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Free energy formalism for polymer adsorption: Self-consistent field theory for weak adsorption

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Polymer adsorption has been widely investigated in the context of self-consistent mean-field theories. As a further simplification, the “ground state dominance approximation” is often made, treating the polymer chains as infinitely long. For short polymers, or not so concentrated polymer solutions, corrections to ground state dominance may be important, however. In this work, we discuss analytical solutions to the full self-consistent field equations, valid for any chain length, in the limit of weak adsorption. We show how the resulting equations may be put into a free energy functional formalism, in analogy to the de Gennes–Lifshitz free energy for infinitely long polymer chains. Analytical expressions are derived for polymer density profiles, surface tension and the interaction potential between two planar, polymer-adsorbing surfaces. Particular attention is paid to the distal ordering of the polymer coils that shows up as oscillations in the polymer density profile and interaction potential at the scale of the polymer’s radius of gyration. © 2003 American Institute of Physics. [DOI: 10.1063/1.1588998]

I. INTRODUCTION

Polymer surfaces have attracted considerable attention in recent years both from an experimental and a theoretical point of view. Interest in these systems is driven by practical applications, but also because it serves as a theoretical example of a confined polymer system.^{1–3} More recently, interest has surged in the study of the interplay between colloidal particles and polymers in solution.^{4–9} Understanding the interaction between colloidal particles, as mediated through the polymer solution, supplies means to understand the mechanisms behind polymer induced colloidal stabilization and crystallization. This may be helpful in formulating conditions under which colloidal particles or globular proteins may crystallize.

Theoretically, the interplay of polymers and surfaces has been extensively studied. Various models for the interaction of the polymer and the (colloidal) surface have been discussed; irreversibly adsorbed or grafted polymers,¹⁰ reversibly adsorbed polymers,^{1,2} and polymers depleted from the surface.^{3,7–9} In the latter case, the polymer density is assumed to be zero at the surface so that a depletion layer exists around each particle. In these calculations, notably by Eisenriegler^{3,7} and by others,^{9,11} analytical solutions of the Edwards equations in the context of the so-called self-consistent field theory could be obtained.

Surfaces with *enhanced* polymer adsorption have first been studied by de Gennes^{1,12} in self-consistent field theory, and by Scheutjens and Fleer in a lattice model for polymers.¹³ In the de Gennes model, the so-called *ground state dominance approximation*^{1,14,15} is made in which the polymer chain length is essentially set to infinity. A result of

the de Gennes model is that the polymer segment density profile is a monotonically decaying function and that the interaction between two planar surfaces is attractive at all separations. Various models have extended the de Gennes model to determine finite chain length corrections to, e.g., surface tension, polymer segment density profile, surface–surface interactions, etc.^{16–20} Such calculations are of particular interest since the polymer chain length is an important parameter in experiments,²¹ computer simulations,^{22–24} and numerical solutions of lattice models.¹³ Variation of the chain length thus provides a more stringent testing of theoretical models. Moreover, it was expected,^{25,26} and later verified,^{16–20} that in certain situations, the “tails” of the polymer chain become important, leading to *qualitatively* different behavior.

Extensions to the ground state dominance model were first investigated by Semenov *et al.*¹⁶ The presence of tails was taken 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 numerical solutions of the lattice self-consistent mean-field theories.¹⁷ Furthermore, it was shown that the interaction between two planar surfaces becomes weakly repulsive at larger distances.¹⁸

It was subsequently shown by Semenov that the two-order parameter model could be cast into a free energy formalism of a *single* order parameter¹⁹ for which the Euler–Lagrange equations are the Edwards equations, just as de Gennes had done previously in the context of the ground state dominance approximation.¹² A free energy functional

was proposed¹⁹ to describe the free energy correctly to $\mathcal{O}(1/N^2)$. This means that the *three* leading contributions in an expansion in $1/N$ to the free energy are captured: (1) the ground state dominance contribution; (2) the leading correction to ground state dominance of $\mathcal{O}(1/N)$, which gives a description on the same level as the two-order parameter model;²⁷ (3) terms of $\mathcal{O}(1/N^{3/2})$. These last terms were shown to be responsible for a weak, oscillatory interaction potential at large distances between two planar surfaces.¹⁹ Similar oscillations were also observed in the segment density profile in analytical work by Semenov *et al.* and in numerical solutions of the Scheutjens and Fler lattice model for polymers.²⁸

In this article, we investigate the surface tension, segment density profiles, and interaction potential for (planar) polymer-adsorbing surfaces. Analytical expressions, valid for any polymer length, are derived in the limit of *weakly* adsorbing polymers. Our expression for the free energy is consistent with the linear response model for bulk polymers¹ and the Semenov single order parameter free energy.¹⁹ We pay particular attention to the segment density profile at large distances from the surface and the interaction between surfaces at large separations.

The outline of the paper is as follows: In the next section we discuss the self-consistent field theory in the context of which our calculations are made. In Secs. III and IV we provide a detailed derivation of the free energy from the Edwards equations in the case of weak external fields (Sec. III) and weak polymer adsorption (Sec. IV). In Secs. V and VI, the free energy derived is used to determine surface tension, segment density profiles, and interaction potential for polymer adsorbing surfaces. We end with a discussion of results.

II. SELF-CONSISTENT FIELD THEORY

The Green function $G(\mathbf{r}, \mathbf{r}', N)$ describes the statistical weight of a single polymer chain of length N with one end at \mathbf{r} and the other end at \mathbf{r}' . The Green function can be determined by solving the Edwards equation,

$$\frac{\partial}{\partial n} G(\mathbf{r}, \mathbf{r}', n) = \frac{a^2}{6} \nabla^2 G(\mathbf{r}, \mathbf{r}', n) - \frac{U(\mathbf{r})}{k_B T} G(\mathbf{r}, \mathbf{r}', n), \quad (2.1)$$

with initial condition

$$\lim_{n \rightarrow 0} G(\mathbf{r}, \mathbf{r}', n) = \delta(\mathbf{r} - \mathbf{r}'), \quad (2.2)$$

where a is the polymer segment length and $U(\mathbf{r})$ is an as yet unspecified external potential.

In terms of the Green function, one may construct the average segment density,

$$\phi(\mathbf{r}) = N_p \frac{\int_0^N dn \int d\mathbf{r}' \int d\mathbf{r}'' G(\mathbf{r}', \mathbf{r}, n) G(\mathbf{r}, \mathbf{r}'', N-n)}{\int d\mathbf{r}' \int d\mathbf{r}'' G(\mathbf{r}', \mathbf{r}'', N)}, \quad (2.3)$$

where N_p is the total number of polymer chains. This prefactor determines the scale of the Green function. As will

become apparent later, it is chosen such that the density becomes equal to the uniform bulk density, $\phi(\mathbf{r}) = N_p N / V \equiv \phi_b$, for a homogeneous system.

The general solution of the Edwards equation may be formulated in the form of an eigenfunction expansion,

$$G(\mathbf{r}, \mathbf{r}', n) = \sum_k \psi_k(\mathbf{r}) \psi_k^*(\mathbf{r}') e^{-n E_k / k_B T}, \quad (2.4)$$

with the eigenfunctions ψ_k and eigenvalues E_k determined by

$$\frac{a^2}{6} \nabla^2 \psi_k(\mathbf{r}) - \frac{U(\mathbf{r})}{k_B T} \psi_k(\mathbf{r}) = -\frac{E_k}{k_B T} \psi_k(\mathbf{r}). \quad (2.5)$$

In the self-consistent field model, the external potential is interpreted as being induced by the presence of the other polymer segments,¹⁴

$$U(\mathbf{r}) = k_B T v \phi(\mathbf{r}), \quad (2.6)$$

where v is the so-called *excluded volume* parameter. In this way, the set of Eqs. (2.1)–(2.3) becomes self-consistently closed. This approach has formed the basis of many theoretical treatments in the literature.^{1–3}

For very long chains—a more precise criterion is formulated later—only the ground state contribution ($k=0$) in the eigenfunction expansion remains and the summation may be limited to the first term only,

$$G(\mathbf{r}, \mathbf{r}', n) \approx \psi_0(\mathbf{r}) \psi_0^*(\mathbf{r}') e^{-n E_0 / k_B T}. \quad (2.7)$$

This is the so-called *ground state dominance approximation*.¹ The Edwards equation, Eq. (2.1), and segment density, Eq. (2.3), can then be written as

$$\begin{aligned} \frac{a^2}{6} \nabla^2 \psi(\mathbf{r}) &= v |\psi(\mathbf{r})|^2 \psi(\mathbf{r}) - \frac{E_0}{k_B T} \psi(\mathbf{r}), \\ \phi(\mathbf{r}) &= |\psi(\mathbf{r})|^2, \end{aligned} \quad (2.8)$$

where we have defined $\psi(\mathbf{r}) \equiv (N_p N)^{1/2} \psi_0(\mathbf{r})$. It may now be noted¹ that the *same equation* follows from the minimization of the following free energy functional:

$$\frac{F[\psi]}{k_B T} = \int d\mathbf{r} \left[\frac{a^2}{6} |\nabla \psi(\mathbf{r})|^2 + \frac{v}{2} |\psi(\mathbf{r})|^4 - \frac{E_0}{k_B T} |\psi(\mathbf{r})|^2 \right]. \quad (2.9)$$

The last term is added to fix the total number of segments,

$$N_p N = \int d\mathbf{r} |\psi(\mathbf{r})|^2. \quad (2.10)$$

The free energy can be rewritten in terms of the segment density, $\phi(\mathbf{r}) = |\psi(\mathbf{r})|^2$. One then has

$$\frac{F[\phi]}{k_B T} = \int d\mathbf{r} \left[\frac{a^2}{24} \frac{|\nabla \phi(\mathbf{r})|^2}{\phi(\mathbf{r})} + \frac{v}{2} (\phi(\mathbf{r}) - \phi_b)^2 \right], \quad (2.11)$$

where the uniform bulk density, $\phi_b \equiv N_p N / V$, is related to $E_0 / k_B T = v \phi_b$. Furthermore, we subtracted the (constant) bulk free energy in order for the above free energy to be the *excess* free energy.

The expression for the free energy in Eq. (2.11) has been the starting point of many density functional treatments for polymer solutions.¹ Due to the nature of the ground state dominance approximation, this treatment is, however, limited to infinitely long chains and semidilute polymer solutions. The question thus naturally arises whether a similar free en-

ergy density functional may be formulated without making use of the ground state dominance approximation. In the present article we construct such a free energy without making the ground state dominance approximation.

III. INHOMOGENEOUS SYSTEM

Ultimately, we are interested in the case of polymer adsorption onto a solid surface, but for now we start by considering an *infinite* system, without the presence of a surface, in which the segment density profile only depends on one coordinate z , $\phi(\mathbf{r}) = \phi(z)$. Furthermore, often we are only interested in the departure of the density profile with respect to the bulk density at $z = \pm\infty$ and introduce $\delta\phi(z) \equiv \phi(z) - \phi_b$, with $\lim_{z \rightarrow \pm\infty} \phi(z) = \phi_b$.

A further reduction that we make, but could have made quite generally, is to integrate the Green function over one of the chain's ends. This defines the statistical weight of a polymer chain of length n with one end fixed at position \mathbf{r} ,

$$G(\mathbf{r}, n) \equiv \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}', n). \quad (3.1)$$

In the bulk region $G(\mathbf{r}, n) \rightarrow G_b(n)$, which is independent of \mathbf{r} . By solving the Edwards equation with the initial condition [Eq. (2.2)], one finds that in the bulk, $G_b(n) = e^{-v\phi_b n}$. It is now convenient to redefine the statistical weight such so as to absorb this trivial n -dependence,

$$Z(\mathbf{r}, n) \equiv e^{v\phi_b n} \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}', n). \quad (3.2)$$

In the geometry under consideration, we have that $Z(\mathbf{r}, n) = Z(z, n)$. The Edwards equation [Eq. (2.1)] and segment density [Eq. (2.3)] in the self-consistent field approximation [Eq. (2.6)] are then given by

$$\frac{\partial}{\partial n} Z(z, n) = \frac{a^2}{6} \frac{\partial^2}{\partial z^2} Z(z, n) - v(\phi(z) - \phi_b) Z(z, n), \quad (3.3)$$

$$\phi(z) = \frac{\phi_b}{N} \int_0^N dn Z(z, n) Z(z, N-n), \quad (3.4)$$

with the initial condition,

$$\lim_{n \rightarrow 0} Z(z, n) = 1. \quad (3.5)$$

An exact solution of the above coupled differential equations can only be found when certain further approximations are made. In the following we consider *weak* fields leading to small deviations from bulk behavior.

Weak fields: Linear response theory: The assumption of a weak field implies that $\delta\phi(z) \equiv \phi(z) - \phi_b \ll \phi_b$ and $\delta Z(z, n) \equiv Z(z, n) - 1 \ll 1$. Linearization of Eqs. (3.3) and (3.4) then leads to

$$\frac{\partial}{\partial n} \delta Z(z, n) = \frac{a^2}{6} \frac{\partial^2}{\partial z^2} \delta Z(z, n) - v \delta\phi(z), \quad (3.6)$$

$$\delta\phi(z) = \frac{2\phi_b}{N} \int_0^N dn \delta Z(z, n), \quad (3.7)$$

with the initial condition,

$$\lim_{n \rightarrow 0} \delta Z(z, n) = 0. \quad (3.8)$$

We now rewrite these differential equations in terms of a single differential equation for the density $\delta\phi(z)$ alone. From the first integral we then proceed to construct the free energy functional. Only later do we explicitly solve the resulting differential equation for $\delta\phi(z)$ and determine the corresponding excess free energy.

The linearized differential equations can be solved by separating $\delta Z(z, n)$ into one part that no longer depends on n and one that still *does* depend on n : $\delta Z(z, n) \equiv \psi(z) + a(z, n)$. The differential equation in Eq. (3.6) is then split up as

$$\frac{\partial}{\partial n} a(z, n) = \frac{a^2}{6} \frac{\partial^2}{\partial z^2} a(z, n), \quad (3.9)$$

$$\frac{a^2}{6} \frac{\partial^2}{\partial z^2} \psi(z) = v \delta\phi(z), \quad (3.10)$$

with the segment density [Eq. (3.7)] now given by

$$\delta\phi(z) = 2\phi_b \psi(z) + \frac{2\phi_b}{N} \int_0^N dn a(z, n), \quad (3.11)$$

and the initial condition [Eq. (3.8)],

$$\lim_{n \rightarrow 0} a(z, n) = -\psi(z). \quad (3.12)$$

In this section, we obtain a solution to these differential equations for the *infinite* system with no boundaries present, i.e., $-\infty < z < \infty$, and leave the more complicated situation of a *semi-infinite* system in the presence of a solid surface to the next section.

For the infinite system, the solution to the differential equation for $a(z, n)$ in Eq. (3.9), with the initial condition Eq. (3.12), reads

$$a(z, n) = -\left(\frac{3}{2\pi n a^2}\right)^{1/2} \int_{-\infty}^{\infty} dz' \psi(z') \exp\left(\frac{-3(z' - z)^2}{2n a^2}\right). \quad (3.13)$$

Inserting the above expression for $a(z, n)$ into Eq. (3.11), we now have for the density profile in terms of $\psi(z)$,

$$\delta\phi(z) = 2\phi_b \psi(z) - \frac{\phi_b}{R_G} \int_{-\infty}^{\infty} dz' \psi(z') \alpha\left(\frac{z' - z}{2R_G}\right), \quad (3.14)$$

where the radius of gyration $R_G \equiv \sqrt{Na^2/6}$, and where we have defined

$$\alpha(x) \equiv \frac{2}{\sqrt{\pi}} \exp(-x^2) - 2|x| \operatorname{erfc}(|x|). \quad (3.15)$$

The Fourier transform of Eq. (3.14) gives

$$\delta\tilde{\phi}(k) = 2\phi_b \tilde{\psi}(k) - 2\phi_b \tilde{\alpha}(2kR_G) \tilde{\psi}(k), \quad (3.16)$$

where the tilde refers to the Fourier transform of the function, $\tilde{\psi}(k) = \int dz e^{-ikz} \psi(z)$ and $\psi(z) = (2\pi)^{-1} \times \int dk e^{ikz} \tilde{\psi}(k)$. Explicitly, we have $\tilde{\alpha}(x) = (4/x^2) [1 - \exp(-x^2/4)]$. Solving Eq. (3.16) for $\tilde{\psi}(k)$ then gives

$$\tilde{\psi}(k) = \frac{1}{2\phi_b} \frac{\delta\tilde{\phi}(k)}{1 - \tilde{\alpha}(2kR_G)}. \quad (3.17)$$

Next, we Fourier transform the original differential equation for $\psi(z)$ in Eq. (3.10),

$$-\frac{a^2}{6}k^2\tilde{\psi}(k) = v\delta\tilde{\phi}(k). \quad (3.18)$$

With the expression for $\tilde{\psi}(k)$ in Eq. (3.17) inserted into it, this is written as

$$-\frac{1}{\phi_b N} \frac{\delta\tilde{\phi}(k)}{f_D(k^2R_G^2)} = v\delta\tilde{\phi}(k), \quad (3.19)$$

where the Debye function is defined as $f_D(x) \equiv (2/x^2) \times [\exp(-x) - 1 + x]$. The back Fourier transform of Eq. (3.19) then finally yields the equation for $\delta\phi(z)$ sought after

$$-\frac{1}{\phi_b N} \int_{-\infty}^{\infty} dz' \delta\phi(z') \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{e^{ik(z-z')}}{f_D(k^2R_G^2)} = v\delta\phi(z). \quad (3.20)$$

We may now construct the free energy for which the Euler-Lagrange equation is given by the equation above. We find

$$\begin{aligned} \frac{F[\delta\phi]}{A k_B T} &= \frac{1}{2\phi_b N} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \delta\phi(z) \delta\phi(z') \\ &\times \int_{-\infty}^{\infty} \frac{dk}{2\pi} \frac{e^{ik(z-z')}}{f_D(k^2R_G^2)} + \frac{v}{2} \int_{-\infty}^{\infty} dz [\delta\phi(z)]^2. \end{aligned} \quad (3.21)$$

This expression for the free energy, with the corresponding Euler-Lagrange equation in Eq. (3.20), is the main result of this section.

The free energy constructed from Eq. (3.20) is only uniquely defined up to a constant, but we do know that the free energy in Eq. (3.21) should reduce to the expression obtained in the ground state dominance approximation, Eq. (2.11), in the limit $N \rightarrow \infty$. That this is indeed the case may be verified by using that $f_D(k^2R_G^2)^{-1} \approx \frac{1}{2}k^2R_G^2 \rightarrow -(Na^2/12)\delta''(z-z')$, and integrating by parts yielding

$$\frac{F[\delta\phi]}{A k_B T} = \int_{-\infty}^{\infty} dz \left[\frac{a^2}{24\phi_b} [\delta\phi'(z)]^2 + \frac{v}{2} [\delta\phi(z)]^2 \right]. \quad (3.22)$$

One may verify that this expression indeed corresponds to the free energy in Eq. (2.11) with the density expanded around the bulk density. Note that the condition $kR_G \rightarrow \infty$, implies that the description is strictly valid for distances smaller than the polymer's radius of gyration, $z \propto 1/k \ll R_G$.

The first term in the expression for the free energy in Eq. (3.21) could also have been derived from a linear response analysis,

$$\delta F = \frac{1}{2}k_B T \int d\mathbf{r} \int d\mathbf{r}' C_b(\mathbf{r}, \mathbf{r}') \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}'), \quad (3.23)$$

in which $C_b(\mathbf{r}, \mathbf{r}') = C_b(|\mathbf{r} - \mathbf{r}'|)$ is the bulk polymer direct correlation function. For Gaussian chains in solution, the

Fourier transform of the direct correlation function is given by the Debye function,

$$\tilde{C}_b(k)^{-1} = \phi_b N f_D(k^2R_G^2). \quad (3.24)$$

A further important connection with previous work forms the expression for the free energy proposed by Semenov.¹⁹ It has the following form:

$$\begin{aligned} \frac{F_{\text{Sem}}[\phi]}{A k_B T} &= \int_{-\infty}^{\infty} dz \left[\frac{a^2}{24} \frac{\phi'(z)^2}{\phi(z)} + \frac{v}{2} \phi(z)^2 - \frac{2}{N} \phi_b^{1/2} \phi(z)^{1/2} \right. \\ &\quad \left. + \mu \phi(z) \right] + \frac{1}{\phi_b N} \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' [\phi_b^{1/2} \phi(z)^{1/2} \\ &\quad - \phi(z)][\phi_b^{1/2} \phi(z')^{1/2} - \phi(z')] \\ &\quad \times \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{ik(z-z')} \left[\frac{1 - e^{-k^2R_G^2} - k^2R_G^2 e^{-k^2R_G^2}}{e^{-k^2R_G^2} - 1 + k^2R_G^2} \right]. \end{aligned} \quad (3.25)$$

This form for the free energy is derived by Semenov¹⁹ in what is termed the ‘‘main approximation’’ which captures the free energy to $\mathcal{O}(1/N^2)$. It is pointed out by Semenov¹⁹ that the free energy reduces to the free energy in Eq. (3.21), when $\phi(z)$ is expanded around the bulk density ϕ_b . The first term in Eq. (3.25) is the leading correction in $1/N$ to ground state dominance and gives a description on the same level as the two-order parameter model.²⁷

Of course, without the existence of adsorption potentials responsible for the existence of an inhomogeneity in the system, the solution of the Euler-Lagrange equation in Eq. (3.19) for $\delta\tilde{\phi}(k)$ yields the trivial result $\delta\tilde{\phi}(k) = 0$ and, therefore, $\delta\phi(z) = 0$. Since the Edwards equation is the Euler-Lagrange equation that minimizes the free energy in Eq. (3.21), this result indicates that, from an energetic point of view, the most profitable situation is when $\phi(z) = \phi_b$, everywhere. Of more interest is therefore the *semi-infinite* system ($0 \leq z < \infty$), considered next, in which the value of the density at the surface differs from the bulk value due the presence of an interaction with a solid surface.

IV. POLYMER ADSORPTION

We now turn to the situation of a polymer solution in contact with a solid surface (wall), located at $z = 0$. The solid surface is considered to be impenetrable to the polymer so that the density is defined only for $z > 0$ [see the density profile in Fig. 1(a)]. An attractive interaction with the wall is considered at $z = 0$,

$$\frac{U_{\text{wall}}(z)}{k_B T} = -\frac{a^2}{6} \frac{1}{d} \delta(z). \quad (4.1)$$

The inverse of the extrapolation length, d , is a measure of the surface interaction strength and is responsible for an enhanced polymer adsorption, $\phi(0) > \phi_b$, when $d > 0$.

Even though the solid surface is considered to be impenetrable, so that $\phi(z) = 0$ for $z < 0$, the polymer segment density is not equal to zero at the wall in this treatment

$[\phi(0) \neq 0]$. Such a description is therefore expected to be valid only for enhanced polymer adsorption and for distances beyond a certain microscopic distance ($\propto a$) away from the surface.¹

Eisenriegler and co-workers^{3,7,8} and others¹¹ have addressed the related problem of polymer depletion, in which there is no additional interaction with the wall considered, assuming the (Dirichlet) boundary condition, $\phi(0) = 0$. They showed that under these circumstances analytic solutions for the polymer partition function could be obtained. In the present situation, such an analytic solution cannot be obtained in general. However, when we assume that the external fields are weak, i.e., when we consider the case of *weak adsorption*, an analytic solution can indeed be formulated.

Weak adsorption: Before turning to the formulation of the appropriate boundary conditions in the case of polymer adsorption, we come back to the expression for the free energy in the ground state dominance approximation. The free energy for weak adsorption is then given by Eq. (3.22) to which a term containing the interaction with the solid surface is added,¹

$$\begin{aligned} \frac{F[\delta\phi]}{A k_B T} &= \int_0^\infty dz \left[\frac{a^2}{24 \phi_b} [\delta\phi'(z)]^2 + \frac{v}{2} [\delta\phi(z)]^2 \right] \\ &\quad - \frac{a^2}{6} \frac{1}{d} \phi(0). \end{aligned} \quad (4.2)$$

The minimization of the above free energy leads to the following Euler–Lagrange equation and boundary condition for $\delta\phi(z)$:

$$\begin{aligned} \frac{a^2}{12\phi_b} \delta\phi''(z) &= v \delta\phi(z), \\ \delta\phi'(0) &= -\frac{2}{d} \phi_b. \end{aligned} \quad (4.3)$$

We turn next to the evaluation of the full free energy, which we expect to reduce to Eq. (4.2) in the limit $N \rightarrow \infty$.

Since the presence of the solid surface precludes the polymer for $z < 0$, the partition function $Z(z, n)$ is defined only for $z \geq 0$. It turns out to be mathematically convenient to extend $Z(z, n)$ also for $z < 0$. Here we choose to extend *symmetrically* [see Fig. 1(b)] and define a partition function $Z_e(z, n)$ defined for *all* z as

$$Z_e(z, n) = Z(-z, n)\Theta(-z) + Z(z, n)\Theta(z), \quad (4.4)$$

where $\Theta(x)$ is the Heaviside-function.

The presence of the potential induced by the surface modifies the external field in Eq. (2.6). The result is that the Edwards equation in Eq. (3.3) now becomes

$$\begin{aligned} \frac{\partial}{\partial n} Z_e(z, n) &= \frac{a^2}{6} \frac{\partial^2}{\partial z^2} Z_e(z, n) - v(\phi_e(z) - \phi_b) Z_e(z, n) \\ &\quad + \frac{a^2}{3} \frac{1}{d} \delta(z) Z_e(z, n). \end{aligned} \quad (4.5)$$

Since the term containing the second derivative with respect to z is the only term that varies rapidly as a function of z near

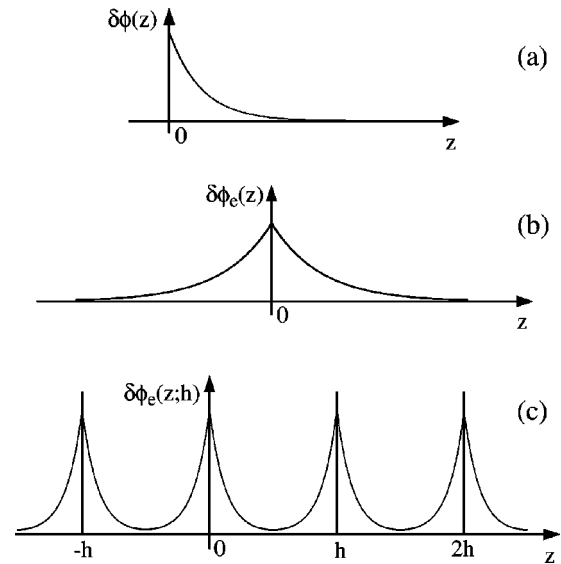


FIG. 1. Sketches of the polymer density profile as a function of the distance to a solid surface. (a) $\delta\phi(z)$ is the polymer density profile near a single surface at $z=0$; (b) $\delta\phi_e(z)$ is the same density profile as in (a), symmetrically extended to $z < 0$; (c) $\delta\phi_e(z;h)$ is the polymer density profile between two surfaces at $z=0$ and $z=h$, periodically extended to whole space.

$z=0$, the above differential equation reduces to the usual Edwards equation in Eq. (3.3) with the additional term leading to the boundary condition,

$$\left. \frac{\partial}{\partial z} Z(z, n) \right|_{z=0} = -\frac{1}{d} Z(z, n) \Big|_{z=0}. \quad (4.6)$$

Again, we introduce $\delta Z(z, n) = Z(z, n) - 1 = a_e(z, n) + \psi_e(z)$, and the symmetrically extended functions $a_e(z, n)$ and $\psi_e(z)$, and expand in $\delta Z(z, n) \ll 1$. The differential equation for $a_e(z, n)$ then becomes

$$\frac{\partial}{\partial n} a_e(z, n) = \frac{a^2}{6} \frac{\partial^2}{\partial z^2} a_e(z, n). \quad (4.7)$$

One may, again, verify that this expression reduces to the equation obtained in Eq. (3.9), now complemented by the boundary condition,

$$\left. \frac{\partial}{\partial z} a_e(z, n) \right|_{z=0} = 0. \quad (4.8)$$

The differential equation for $\psi_e(z)$ reads

$$\frac{a^2}{6} \frac{\partial^2}{\partial z^2} \psi_e(z) = v \delta\phi_e(z) - \frac{a^2}{3} \frac{1}{d} \delta(z). \quad (4.9)$$

This expression reduces to the equation obtained in Eq. (3.10) with the additional term leading to the boundary condition,

$$\left. \frac{\partial}{\partial z} \psi_e(z) \right|_{z=0} = -\frac{1}{d}. \quad (4.10)$$

We may now solve the differential equation for $a_e(z, n)$ in Eq. (3.9) taking into account the boundary condition in Eq. (4.8). One may show that

$$a(z, n) = - \left(\frac{3}{2\pi n a^2} \right)^{1/2} \int_0^\infty dz' \psi(z') \left[\exp \left(\frac{-3(z'+z)^2}{2n a^2} \right) + \exp \left(\frac{-3(z'-z)^2}{2n a^2} \right) \right] \quad (z > 0). \quad (4.11)$$

The segment density profile is obtained by inserting the above expression for $a(z, n)$ into Eq. (3.11). We then arrive at

$$\delta\phi(z) = 2 \phi_b \psi(z) - \frac{\phi_b}{R_G} \int_0^\infty dz' \psi(z') \times \left[\alpha \left(\frac{z'+z}{2R_G} \right) + \alpha \left(\frac{z'-z}{2R_G} \right) \right] \quad (z > 0), \quad (4.12)$$

where $\alpha(x)$ is defined earlier [Eq. (3.15)]. This expression for $\delta\phi(z)$ is symmetrically extended for $z < 0$,

$$\delta\phi_e(z) = 2 \phi_b \psi_e(z) - \frac{\phi_b}{R_G} \int_{-\infty}^\infty dz' \psi_e(z') \alpha \left(\frac{z'-z}{2R_G} \right). \quad (4.13)$$

One may note that the above expression for the symmetrically extended density profile is the same as the expression for $\delta\phi(z)$ in the previous section, Eq. (3.14).

In order to proceed as before, we need to determine the Fourier transform of Eq. (4.13) and the Edwards equation in Eq. (4.9). One finds

$$\delta\tilde{\phi}_e(k) = 2 \phi_b \tilde{\psi}_e(k) - 2 \phi_b \tilde{\alpha}(2kR_G) \tilde{\psi}_e(k), \quad (4.14)$$

$$-\frac{a^2}{6} k^2 \tilde{\psi}_e(k) = v \delta\tilde{\phi}_e(k) - \frac{a^2}{3} \frac{1}{d}. \quad (4.15)$$

Substituting the expression for $\tilde{\psi}_e(k)$ in Eq. (4.15) into Eq. (4.14) gives

$$-\frac{a^2}{12 \phi_b} \frac{k^2}{1 - \tilde{\alpha}(2kR_G)} \delta\tilde{\phi}_e(k) = v \delta\tilde{\phi}_e(k) - \frac{a^2}{3} \frac{1}{d}. \quad (4.16)$$

The back Fourier transform of this equation gives

$$\frac{1}{4 \phi_b N} \int_{-\infty}^\infty dz' \delta\phi_e''(z') \alpha_D \left(\frac{z-z'}{2R_G} \right) = v \delta\phi_e(z) - \frac{a^2}{3} \frac{1}{d} \delta(z), \quad (4.17)$$

where we have defined

$$\alpha_D(x) \equiv \int_{-\infty}^\infty \frac{dk}{2\pi} \frac{e^{ikx}}{1 - \tilde{\alpha}(k)}. \quad (4.18)$$

Again, we may construct the free energy for which the Euler-Lagrange equation is equal to the Edwards equation in Eq. (4.17). One finds

$$\frac{F_e[\delta\phi_e]}{A k_B T} = \frac{-1}{8 \phi_b N} \int_{-\infty}^\infty dz \int_{-\infty}^\infty dz' \delta\phi_e(z) \delta\phi_e''(z') \times \alpha_D \left(\frac{z-z'}{2R_G} \right) + \frac{v}{2} \int_{-\infty}^\infty dz [\delta\phi_e(z)]^2 - \frac{a^2}{3} \frac{1}{d} \phi_e(0), \quad (4.19)$$

where $\phi_e(0) = \phi_b + \delta\phi_e(0)$. From the symmetrically extended free energy, we may now go back to the free energy in terms of $\phi(z)$ instead of $\phi_e(z)$. Keeping in mind that the free energy of the symmetrically extended system is twice the free energy of the semi-infinite system, i.e., $F_e = 2F$, we find

$$\frac{F[\delta\phi]}{A k_B T} = \frac{1}{8 \phi_b N} \int_0^\infty dz \int_0^\infty dz' \delta\phi'(z) \delta\phi'(z') \times \left[\alpha_D \left(\frac{z-z'}{2R_G} \right) - \alpha_D \left(\frac{z+z'}{2R_G} \right) \right] + \frac{v}{2} \int_0^\infty dz [\delta\phi(z)]^2 - \frac{a^2}{6} \frac{1}{d} \phi(0). \quad (4.20)$$

In this way we have constructed the free energy functional for weak polymer adsorption. We should verify that this expression for the free energy reduces to the free energy given in Eq. (4.2) for ground state dominance when $N \rightarrow \infty$. One may show that this is indeed the case by using that in this limit $\alpha_D((z \pm z')/2R_G) \rightarrow (N a^2/3) \delta(z \pm z')$.

V. POLYMER DENSITY PROFILE AND SURFACE TENSION

In this section we turn our attention to obtaining explicit solutions for the segment density profile and surface tension.

A. Polymer density profile

An explicit solution for the polymer segment density profile is obtained by solving $\delta\tilde{\phi}_e(k)$ from Eq. (4.16). This gives

$$\delta\tilde{\phi}_e(k) = \frac{4 \phi_b \xi_b^2}{d} \left[\frac{k^2 R_G^2 - 1 + \exp(-k^2 R_G^2)}{k^4 \xi_b^2 R_G^2 + 4 k^2 R_G^2 - 4 + 4 \exp(-k^2 R_G^2)} \right], \quad (5.1)$$

where the bulk correlation length, $\xi_b \equiv a/(3v\phi_b)^{1/2}$. The Fourier transform of $\delta\tilde{\phi}_e(k)$ is

$$\delta\phi_e(z) = \frac{\phi_b \xi_b}{\pi d} \int_{-\infty}^\infty dk e^{2ikz/\xi_b} \times \left[\frac{4 k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)}{4 k^4 + 4 k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)} \right], \quad (5.2)$$

where we have introduced the parameter ε as the (square of) the bulk correlation length, ξ_b , divided by the polymer's radius of gyration,

$$\varepsilon \equiv \frac{\xi_b^2}{R_G^2} = \frac{2}{v \phi_b N}. \quad (5.3)$$

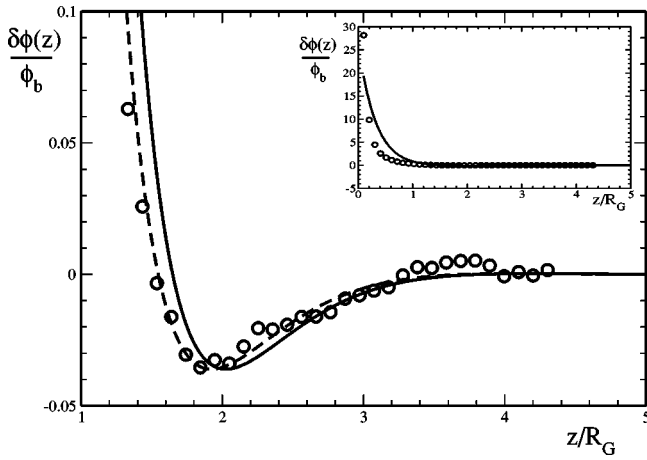


FIG. 2. Polymer segment density profiles, $\delta\phi(z)/\phi_b$, as a function of z/R_G from MC simulations (Ref. 23) (circles) with the analytical expression in Eq. (5.4) (solid curve). In the MC simulations: $N=200$, $a^3\phi_b=0.0216$; $R_G/a=9.76$; surface interaction strength $\varepsilon_s=1.0 k_B T$ (Ref. 23). In Eq. (5.4): $v=a^3$; $\varepsilon\approx 0.46$; $d=(1/3)a/\sqrt{6}$. The inset shows the same polymer segment density profile on a full scale. The dashed curve is Eq. (5.4) shifted by a lattice distance a .

The segment density profile $\delta\phi(z)$ thus becomes

$$\delta\phi(z) = \frac{2\phi_b\xi_b}{\pi d} \int_0^\infty dk \cos\left(\frac{2kz}{\xi_b}\right) \times \left[\frac{4k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)}{4k^4 + 4k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)} \right]. \quad (5.4)$$

This expression is our final result for the segment density profile valid for any chain length. We first investigate Eq. (5.4) by comparing it to the segment density profile obtained in MC simulations by de Joannis *et al.*²³ In Fig. 2, the reduced segment density $\delta\phi(z)/\phi_b$ is shown as a function of z/R_G . For the MC simulations (circles), the following parameter values were used: chain length $N=200$, bulk density $a^3\phi_b=0.0216$, radius of gyration $R_G/a=9.76$, and surface interaction strength $\varepsilon_s=1.0 k_B T$.²³ For the evaluation of the analytical expression in Eq. (5.4) (solid curve), we have set $v=a^3$ (good solvent), which gives $\varepsilon\approx 0.46$. The relation between the value of ε_s and the extrapolation length d is less transparent; we have now set $d=1/3$ in units of $a/\sqrt{6}$. The value of d determines the scale of $\delta\phi(z)$ and is chosen such that the depth of the minima for the segment density profiles are approximately equal.

Even though the adsorption strength is quite high in the MC simulations, Eq. (5.4) gives a fair description of the full polymer segment density profile (inset Fig. 2). Good agreement is obtained for the ‘‘overshoot’’ of the polymer segment density profile, which may be further improved by shifting the density profile by a lattice distance a (dashed curve).

We may further investigate the expression for the segment density profile in Eq. (5.4) by expanding in $\varepsilon\ll 1$. Since small ε implies large N , we thus should reproduce the results derived previously in the ground state dominance approximation¹ and those by Semenov *et al.*^{16,19} The three leading terms in the expansion in ε of Eq. (5.4) are

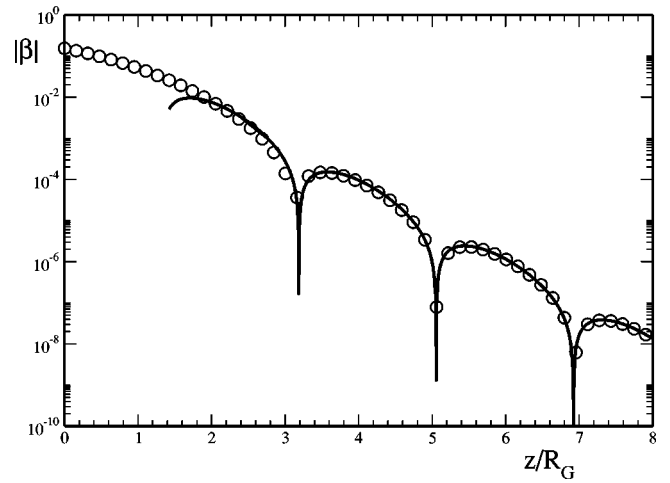


FIG. 3. Numerical solution for $|\beta(z/R_G)|$ as a function of z/R_G (circles); the solid curve is the approximate expression for the asymptotic behavior ($z\gg R_G$) given by Eq. (5.9).

$$\delta\phi(z) = \frac{2\phi_b\xi_b}{\pi d} \int_0^\infty dk \left[\frac{\cos(2kz/\xi_b)}{k^2+1} \right] - \varepsilon \frac{\phi_b\xi_b}{2\pi d} \times \int_0^\infty dk \left[\frac{\cos(2kz/\xi_b)}{(k^2+1)^2} \right] - \varepsilon^{3/2} \frac{\phi_b\xi_b}{4\pi d} \int_0^\infty dt \cos\left(\frac{tz}{R_G}\right) \times \left[\frac{1 - e^{-t^2} - t^2 e^{-t^2}}{e^{-t^2} - 1 + t^2} \right] + \mathcal{O}(\varepsilon^2), \quad (5.5)$$

where we have defined $t\equiv 2kR_G/\xi_b$. The first two integrals can be carried out

$$\delta\phi(z) = \frac{\phi_b\xi_b}{d} \left[e^{-2z/\xi_b} - \frac{\varepsilon}{8} \left(1 + \frac{2z}{\xi_b} \right) e^{-2z/\xi_b} - \varepsilon^{3/2} \beta\left(\frac{z}{R_G}\right) + \mathcal{O}(\varepsilon^2) \right], \quad (5.6)$$

where we have defined

$$\beta(x) \equiv \frac{1}{4\pi} \int_0^\infty dt \cos(xt) \left[\frac{1 - e^{-t^2} - t^2 e^{-t^2}}{e^{-t^2} - 1 + t^2} \right]. \quad (5.7)$$

The leading term in Eq. (5.6) corresponds to the segment density profile in the ground state dominance approximation. One may verify that this profile indeed satisfies the Euler–Lagrange equation and boundary condition in Eq. (4.3).

Both the leading term and the first correction in ε are exponentially decaying functions of z/ξ_b ; the next term, however, varies as a function of z/R_G . This means that even as this term is subdominant in ε , at distances much larger than the bulk correlation length, it becomes the dominant contribution,^{16,19}

$$\delta\phi(z) = -\frac{\phi_b\xi_b}{d} \varepsilon^{3/2} \beta\left(\frac{z}{R_G}\right) + \mathcal{O}(\varepsilon^2) \quad (z\gg\xi_b). \quad (5.8)$$

In Fig. 3, we have plotted $\beta(z/R_G)$ (circles) as a function of z/R_G . [To show $\beta(z/R_G)$ on a logarithmic scale the absolute value has been taken.] One finds that at large distances, $\beta(z/R_G)$ exhibits an oscillatory behavior. These oscillations

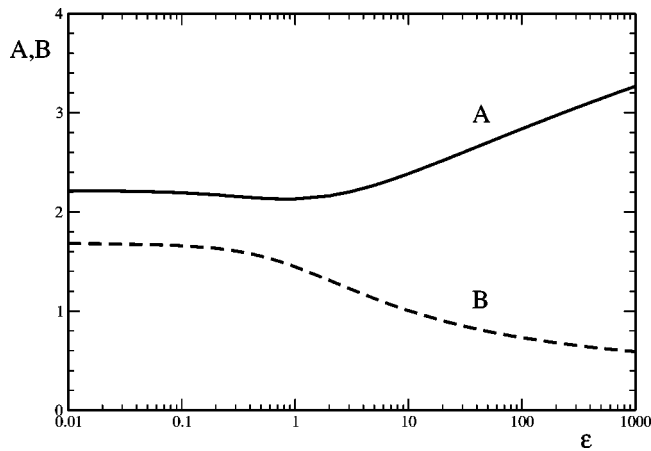


FIG. 4. The coefficients A (solid curve) and B (dashed curve), that determine the exponential decay and the oscillation period of the polymer density profile, respectively [see Eq. (5.11)], as a function of $\varepsilon = 2/(\nu \phi_b N)$.

are also observed²⁸ in numerical solutions of the density profile in the Scheutjens and Fler lattice model for polymers.

It is interesting to further quantify the behavior of the density profile at large distances, $z \gg R_G$. One may show that, for large x [see also Eq. (118) in Ref. 16],

$$\beta(x) = C_0 e^{-A_0 x} \sin(B_0 x + \alpha_0) \quad (x \gg 1), \quad (5.9)$$

where

$$\begin{aligned} A_0 &\equiv \text{Im}[W(1, -1/e) + 1]^{1/2} \approx 2.217792\dots, \\ B_0 &\equiv \text{Re}[W(1, -1/e) + 1]^{1/2} \approx 1.682188\dots, \\ C_0 &\equiv -\frac{1}{4}\sqrt{A_0^2 + B_0^2} \approx -0.695897\dots, \\ \alpha_0 &\equiv \arctan(A_0/B_0) \approx 0.921879\dots, \end{aligned} \quad (5.10)$$

with $W(k, x)$ the Lambert W -function.²⁹ The polymer density profile therefore falls as an oscillating exponential on the scale of the polymer's radius of gyration. The asymptotic behavior as given by Eq. (5.9) is shown as the solid curve in Fig. 3.

The asymptotic behavior of the density profile was determined under the assumption that ε is small. It is interesting to investigate the asymptotic behavior of the density profile directly from the full expression in Eq. (5.4). One finds that also then the density profile is a decaying sinusoid,

$$\delta\phi(z) \propto e^{-(Az/R_G)} \sin\left(\frac{Bz}{R_G} + \alpha\right) \quad (z \gg R_G). \quad (5.11)$$

The coefficients A and B , that determine the exponential decay and the oscillation period of the polymer density profile, respectively, depend (moderately) on ε (see Fig. 4). In the limit $\varepsilon \rightarrow 0$, A and B are equal to the values A_0 and B_0 in Eq. (5.10). The value of the coefficients A and B were phenomenologically determined in Ref. 28 by fitting Eq. (5.11) to their numerically obtained density profiles. It was found that $A_{\text{num}} \approx 1/0.19\sqrt{6} \approx 2.1$ and $B_{\text{num}} \approx 2\pi/1.5\sqrt{6} \approx 1.7$ in excellent agreement with the analytical results in Eq. (5.10).

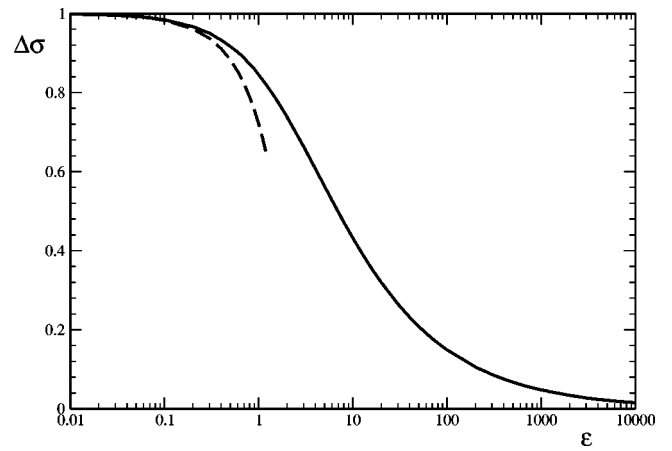


FIG. 5. Reduced surface tension $\Delta\sigma/\Delta\sigma_{\varepsilon=0}$ as a function of $\varepsilon = 2/(\nu \phi_b N)$ (solid curve). The dashed curve is the asymptotic expression for $\Delta\sigma$ given in Eq. (5.16).

B. Surface tension

The surface tension is obtained by inserting the density profile in Eq. (5.2) into the expression for the free energy given by Eq. (4.19) [or the density profile in Eq. (5.4) into Eq. (4.20)]. However, the expression for the free energy may be simplified by first using the Euler–Lagrange equation in Eq. (4.17). Multiplying both sides in Eq. (4.17) by $\frac{1}{2}\delta\phi_e(z)$, integrating over z , and adding the result to the free energy in Eq. (4.19), one finds

$$\frac{F_e}{A k_B T} = \frac{2\sigma}{k_B T} = -\frac{a^2}{3} \frac{\phi_e(0)}{d} + \frac{a^2}{6} \frac{1}{d} \delta\phi_e(0), \quad (5.12)$$

so that the surface tension is given by

$$\frac{\sigma}{k_B T} = -\frac{a^2}{6} \frac{\phi_b}{d} - \frac{a^2}{12} \frac{1}{d} \delta\phi(0). \quad (5.13)$$

The first term in this expression is the constant contribution to the surface tension that remains even when the density profile is equal to the bulk density everywhere, $\phi(z) = \phi_b$. To show more directly the influence of polymer adsorption on the surface tension, it is therefore convenient to subtract this constant,

$$\frac{\Delta\sigma}{k_B T} \equiv \frac{\sigma}{k_B T} + \frac{a^2}{6} \frac{\phi_b}{d} = -\frac{a^2}{12} \frac{1}{d} \delta\phi(0). \quad (5.14)$$

Inserting $z=0$ in Eq. (5.4) thus gives for the surface tension,

$$\begin{aligned} \frac{\Delta\sigma}{k_B T} &= -\frac{a^2}{6} \frac{\phi_b \xi_b}{d^2} \frac{1}{\pi} \int_0^\infty dk \\ &\times \left[\frac{4k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)}{4k^4 + 4k^2 - \varepsilon + \varepsilon \exp(-4k^2/\varepsilon)} \right]. \end{aligned} \quad (5.15)$$

This is our final result for the surface tension valid for all values of the parameter ε . In Fig. 5, the rescaled surface tension, $\Delta\sigma/\Delta\sigma_{\varepsilon=0}$, is shown as a function of ε (solid curve). As expected, the contribution to the surface tension due to polymer adsorption decreases when the polymer chain length becomes shorter ($\varepsilon \rightarrow \infty$).

It is interesting to compare this expression to previous results obtained in the limit of large polymer length. In an expansion in ε we find for $\Delta\sigma$,

$$\frac{\Delta\sigma}{k_B T} = -\frac{a^2}{12} \frac{\phi_b \xi_b}{d^2} \left[1 - \frac{\varepsilon}{8} - \beta(0) \varepsilon^{3/2} + \mathcal{O}(\varepsilon^2) \right], \quad (5.16)$$

with

$$\beta(0) = \frac{1}{4\pi} \int_0^\infty dt \left[\frac{1 - e^{-t^2} - t^2 e^{-t^2}}{e^{-t^2} - 1 + t^2} \right] \approx 0.154042\dots \quad (5.17)$$

For $\varepsilon=0$, the ground state dominance result in the weak adsorption limit is recovered.¹ The asymptotic formula in Eq. (5.16) is shown as the dashed curve in Fig. 5. The expansion deviates from the full expression when $\varepsilon \approx 1$.

VI. INTERACTION BETWEEN TWO PLANAR SURFACES

In this section, we consider the density profile and interaction energy of two planar surfaces separated at a distance h . This calculation is of particular interest for the description of the interaction between colloidal particles mediated by a polymer solution.

A. Polymer density profile

The calculation presented here is closely related to the case of polymer adsorption onto a single planar surface. Again, it is convenient to extend the polymer density profile (between $0 \leq z \leq h$) to the whole space. Here, we extend the density profile *periodically* [see Fig. 1(c)]. Instead of a single delta function, the external potential that induces such a periodic profile is an infinite sum of delta functions. The Euler–Lagrange equation for the extended density profile, $\delta\phi_e(z;h)$, thus becomes [cf. Eq. (4.17)],

$$\begin{aligned} & \frac{1}{4\phi_b N} \int_{-\infty}^\infty dz' \delta\phi_e''(z';h) \alpha_D \left(\frac{z-z'}{2R_G} \right) \\ & = v \delta\phi_e(z;h) - \frac{a^2}{3} \frac{1}{d} \sum_{n=-\infty}^\infty \delta(z-nh). \end{aligned} \quad (6.1)$$

The total free energy is then [cf. Eq. (4.19)],

$$\begin{aligned} \frac{F_e[\delta\phi_e]}{A k_B T} &= \frac{-1}{8\phi_b N} \int_{-\infty}^\infty dz \int_{-\infty}^\infty dz' \delta\phi_e(z;h) \delta\phi_e''(z';h) \\ & \times \alpha_D \left(\frac{z-z'}{2R_G} \right) + \frac{v}{2} \int_{-\infty}^\infty dz [\delta\phi_e(z;h)]^2 \\ & - \frac{a^2}{3} \frac{1}{d} \sum_{n=-\infty}^\infty \int_{-\infty}^\infty dz \phi_e(z;h) \delta(z-nh). \end{aligned} \quad (6.2)$$

The density profile $\delta\phi_e(z;h)$ is obtained by solving the Euler–Lagrange equation in Eq. (6.1). Again, it is convenient to Fourier transform the Euler–Lagrange equation in Eq. (6.1), and then solve for $\delta\tilde{\phi}_e(k;h)$. One finds

$$\begin{aligned} \delta\tilde{\phi}_e(k;h) &= \frac{4\phi_b \xi_b^2}{d} \sum_{n=-\infty}^\infty e^{inhk} \\ & \times \left[\frac{k^2 R_G^2 - 1 + \exp(-k^2 R_G^2)}{k^4 \xi_b^2 R_G^2 + 4k^2 R_G^2 - 4 + 4\exp(-k^2 R_G^2)} \right]. \end{aligned} \quad (6.3)$$

The back Fourier transform gives the segment density profile,

$$\begin{aligned} \delta\phi(z;h) &= \frac{\phi_b \xi_b^2}{h d} \sum_{n=-\infty}^\infty \cos\left(\frac{2\pi n z}{h}\right) \\ & \times \left[\frac{4k_n^2 - \varepsilon + \varepsilon \exp(-4k_n^2/\varepsilon)}{4k_n^4 + 4k_n^2 - \varepsilon + \varepsilon \exp(-4k_n^2/\varepsilon)} \right], \end{aligned} \quad (6.4)$$

where we have defined $k_n \equiv n\pi\xi_b/h$. This is the final expression for the segment density profile between two plates at distance h valid for all ε . One may verify that at infinite separation ($h \rightarrow \infty$), the summation reduces to an integration and Eq. (6.4) reduces to the previous expression in Eq. (5.4).

Again, one may expand the segment density in ε ,

$$\begin{aligned} \delta\phi(z;h) &= \frac{\phi_b \xi_b}{d} \left\{ \frac{\cosh((2z-h)/\xi_b)}{\sinh(h/\xi_b)} \right. \\ & - \frac{\varepsilon}{8} \left[\frac{(h/\xi_b) \cosh((2z-h)/\xi_b)}{\sinh^2(h/\xi_b)} \right. \\ & \left. \left. + \frac{\cosh((2z-h)/\xi_b) - (2z/\xi_b) \sinh((2z-h)/\xi_b)}{\sinh(h/\xi_b)} \right] \right\} \\ & - \varepsilon^{3/2} \beta\left(\frac{z}{R_G}; \frac{h}{R_G}\right) + \mathcal{O}(\varepsilon^2), \end{aligned} \quad (6.5)$$

where we have defined

$$\beta(x;y) \equiv \frac{1}{4y} \sum_{n=-\infty}^\infty \cos(xt_n) \left[\frac{1 - e^{-t_n^2} - t_n^2 e^{-t_n^2}}{e^{-t_n^2} - 1 + t_n^2} \right], \quad (6.6)$$

and where $t_n \equiv 2\pi n/y$. The function $\beta(x;y)$ is defined such that it reduces to $\beta(x)$ defined in Eq. (5.7) when $y \rightarrow \infty$. The leading term in Eq. (6.5) is the ground state dominance result for the polymer density profile between two planar polymer-adsorbing surfaces in the weak adsorption limit.

B. Interaction potential

We now turn to the derivation of the interaction potential between two planar surfaces. Consider again the free energy for the whole system as given by Eq. (6.2). Like the surface tension for the single surface, this expression may be reduced by first using the Euler–Lagrange equation in Eq. (6.1). One then obtains,

$$\frac{F_e(h)}{A k_B T} = -\frac{a^2}{6} \frac{1}{d} \sum_{n=-\infty}^\infty [2\phi_b + \delta\phi_e(nh;h)]. \quad (6.7)$$

For the free energy of the two-surface system, one therefore has

$$\frac{F(h)}{A k_B T} = -\frac{a^2}{3} \frac{1}{d} \phi_b - \frac{a^2}{6} \frac{1}{d} \delta\phi(0;h). \quad (6.8)$$

The interaction potential $U(h)$ is defined as the free energy (per unit area) of the two-surface system with the free energy at infinite separation subtracted,

$$\frac{U(h)}{k_B T} = -\frac{a^2}{6} \frac{\phi_b \xi_b}{\pi d^2} \left\{ \frac{\pi \xi_b}{h} \sum_{n=-\infty}^{\infty} \left[\frac{4 k_n^2 - \varepsilon + \varepsilon \exp(-4 k_n^2/\varepsilon)}{4 k_n^4 + 4 k_n^2 - \varepsilon + \varepsilon \exp(-4 k_n^2/\varepsilon)} \right] - \int_{-\infty}^{\infty} dk \left[\frac{4 k^2 - \varepsilon + \varepsilon \exp(-4 k^2/\varepsilon)}{4 k^4 + 4 k^2 - \varepsilon + \varepsilon \exp(-4 k^2/\varepsilon)} \right] \right\}. \quad (6.10)$$

An alternative but equivalent expression may be derived in terms of the density profile of the *single* surface. This expression is derived by using the fact that the density profile of the two-surface system is given by the sum of all the single-surface density profiles, $\delta\phi(z;h) = \sum_n \delta\phi(z+nh)$. The interaction potential may therefore also be written as

$$\begin{aligned} \frac{U(h)}{k_B T} &= -\frac{a^2}{3} \frac{1}{d} \sum_{n=1}^{\infty} \delta\phi(nh) \\ &= -\frac{2 a^2 \phi_b \xi_b}{3 \pi d^2} \sum_{n=1}^{\infty} \int_0^{\infty} dk \cos\left(\frac{2nhk}{\xi_b}\right) \\ &\quad \times \left[\frac{4 k^2 - \varepsilon + \varepsilon \exp(-4 k^2/\varepsilon)}{4 k^4 + 4 k^2 - \varepsilon + \varepsilon \exp(-4 k^2/\varepsilon)} \right]. \quad (6.11) \end{aligned}$$

This expression, or the equivalent expression in Eq. (6.10), is our final result for the interaction potential valid for all ε . One may expand in ε to compare with previous results

$$\begin{aligned} \frac{U(h)}{k_B T} &= -\frac{a^2 \phi_b \xi_b}{3 d^2} \left[\frac{1}{e^{2h/\xi_b} - 1} \right. \\ &\quad - \frac{\varepsilon}{32} \frac{(2h/\xi_b) + 1 - e^{-2h/\xi_b}}{\sinh^2(h/\xi_b)} \\ &\quad \left. - \varepsilon^{3/2} \sum_{n=1}^{\infty} \beta\left(\frac{nh}{R_G}\right) + \mathcal{O}(\varepsilon^2) \right]. \quad (6.12) \end{aligned}$$

The leading term in Eq. (6.12) corresponds to the interaction potential in the ground state dominance approximation. The negative sign indicates that the interaction between two plates is *attractive*.^{18,30}

The leading term and the first correction in ε , are exponentially decaying functions of h/ξ_b ; the next term, however, varies as a function of h/R_G . Therefore, at distances much larger than the bulk correlation length, it becomes the dominant contribution,

$$\frac{U(h)}{k_B T} = \frac{a^2 \phi_b \xi_b}{3 d^2} \varepsilon^{3/2} \sum_{n=1}^{\infty} \beta\left(\frac{nh}{R_G}\right) + \mathcal{O}(\varepsilon^2) \quad (h \gg \xi_b). \quad (6.13)$$

In Fig. 6, $\sum_n \beta(nh/R_G)$ is plotted as a function of h/R_G . [To show $\sum_n \beta(nh/R_G)$ on a logarithmic scale the absolute value has been taken.] One may identify different regimes; at intermediate distances, $\xi_b \ll h \ll R_G$, an approximate expres-

$$\frac{U(h)}{k_B T} \equiv \frac{F(h)}{A k_B T} - \frac{2\sigma}{k_B T} = -\frac{a^2}{6} \frac{1}{d} [\delta\phi(0;h) - \delta\phi(0;\infty)]. \quad (6.9)$$

The interaction potential is obtained by inserting the expression for the density profile given in Eq. (6.4),

sion for $\beta(x)$ is derived by replacing the term in square brackets in Eq. (5.7) with a Gaussian for small t . The summation over n is subsequently approximated by an integral,

$$\begin{aligned} \sum_{n=1}^{\infty} \beta\left(\frac{nh}{R_G}\right) &\approx \frac{1}{4\pi} \sum_{n=1}^{\infty} \int_0^{\infty} dt \cos\left(\frac{nh t}{R_G}\right) e^{-(t^2/3)} \\ &= \frac{\sqrt{3}}{8\sqrt{\pi}} \sum_{n=1}^{\infty} e^{-(3h^2 n^2/R_G^2)} \approx \frac{R_G}{8h}. \quad (6.14) \end{aligned}$$

This approximation for intermediate distances is shown as the solid curve in Fig. 6. For the full interaction potential in this region we thus have

$$\frac{U(h)}{k_B T} = \frac{\phi_b \xi_b^4}{4 d^2 N} \frac{1}{h} \quad (\xi_b \ll h \ll R_G). \quad (6.15)$$

The sign of this contribution is *positive* indicating that beyond a certain distance the interaction becomes *repulsive*. This distance is of the order of the bulk correlation length.

At large separations, $h \gg R_G$, the summation over n may be limited to the first term only, $\sum_n \beta(nh/R_G) \approx \beta(h/R_G)$. The asymptotic behavior of $\beta(x)$ was previously given in Eq. (5.9) and is shown as the solid curve in Fig. 6. We thus find for the interaction potential,

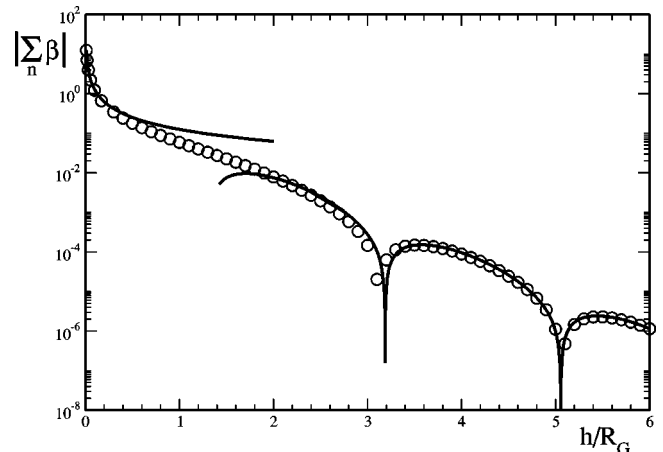


FIG. 6. Numerical solution for $|\sum_n \beta(nh/R_G)|$ as a function of h/R_G (circles); the solid curves are the approximate expressions for the asymptotic behavior in the regions $\xi_b \ll h \ll R_G$ and $h \gg R_G$, given by Eqs. (6.14) and (5.9), respectively.

$$\frac{U(h)}{k_B T} = -\frac{2\phi_b \xi_b^4}{d^2 N R_G} C_0 e^{-(A_0 h/R_G)} \sin\left(\frac{B_0 h}{R_G} + \alpha_0\right) \quad (h \gg R_G \gg \xi_b). \quad (6.16)$$

At these large separations, the interaction between two planar surfaces is oscillatory¹⁹ and falls off exponentially with h/R_G . This feature is preserved also when ε is not small,

$$U(h) \propto e^{-(Ah/R_G)} \sin\left(\frac{Bh}{R_G} + \alpha\right) \quad (h \gg R_G \approx \xi_b), \quad (6.17)$$

with the numerical value of the coefficients A and B , that determine the exponential decay and the oscillation period of the interaction potential, given previously in Fig. 4.

VII. DISCUSSION

In this article, we have investigated the surface tension, segment density profile, and interaction potential for polymer adsorbing (planar) surfaces. Analytical expressions for these quantities, valid for any polymer length, are derived in the limit of *weakly* adsorbing polymers. Particular attention is paid to the behavior of the segment density profile at large distances and the interaction potential between two polymer-adsorbing surfaces at large separations.

The relevant parameter connected to the polymer chain length is the square of the ratio of the bulk correlation length and the polymer's radius of gyration, $\varepsilon \equiv \xi_b^2/R_G^2 = 2/(v\phi_b N)$. When $\varepsilon \ll 1$, i.e., $R_G \gg \xi_b$, the contributions to the segment density profile and the interaction potential may be investigated in an expansion in ε . The three leading contributions dominate the polymer density profile in three different spatial regions: the zeroth order term, corresponding to the ground state dominance, dominates the density profile due to loops near the wall; the leading order correction of $\mathcal{O}(1/N)$ due to tails gives a description at an intermediate region of the order of the bulk correlation length; terms of $\mathcal{O}(1/N^{3/2})$, which dictate the density profile at the region of the order of the polymer coil size R_G .^{16,19} This last term is responsible for the (oscillatory) decay of the density profile and the interaction potential on the scale of the polymer's radius of gyration.

The picture that emerges from the expansion in ε is the following: the *polymer density profile* decays exponentially as z/ξ_b close to the solid surface, "overshoots" at a certain distance (typically, a few ξ_b), and then decays exponentially as z/R_G in an oscillatory way with a period determined by R_G . This overshoot in the segment density profile was previously obtained in analytical work and computer simulations^{23,31} and agrees quantitatively with our expression for the segment density profile in Eq. (5.4) (see Fig. 2). The oscillatory decay on the scale of R_G that follows the overshoot was previously observed²⁸ in numerical solutions of the Scheutjens and Fleer lattice model for polymers. The parameters that describe the exponential decay and the oscillation period of the polymer density profile determined from the numerical profiles²⁸ are in excellent agreement with our analytical results [Eq. (5.10)]. An interpretation of these oscillations in terms of a liquidlike ordering of the polymer

coils is tempting, but it should be kept in mind that the polymer coils are still highly entangled forming a transient network of mesh size ξ_b .

A similar picture emerges for the *interaction potential* between two polymer-adsorbing surfaces; at close separation, the interaction is *attractive* and decays exponentially as h/ξ_b . At a separation of typically a few ξ_b , the interaction becomes *repulsive* and then oscillates between an exponentially decreasing attractive/repulsive interaction on a scale determined by R_G . The repulsive interaction was previously obtained in the context of the two-order parameter model,¹⁸ whereas the presence of oscillations on the scale of R_G was previously noted by Semenov.¹⁹

We have assumed that deviations from bulk behavior are small—an assumption which holds for weak adsorption, but which also holds for strong adsorption at large distances. The description given for the distal behavior of the density profile and interaction potential is therefore also valid for *strong* polymer adsorption, up to a possible shift in the distance to the solid surface (see, e.g., Fig. 2). Furthermore, an important benefit from the expressions derived here, is that it is also possible to investigate the distal behavior of the segment density profile and the interaction potential when ε is *not* small. These results are especially relevant when the polymer chain length is not so large or, even when N is large, when the bulk polymer concentration is low.

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¹P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).

²G. J. Fleer, M. A. Cohen-Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Elsevier, London, 1993).

³E. Eisenriegler, *Polymers Near Interfaces* (World Scientific, Singapore, 1993).

⁴T. Odijk, *Macromolecules* **29**, 1842 (1996); *Physica A* **278**, 347 (2000).

⁵A. Johner, J.-F. Joanny, S. Diez-Orrite, and J. Bonet-Avalos, *Europhys. Lett.* **56**, 549 (2001).

⁶R. Tuinier, G. A. Vliegenthart, and H. N. W. Lekkerkerker, *J. Chem. Phys.* **113**, 10768 (2000).

⁷A. Hanke, E. Eisenriegler, and S. Dietrich, *Phys. Rev. E* **59**, 6853 (1999).

⁸R. Maassen, E. Eisenriegler, and A. Bringer, *J. Chem. Phys.* **115**, 5292 (2001).

⁹A. A. Louis, P. G. Bolhuis, E. J. Meijer, and J. P. Hansen, *J. Chem. Phys.* **117**, 1893 (2002).

¹⁰S. T. Milner, T. A. Witten, and M. E. Cates, *Macromolecules* **21**, 2610 (1988); A. N. Semenov, *Sov. Phys. JETP* **61**, 733 (1985).

¹¹D. T. Wu, G. H. Fredrickson, J.-P. Carton, A. Ajdari, and L. Leibler, *J. Polym. Sci., Part B: Polym. Phys.* **33**, 2373 (1995).

¹²P. G. de Gennes, *Macromolecules* **14**, 1637 (1981); **15**, 492 (1982).

¹³J. M. H. M. Scheutjens and G. J. Fleer, *J. Phys. Chem.* **83**, 1619 (1979); **84**, 178 (1980); *Macromolecules* **18**, 1882 (1985).

¹⁴S. F. Edwards, *Proc. Phys. Soc.* **85**, 613 (1965); **88**, 265 (1966).

¹⁵I. M. Lifshitz, *Sov. Phys. JETP* **28**, 1280 (1969); I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khoklov, *Rev. Mod. Phys.* **50**, 683 (1978).

¹⁶A. N. Semenov, J. Bonet-Avalos, A. Johner, and J.-F. Joanny, *Macromolecules* **29**, 2179 (1996).

- ¹⁷A. Johner, J. Bonet-Avalos, C. C. van der Linden, A. N. Semenov, and J.-F. Joanny, *Macromolecules* **29**, 3629 (1996).
- ¹⁸J. Bonet-Avalos, J.-F. Joanny, A. Johner, and A. N. Semenov, *Europhys. Lett.* **35**, 97 (1996); A. N. Semenov, J.-F. Joanny, A. Johner, and J. Bonet-Avalos, *Macromolecules* **30**, 1479 (1997).
- ¹⁹A. N. Semenov, *J. Phys. II* **6**, 1759 (1996).
- ²⁰A. N. Semenov, J.-F. Joanny, and A. Johner, "Polymer adsorption: Mean-field theory and ground state dominance approximation," in *Theoretical and Mathematical Models in Polymer Research*, edited by A. Grosberg (Academic, San Diego, 1998).
- ²¹P. F. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
- ²²K. Binder, *Monte Carlo and Molecular Simulations in Polymer Sciences* (Oxford University Press, Oxford, 1995).
- ²³J. de Joannis, C.-W. Park, J. Thomatos, and I. A. Bitsanis, *Langmuir* **17**, 69 (2001).
- ²⁴J. de Joannis, R. K. Ballamudi, C.-W. Park, J. Thomatos, and I. A. Bitsanis, *Europhys. Lett.* **56**, 200 (2001).
- ²⁵J. M. H. M. Scheutjens and G. J. Fleer, in *The Effect of Polymers on Dispersion Properties*, edited by Th. F. Tadros (Academic, New York, 1982).
- ²⁶A. N. Semenov and J.-F. Joanny, *Europhys. Lett.* **29**, 279 (1995).
- ²⁷K. I. Skau and E. M. Blokhuys, *Macromolecules* **36**, 4637 (2003).
- ²⁸J. van der Gucht, N. A. M. Besseling, J. van Male, and M. A. Cohen Stuart, *J. Chem. Phys.* **113**, 2886 (2000).
- ²⁹E. W. Weisstein, *CRC Concise Encyclopedia of Mathematics* (CRC, Boca Raton, 1999).
- ³⁰J.-F. Joanny, L. Leibler, and P. G. de Gennes, *J. Polym. Sci., Polym. Phys. Ed.* **17**, 1073 (1979).
- ³¹P. G. Bolhuis, A. A. Louis, J. P. Hansen, and E. J. Meijer, *J. Chem. Phys.* **114**, 4296 (2001).