Equilibrium Polymers at Interfaces: Analytical Self-Consistent-Field Theory

J. van der Gucht, N. A. M. Besseling,* and G. J. Fleer

Dutch Polymer Institute/Wageningen University, Laboratory of Physical Chemistry and Colloid Science, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

Received August 11, 2003; Revised Manuscript Received January 27, 2004

ABSTRACT: An analytical mean-field theory is constructed for equilibrium (or "living") polymers with excluded volume at a surface. Within a mean-field approximation, exact analytical expressions are obtained for the monomer concentration profile at the surface and for the excess amount, both for adsorbing and nonadsorbing surfaces, and for the whole concentration range from the dilute to the marginal regime. A ground-state approximation is not needed. For nonadsorbing polymers there is a depletion layer next to the surface with a thickness that passes through a maximum as a function of the monomer concentration. If the equilibrium polymers adsorb on the surface, their behavior is qualitatively different from that of monodisperse chains. For weak adsorption, the excess amount increases gradually as the adsorption energy increases. At a certain finite value of the adsorption energy (which depends on the average length of the chains in the bulk), the excess amount starts to increases very rapidly by orders of magnitude. For chains without excluded volume the excess amount diverges at this point, whereas for real chains it remains finite. Adsorption isotherms of equilibrium polymers show a similar behavior: a gradual increase at low concentrations, then a very steep increase at some finite concentration, and a plateau at higher concentrations.

1. Introduction

The behavior of polymer chains at interfaces is a topic of considerable interest, both from a theoretical and an experimental point of view.[1,2] A surface affects a polymer coil in two ways: (i) it reduces the conformational entropy, and (ii) it may have an energetic interaction with the polymer segments. If this energetic interaction is too weak to compensate the entropy loss, the polymers avoid the region close to the surface. This region of lower polymer concentration is called the depletion layer. On the other hand, if the energetic gain is larger than the entropy loss, the chains adsorb on the surface.

Several theoretical models have been proposed to describe polymers near a surface. Scheutjens and Fleer[1,3,4] developed a self-consistent-field lattice theory, which proved to be successful in describing polymer adsorption and depletion. Within a mean-field approximation, this model gives exact results for the concentration profile and the excess amount of polymer near the surface. The model of Scheutjens and Fleer relies on numerical calculations. Most analytical mean-field calculations have been performed using continuum models. Edwards[5] used the analogy between the conformation of a polymer chain and the path of a diffusing particle to describe the conformational statistics of a polymer chain by a diffusion-like equation. For ideal chains without excluded-volume interactions, Edwards' equation can be solved exactly to yield an analytical expression for the concentration profile of segments near an adsorbing or a nonadsorbing surface.[2,6−8] The ideal chain approximation is valid for very dilute solutions of polymers at the theta temperature near a nonadsorbing or a weakly adsorbing surface. At higher concentrations (or for strong adsorption) excluded-volume interactions cannot be neglected. Only approximate solutions have been obtained for this case, mainly within the so-called ground-state dominance approximation.[9,10] For depletion or weak adsorption from marginal solutions, this approximation gives rather good agreement with exact numerical mean-field calculations.[11] For strong adsorption, however, the agreement is not as good, because the ground-state approximation neglects tails in the adsorbed layer. To account for the tails, Semenov et al.[10] presented a mean-field theory that goes beyond ground-state dominance. Their approach was in reasonable agreement with numerical mean-field calculations.[11,12]

The theoretical description of polymers at surfaces has focused mainly on monodisperse polymers. Polydisperse chains have received far less attention.[13−17] In this paper, we consider a special class of polymers, in which the bonds between monomers are not covalent, but based on reversible interactions. Such chains are called equilibrium polymers (or "living polymers" or "supramolecular polymers"). Examples of equilibrium polymers are wormlike micelles[18] and supramolecular polymers based on hydrogen bonding.[19−24] The difference with classical polymers is that the bonds between the segments can break and recombine on experimental time scales. As a result, the chain length distribution in such systems is not fixed but is determined by thermodynamic equilibrium and responds to variable conditions. Within a mean-field approximation, the equilibrium chain length distribution in a homogeneous system of equilibrium polymers is exponential:[18,25]

$$\rho_0(N) = \frac{\rho_0}{\langle N_0\rangle^2}\exp\left(-\frac{N}{\langle N_0\rangle}\right) \qquad (1)$$

where $\rho_0(N)$ is the number of chains of length N per unit volume, ρ_0 is the total concentration of segments, and $\langle N_0\rangle$ is the number-averaged chain length. The chain length N is expressed in terms of the number of segments. For equilibrium polymers, $\langle N_0\rangle$ is not fixed

---

* Corresponding author. E-mail: klaas.besseling@wur.nl.

10.1021/ma0351773 CCC: $27.50

but it depends on the segment concentration ρ_0 and on the strength of the bonds between the monomers E (often called the scission energy or the end-cap energy):

$$\langle N_0 \rangle = \sqrt{\rho_0 b^3}\exp\left(\frac{E}{2kT}\right) \tag{2}$$

Here, b^3 is the volume of a segment and $\rho_0 b^3$ is a dimensionless concentration.

Relatively little is known about the behavior of equilibrium polymers near surfaces. Most attention has been given to the case of nonadsorbing chains. Schmitt et al.[26] presented an analytical model for a solution of ideal equilibrium polymer chains confined between two repulsive (nonadsorbing) walls. Excluded-volume interactions were not accounted for in this approach. Analytical expressions were obtained for the average monomer concentration in the gap, the average length of the chains, and the interaction between the surfaces. Rouault and Milchev[27] used Monte Carlo simulations to calculate the average chain length of concentrated equilibrium polymers confined between two surfaces. In a recent paper, we used a numerical self-consistent-field lattice theory to describe equilibrium polymers near a nonadsorbing surface.[28] Concentration profiles were calculated and the thickness of the depletion layer was investigated as a function of the polymer concentration and the strength of the bonds between the monomers. In dilute solutions, the depletion layer thickness is proportional to the average radius of gyration of the chains, which increases with increasing monomer concentration as a result of the growth of the chains (see eq 2). Above the overlap concentration, the depletion layer thickness is proportional to the correlation length of the solution ξ, which decreases with increasing concentration as $\xi \sim \rho_0^{-1/2}$ within the mean-field approximation (so-called marginal regime).[1] At intermediate concentration, the depletion layer thickness passes through a maximum.

Adsorbing equilibrium polymers have received less attention.[29,30] In a recent paper,[31] we considered ideal equilibrium polymers (without excluded volume) confined between two surfaces with arbitrary interaction between the polymer segments and the surface. We were able to obtain exact analytical expressions for the concentration profile, the average length of the chains, and the disjoining pressure on the surfaces. For nonadsorbing surfaces, our results were the same as those of Schmitt et al.[26] For adsorbing equilibrium polymers, we found that the behavior is qualitatively different from that of monodisperse chains. With increasing adsorption energy of the polymer segments, the adsorbed amount diverges continuously at a certain value of the adsorption energy which depends on the average chain length (a second-order phase transition). Obviously, the ideal chain description is not valid in this regime, because excluded-volume interactions in the adsorbed layer will become very important.

In this paper, we construct an analytical mean-field theory for equilibrium polymers near a surface, based on Edwards' diffusion equation. We consider both adsorbing and nonadsorbing equilibrium polymers over the whole concentration range from the dilute to the marginal regime. In section 2.1, we give a general description of the analytical self-consistent-field theory of polymers near a surface. In section 2.2, we apply this to equilibrium polymers. We will show that, unlike for monodisperse homopolymers, for equilibrium polymers it is not necessary to use the ground-state approximation. Exact analytical expressions can be obtained for the concentration profile and the excess amount of polymer near the surface. In section 3 we discuss the results of our model for nonadsorbing chains. Adsorbing equilibrium polymers will be considered in section 4.

2. Self-Consistent-Field Theory

2.1. General Theory. In this section, we give a brief description of the general self-consistent-field theory of polydisperse polymers near a surface. In section 2.2, we apply this theory to a solution of equilibrium polymers with an exponential chain length distribution (eq 1).

We consider a polydisperse solution of polymer chains in contact with a solid, impenetrable surface. There is full equilibrium between the surface region and the bulk solution. A short ranged adsorption potential $u^a(z)$ accounts for the interactions between the polymer segments and the surface. The interactions between polymer segments are treated in a mean-field approximation. Within this approximation, segment–segment interactions are replaced by an effective potential that depends on the local concentration of segments $\rho(z)$. We assume that the concentration of segments is not very high, so that binary interactions between segments dominate. The total potential of a polymer segment at a distance z from the surface with respect to that in the bulk is then:

$$\frac{u(z)}{kT} = \frac{u^a(z)}{kT} + v(\rho(z) - \rho_0) \tag{3}$$

Here the first term accounts for the interactions with the surface and the second term represents the segment–segment interactions, with v the excluded-volume parameter and ρ_0 the concentration of segments in the bulk (at $z \to \infty$). The excluded-volume parameter v can be related to the Flory–Huggins polymer–solvent interaction parameter χ:

$$v = b^3(1 - 2\chi) \tag{4}$$

For a good solvent ($\chi < 1/2$), v is a positive constant. In an athermal solvent ($\chi = 0$), there are only hard-core interactions between segments and v is equal to the volume of a segment b^3.

The probability of a conformation of a polymer chain in the potential field $u(z)$ can be quantified by the end-point distribution $G(z, N)$. This gives the statistical weight of a chain (or chain section) of N segments with one end fixed at a position z as compared to that of a chain of the same length in the bulk. The concentration of end segments belonging to chains of length N is proportional to this:

$$\rho_N^{\mathrm{e}}(z) = 2\rho_0(N)G(z, N) \tag{5}$$

where the factor $\rho_0(N)$ denotes the number concentration of chains of length N in the bulk. It is a normalization factor, ensuring that in the bulk, for $z \to \infty$ (where $G(z, N) = 1$), $\rho_N^{\mathrm{e}}(\infty) = 2\rho_0(N)$ (since every chain has two ends).

The statistical weight of a chain of length N with its nth monomer at position z is equal to $G(z, n)G(z, N - n)$, where the two factors correspond to the two walks from either end of the chain toward segment n at position z. We assume that the average length of the chains is large, so that the contributions of small chains are negligible, and n and N can be treated as continuous variables. The total contribution of chains of length N to the local segment concentration can then be found by integration over all segments n:

$$\rho_N(z) = \rho_0(N) \int_0^N G(z, n)G(z, N - n)\, \mathrm{d}n \qquad (6)$$

where the factor $\rho_0(N)$ ensures that $\rho_N(\infty) = \rho_0(N)N$. The total segment concentration can be found by integration over all N:

$$\rho(z) = \int_0^\infty \rho_N(z)\mathrm{d}N \qquad (7)$$

The distribution function $G(z, N)$, and thus the segment concentration $\rho(z)$, depends on the potential $u(z)$. The potential, in turn, depends on the segment concentration (eq 3). The solution must be self-consistent. As pointed out by Edwards, the end-point distribution $G(z, N)$ in a potential field $u(z)$ satisfies a diffusion-like equation[5]

$$\frac{\partial G(z, N)}{\partial N} = \frac{b^2}{6}\frac{\partial^2 G(z, N)}{\partial z^2} - \frac{u(z)}{kT}G(z, N) \qquad (8)$$

where we assume that the chain length is large ($N \gg 1$), so that N may be treated as a continuous variable. Here, the monomer size b specifies the average random-walk step length. The starting point of the chain may be anywhere (for $z \geq 0$), so that the initial condition is

$$G(z, 0) = 1 \qquad (9)$$

To proceed, we assume that the adsorption potential $u^a(z)$ is nonzero only in a very thin layer near the surface, of the order of the monomer size b. As shown by De Gennes,[32] the effect of such a localized adsorption potential can be taken into account by an effective boundary condition at the surface (at $z = 0$):

$$\left[\frac{1}{G}\frac{\partial G}{\partial z}\right]_{z=0} = -c \qquad (10)$$

The parameter c is the inverse of the so-called extrapolation length. It specifies the interactions of the segments with the surface. In the case of depletion (a nonadsorbing surface) $c < 0$, while in the case of adsorption $c > 0$. At the adsorption/depletion transition $c = 0$. The adsorption parameter c can be related to the adsorption energy of the polymer segments and the temperature.[12,33,35] Close to the adsorption threshold c varies as $c \simeq (\chi_s - \chi_{sc})$ where $\chi_s = -(u_p^a - u_0^a)/kT$ is the difference between the adsorption energy of a polymer segment u_p^a and that of a solvent molecule u_0^a, and χ_{sc} is the value of χ_s at the adsorption/depletion transition (where the adsorption energy is just sufficient to compensate the entropy loss of a chain). For $\chi_s < \chi_{sc}$ ($c < 0$) the polymers are depleted, whereas for $\chi_s > \chi_{sc}$ ($c > 0$) the polymers adsorb.

An exact solution of eq 8 with boundary conditions 9 and 10 has been obtained only for $u(z) = 0$, i.e., for very dilute polymer solutions where excluded-volume interactions are negligible.[2,6,7,34] For polymers with excluded-volume interactions, only approximate solutions have been obtained.[9,10] The end-point distribution is then expanded in a series of eigenfunctions: $G(z, N) = \sum_k \psi_k(z)e^{\epsilon_k N}$. Assuming that the eigenfunction ψ_0 with the largest eigenvalue dominates (ground-state approximation), approximate analytical expressions can be obtained for the end-point distribution $G(z, N) \approx \psi_0(z)e^{\epsilon_0 N}$. As follows from eq 6, within this ground-state approximation, all segments belonging to chains of the same length have the same probability distribution, irrespective of their position within the chain. As a result, it does not account for the tails of adsorbed polymers, which are important in the outer region of the adsorbed layer.[1,3,10−12] Although some progress has been made to go beyond the ground-state approximation,[10] exact analytical solutions of eq 8 with the mean-field potential 3 have not been obtained, so far.

In the next section we apply the self-consistent-field equations to a solution of equilibrium polymers in contact with a surface. We will show that for such polymers, we can obtain *exact* expressions for the concentration profile and the excess amount using the mean-field potential, eq 3. It is not necessary to assume ground-state dominance.

2.2. Equilibrium Polymers at a Surface. To describe equilibrium polymers at a surface, we need to substitute the chain length distribution given by eq 1 in eq 6. As a result of the exponential chain length distribution of equilibrium polymers, the integral in eq 7 can be rewritten as

$$\rho(z) = \frac{\rho_0}{\langle N_0\rangle^2}[\tilde{G}(z, s)]^2 = \rho_0[g(z, s)]^2 \qquad (11)$$

where $\tilde{G}(z, s)$ denotes the Laplace transform of $G(z, N)$ with respect to the variable N:

$$\tilde{G}(z, s) = \int_0^\infty G(z, N)\mathrm{e}^{-sN}\, \mathrm{d}N \qquad (12)$$

with the Laplace variable $s \equiv \langle N_0\rangle^{-1}$, where $\langle N_0\rangle$ is the number-averaged chain length in the homogeneous bulk solution. In eq 11, we have used the convolution theorem for Laplace transforms. In the second equality, we have defined the function $g(z, s) \equiv \tilde{G}(z, s)/\langle N_0\rangle$. Similarly, for the total concentration of chain ends at position z, we can write (using eqs 1, 5, and 12):

$$\rho^{\mathrm{e}}(z) = \int_0^\infty \rho_N^{\mathrm{e}}(z)\mathrm{d}N = \frac{2\rho_0}{\langle N_0\rangle}g(z, s) \qquad (13)$$

We see that the concentration profile $\rho(z)$ can be computed directly from the Laplace transform of the end-point distribution. Substitution of eq 11 in eq 3 gives an equation for the potential $u(z)$ in terms of $g(z, s)$. The differential equation for $g(z, s)$ is obtained by performing a Laplace transform on the diffusion eq 8, and substituting $\tilde{G} = \langle N_0\rangle\, g = g/s$. This gives, after some rearrangement

$$R_0^{\,2}\frac{\mathrm{d}^2 g(z, s)}{\mathrm{d}z^2} = x[g(z, s)]^3 + (1 - x)g(z, s) - 1 \qquad (14)$$

with

$$R_0 = b\sqrt{\frac{\langle N_0\rangle}{6}} \quad \text{and} \quad x = v\rho_0\langle N_0\rangle \qquad (15)$$

Here R_0 is the unperturbed radius of gyration of a chain with a length equal to the average length in the bulk $\langle N_0\rangle$. (Hereafter, we will loosely call R_0 the “average radius of gyration".) The dimensionless parameter x depends on the solvency conditions, and on the concentration and the average chain length in the bulk. The physical meaning of the parameter x can be understood by considering the expansion of the Flory–Huggins (or mean-field) expression for the osmotic pressure, which is fully in line with the present treatment:[1,25]

$$\frac{\Pi}{kT} \approx \frac{\rho_0}{\langle N_0 \rangle} + \frac{1}{2} v {\rho_0}^2 + ... \tag{16}$$

In dilute solutions the first term is dominant (the ideal regime), while above the overlap concentration (in the marginal regime) the second term dominates. The crossover from the ideal regime to the marginal regime occurs when $\rho_0/\langle N_0\rangle \approx v{\rho_0}^2$ or when $x \approx 1$. Hence, the parameter x indicates the concentration regime: in the dilute regime $x < 1$, while in the marginal regime $x > 1$.

After multiplication by $\mathrm{d}g/\mathrm{d}z$ and integration, eq 14 becomes

$${R_0}^2\left(\frac{\mathrm{d}g}{\mathrm{d}z}\right)^2 = \frac{1}{2}xg^4 + (1-x)g^2 - 2g + 1 + \frac{x}{2} \tag{17}$$

where the integration constant $1 + x/2$ is found using $g = 1$ (see eq 11) and $\mathrm{d}g/\mathrm{d}z = 0$ in the bulk. This differential equation can be solved by integration, giving z as a function of g. Inversion then yields $g(z, s)$:

$$g(z, s) = 1 + \frac{2 + 4x}{\mathrm{sign}(c)\sqrt{2x}\sinh\left(\frac{z+p}{d}\right) - 2x} \tag{18}$$

where $\mathrm{sign}(c) = 1$ for adsorbing chains ($c \geq 0$), and $\mathrm{sign}(c) = -1$ for nonadsorbing chains ($c < 0$). The parameter p is an integration constant (with the dimension of length), and the length scale d is defined as

$$d = \frac{R_0}{\sqrt{1+2x}} \tag{19}$$

It depends on the average dimension of the chains and on the bulk concentration, and can be approximated as

$$d \approx \begin{cases} R_0 & \text{for } x \ll 1 \\ \xi = \frac{1}{2}b(3v\rho_0)^{-1/2} & \text{for } x \gg 1 \end{cases} \tag{20}$$

At low concentrations the characteristic length scale d is equal to the average radius of gyration R_0, which increases with the monomer concentration for equilibrium polymers (see eqs 15 and 2). At high concentrations, d corresponds to the bulk correlation length ξ which is equal to $b/(2\sqrt{3v\rho_0})$ in a mean-field approximation (in the marginal regime),[1] and decreases with increasing concentration. It follows that d must pass through a maximum at intermediate concentration (see also section 3). Figure 1 contains some typical plots of d vs ρ_0 (dashed curves).

The integration constant p in eq 18 is determined by the boundary condition at the surface, eq 10, which becomes in terms of $g(z, s)$:

$$\left[\frac{1}{g}\frac{\mathrm{d}g}{\mathrm{d}z}\right]_{z=0} = -c \tag{21}$$

Substitution of eq 18 gives a relation between p, x, c, and d.

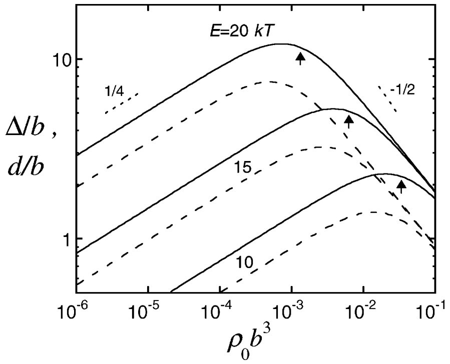

Figure 1. Depletion layer thickness Δ and characteristic length d as a function of concentration for several values of the bonding energy E, for $\chi = 0$. The solid curves refer to Δ, the dashed curves to d. Arrows indicate the concentration where $x = 1$ (i.e., the crossover from the dilute to the marginal regime).

$$C = \frac{\sqrt{2x}(1+2x)\cosh\left(\frac{p}{d}\right)}{\left[\mathrm{sign}(c)\sinh\left(\frac{p}{d}\right) - \sqrt{2x}\right]\left[x\sinh\left(\frac{p}{d}\right) + \mathrm{sign}(c)\sqrt{2x}(1+x)\right]} \tag{22}$$

where we have introduced the dimensionless adsorption parameter

$$C = cd = \frac{cR_0}{\sqrt{1+2x}} \tag{23}$$

Here, C is defined as the ratio between the length scale d given by eq 19 and the extrapolation length $1/c$. (Note that in ref 31, where we considered ideal chains with $x = 0$, we used $C = cR_0$. Equation 23 is a generalization of this for the whole concentration regime.) Equation 22 can be solved for p/d as a function of C and x, but this expression is too long to display here. For several limiting cases, limiting expressions can be obtained. These will be discussed in the following sections.

The concentration profile $\rho(z)$ is obtained from $g(z, s)$ after substitution of eq 18 in eq 11. The excess amount of segments per unit surface area can be obtained as

$$\theta^{\mathrm{ex}} = \int_0^\infty (\rho(z) - \rho_0)\,\mathrm{d}z = \frac{2\rho_0 d[\mathrm{e}^{-p/d} + \mathrm{sign}(c)\sqrt{2x}][1+2x]}{x[\sinh(p/d) - \mathrm{sign}(c)\sqrt{2x}]} \tag{24}$$

The dimensionless normalized excess amount $\theta^{\mathrm{ex}}/(\rho_0 d)$ is a function of two dimensionless parameters, x and p/d (or C).

In this section we have derived expressions for the concentration profile of equilibrium polymers near a surface and for the excess amount. These expressions are exact provided that the mean-field potential is given by eq 3. They are valid for both nonadsorbing and adsorbing polymers and for both the dilute and marginal concentration regime. In section 3 we will discuss in more detail the case of nonadsorbing equilibrium polymers ($c < 0$). In section 4, we consider adsorbing

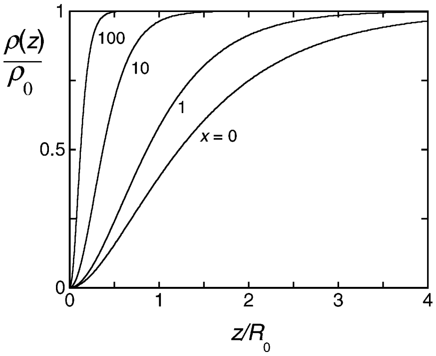

Figure 2. Segment concentration profiles for nonadsorbing equilibrium polymers ($c \rightarrow -\infty$) for several values of x.

equilibrium polymers. Where possible, we will derive simplified equations for $\rho(z)$ and θ^{ex}.

3. Nonadsorbing Equilibrium Polymers

In this section, we consider nonadsorbing equilibrium polymers for which the adsorption energy of a polymer segment is insufficient to compensate the entropy loss near the surface ($c < 0$). The partition function $g(z, s)$ is then given by eq 18 with $\mathrm{sign}(c) = -1$. We take $c \rightarrow -\infty$ here, which corresponds to the boundary condition $g(0, s) = 0$ on the surface (a hard wall). For c less negative, the results are qualitatively the same.

For $c \rightarrow -\infty$, eq 22 gives the following expression for the parameter p in eq 18:

$$p = d\ \mathrm{arcsinh}\left(\frac{2 + 2x}{\sqrt{2x}}\right) \tag{25}$$

which can be substituted in eq 18 to yield an exact explicit expression for $g(z, s)$. Substitution in eq 11 then gives the concentration profile of segments. The segment concentration profile for nonadsorbing equilibrium polymers is shown in Figure 2 as a function of the reduced distance to the surface z/R_0 for several values of x (corresponding to several bulk concentrations of monomers; note that R_0 increases with the bulk concentration ρ_0).

For very dilute solutions ($x \ll 1$) the polymer concentration $\rho(z)$, given by eqs 11, 18, and 25 simplifies to

$$\rho(z) = \rho_0(1 - \mathrm{e}^{-z/R_0})^2 \tag{26}$$

which is exactly the result for ideal chains without excluded-volume interactions.[31] The thickness of the depletion layer is of order R_0. As x increases, the depletion layer becomes thinner (see Figure 2). For $x \gg 1$ (in the marginal regime), eqs 11, 18, and 25 can be simplified to

$$\rho(z) = \rho_0 \tanh^2\left(\frac{z}{2\xi}\right) \tag{27}$$

where $\xi = b/(2\sqrt{3v\rho_0})$ is the bulk correlation length in the marginal regime.[1] For large distances ($z \gg \xi$), the concentration decays exponentially toward the bulk value with a decay length $d \approx \xi$: $\rho(z) \approx \rho_0(1-4\mathrm{e}^{-z/\xi})$. Equation 27 is exactly the same result as found using a ground-state approximation.[9,34] Hence, this solution, which is approximate for monodisperse conventional polymers, is exact for equilibrium polymers if the mean molecular field is given by eq 3. The profile depends only on the polymer concentration and not on the average chain length. This is a well-known result for polymer solutions above the overlap concentration. We note that for monodisperse polymers, using approaches that avoid the ground-state approximation, a nonmonotonic concentration profile has been found for concentrations above the overlap concentration.[10,36] For equilibrium polymers, we do not find such a nonmonotonic behavior. It can be seen from eq 18 that the profile is monotonic for all C and x.

A measure Δ for the thickness of the depletion layer can be obtained from the excess amount as $\Delta = -\theta^{\mathrm{ex}}/\rho_0$. Substitution of eqs 25 and 19 in eq 24 gives an exact expression for Δ as a function of x, valid for the whole concentration range:

$$\Delta = \frac{R_0}{x}(2\sqrt{1 + 2x} - \sqrt{2(x + 2)}) \tag{28}$$

After substitution of eqs 15 and 2, we obtain Δ as a function of ρ_0 and E. The result is shown in Figure 1 (the full curves). Two regimes can be recognized in this Figure. At low concentrations Δ is determined by the average size R_0 of the chains, which increases with increasing concentration ρ_0 and increasing scission energy E (see eq 2). At high concentrations, above the overlap concentration, Δ is determined by the bulk correlation length ξ, which decreases with increasing concentration and is independent of E. At intermediate concentration, Δ passes through a maximum.

The asymptotic behaviors follow by expansion of eq 28:

$$\Delta \approx \begin{cases} \frac{3}{2}R_0 \sim {\rho_0}^{1/4} \exp\left(\frac{E}{4kT}\right) & \text{for } x \ll 1 \\ 2\xi \sim {\rho_0}^{-1/2} & \text{for } x \gg 1 \end{cases} \tag{29}$$

Note that the depletion layer thickness in dilute solutions of equilibrium polymers ($\Delta = {}^{3}/_{2}R_0$) is slightly larger than that of ideal monodisperse chains[2,7,34] ($\Delta = 2R/\sqrt{\pi}$). The maximum of the depletion layer thickness occurs around $x \approx 1$, which corresponds to a segment concentration $\rho_0^* \simeq b^{-3} \exp(-E/3kT)$.

An alternative definition of the depletion layer thickness can be obtained from the concentration profile. It follows from eqs 11 and 18 that at large distances ($z \gg d$) the concentration decays exponentially toward the bulk value: $|\rho(z) - \rho_0| \sim \mathrm{e}^{-z/d}$. The decay length d provides an alternative measure for the thickness of the depletion layer. It is given by eq 19 and is also plotted in Figure 1 (the dashed curves). It can be seen that d follows qualitatively the same trend as Δ. The same scaling with concentration is found in the dilute and marginal regime (compare eqs 20 and 29).

The results of Figure 1 are in excellent agreement with recent results obtained using a numerical self-consistent-field lattice model.[28] Only at very high concentrations do the numerical results show a faster decrease of the depletion layer thickness with concentration than predicted by eq 29. This is due to higher-order interactions between segments that are neglected in eq 3. Also for very small ρ_0 and E (where the average length of the chains is only a few segments) the present model deviates from the numerical results. The reason is obvious: the Edwards equation is not valid for small $\langle N_0 \rangle$, and also eq 2 does not apply. A more detailed

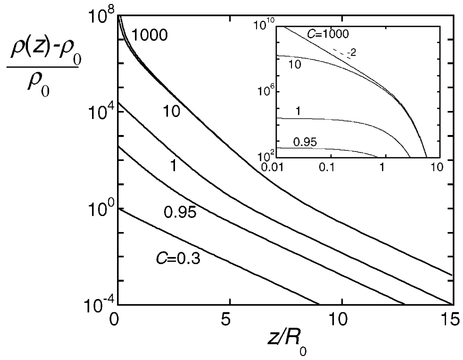

Figure 3. Excess segment concentration profiles for equilibrium polymers adsorbing from dilute solution ($x = 10^{-6}$) for several values of C. The main figure is semilogarithmic, the inset shows the profiles on a double-logarithmic scale.

comparison with the numerical model of ref 28 is made in the appendix.

4. Adsorbing Equilibrium Polymers

In this section, we consider adsorbing equilibrium polymers for which the gain in adsorption energy is larger than the entropy loss near the surface ($\chi_s > \chi_{sc}$, $c > 0$). The partition function $g(z, s)$ for this case is given by eq 18 with sign(c) = 1. We will discuss concentration profiles for adsorption from dilute and marginal solutions, and study the excess amount of segments at the surface as a function of the adsorption strength and the concentration.

Adsorption from Dilute Solution: Concentration Profiles. For $x \ll 1$, the concentration profile (eqs 11 and 18) can be written as

$$\rho(z) = \rho_0\left[1 + \frac{2}{\sqrt{2x}\,\sinh\left(\frac{z+p}{d}\right)}\right]^2 \tag{30}$$

with $d \approx R_0$ and with the parameter p given by eq 22. In Figure 3, excess concentration profiles ($\rho(z) - \rho_0$), as given by eq 30, are shown for $x = 10^{-6}$ and for several values of the adsorption strength $C \approx cR_0$. Obviously, the concentration in the adsorbed layer increases strongly with increasing adsorption strength. Also the shape of the curves depends on the value of C.

The characteristic features observed in Figure 3 can be deduced by examining approximate expressions for the various regimes. These can be obtained by expanding eq 22 in terms of x. This yields the following limiting expressions for p:

$$p \approx \begin{cases} d\ln\left(\dfrac{4-4C}{C\sqrt{2x}}\right) & \text{for } (1-C) \gg \sqrt{2x} \\ d/C = 1/c & \text{for } C \gg 1 \end{cases} \tag{31}$$

For weak adsorption ($(1 - C) \gg \sqrt{2x}$), eqs 31 and 30 yield the following expression for the concentration profile:

$$\rho(z) = \rho_0\left(1 + \frac{Ce^{-z/d}}{1-C}\right)^2 \tag{32}$$

with $d \approx R_0$ and $C \approx cR_0$. This is exactly the same result as obtained for ideal chains without excluded-volume interactions ($v = 0$).[31] For $x = 10^{-6}$, eq 32 describes the profile very well for values of $C < 0.99$. According to eq 32, the excess concentration ($\rho(z) - \rho_0$) is a sum of two exponentials, with decay lengths R_0 and $R_0/2$. For $|C| \ll 1$, the term with the longest decay length dominates, and eq 32 can be further simplified to $\rho(z) \approx \rho_0(1 + 2Ce^{-z/d})$: the segment concentration decays exponentially toward the bulk value with a decay length $d \approx R_0$. This can be seen in Figure 3 for $C = 0.3$.

For higher adsorption strength, both exponential terms are important. The shortest decay length $R_0/2$ dominates at short distance, and the longest decay length R_0 dominates at large distance. In Figure 3, this can be seen for $C = 0.95$.

For strong adsorption ($C \gg 1$), the concentration profile becomes more complicated (see Figure 3) and is given by the full expression 30 with $p \approx 1/c$. The profile can be subdivided into four regions. For $z \leq p$ the concentration profile depends strongly on the adsorption strength C. This region is called the proximal region,[12,37] and p could be called the proximal length. The concentration in the proximal region is of order $\rho(0) \approx 2\rho_0 d^2/(xp^2) \approx (cb)^2/(3v)$. Note that for $(cb)^2 > 3(1 - 2\chi)$ the model predicts a volume fraction of train segments $\rho(0)b^3$ larger than unity. For this case, the region close to the surface is not well described by our model and higher-order interactions between segments should be taken into account. For $z \gg p$, the profile does not depend on C (see also Figure 3). In the so-called central region[37] ($p \ll z \ll d$) the profile follows the mean-field power-law: $\rho(z) \approx 2\rho_0 d^2/(xz^2) \approx b^2/(3vz^2)$ (see inset in Figure 3). For $d \ll z \ll - d \ln x$, the profile decays exponentially with a decay length $d/2$ which is determined by the average radius of gyration: $\rho(z) \approx (8\rho_0/x)e^{-2z/d} \approx (8/v\langle N_0\rangle)e^{-2z/R_0}$. Finally, for very large distances ($z \gg - d \ln x$) the concentration approaches the bulk value as $\rho(z) \approx \rho_0[1 + (8/\sqrt{2x})e^{-z/R_0}]$. Of course, these four regions can only be observed clearly if the length scales are well separated. This is the case for large c, low ρ_0 and large $\langle N_0\rangle$ (i.e., large E).

The inner three regions of the profile (where $z \ll - d \ln x$ and $\rho(z) \gg \rho_0$), are also found if we solve eq 8 using a ground-state approximation.[38] As tails are neglected in the ground-state approximation, this means that in the inner part of the profile only loops are important. Hence, the exponential part of the profile with a decay length $d/2$ is due to the loops. Deviations from the ground-state approximation occur only for $z > - d \ln x$ where the concentration is almost equal to the bulk value. In this region, tails become important. The decay length associated with the tails is equal to d.[1,10,12] This is also the decay length of the profile for the chain-ends (eqs 13 and 18): $[\rho^e(z) - 2\rho_0/\langle N_0\rangle] \sim \exp(- z/d)$ for $z \gg d$.

It is instructive to compare the features of the profile to those observed for adsorption of monodisperse homopolymers. The proximal length $p \approx 1/c$ is the same for equilibrium polymers as for monodisperse polymers. The length scale d (the distal length), however, is larger for equilibrium polymers than for monodisperse chains of length equal to the average length $\langle N_0\rangle$ in the bulk. For monodisperse polymers, the distal length equals $R/\sqrt{\ln(1/\rho_0 b^3)}$,[10,11,12] which is lower than the radius of gyration R by a factor of 3−5 for typical small values of $\rho_0 b^3$. For equilibrium polymers, on the other hand, the distal length (eq 19) is approximately equal to the average radius of gyration R_0. As a result, the crossover from the central to the distal regime occurs at a larger distance from the surface than for homopolymers. Physically, this may be understood as follows: In the central regime the concentration is locally in the marginal concentration regime.[37] The crossover to the distal regime occurs when the local concentration drops below the overlap threshold. This overlap concentration is lower for longer chains. For equilibrium polymers (and other polydisperse chains), long chains are preferentially adsorbed. As a result the average length is higher in the adsorbed layer and the corresponding overlap concentration is lower. The crossover to the distal regime therefore occurs for lower $\rho(z)$, i.e., at a larger distance from the surface.

The ground-state approximation for homopolymers predicts a distal regime where the profile decays exponentially with a decay length $d/2$, similar to the first exponential regime observed for equilibrium polymers. This decay length is due to the loops. A more detailed analysis, however, shows that tails cannot be neglected in the distal region.[1,3,10,12] For monodisperse chains, the crossover from the loops-dominated regime to the tails-dominated regime occurs at a distance z^* from the surface which is comparable to d. As a result, tails dominate for $z \gg d$, so that the exponential decay with length scale $d/2$ (due to the loops) cannot be observed in the overall profile, and the only visible decay length is that of the tails, d. This is also seen in numerical calculations using the Scheutjens–Fleer theory.[3,11] For equilibrium polymers, on the other hand, the exponential decay for the loops (decay length $d/2$) and that for the tails (decay length d) can both be seen in the profile (see Figure 3). Apparently, the crossover distance z^* from the loops-dominated to the tails-dominated regime is much larger than d in this case. The reason z^* is so much larger for equilibrium polymers than for homopolymers is that tails seem to be much less important for equilibrium polymers. As discussed above, tails only start to play a role in the region where the concentration is almost equal to the bulk value.

The reason tails are not very important for equilibrium polymers is that the average length of the adsorbed chains is much higher than that of chains in the bulk. In the regime of strong adsorption (where $\theta^{ex} \approx \Gamma$ with Γ the adsorbed amount), the average length of adsorbed chains can be calculated as

$$\langle N^a \rangle = \frac{\theta^{ex}}{\frac{1}{2}\int_0^\infty [\rho^e(z) - \rho_0/\langle N_0 \rangle]\,dz} \approx \frac{2C}{\sqrt{2x}\,\ln(2C)}\langle N_0 \rangle \quad \text{for } x \ll 1,\ C \gg 1 \tag{33}$$

Clearly $\langle N^a \rangle \gg \langle N_0 \rangle$ (for example for $x = 10^{-6}$ and $C = 10$, $\langle N^a \rangle \approx 10^5 \langle N_0 \rangle$). For such long chains, tails are not very important. Another way to look at it is that for equilibrium polymers, the ends of two tails can combine and form a loop. For high values of the binding energy, this is favorable, so that tails are suppressed in this case.

Adsorption from Marginal Solution: Concentration Profiles. For adsorption from marginal solutions ($x \gg 1$), the parameter p/d is large for all C. Hence, we may replace $\sinh[(z + p)/d]$ in eq 18 with $(^1/_2) \exp[(z + p)/d]$. The parameter d is now equal to ξ (see eq 20). Using this, we find from eq 11 in combination with 18 for the concentration profile for adsorption from marginal solutions

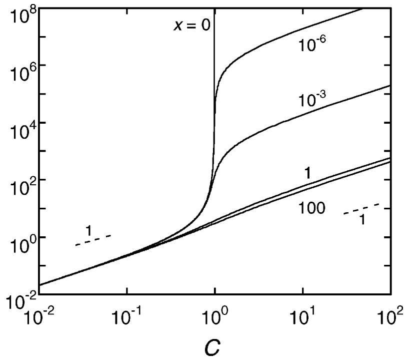

Figure 4. Excess amount of segments at the surface as a function of the adsorption strength C for several values of x.

$$\rho(z) \approx \rho_0 \coth^2\left(\frac{z + a}{2\xi}\right) \tag{34}$$

where $a = p - 2\xi\ln(2\sqrt{2x})$ gives a new definition for the proximal length in the marginal regime. The following relation can be derived for a (using eq 22):

$$a \approx \xi \ln\left[\frac{1 + \sqrt{1 + C^2}}{C}\right] \tag{35}$$

Equation 34 is exactly the same result as found using a ground-state approximation.[9,10] The profile does not depend on the chain length. The characteristics of the profile are easily seen from eq 34. For weak adsorption ($c \ll \xi^{-1}$), eq 35 reduces to $a \approx \xi\ln(2/C)$. Equation 34 then gives $\rho(z) \approx \rho_0(1 + 2Ce^{-z/\xi})$; i.e., the concentration decays exponentially toward the bulk value with a decay length ξ. For $c \gg \xi^{-1}$ (strong adsorption), $a \approx 1/c$, and the profile can be divided into three regions. For $z \ll \xi$, the profile is the same as for adsorption from dilute solution. In the proximal region (for $z < a$), the concentration is on the order of $\rho(0) \approx \rho_0 C^2 = (cb)^2/(3v)$ and in the central region (for $a \ll z \ll \xi$), the profile decays as a power law: $\rho(z) \approx \rho_0(\xi/z)^2 = b^3/(3vz^2)$. At large distances $z \gg \xi$, $\rho(z)$ approaches the bulk concentration exponentially: $\rho(z)/\rho_0 \approx 1 + 4e^{-2z/\xi}$.

Semenov et al.[10] predicted that for monodisperse polymers corrections to the ground-state approximation would lead to a nonmonotonic concentration profile in the marginal regime (as for nonadsorbing chains). We find here that for equilibrium polymers, the profile is monotonic for all C and x.

Surface Excess. The normalized excess amount of segments at the surface $\theta^{ex}/(\rho_0 d)$ is shown in Figure 4 as a function of the dimensionless adsorption strength C for several values of x. Two regimes can be observed in this figure. For weak adsorption ($|C| \ll 1$), the curves for different x fall on one single curve. Hence, the normalized excess amount $\theta^{ex}/(\rho_0 d)$ is a universal function of C in this regime. As C approaches unity the curves start to differ and in the strong adsorption regime the normalized excess amount depends strongly on x. Below, we will discuss these two regimes in detail.

Approximate expressions for θ^{ex} for weak adsorption ($0 < C \ll 1$) and for strong adsorption ($C \gg 1$) can be obtained by expanding eq 22. This yields

$$\frac{\theta^{ex}}{\rho_0 d} \approx \begin{cases} 2C & \text{for } |C| \ll 1 \\ 2C(1+2x)x^{-1} & \text{for } C \gg 1 \end{cases} \tag{36}$$

Both for weak and for strong adsorption, the excess amount increases linearly with C (see also Figure 4). Indeed, for $|C| \ll 1$, the normalized excess amount $\theta^{ex}/(\rho_0 d)$ does not depend on x. In the strong adsorption regime, however, it depends very strongly on x. For $x \ll 1$, the excess amount becomes very large: $\theta^{ex}/(\rho_0 d) \approx 2C/x$. For marginal solutions ($x \gg 1$), $\theta^{ex}/(\rho_0 d) \approx 4C$ for $C \gg 1$.

For adsorption from dilute solution ($x \ll 1$), the excess amount increases very rapidly when C approaches unity (see Figure 4). For ideal chains ($x = 0$), the excess amount diverges continuously, and goes to infinity at $C \rightarrow 1$ (a second-order phase transition). As discussed in a recent paper about ideal equilibrium polymers,[31] this behavior is qualitatively different than that of ideal monodisperse polymers. For the latter, the adsorbed amount increases gradually with increasing adsorption strength, but remains finite. It can be seen in Figure 4 that for equilibrium polymers with excluded-volume interactions, the adsorbed amount also remains finite, because the excluded-volume interactions between segments hinder the accumulation of segments near the surface. For $x \ll 1$, a reminiscence of the phase transition is still visible, however: even though the surface excess does not diverge at $C = 1$, it increases very steeply with ln C. The slope of a plot of θ^{ex} vs C changes by a factor $1/x$ around $C = 1$. The steep increase of the excess amount around $C = 1$ is typical for equilibrium polymers. It is not found for monodisperse polymers.

For adsorption from more concentrated solutions ($x > 1$), nothing special happens at $C = 1$. For $x \gg 1$, the ratio p/d is large for all C. Approximate expressions for p and θ^{ex} can then be obtained by replacing $\sinh[(z + p)/d]$ in eqs 22 and 24 by $(^1/_2)\exp[(z + p)/d]$. This yields the following expression, which is valid for for all C (not only for adsorption, but also for depletion):

$$\frac{\theta^{ex}}{\rho_0 d} \approx 2(C - 1 + \sqrt{1 + C^2}) \tag{37}$$

Hence, the normalized excess amount $\theta^{ex}/(\rho_0 d)$ does not depend on x for $x \gg 1$, which can also be seen in Figure 4.

Adsorption Isotherms. So far, we have considered concentration profiles and excess amounts in terms of the dimensionless parameters x and C. These results are valid for equilibrium polymers, but also for covalent polymers with an exponential chain length distribution (e.g., condensation polymers), provided that the bulk reservoir is (virtually) infinitely large. The major difference with covalent polymers is that for equilibrium polymers, the average length $\langle N_0 \rangle$ is a function of the concentration ρ_0 (see eq 2). As a result, the concentration dependence of the excess amount is quite different for equilibrium polymers than for covalent polymers with an exponential distribution.

With increasing concentration the parameter x (eq 15) increases monotonically as $x \sim \rho_0^{3/2}$. The crossover from the dilute to the marginal regime occurs when $x \simeq 1$, i.e., at a concentration

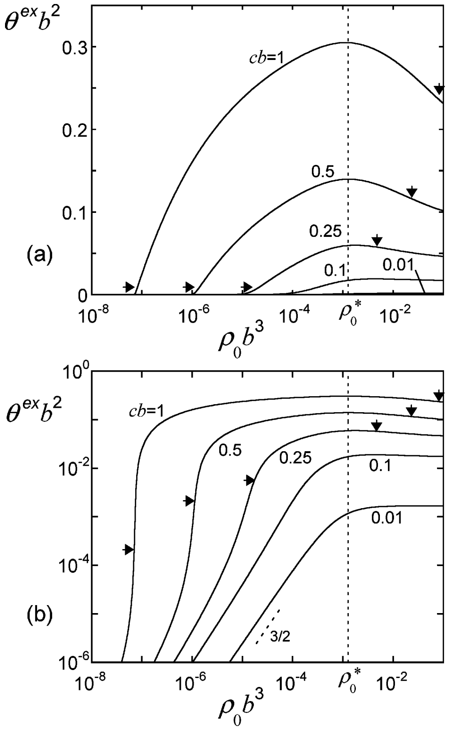

Figure 5. Adsorption isotherms for monomers with a scission energy of $20kT$ and for several values of the adsorption strength c and for $\chi = 0$ on a lin−log scale (a) and on a log−log scale (b). Vertical dashed line indicates the crossover concentration ρ_0^* from the dilute to the marginal concentration regime. Arrows indicate the concentration where $C = 1$: the horizontal arrow in the dilute and the vertical arrow in the marginal regime. At concentrations between the two arrows, $C > 1$.

$$\rho_0^* \simeq \frac{e^{-E/3kT}}{bv^{2/3}} \tag{38}$$

where we have used eqs 15 and 2. The parameter C (eq 23) is a nonmonotonic function of the concentration. For dilute solutions ($x \ll 1$), it increases as $C \approx cR_0 \sim \rho_0^{1/4}$, while for marginal solutions ($x \gg 1$), it decreases as $C \approx cR_0/\sqrt{2x} \sim \xi \sim \rho_0^{-1/2}$. For constant c and E, it reaches a maximum value at a concentration $\rho_0 = 4^{-2/3}\rho_0^* \approx 0.4\,\rho_0^*$:

$$C^{max} = \frac{2^{2/3}cb^{3/2}e^{E/6kT}}{6v^{1/6}} \tag{39}$$

Substitution of eqs 19, 15, and 2 in eq 24 gives the excess amount as a function of c, ρ_0, and E. In Figure 5, the excess amount θ^{ex} is shown as a function of the monomer concentration for monomers with a scission energy of $20kT$ for several values of c. The vertical line indicates the crossover concentration ρ_0^* (eq 38), and the arrows indicate the concentration where $C = 1$: in the concentration range between the arrows $C > 1$. Several regimes can be observed in this figure, depending on the value of c.

For very weak adsorption ($cb \ll e^{-E/6kT}$) we have $C \ll 1$ over the whole concentration range (see eq 39). The excess amount then equals $\theta^{\mathrm{ex}} \approx 2C\rho_0 d$ according to eq 36. Substitution of eqs 15 and 2 gives

$$\theta^{\mathrm{ex}} \approx \frac{cb^{7/2}\rho_0^{3/2}\mathrm{e}^{E/2kT}}{3[1 + 2v\rho_0 b^{3/2}\mathrm{e}^{E/2kT}]} \tag{40}$$

At low concentrations ($\rho_0 \ll \rho_0^*$), the excess amount increases as $\theta^{\mathrm{ex}} \sim c\rho_0^{3/2}\mathrm{e}^{E/2kT}$. At higher concentrations ($\rho_0 \gg \rho_0^*$) it reaches a plateau: $\theta^{\mathrm{ex}}_{\mathrm{max}} \approx (^1/_6)cb^2/v$. This behavior can be seen in Figure 5b for $c = 0.01$

For larger values of c the shape of the adsorption isotherm changes. If c is large enough, there is a concentration range where $C > 1$ (in between the horizontal and vertical arrows in Figure 5). As seen in Figure 4, the excess amount increases drastically around $C = 1$ for dilute solutions. This can also be seen in Figure 5. At very low concentrations, $C \ll 1$, and the excess amount (given by eq 40) is small. With increasing concentration, $\langle N_0 \rangle$ increases and also C increases. When $C \to 1$ (indicated by the horizontal arrows in Figure 5), the excess amount starts to increase rapidly (this is particularly obvious on the double-logarithmic scale of Figure 5b). For larger values of c this steep increase occurs at lower concentrations. As the concentration increases further the excess amount levels off. For very strong adsorption ($C \gg 1$), the excess amount reaches a plateau: $\theta^{\mathrm{ex}} \approx (^1/_3)cb^2/v$ (see eq 36 with eq 15 and see eq 2). In the marginal regime ($\rho_0 \gg \rho_0^*$), C decreases proportionally to ξ, and consequently, also θ^{ex} decreases. The reason is that the concentration decays more rapidly toward the bulk value for higher concentrations (ξ decreases), so that the periphery of the profile contributes less to θ^{ex}. This behavior is similar to the decrease of the depletion layer thickness for nonadsorbing equilibrium polymers in the marginal regime (section 3). The maximum of the excess amount occurs when $C \approx C^{\mathrm{max}}$, i.e., at $\rho_0 \approx \rho_0^*$.

In the calculation of the adsorption isotherms, we have assumed that the parameter c does not depend on the concentration. In reality, c may depend on the concentration for fixed χ_{s}, because the average surroundings of a polymer segment is different near the surface than in the bulk. This is a weak effect, however; see also the Appendix.

5. Concluding Remarks

We have developed an analytical mean-field theory for equilibrium polymers at a surface. Both adsorbing and nonadsorbing polymers were considered at bulk concentrations ranging from the dilute to the marginal concentration regime. Because of the exponential chain length distribution in the bulk solution, we could make use of the properties of Laplace transforms to obtain exact analytical expressions for the concentration profile and the excess amount of polymers at the surface. In this way, the usual ground-state approximation can be avoided.

This paper was written with predominantly equilibrium polymers in mind for which the chain length distribution adapts to the concentration according to eq 2. However, most results apply also to covalent polydisperse polymers with an exponential chain length distribution. The obvious exception is for those results where the concentration dependence of the average chain length is explicitly addressed.

For a nonadsorbing surface, there is a depletion layer near the surface where the polymer concentration is lower than in the bulk. An analytical expression was derived for the depletion layer thickness. It passes through a maximum as a function of concentration. In dilute solutions, it is proportional to the average radius of gyration of the chains, which increases with concentration, and in the marginal regime, it corresponds to the bulk correlation length which decreases with concentration.

For adsorbing surfaces, the concentration profile has similar characteristics as for adsorption of monodisperse chains, but there are also important differences. The distal length is larger for equilibrium polymers than for homopolymers. As a result, the central regime extends further from the surface. Furthermore, tails are much less important for equilibrium polymers than for homopolymers. This may have consequences for the interactions between two surfaces covered with adsorbed polymer layers. For homopolymers, the presence of tails causes a repulsive barrier at intermediate surface separations, which may be sufficient to cause stabilization of colloidal dispersions.[39] For equilibrium polymers, with much fewer tails, this repulsion is probably much weaker or even absent.

The dependence of the excess amount on the adsorption energy is qualitatively different for equilibrium polymers than for monodisperse chains. For weak adsorption the excess amount is small and increases linearly with the adsorption energy. As the adsorption energy reaches a certain finite value (which depends on the average length of the chains), the excess amount starts to increase very rapidly by orders of magnitude. For ideal chains without excluded-volume interactions, the adsorbed amount diverges at this point (a second-order phase transition). For chains with excluded-volume interactions a reminiscence of this phase transition is still visible (a very steep increase of the adsorbed amount), but the excess amount remains finite.

We also calculated adsorption isotherms for equilibrium polymers for several values of the adsorption energy. At low concentrations, the adsorbed amount is low and increases gradually as a power law $\theta^{\mathrm{ex}} \sim {\rho_0}^{3/2}$ with concentration. If the adsorption energy is sufficiently high, there is a certain concentration where the adsorbed amount starts to increase very rapidly. For chains without excluded volume, the excess amount diverges at this point, but for chains with excluded volume, it remains finite. At higher concentrations, the excess amount saturates at a plateau, and for very high concentrations, it decreases again.

In our model, we have only taken into account binary interactions between segments. At very strong adsorption this may not be accurate, because the concentration in the adsorbed layer may become very high. Therefore, the excess amount for this regime may be overestimated by our calculations.

Another limitation of our model is that we use a mean-field approach in which excluded-volume correlations are neglected. As a result it neglects swelling of polymer chains in a good solvent. For not too long chains in marginal solvents ($v/b^3 \lesssim \langle N_0 \rangle^{-1/2}$), correlations are not very important and the mean-field treatment is rather good.[10,1,40] For concentrations above the overlap value, the fluctuations that are characteristic for the semidilute regime are neglected. However, for $v/b^3 \lesssim$

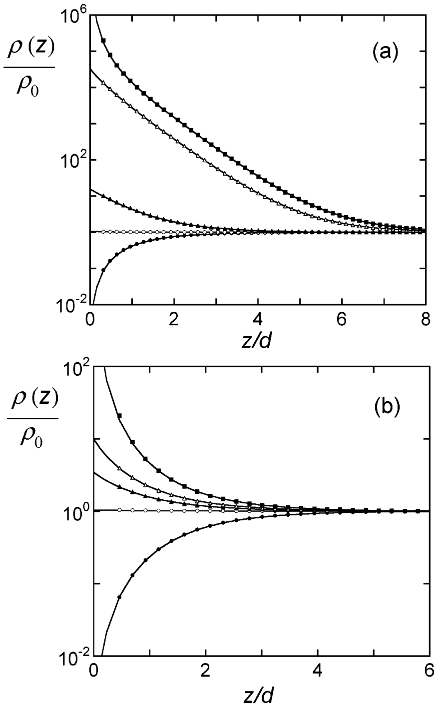

Figure 6. Comparison between density profiles obtained with the numerical lattice model (symbols) and the analytical continuum model (full curves) for monomers with a scission energy of $25kT$ and for several adsorption energies, from bottom to top: (●) $\chi_s = 0$, $c = -5$; (○) $\chi_s = 0.223$, $c = 0.005$; (▲) $\chi_s = 0.26$, $c = 0.1$; (△) $\chi_s = 0.3$, $c = 0.3$; (■) $\chi_s = 1$, $c = 25$. (a) Dilute solution: $\phi_M^b = 10^{-6}$, $\langle\hat{N}_0\rangle = 155$, $x = 10^{-4}$, $d = 6.2$. (b) Marginal solution: $\phi_M^b = 10^{-2}$, $\langle\hat{N}_0\rangle = 15\,500$, $x = 10^2$, $d = 4.3$.

$\rho_0 b^3$ there is a crossover to the marginal regime, where fluctuations are unimportant and where the mean-field treatment is valid.[1,40] For Θ solvents ($\chi = 0.5$) the excluded-volume parameter v vanishes and three-segment interactions dominate.

In this paper we have only considered the total segment concentration $\rho(z)$, which is obtained after integration over all chain lengths (eq 7). As a result, no information is obtained about the distribution of chain lengths near the surface. To obtain the chain length distribution, one would have to perform an inverse Laplace transform on the distribution function $g(z, s)$, eq 18. Unfortunately, we could not do this analytically. It is to be expected, however, that the distribution is very different from that in the bulk of the solution: it is well-known that in the case of depletion short chains are favored near the surface, whereas in the case of adsorption long chains are favored.[1,13,16,28,26,35]

Acknowledgment. We thank Frans Leermakers for helpful discussions.

Appendix: Comparison to Numerical Lattice Theory

In ref 28, a numerical lattice theory was used to describe equilibrium polymers near surfaces. In this appendix, we compare the results obtained using this lattice model to the analytical density profiles, given by eqs 11, 18, and 22. The parameters in the numerical calculations are the volume fraction of monomers ϕ_M^b, the average length $\langle\hat{N}_0\rangle$ (expressed in lattice monomers), the adsorption energy χ_s (i.e., the contact energy between a monomer and the surface), and the contact energy between segments and solvent molecules. These must be related to the parameters R_0, x, and c occurring in the analytical theory. For chains on a cubic lattice without the possibility of back-folding (as in ref 28), the Kuhn length b is equal to $^3/_2 l$ with l being the lattice spacing.[41] Hence, the average length expressed in Kuhn segments is $\langle N_0\rangle = {}^2/_3\langle\hat{N}_0\rangle$ and the average radius of gyration is $R_0 = {}^1/_2 l\langle\hat{N}_0\rangle^{1/2}$. For athermal chains (no interactions between monomers and solvent, i.e., $\chi = 0$) this gives $x = v\rho_0\langle N_0\rangle = {}^2/_3\phi_M^b\langle\hat{N}_0\rangle$ (with $\phi_M^b = \rho_0 b^3$). The main difficulty in comparing lattice and continuum models is related to the different boundary conditions in the two models. For ideal chains on a cubic lattice *with* the possibility of back-folding a relation between the lattice adsorption parameter χ_s and the continuum adsorption parameter c in the limit of zero concentration was derived by Gorbunov et al.[33,35] This relation is not valid for the present case, however, because in the model of ref 28 back-folding is not allowed.

A detailed comparison between the boundary conditions in the two models is beyond the scope of this appendix, so we use c as an adjustable parameter for fitting the lattice profiles. In Figure 6, density profiles obtained using both models are shown for dilute and marginal solutions and for several values of the adsorption energy. The agreement between the two models is excellent. The critical adsorption energy χ_{sc} (where $c = 0$) is approximately $\ln(5/4) \approx 0.223$. Moreover, we find that the relation between c and χ_s does not depend very strongly on the monomer concentration: for the same χ_s, the numerical data for the two concentrations can be fitted with approximately the same value of c.

References and Notes

(1) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman and Hall: London, 1993.
(2) Eisenriegler, E. *Polymers near Surfaces*; World Scientific: Singapore, 1993.
(3) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83,* 1619.
(4) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84,* 178.
(5) Edwards, S. F. *Proc. Phys. Soc.* **1965**, *85,* 613.
(6) Gorbunov, A. A.; Skvortsov, A. M. *Adv. Colloid Interface Sci.* **1995**, *62,* 31.
(7) Eisenriegler, E. *J. Chem. Phys.* **1983**, *79,* 1052.
(8) Lépine, Y.; Caillé, A. *Can. J. Phys.* **1978**, *56,* 403.
(9) De Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, and London, 1979.
(10) Semenov, A. N.; Bonet-Avalos, J.; Johner, A.; Joanny, J. F. *Macromolecules* **1996**, *29,* 2179.
(11) Johner, A.; Bonet-Avalos, J.; Van der Linden, C. C.; Semenov, A. N.; Joanny, J. F. *Macromolecules* **1996**, *29,* 3629.
(12) Fleer, G. J.; Van Male, J.; Johner, A. *Macromolecules* **1999**, *32,* 825.
(13) Roefs, S. P. F. M.; Scheutjens, J. M. H. M.; Leermakers, F. A. M. *Macromolecules* **1994**, *27,* 4810.
(14) Hariharan, A.; Kumar, S. K.; Russell, T. P. *Macromolecules* **1990**, *23,* 3584.
(15) Van der Gucht, J.; Besseling, N. A. M.; Fleer, G. J. *Macromolecules* **2002**, *35,* 6732.
(16) Sear, R. P. *J. Chem. Phys.* **1999**, *111,* 2255.
(17) Fleer, G. J. *Macromol. Symp.* **1997**, *113,* 177.
(18) Cates, M. E.; Candau, S. J. *J. Phys. Cond. Matter* **1990**, *2,* 6869.
(19) Lehn, J.-M. *Supramolecular Chemistry, Concepts and Perspectives*; VCH: Weinheim, Germany, 1995.
(20) Ciferri, A. *Supramolecular polymers*; Marcel Dekker: New York, 2000.

(21) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601−1604.
(22) Zimmerman, N.; Moore, J. S.; Zimmerman, S. C. *Chem. Ind.* **1998**, 604−610.
(23) Boileau, S.; Bouteiler, L.; Lauprêtre, F.; Lortie, F. *New J. Chem.* **2000**, *24*, 845−848.
(24) Fogleman, E. A.; Yount, W. C.; Xu, J.; Craig, S. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 4026.
(25) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(26) Schmitt, V.; Lequeux, F.; Marques, C. M. *J. Phys. II* **1993**, *3*, 891.
(27) Rouault, Y.; Milchev, A. *Macromol. Theor. Simul.* **1997**, *6*, 1177.
(28) Van der Gucht, J.; Besseling, N. A. M. *Phys. Rev. E* **2002**, *65*, 51801.
(29) Milchev, A.; Landau, D. P. *J. Chem. Phys.* **1996**, *104*, 9161.
(30) Van der Gucht, J.; Besseling, N. A. M.; Cohen Stuart, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 6202.
(31) Van der Gucht, J.; Besseling, N. A. M.; Fleer, G. J. *J. Chem. Phys.* **2003**, *119*, 8175.
(32) De Gennes, P. G. *Rept. Prog. Phys.* **1969**, *32*, 187.
(33) Gorbunov, A. A.; Skvortsov, A. M.; Van Male, J.; Fleer, G. J. *J. Chem. Phys.* **2001**, *114*, 5366.
(34) Fleer, G. J.; Skvortsov, A. M.; Tuinier, R. *Macromolecules* **2003**, *36*, 7857.
(35) Van der Gucht, J.; Besseling, N. A. M.; Fleer, G. J. *Macromolecules* **2002**, *35*, 2810.
(36) Van der Gucht, J.; Besseling, N. A. M.; Van Male, J.; Cohen Stuart, M. A. *J. Chem. Phys.* **2000**, *113*, 2886.
(37) De Gennes, P. G. *Macromolecules* **1981**, *14*, 1637.
(38) Within the GSA, the profile is given by $\rho(z) = b^3/(3vd^2\sinh^2[(z + p)/d])$. The distal length equals $d = b/\sqrt{6\epsilon}$ with ϵ the ground-state eigenvalue. For polydisperse chains ϵ is found from[17] $\int_0^\infty \rho(N) N e^{\epsilon N}\, dN = 1$. For equilibrium polymers (eq 1) this gives $\epsilon = \langle N_0 \rangle^{-1}(1 - \sqrt{\rho_0}) \approx \langle N_0 \rangle^{-1}$, so that $d \approx R_0$. The GSA thus gives the same profile as eq 30, but without the term unity in brackets.
(39) Semenov, A. N.; Joanny, J. F.; Johner, A.; Bonet-Avalaos, J. *Macromolecules* **1997**, *30*, 1479.
(40) Grosberg, A. Y.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; AIP Press: New York, 1994.
(41) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.

MA0351773