \tilde{d} \equiv d/\xi_b, \quad \phi(x) \equiv \phi_b f_0(x)^2 \quad (2.22)$$

Furthermore, we introduce as a small parameter the (square of) the bulk correlation length, ξ_b, divided by $R_G \equiv \sqrt{Na^2/6}$, the polymer's radius of gyration:

$$\epsilon \equiv \frac{{\xi_b}^2}{{R_G}^2} = \frac{2}{v\phi_b N} \quad (2.23)$$

In order for ϵ to be small, the bulk polymer density $v\phi_b \gg 2/N$, i.e., the expansion is expected to fail for very dilute polymer solutions. On the other hand, for concentrated polymer solutions, where the bulk polymer density is much higher than the overlap concentration, $v\phi_b \gg 1/\sqrt{N}$, this type of mean-field theory is also expected to break down. Our model is therefore most relevant for *semidilute* polymer solutions.

The free energy in eq 2.17 is written as

$$\tilde{F}[f_0] \equiv \frac{2}{v\xi_b{\phi_b}^2}\frac{F[f_0]}{Ak_BT} = \int_0^\infty dx\,[(f_0')^2 + g(f_0)\,] - \frac{1}{\tilde{d}}\,{f_{0,w}}^2 \quad (2.24)$$

where $g(f_0)$ is given by

$$g(f_0) = ({f_0}^2 - 1)^2 + \epsilon\,(f_0 - 1)^2 \quad (2.25)$$

The Euler–Lagrange equation to the free energy in eq 2.24 reads

$$f_0''(x) = \frac{1}{2}\,g'(f_0) \Rightarrow f_0'(x)^2 = g(f_0) \quad (2.26)$$

which gives

$$f_0'(x) = -\sqrt{g(f_0)} = -\,(f_0 - 1)({f_0}^2 + 2f_0 + 1 + \epsilon)^{1/2} \quad (2.27)$$

As a boundary condition to the above first-order differential equation, we have $f'_{0,w} = -\,f_{0,w}/\tilde{d}$. The initial value $f_{0,w} \equiv f_0(0)$ is thus obtained by solving the following algebraic equation:

$$\frac{1}{\tilde{d}}f_{0,w} = (f_{0,w} - 1)({f_{0,w}}^2 + 2f_{0,w} + 1 + \epsilon)^{1/2} \quad (2.28)$$

The profile obtained as an explicit solution to the differential equation reads

$$f_0(x) = 1 + \frac{8\,(\epsilon + 4)}{16\,\exp(\beta(x + x_w)) - 16 - \epsilon\,\exp(-\beta(x + x_w))} \quad (2.29)$$

where we have defined

$$\exp(\beta x_w) \equiv \frac{2 + 2\,f_{0,w} + \epsilon + \alpha\beta}{4\,(f_{0,w} - 1)}$$

$$\alpha \equiv ({f_{0,w}}^2 + 2f_{0,w} + 1 + \epsilon)^{1/2}$$

$$\beta \equiv (\epsilon + 4)^{1/2} \quad (2.30)$$

This analytical result for the order parameter profile was derived without making any further approximations. However, it should be kept in mind that the free energy in eq 2.17 captures only the leading order correction (in $1/N$) to ground state dominance. The result is that only the two leading terms in an expansion in ϵ are physically relevant: $f_0(x) = f_{0,0}(x) + \epsilon\, f_{0,1}(x) + ...$, with

$$f_{0,0}(x) = \frac{1}{\tanh(x + x_0)}$$

$$f_{0,1}(x) = -\frac{(5e^{4x_0} - 8e^{2x_0} + 4 - e^{-4x_0})}{32(e^{4x_0} + 1)\sinh^2(x + x_0)} - \frac{(4x + 4e^{-2x-2x_0} - e^{-4x-4x_0} - 3)}{32\sinh^2(x + x_0)} \quad (2.31)$$

where we have defined $x_0 \equiv (^1/_2)$ arcsinh$(2\tilde{d})$. These expressions can be used to analyze the limiting behavior of the segment density profile for strong and weak adsorption. For weak adsorption, we have

$$\frac{\phi(z)}{\phi_b} = 1 + \frac{1}{\tilde{d}}\left[e^{-2z/\xi_b} - \frac{\epsilon}{8}\left(1 + \frac{2z}{\xi_b}\right)e^{-2z/\xi_b} + ...\right] \quad (2.32)$$

In the case of strong adsorption, one finds the characteristic $1/z^2$ behavior[1] of the segment density profile close to the solid surface

$$\frac{\phi(z)}{\phi_b} = \frac{{\xi_b}^2}{z^2} \quad (2.33)$$

This result is unaffected by the finite chain length corrections which implies that for strong adsorption, the segment density profile in the immediate vicinity of the wall is unaffected by the length of the polymer chain.

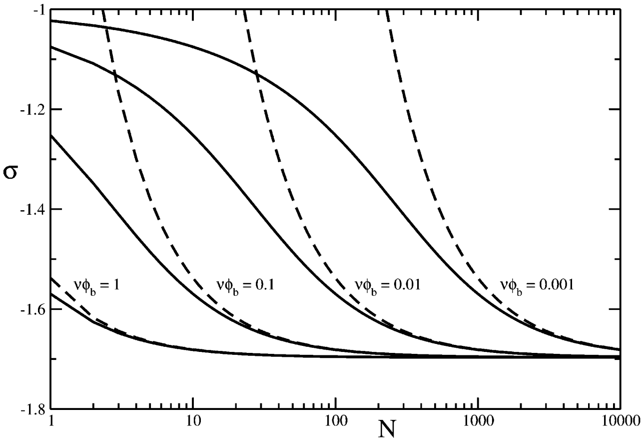

Figure 2. Surface tension $\tilde{\sigma}$ as a function of chain length. The adsorption strength $\tilde{d} = 1$; the bulk polymer density ranges from $v\phi_b = 0.001$ to $v\phi_b = 1$. The solid line is eq 2.36; the dashed line is eq 2.37 combined with eq 2.38.

The surface tension is given by the surface free energy with the order parameter profile, as determined by the Euler–Lagrange equation, inserted into it:

$$\tilde{\sigma} \equiv \frac{2}{v\xi_b{\phi_b}^2}\frac{\sigma}{k_BT} = 2\int_0^\infty dx\,[f_0'(x)^2] - \frac{1}{\tilde{d}}\,{f_{0,w}}^2 \quad (2.34)$$

The surface tension can be conveniently rewritten as an integral over f:[26]

$$\tilde{\sigma} = 2\int_1^{f_{0,w}} df_0\sqrt{g(f_0)} - \frac{1}{\tilde{d}}\,{f_{0,w}}^2 \quad (2.35)$$

The value of the surface tension is thus calculated either by inserting the density profile in eq 2.29 back into eq 2.34, or by direct evaluation of the density integral formula above. In either case, the result is

$$\tilde{\sigma} = \frac{2}{3}\,\alpha\,f_{0,w}(f_{0,w} - 1) + \frac{2}{3}(2 - \epsilon)(\beta - \alpha) - 2\epsilon\ln\left(\frac{1 + f_{0,w} + \alpha}{2 + \beta}\right) - \frac{1}{\tilde{d}}\,{f_{0,w}}^2 \quad (2.36)$$

This analytical result for the surface tension was derived without making any further approximations. However, it should again be kept in mind that only the two leading terms in an expansion in ϵ are physically relevant:

$$\tilde{\sigma} = \tilde{\sigma}_0 + \epsilon\,\tilde{\sigma}_1 + ... \quad (2.37)$$

Expanding eq 2.36 in ϵ gives as explicit expressions

$$\tilde{\sigma}_0 = \frac{4}{3} - \frac{4}{3\tanh(x_0)} - \frac{\cosh(x_0)}{3\sinh^3(x_0)}$$

$$\tilde{\sigma}_1 = \frac{1}{\tanh(x_0)} - 1 + 2\ln(1 - e^{-2x_0}) \quad (2.38)$$

The result for $\tilde{\sigma}_0$ was first derived in ref 15. In Figure 2, the surface tension is plotted as a function of chain length at fixed $\tilde{d} = 1$ and for various values of $v\phi_b$. The solid line is the full result in eq 2.36 with the dashed line the two leading terms (eqs 2.37 and 2.38). Even though the relevant variable is the combination $\epsilon = 2/(Nv\phi_b)$, we have chosen to plot the surface tension as a function of N for various $v\phi_b$. The condition that ϵ is small implies that $N \gg 1/(v\phi_b)$. This limit corresponds (for each $v\phi_b$) roughly to the point where the solid and dashed lines deviate. The leading order correction to the surface tension is always positive indicating that the lowering of the surface tension due to the presence of adsorbed polymer is *reduced* when the polymer chain becomes shorter. The magnitude of this effect is appreciable ($\simeq$10%) already for large polymer chains ($N \simeq 1000$) when the bulk density is low ($v\phi_b \simeq 0.001$).

It is instructive to consider the behavior of $\tilde{\sigma}_1$ in the weak adsorption limit ($d \gg \xi_b$):

$$\tilde{\sigma}_1 = \frac{1}{16}\frac{1}{\tilde{d}^2} + \frac{1}{48}\frac{1}{\tilde{d}^3} + \mathcal{O}\left(\frac{1}{\tilde{d}^4}\right) \quad (2.39)$$

This result for $\tilde{\sigma}_1$ can be combined with the limiting behavior for $\tilde{\sigma}_0$. To show this in more detail, we subtract from the surface tension the constant contribution to σ that remains even when the density profile is equal to the bulk density everywhere $\phi(z) = \phi_b$. One can then write

$$\Delta\sigma \equiv \sigma + k_BT\frac{a^2\phi_b}{6\,d} = -\frac{a^4\,k_BT}{36v\xi_b d^2}\left(1 - \frac{\epsilon}{8} + ...\right) \quad (2.40)$$

This expression more clearly shows that the lowering of the surface tension due to the presence of adsorbed polymer is *reduced* when the polymer chain becomes shorter. One may show[27] that the next term in the expansion of the surface tension in eq 2.40 goes as $\simeq -0.1540\epsilon^{3/2}$.

For completeness we also give the expression for $\tilde{\sigma}_1$ in the case of *strong* polymer adsorption ($d \ll \xi_b$):

$$\tilde{\sigma}_1 = \frac{1}{\tilde{d}} + (2\ln(2\tilde{d}) - 1)\,\tilde{d} + \mathcal{O}(\tilde{d}^2) \quad (2.41)$$

3. Semenov Model for Adsorption onto Curved Surfaces

We now extend our analysis to curved surfaces. In particular, we are interested in determining the coefficients of an expansion of the free energy to second order in the curvature: the spontaneous radius of curvature, R_0, and the rigidity constants k and $\bar{k}$. In general geometry, the free energy functional in the Semenov model reads as follows:

$$\frac{F[\phi]}{k_BT} = \int d\vec{r}\left[\frac{a^2}{24}\frac{|\vec{\nabla}\phi(\vec{r})|^2}{\phi} + G(\phi)\right] - \frac{A}{d}\frac{a^2}{6}\phi_w \quad (3.1)$$

We rescale the variables as done previously; see eq 2.22. The rescaled free energy is then given by

$$\tilde{F}[f] = \frac{1}{A}\int d\vec{x}\,[|\vec{\nabla}f(\vec{x})|^2 + g(f)] - \frac{1}{\tilde{d}}\,{f_w}^2 \quad (3.2)$$

with the Euler–Lagrange equation and boundary condition as follows:

$$\Delta f(\vec{x}) = \frac{1}{2}\,g'(f), \quad \hat{n}\cdot\vec{\nabla}f_w = -\frac{1}{\tilde{d}}f_w \quad (3.3)$$

To derive the curvature parameters, both order param-

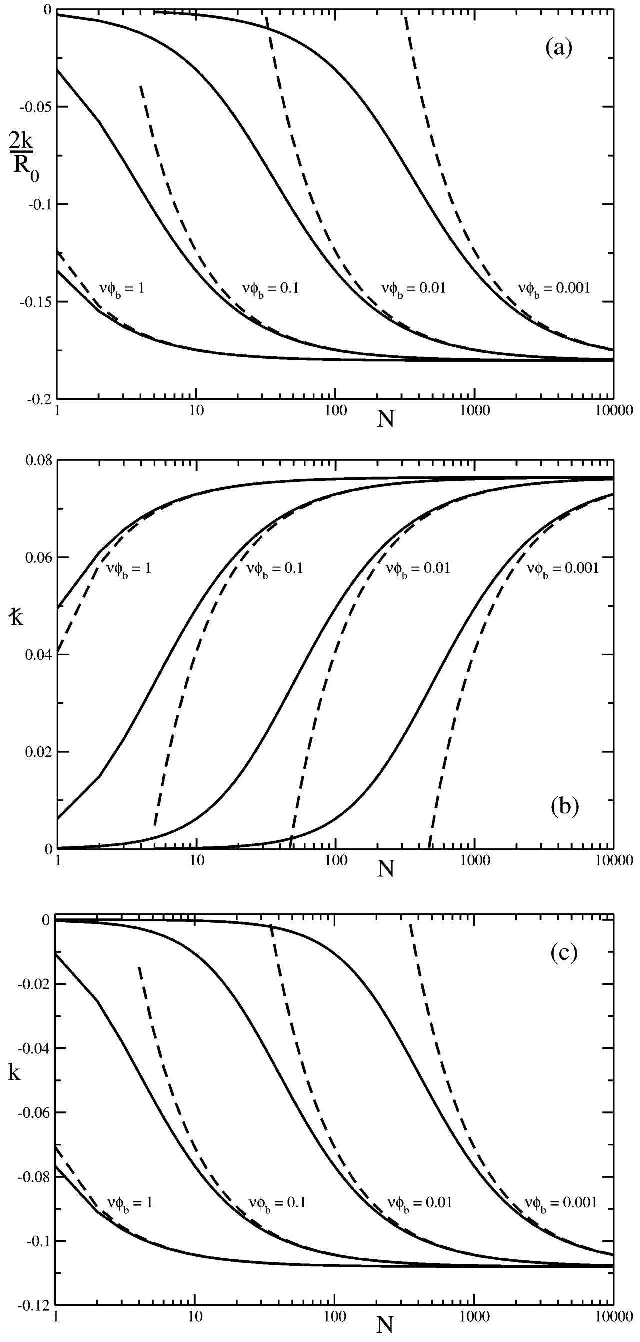

Figure 3. Curvature parameters as a function of chain length; (a) the spontaneous curvature $\tilde{c}_0$, (b) the Gaussian rigidity $\tilde{\bar{k}}$, (c) the bending rigidity $\tilde{k}$. The adsorption strength $\tilde{d} = 1$; the bulk polymer density ranges from $v\phi_b = 0.001$ to $v\phi_b = 1$. The solid lines are numerical evaluations of the integral expressions in eqs 3.7 and 3.8. The dashed lines are the two leading contributions, eq 3.10 combined with eq 3.11.

eter profile and free energy are expanded to second order in curvature for a spherically and cylindrically shaped surface.[28] For example, in the spherical geometry we have

$$f_s(x) = f_0(x) + \frac{1}{R}\, f_{s,1}(x) + \frac{1}{R^2}\, f_{s,2}(x) + \dots \qquad (3.4)$$

where R is the sphere's radius. In this expansion, the Euler−Lagrange equation and boundary condition are given to zeroth and first order by

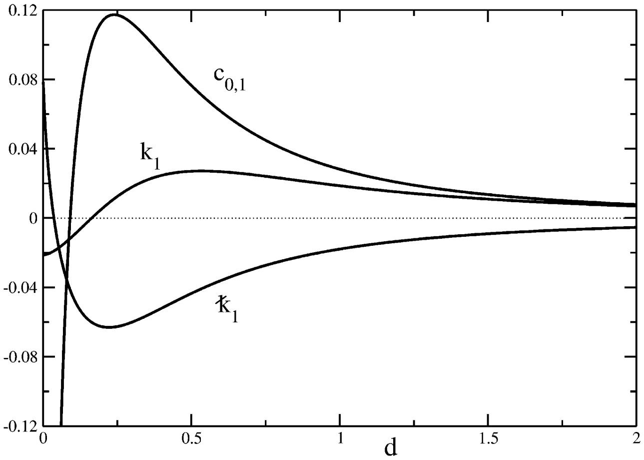

Figure 4. Leading order corrections to the curvature parameters: $\tilde{c}_{0,1}$, $\tilde{\bar{k}}_1$, and $\tilde{k}_1$, plotted as a function of the adsorption strength (strong adsorption when $\tilde{d} \ll 1$).

$$f_0''(x) = \frac{1}{2}\, g'(f_0), \quad f_{0,w}' = -\frac{1}{\tilde{d}} f_{0,w}$$

$$f_{s,1}''(x) = \frac{1}{2}\, g'(f_0)\, f_{s,1}(x) - 2\, f_0'(x), \quad f_{s,1,w} = -\frac{1}{\tilde{d}}\, f_{s,1,w} \qquad (3.5)$$

The spontaneous radius of curvature, R_0, and the rigidity constants k and $\bar{k}$, are given by[14,15,28]

$$\tilde{c}_0 \equiv \left(\frac{2}{v\xi_b^{\,2}\phi_b^{\,2}k_BT}\right)\frac{2k}{R_0} = -2\int_0^\infty dx\, [x\, f_0'(x)^2]$$

$$\tilde{\bar{k}} \equiv \left(\frac{2}{v\xi_b^{\,3}\phi_b^{\,2}k_BT}\right)\bar{k} = 2\int_0^\infty dx\, [x^2\, f_0'(x)^2]$$

$$\tilde{k} \equiv \left(\frac{2}{v\xi_b^{\,3}\phi_b^{\,2}k_BT}\right) k = -\int_0^\infty dx\, [f_0'(x) f_{s,1}(x)] \qquad (3.6)$$

The expressions for the spontaneous radius of curvature, R_0, and the rigidity constants associated with Gaussian curvature, $\bar{k}$, can be rewritten as integrals over f, similar to the expression for the surface tension in eq 2.34:

$$\tilde{c}_0 = -2\int_1^{f_w} df \sqrt{g(f)} \int_f^{f_w} df' \frac{1}{\sqrt{g(f')}}$$

$$\tilde{\bar{k}} = 2\int_1^{f_w} df \sqrt{g(f)} \left[\int_f^{f_w} df' \frac{1}{\sqrt{g(f')}}\right]^2 \qquad (3.7)$$

One may show that the bending rigidity constant, k, is given by

$$\tilde{k} = \frac{4\tilde{d}}{\sqrt{g(f_w)}\,[2\sqrt{g(f_w)} - \tilde{d}g'(f_w)]}\,[\int_1^{f_w} df \sqrt{g(f)}]^2 - 2\int_1^{f_w} df \sqrt{g(f)} \int_f^{f_w} df' \frac{1}{\sqrt{g(f')}^3} \int_1^{f'} df'' \sqrt{g(f'')} \qquad (3.8)$$

Explicit results for the value of $\tilde{c}_0$, $\tilde{\bar{k}}$, and $\tilde{k}$ are obtained by inserting the functional form for $g(f)$ (eq 2.25) into eqs 3.7 and 3.8 and evaluating the resulting integrals numerically. Typical results for the various curvature parameters as a function of chain length are shown as the solid lines in Figure 3. Again, it should be kept in mind that the physical relevance of these expressions for the curvature parameters is restricted to the first two terms in an expansion in ϵ:

$$\tilde{c}_0 = \tilde{c}_{0,0} + \epsilon\, \tilde{c}_{0,1} + ...$$
$$\tilde{\tilde{k}} = \tilde{\tilde{k}}_0 + \epsilon\, \tilde{\tilde{k}}_1 + ...$$
$$\tilde{k} = \tilde{k}_0 + \epsilon\, \tilde{k}_1 + ... \qquad (3.9)$$

An explicit calculation gives[15]

$$\tilde{c}_{0,0} = -\frac{1}{3\sinh^2(x_0)} - \frac{4}{3}\ln(1 - \mathrm{e}^{-2x_0})$$
$$\tilde{\tilde{k}}_0 = -\frac{2}{3} + \frac{2}{3\tanh(x_0)} - \frac{4}{3}\,\mathrm{dilog}(1 - \mathrm{e}^{-2x_0})$$
$$\tilde{k}_0 = -\frac{(27\mathrm{e}^{2x_0} + 5 - \mathrm{e}^{-2x_0} + \mathrm{e}^{-4x_0})}{18(\mathrm{e}^{2x_0} - 1)(\mathrm{e}^{4x_0} + 1)} \qquad (3.10)$$

and

$$\tilde{c}_{0,1} = -\frac{(4\mathrm{e}^{2x_0} - 7 + \mathrm{e}^{-4x_0})}{12(\mathrm{e}^{4x_0} + 1)} + \mathrm{dilog}(1 - \mathrm{e}^{-2x_0}) + \frac{2}{3}\ln(1 - \mathrm{e}^{-2x_0})$$
$$\tilde{\tilde{k}}_1 = -\frac{(3\mathrm{e}^{2x_0} - \mathrm{e}^{-2x_0})}{12(\mathrm{e}^{4x_0} + 1)} - \frac{(5\mathrm{e}^{4x_0} - 8\mathrm{e}^{2x_0} + 4 - \mathrm{e}^{-4x_0})}{12(\mathrm{e}^{4x_0} + 1)}\ln(1 - \mathrm{e}^{-2x_0}) + \frac{5}{6}\,\mathrm{dilog}(1 - \mathrm{e}^{-2x_0}) - \mathrm{Li}_3(\mathrm{e}^{-2x_0})$$
$$\tilde{k}_1 = -\frac{1}{288\,(\mathrm{e}^{4x_0} + 1)^3}[456\mathrm{e}^{10x_0} - 354\mathrm{e}^{8x_0} + 1272\mathrm{e}^{6x_0} - 281\mathrm{e}^{4x_0} + 792\mathrm{e}^{2x_0} - 143 + 168\mathrm{e}^{-2x_0} + 37\mathrm{e}^{-4x_0} - 3\mathrm{e}^{-8x_0}] - \frac{(13\mathrm{e}^{4x_0} - 16\mathrm{e}^{2x_0} + 4 - \mathrm{e}^{-4x_0})}{12\,(\mathrm{e}^{4x_0} + 1)}\ln(1 - \mathrm{e}^{-2x_0}) + \frac{1}{2}\,\mathrm{dilog}(1 - \mathrm{e}^{-2x_0}) \qquad (3.11)$$

where the polylogs $\mathrm{Li}_n(z)$ and $\mathrm{dilog}(z)$ are defined in the Appendix.

The two leading contributions, eq 3.10 with eq 3.11, are shown as the dashed curves in Figure 3. Again, the validity limit of the expansion in ϵ corresponds (for each $v\phi_b$) roughly to the point where the solid and dashed lines deviate. The curves in Figure 3 show that the leading order correction to the curvature parameters is significant already for large polymer chains, especially when the bulk polymer density is low. Furthermore, when the polymer chain becomes shorter, the effect of polymer adsorption on the curvature parameters is reduced. However, this is not a general result, and it is only valid when the adsorption strength is sufficiently weak. This is shown in Figure 4, where we have plotted the leading order corrections to the curvature parameters as a function of the adsorption strength. For large $\tilde{d}$, i.e., weak adsorption, the leading order corrections are such that they are opposite in sign to the ground state dominance results ($\tilde{c}_{0,1}$ and $\tilde{k}_1$ are positive and $\tilde{\tilde{k}}_1$ is negative); for small $\tilde{d}$, i.e., strong adsorption, they *enhance* the effect.

These results are further demonstrated by considering the limiting behavior. In the weak adsorption limit ($d \gg \xi_b$) one finds the following:

$$\tilde{c}_{0,1} = \frac{1}{32}\frac{1}{\tilde{d}^2} + \frac{1}{288}\frac{1}{\tilde{d}^3} + \mathcal{O}\left(\frac{1}{\tilde{d}^4}\right)$$
$$\tilde{\tilde{k}}_1 = -\frac{3}{128}\frac{1}{\tilde{d}^2} + \frac{1}{576}\frac{1}{\tilde{d}^3} + \mathcal{O}\left(\frac{1}{\tilde{d}^4}\right)$$
$$\tilde{k}_1 = \frac{9}{256}\frac{1}{\tilde{d}^2} - \frac{1}{96}\frac{1}{\tilde{d}^3} + \mathcal{O}\left(\frac{1}{\tilde{d}^4}\right) \qquad (3.12)$$

The leading order corrections all scale as $1/\tilde{d}^2$ just as the ground state dominance results for $\tilde{c}_{0,0}$, $\tilde{\tilde{k}}_0$, and $\tilde{k}_0$.[15] We can therefore write

$$\frac{2k}{R_0} = -\frac{a^4\; k_\mathrm{B}T}{144\, v d^2}\left(1 - \frac{\epsilon}{4} + ...\right)$$
$$\bar{k} = \frac{a^4\; k_\mathrm{B}T\xi_\mathrm{b}}{288\;\; v d^2}\left(1 - \frac{3\epsilon}{8} + ...\right)$$
$$k = -\frac{a^4\; k_\mathrm{B}T\xi_\mathrm{b}}{192\;\; v\; d^2}\left(1 - \frac{3\epsilon}{8} + ...\right) \qquad (3.13)$$

These expressions show more clearly that in the weak adsorption limit, the influence on the curvature parameters caused by the presence of adsorbed polymer is reduced when the polymer chain becomes shorter.

For strong adsorption($d \ll \xi_b$), one has

$$\tilde{c}_{0,1} = \frac{2}{3}\ln(2\tilde{d}) + \frac{\pi^2}{6} + \frac{1}{12} + (2\ln(2\tilde{d}) - 3)\,\tilde{d} + \mathcal{O}(\tilde{d}^2)$$
$$\tilde{\tilde{k}}_1 = \frac{5\pi^2}{36} - \frac{1}{12} - \zeta(3) + \left(\frac{4}{3}\ln(2\tilde{d}) + \frac{\pi^2}{3} - \frac{11}{6}\right)\tilde{d} + \mathcal{O}(\tilde{d}^2)$$
$$\tilde{k}_1 = -\frac{27}{32} + \frac{\pi^2}{12} + \mathcal{O}(\tilde{d}^2) \qquad (3.14)$$

where the ζ-function is defined in the Appendix.

These results show that when the adsorption is sufficiently strong, one finds the somewhat surprising result that shortening the polymer chain *enhances* the effect on the curvature parameters induced by adsorbing polymer.

4. Discussion

In this article, we have investigated the chain length dependence of the curvature properties of polymer adsorbed surfaces. Our calculations are done in the context of the Semenov model[23] for the free energy which captures the leading correction to the free energy in an expansion in $1/N$. Analytic expressions are derived for the leading corrections to the surface tension and curvature parameters.

For an infinite chain, it is well-established that the ground state dominance model predicts that the addition of polymer reduces the surface tension, induces a spontaneous curvature toward the polymers, gives a positive contribution to the Gaussian rigidity, and reduces the value of the bending rigidity. We find that if the adsorption strength is sufficiently low, the leading correction due to the finiteness of the polymer chain to

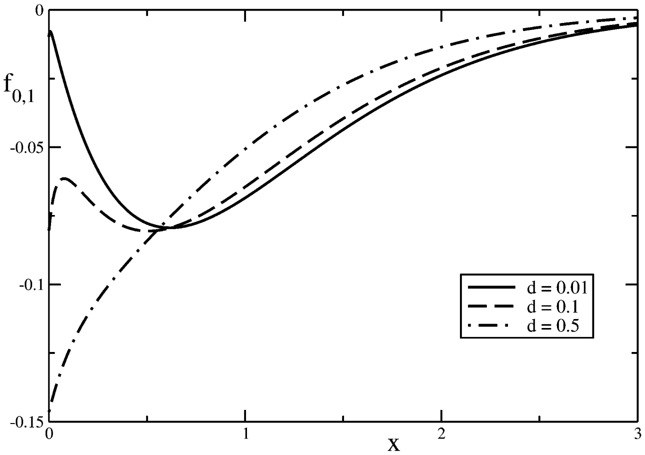

Figure 5. Order parameter profile $f_{0,1}(x)$ as a function of x for various values of the adsorption strength: solid line, $\tilde{d} = 0.01$; dashed line, $\tilde{d} = 0.1$; dot−dashed line, $\tilde{d} = 0.5$.

the surface tension and curvature parameters is to *reduce* the effect of polymer adsorption on these coefficients. The magnitude of this effect may be considerable already for long polymer chains, especially when the bulk polymer density is low.

For strong adsorption, we find that the leading contribution to the curvature parameter *changes sign*. This means that shortening the polymer chains now *enhances* the effect polymers have on the curvature parameters. This seems a bit surprising since it is expected that, for very short chains, the influence of these chains becomes less pronounced. Still, our result is not necessarily in contradiction with this expectation since for small N *all* the terms in the expansion in $1/N$ are important.

One would like to understand the *physical reason* behind this “enhancement effect”. Mathematically, the effect is traced back to the nonmonotonic behavior of the leading correction to the segment density profile $f_{0,1}(x)$, which is directly linked to the leading corrections to the spontaneous curvature ($\tilde{c}_{0,1}$) and the Gaussian rigidity ($\tilde{\bar{k}}$). (An equivalent argument can be made for the bending rigidity ($\tilde{k}_1$) which is determined by the behavior of $f_{1,1}(x)$.)

In Figure 5, we have plotted $f_{0,1}(x)$ for various values of the adsorption strength. For weak adsorption, $f_{0,1}(x)$ monotonically increases to zero at large distances indicating that short chains adsorb less. For strong adsorption, two regions may be identified: in the vicinity of the wall the segment density profile is dominated by polymer “loops”. In this region $f_{0,1}(x)$ is close to zero indicating that the polymer density is independent of chain length. At somewhat larger distances from the wall the profile is dominated by the polymer “tails”.[2,24] Here $f_{0,1}(x)$ goes through a minimum and then monotonically increases to zero at large distances. One may therefore conclude that, although the total adsorption is less when the chain length is reduced, the segregation between a region dominated by loops and a region dominated by tails is more pronounced leading to steeper gradients in the polymer segment density profile. This is then ultimately responsible for an enhancement of the polymer contribution to the curvature parameters in the case of strong adsorption.

We end with a discussion of the limitations of our theoretical treatment. Corrections to the curvature parameters were calculated to leading order in $1/N$. We showed that the leading correction to the segment density profile gives a modified density profile that varies on the scale of the bulk correlation length, as does the ground state dominance profile. One expects[23,27] higher order corrections ($\mathcal{O}(1/N^{3/2})$) to give modifications to the segment density profile on the scale of the polymer’s radius of gyration. Although these higher order corrections dominate the segment density profile when $z \gg \xi_b$, they remain subdominant when it concerns the curvature parameters since these are expressed in terms of integrals over the entire region of inhomogeneity.

A subtle point concerns the dimensional dependence of our analysis. Since all our results are derived within mean-field theory, it is implied that the critical exponents are those of a polymer system embedded in four dimensions. In our derivation of the curvature parameters we explicitly consider the geometry to be that of a two-dimensional surface curved in three-dimensional space, which is arguably inconsistent with the mean-field assumption. It seems hard to avoid such an inconsistency, however, and it is a critique which applies to all mean-field calculations of curvature properties.

The interaction with the solid surface is modeled by the extrapolation length d giving an effective interaction. Details of the structure of the wall (e.g., surface roughness, surface heterogeneity) and the full wall−polymer interaction potential are therefore not explicitly considered. It is expected that these factors influence the polymer segment density in the very vicinity of the wall. In the present calculations, the scale of the segment density profile is set by the bulk correlation length. One expects that the detailed structure of the wall is unimportant as long as the bulk correlation length is much larger than the microscopic length scale associated with this structure.

Formally, in the calculation presented the surface is taken to be that of an undeformable, attractive solid wall so that the main application of our results to experiments is for, e.g., polymer adsorption onto a colloidal particle. However, our results should also be of interest to the description of polymer adsorption on more flexible surfaces such as membranes,[29] for which the essential physics is captured by the Helfrich free energy.

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A. Mathematical Functions

As a reference, we provide definitions of the special functions used.

The polylogarithm function is defined as

$$\mathrm{Li}_n(z) \equiv \sum_{k=1}^{\infty} \frac{z^k}{k^n} \tag{A.1}$$

The dilogarithm function is defined as

$$\mathrm{dilog}(z) \equiv \mathrm{Li}_2(z) \equiv \int_1^z \mathrm{d}t \frac{\ln t}{(1-t)} \tag{A.2}$$

The Riemann ζ-function is defined as

$$\zeta(n) \equiv \mathrm{Li}_n(1) \equiv \sum_{k=1}^{\infty} \frac{1}{k^n} \tag{A.3}$$

$$\zeta(3) \simeq 1.202056903... \tag{A.4}$$

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