Chain-Length Dependence of the Polymer Surface Excess near the Adsorption/Depletion Transition

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ABSTRACT: The behavior of a solution of ideal polymers at a surface near the adsorption/depletion transition is investigated using a lattice model. A very simple relation was found for the surface excess θ^{ex} of a polymer molecule of length N close to the adsorption/depletion transition: $\theta^{ex}/\phi^b = A[B + (\chi_s - \chi_{sc}^{\infty})N]$, where ϕ^b is the bulk volume fraction of polymer, $A \approx 5/6$ and $B \approx 1/5$ are constants, χ_s is the Silberberg adsorption parameter, and χ_{sc}^{∞} is the critical adsorption energy for infinite chain lengths. The adsorption/depletion transition shifts to lower χ_s values with decreasing chain length. This effect is strongly enhanced if the end segments of the chain adsorb preferentially. A continuum model was used to obtain analytical expressions. The agreement between lattice and continuum descriptions is quite good. The chain-length dependence of the adsorption/depletion transition for homopolymers is not found in the continuum model, however. The results in this paper may be relevant for example for critical chromatography.

1. Introduction

The behavior of polymer solutions at interfaces is of considerable interest, both from a theoretical point of view and because of its practical relevance.[1] 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. The equilibrium configuration is a result of the balance between these two factors. If the affinity of polymer segments for the surface is below a certain threshold, the polymer chains are depleted from the surface, and above the threshold they are adsorbed. At the point where the entropic effects are exactly compensated by the energetic effects, there is a transition from the depletion to the adsorption regime. This point corresponds to the adsorption/depletion transition and is important in polymer adsorption theories.[1] For infinitely long chains the transition is second order, and we may speak about a critical adsorption energy.[1]

The adsorption/depletion transition is of particular interest in critical chromatography,[2,3] i.e., chromatography of polymers under critical adsorption conditions. This technique is based on the assumption that the separation of homopolymers with respect to molar mass is absent under such conditions. In other words, the adsorption/depletion transition is assumed to be independent of the chain length. As a result, the retention is solely governed by small differences in the chemical structure of the polymer chains. Detailed calculations, however, indicate that the adsorption/depletion transition for finite chains does vary with chain length.[4−6] This observation may seriously affect the interpretation of critical chromatography experiments. Hence, a full understanding of the behavior of polymer chains near the adsorption/depletion point is necessary.

A variety of theoretical methods have been used to describe polymer solutions near surfaces. Scheutjens and Fleer[1,4,7] developed a self-consistent-field lattice theory, which proved to be successful in describing polymer adsorption and depletion. Their numerical model uses a mean-field approximation in which correlations between the occupations of sites within the same layer are neglected. A drawback of any model that relies on numerical calculations is, obviously, that it is difficult to recognize general trends. No exact general analytical solutions for the self-consistent-field equations have been found, however. On the other hand, there are continuum models which can be solved analytically for some cases.[8−10] The description of a polymer chain in a continuum approach is analogous to the Brownian motion of a particle. The equivalence between the continuum and the lattice approach is well established.[1,11,5] Recently, Gorbunov et al.[5] made a quantitative comparison for an ideal chain anchored to a surface. To that end, they introduced in the continuum model a finite size of the adsorbed segments, which is automatically accounted for in a lattice. The agreement between the continuum and lattice results was then found to be virtually quantitative.

In section 2 we use a lattice model to study polymer adsorption and depletion under conditions close to the adsorption/depletion transition. The shift of this transition with chain length is investigated. It will be shown that there is a very simple expression that relates the surface excess of a polymer to its chain length and bulk concentration. The transition point is defined as the point where this surface excess is zero. The numerical results are compared to a continuum model in section 3. In section 4 we investigate the effect of chemically different end segments on the adsorption of polymers near the adsorption/depletion point. Finally, in section 5 we discuss in some detail the range of validity of the results of sections 2 and 3.

2. Numerical Lattice Theory

2.1. Model. Lattice models are very powerful tools to count conformations of polymer chains.[1] The space adjoining a solid surface is divided into a number of parallel lattice layers. Segments in the first layer, at z

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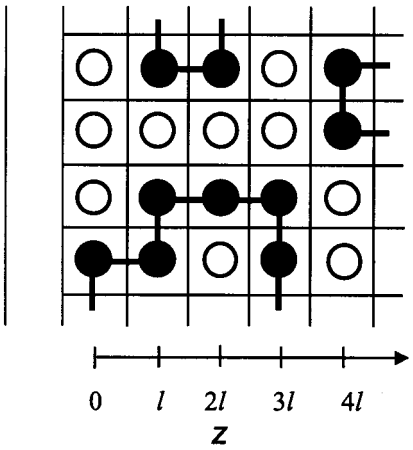

Figure 1. A two-dimensional representation of a three-dimensional cubic lattice. Open circles denote solvent molecules, and filled circles refer to polymer segments. Polymer segments and solvent molecules are restricted to the region $z \geq 0$.

$= 0$, are adsorbed. Nonadsorbed segments are at $z = l$, $2l$, ..., Ml, where l is the thickness of a lattice layer (Figure 1). The region $z < 0$ is forbidden for chain segments and solvent molecules. A reflecting boundary condition is imposed at $z = Ml$ in this study. Here, M is taken large enough so that near Ml bulk properties prevail, in order to avoid boundary effects. The lattice geometry is defined by the lattice constant λ, which is the fraction of neighboring sites that a lattice site has in an adjacent layer. The fraction of neighbors in the same layer is equal to $1 - 2\lambda$. In this paper we use a simple cubic lattice with $\lambda = {}^1/_6$.

We consider a very dilute solution of polymer chains, all composed of chemically identical segments. (In section 4 we allow the end segments to be different.) All lattice sites are occupied by either a polymer segment or a solvent molecule. The system is in equilibrium with a bulk solution, the composition of which defines the chemical potential. The excess of polymer near the surface expressed in equivalent lattice layers is denoted θ^{ex}. The total excess amount of polymer for chains of length N is equal to N times the excess of end segments. It can be calculated as

$$\theta^{ex} = N \sum_{z/l=0}^{M} \phi(z,N) - \phi^b(N) \tag{1}$$

where $\phi(z,N)$ and $\phi^b(N)$ are the volume fractions of end segments (segments with ranking number N) at a distance z from the surface and in the bulk, respectively. Obviously, $\phi^b(N) = \phi^b/N$, where ϕ^b is the bulk volume fraction of polymer. An alternative way to compute θ^{ex} is summing over $\phi(z) - \phi^b$, where $\phi(z)$ is the overall segment concentration. As every chain has exactly one segment with ranking number N, the results are identical.

Polymer chains can adopt many different conformations. The conformation of a chain is specified by the sequence of layers in which the successive segments of the chain are situated. The equilibrium situation corresponds to the most probable set of conformations.

The segmental weighting factor $G(z)$ gives the relative preference of a detached polymer segment to be in layer z rather than in the bulk of the solution:

$$G(z) = e^{-u(z)/kT} \tag{2}$$

where $u(z)$ is the local potential of a polymer segment with respect to the bulk solution. Since we consider ideal chains, the segments do not interact with each other, and the only contribution to $u(z)$ arises from a short-range interaction with the surface:

$$\frac{u(z)}{kT} = \begin{cases} \infty & \text{if } z < 0 \\ -\chi_s & \text{if } z = 0 \\ 0 & \text{if } z \geq l \end{cases} \tag{3}$$

where χ_s is a dimensionless adsorption energy parameter, reflecting the energetic effect of displacing a polymer segment by a solvent molecule on the surface:[12]

$$\chi_s = -\frac{u_p^a - u_0^a}{kT} \tag{4}$$

Here u_p^a is the adsorption energy of a polymer segment and u_0^a that of a solvent molecule. The transition between positive adsorption ($\theta^{ex} > 0$) and negative adsorption (depletion, $\theta^{ex} < 0$) of a polymer chain occurs at a threshold value of χ_s, denoted χ_{sc}^N. A segmental adsorption energy $\chi_s = \chi_{sc}^N$ just compensates for the conformational entropy loss due to the presence of the surface. For $\chi_s < \chi_{sc}^N$ the polymer is depleted from the surface, and for $\chi_s > \chi_{sc}^N$ it adsorbs. As we will see, χ_{sc}^N is a (weak) function of the chain length N. For infinite chain length χ_{sc}^N equals the critical adsorption energy, given by[1,13]

$$\chi_{sc}^{\infty} = -\ln(1 - \lambda) \tag{5}$$

For each segment s of a polymer molecule of N segments we can write an end-point distribution function $G(z,s)$. It gives the statistical weight of all possible walks starting from segment 1 in an arbitrary layer in the lattice and ending at a segment s in layer z. The end-point distribution functions can be calculated from the weighting factors $G(z)$ of polymer segments through the recurrence relation:

$$G(z, s+1) = G(z)\{\lambda G(z-1, s) + (1 - 2\lambda)G(z, s) + \lambda G(z+1, s))\} \tag{6}$$

with the initial condition $G(z,1) = G(z)$. The volume fraction of end segments in layer z is proportional to the end-point distribution function:

$$\phi(z,N) = \frac{\phi^b}{N} G(z,N) \tag{7}$$

where the factor ϕ^b/N is a normalization factor, giving $\phi^b(N) = \phi^b/N$. The solution of eq 6 can be found numerically. Hence, the distribution of end segments is obtained. Equation 1 can now be rewritten using eq 7:

$$\theta^{ex} = \phi^b \sum_{z/l=0}^{M} (G(z,N) - 1) \tag{8}$$

2.2. Numerical Results. As an example, the volume fraction profiles of end segments of a very dilute solution of polymer chains of 500 segments at three values of χ_s

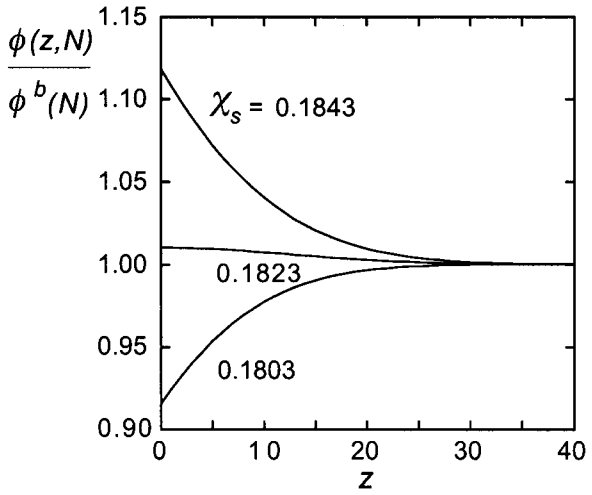

Figure 2. Volume fraction profiles of end segments of a very dilute solution of polymer chains of 500 segments for three different values of χ_s. Calculated points are connected by straight lines.

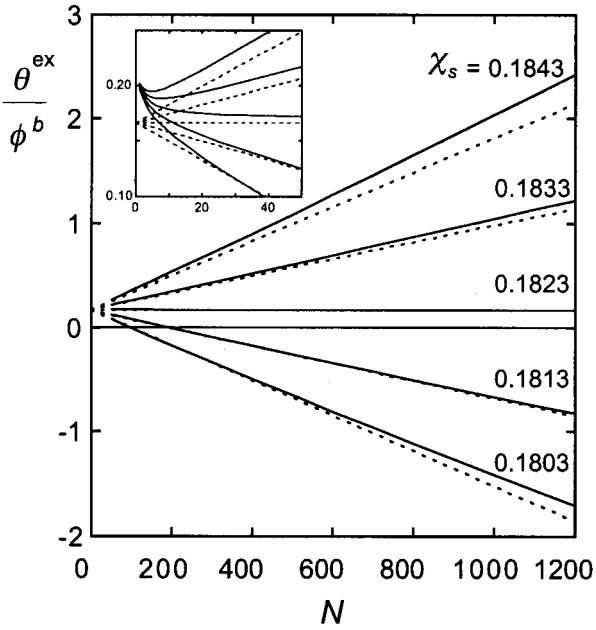

Figure 3. θ^{ex}/ϕ^b as a function of the chain length N for several values of χ_s. Calculated points are connected by straight lines; the dashed lines represent eq 9 with $A = {}^5/_6$ and $B = {}^1/_5$ (see eq 32). Inset: magnification for $N \leq 50$.

close to $\chi_{sc}^{\infty} \approx 0.1823$ are plotted in Figure 2. The surface excess θ^{ex} of polymer is calculated with eq 1 or 8. Figure 3 shows the surface excess relative to the bulk volume fraction as a function of the chain length for several values of χ_s close to χ_{sc}^{∞}. The main figure contains numerical data for $N > 50$; the solid lines were obtained by connecting the data points by straight lines. In very good approximation, θ^{ex}/ϕ^b is linear in N in this range. The inset of Figure 3 shows an expanded view for short chains, for which deviations of this linearity show up. In section 5 we will discuss these deviations in more detail.

If we fit the numerical data for $N > 50$ and $|\theta^{ex}/\phi^b| < 1$ to a straight line, we find a nearly constant intercept of 0.167 on the vertical axis and a slope which is, in good approximation, proportional to $\chi_s - \chi_{sc}^{\infty}$. Hence, the surface excess for long chains near the adsorption/depletion transition is very accurately described by

$$\frac{\theta^{ex}}{\phi^b} = A(B + (\chi_s - \chi_{sc}^{\infty})N) \tag{9}$$

with χ_{sc}^{∞} given by eq 5. For χ_s values close to the adsorption threshold, the parameter $A \approx 0.833 \approx {}^5/_6$ and the parameter $B \approx 0.200 \approx {}^1/_5$. For $\chi_s = \chi_{sc}^{\infty}$ the slope of the line becomes zero and, for not too small chain lengths, $\theta^{ex}/\phi^b = AB \approx {}^1/_6$, irrespective of chain length. For $\chi_s > \chi_{sc}^{\infty}$, all θ^{ex} are positive and increase with increasing chain length. For $\chi_s \lesssim \chi_{sc}^{\infty}$, on the other hand, there is a positive adsorption of relatively short chains and a negative adsorption (depletion) of long ones. The dashed lines in Figure 3 correspond to eq 9 with $A = {}^5/_6$ and $B = {}^1/_5$, which is the prediction of the continuum model (eq 26) with an offset ${}^1/_6$ added to it. This equation is very good if $|\chi_s - \chi_{sc}^{\infty}|$ is small. For somewhat larger values of $|\chi_s - \chi_{sc}^{\infty}|$, θ^{ex} is still a linear function of N, but the slope, and to a lesser extent the intercept, deviate from the above-mentioned values. Also for very small chain lengths (inset in Figure 3), deviations from linearity occur.

The adsorption/depletion transition ($\chi_s = \chi_{sc}^{N}$) is defined as the point where $\theta^{ex} = 0$. For $\chi_s > \chi_{sc}^{N}$, the surface excess is positive, and for $\chi_s < \chi_{sc}^{N}$ it is negative. From eq 9 it is easily seen that χ_{sc}^{N} is a function of the chain length N. For infinitely long chains, χ_{sc}^{N} has a limiting value χ_{sc}^{∞}. For finite chain lengths, it is given by

$$\chi_{sc}^{N} = \chi_{sc}^{\infty} - \frac{B}{N} \tag{10}$$

Gorbunov et al. derived this result for end-grafted chains, using a mapping of a continuum model on a lattice.[5] They found $B = {}^1/_5$. In section 3 we consider the continuum description of a solution containing free polymer chains in contact with a surface. Equation 10 can also be read as an expression for the chain length for which, at a given χ_s that is somewhat smaller than χ_{sc}^{∞}, $\theta^{ex} = 0$:

$$N_c = \frac{B}{\chi_{sc}^{\infty} - \chi_s} \tag{11}$$

At an adsorption strength χ_s, chains of this length have just a vanishing surface excess. Shorter chains have a positive surface excess because the energetic reward for the adsorption exceeds the entropic penalty. Longer chains will be depleted from the surface because the entropic penalty is larger than the energetic attraction. For $\chi_s \lesssim \chi_{sc}^{\infty}$ eq 9 can now be rewritten using eq 11:

$$\frac{\theta^{ex}}{\phi^b} = AB\left(1 - \frac{N}{N_c}\right) \tag{12}$$

Hence, the relation between the surface excess and the chain length near the adsorption/depletion transition is remarkably simple. This relation was found here by careful examination of numerical results of many calculations. Yet, the situation is somewhat unsatisfactory: a strikingly simple law emerges from extensive numerical calculations using a rather involved model. It would be much more satisfying if such a simple law could be derived from theoretical arguments. Therefore,

in the next section we analyze the situation from an analytical perspective, using some additional assumptions.

3. Analytical Continuum Theory

The continuum description of polymers near a surface is based on a model analogous to the diffusion of a particle in the presence of a surface. The continuum equation describing the distribution of end points is the Edwards equation:[14]

$$\frac{\partial G(z,N)}{\partial N} = \frac{b^2}{6}\frac{\partial^2 G(z,N)}{\partial z^2} - u(z)\,G(z,N) \qquad (13)$$

where b is the segmental length, and $G(z,N)$ is the statistical weight of a chain or chain section of contour length Nb with its end point situated at a distance z from the surface. This equation is the continuum analogue of the lattice recurrence relation, eq 6.[1]

Outside the range of the interaction potential with the surface, the potential $u(z)$ is zero for ideal chains. The effect of the surface is taken into account through the boundary condition. It is well-known from analogous problems in quantum mechanics that the influence of a local wall potential in the asymptotic region (outside the range of the potential) can be related to the logarithmic derivative of the ground-state eigenfunction:[8,9]

$$\left[\frac{1}{\psi_0(z)}\frac{\partial \psi_0(z)}{\partial z}\right]_{z=0} = -c \qquad (14)$$

where $\psi_0(z)$ is the ground-state eigenfunction in the eigenfunction expansion of $G(z,N)$. The parameter c is the inverse of the so-called extrapolation length. It can be related to the adsorption energy parameter χ_s. Eisenriegler[9] argued that the ground-state eigenfunction dominates in the region close to the surface. Hence, it is a reasonable approximation to replace boundary condition 14 by

$$\left[\frac{1}{G(z,N)}\frac{\partial G(z,N)}{\partial z}\right]_{z=0} = -c \qquad (15)$$

The use of this boundary condition enables an explicit solution of the Edwards equation for weak adsorption, around the adsorption/depletion transition, where the concentrations are so low that the assumption $u(z) = 0$ is justified. However, some errors may be introduced upon replacing (14) by (15).

When we take the potential $u(z)$ equal to zero, $G(z,N)$ is a monotonic function of z. (This is not strictly true for the lattice $G(z,N)$ of the previous section.) This means that a positive value of c results in a positive θ^{ex} and a negative value of c in a negative θ^{ex}. At the adsorption/depletion transition $c = 0$. The parameter c has the dimension of inverse length. Analogous to ref 5, it is convenient to introduce a dimensionless adsorption parameter C as

$$C \equiv \frac{cb}{\sqrt{6}} \qquad (16)$$

The solution of eq 13 with $u(z) = 0$ for all z and with boundary condition 15 at the surface and $G(\infty,N) = 1$ in the bulk solution has been derived by Eisenriegler et al.:[9]

$$G(z,N) = \mathrm{erf}(\zeta) + \mathrm{e}^{-\zeta^2} Y(\zeta - \gamma) \qquad (17)$$

where $\mathrm{erf}(x)$ is the error function and $Y(x) = \mathrm{e}^{x^2}\,\mathrm{erfc}(x)$, with $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$ the complementary error function. The parameters ζ and γ are defined as

$$\zeta = \frac{z}{2R} \quad \gamma = cR = C\sqrt{N} \quad \text{with } R = b\sqrt{\frac{N}{6}} \qquad (18)$$

Here R is the radius of gyration of a free Gaussian chain, and ζ is a scaled, dimensionless distance to the surface. The dimensionless parameter γ is a scaled adsorption interaction parameter. The first term in eq 17, which depends only on ζ but not on γ, represents the contribution $G^f(z,N)$ of the free chains not touching the surface. The second term is the contribution $G^a(z,N)$ of the adsorbed chains.

The volume fraction of end segments is directly proportional to the end-point distribution function:

$$\phi(z,N) = \frac{\phi^b}{N} G(z,N) \qquad (19)$$

where ϕ^b/N is a normalization factor. This equation is identical to eq 7 in the lattice model.

The excess amount of polymer is again equal to N times the excess of end-segments. In a continuum model, the summation in eq 8 is replaced by an integral:

$$\theta^{ex} = b^{-1}\phi^b \int_0^\infty [G(z,N) - 1]\,\mathrm{d}z \qquad (20)$$

where we have added a factor b^{-1} so that θ^{ex} is expressed in equivalent monolayers. Integration of eq 17 yields[10]

$$\frac{\theta^{ex}}{\phi^b} = \frac{1}{C\sqrt{6}}\left[Y(-\gamma) - 1 - \frac{2\gamma}{\sqrt{\pi}}\right] \qquad (21)$$

The first two terms represent the integral over $G^a(z,N)$ and the last one that over $G^f(z,N) - 1$. Close to the adsorption/depletion transition ($|C| \ll N^{-1/2}$) the parameter γ is very small. We note that the first terms in the expansion of $Y(-\gamma) - 1$ are $2\gamma/\sqrt{\pi} + \gamma^2$, so that in eq 21 the linear term cancels. Hence, for $|\gamma| \ll 1$, eq 21 reduces to

$$\frac{\theta^{ex}}{\phi^b} = \frac{CN}{\sqrt{6}} \qquad (22)$$

This gives θ^{ex} in terms of the parameter C. If we now find an expression for C, we have θ^{ex} as a function of N.

The parameter C is related to the lattice adsorption parameter χ_s. Gorbunov et al.[5] found a relation between C and χ_s for an ideal chain anchored to a surface, by substituting the continuum partition function in the boundary condition of the lattice model. They showed that the analytical results for this case can be mapped on the results of the lattice theory. We follow the same strategy for the present case of a polymer solution. Thus, we substitute $G(z,N)$ (eq 17) in the lattice boundary condition (eq 6 for $z = 0$):

$$G(0, N+1) = \mathrm{e}^{\chi_s}[(1 - 2\lambda)G(0,N) + \lambda G(l,N)] \qquad (23)$$

A relation between the lattice spacing l and the segmental length b follows from equating the radius of

gyration in both models. This yields[5] $l = b/\sqrt{6\lambda}$, and, hence, in a cubic lattice $l = b$.

For infinite chain length eq 23 yields, with $\lambda = {}^1/_6$,

$$e^{-\chi_s} = \begin{cases} \frac{1}{6}(4 + e^{-C\sqrt{6}})e^{-C^2} & \text{if } C \geqslant 0 \\ \frac{5}{6} - \frac{C}{\sqrt{6}} & \text{if } C \leqslant 0 \end{cases} \tag{24}$$

which is the same result as found by Gorbunov et al. for end-grafted chains.[5] For $|C| \ll 1$ (and hence, $|\chi_s - \chi_{sc}^{\infty}| \ll 1$), which is the relevant situation in this paper, this reduces to

$$C \approx \frac{5}{\sqrt{6}}(\chi_s - \chi_{sc}^{\infty}) \tag{25}$$

For end-grafted chains Gorbunov et al.[5] derived also the first-order correction for finite N in eq 25, resulting in an extra term $N^{-1}/\sqrt{6}$ on the right-hand side of eq 25. As a consequence, the adsorption/depletion transition ($\theta^{ex} = 0$) for an anchored chain of finite length is not situated at $\chi_s = \chi_{sc}^{\infty} = \ln(6/5)$, but at a value of χ_s which is lower by an amount $1/(5N)$. For chains in solution (i.e., using eq 17 in the boundary condition) the correction for finite N is much smaller, and for $C = 0$ it vanishes. Hence, the (small) shift in the adsorption/depletion transition is not predicted by the present continuum model. Yet, in the lattice calculations we found that also for a solution of ideal chains the transition is very close to the point $\chi_s = \ln(6/5) - 1/(5N)$.

Substitution of eq 25 in eq 22 yields

$$\frac{\theta^{ex}}{\phi^b} = \frac{5}{6}(\chi_s - \chi_{sc}^{\infty})N \tag{26}$$

Hence, the continuum model predicts that for $\chi_s > \chi_{sc}^{\infty}$ adsorption takes place ($\theta^{ex} > 0$), whereas for $\chi_s < \chi_{sc}^{\infty}$ depletion occurs ($\theta^{ex} < 0$). At the adsorption/depletion transition $\chi_s = \chi_{sc}^{\infty}$ irrespective of the chain length. If we compare this result with the results of the lattice model (eq 9), we see that indeed a linear relation between θ^{ex} and N is predicted. The slope of the line is in good agreement with the numerical results, especially for small $|\chi_s - \chi_{sc}^{\infty}|$ (see Figure 3). However, whereas the numerical calculations show that the intercept of the line is about 1/6, the continuum model predicts an intercept equal to zero. As a result, the adsorption/depletion transition in the continuum model is not a function of the chain length, whereas the lattice results show that χ_{sc}^{N} decreases with increasing chain length (eq 10). We note that including the $1/(5N)$ correction as discussed above would exactly give an intercept of ${}^1/_6$. From eq 23 with $G(0,N)$ and $G(l,N)$ given by eq 17 there is, however, no justification of this correction. This discrepancy between lattice and continuum results may be attributed to the way the interactions with the wall are accounted for in the continuum model. As discussed before, upon replacing the interaction potential $u(z)$ by boundary condition 14, we disregard the region close to the surface (within the range of the potential). As a result, the contribution of the adsorbed polymer in this region to θ^{ex} is also disregarded. Furthermore, we have assumed that the ground-state eigenfunction dominates near the surface, so that we could use boundary condition 15 instead of 14. Another reason for the discrepancy is that in Eisenrieglers result (eq 17), which is obtained after integration over the position z' of the starting point of the chain, the same value of C applies. In the lattice model a constant χ_s is taken. Application of eq 23 to subconformations with different z' shows that the relation between χ_s and C depends weakly on z', which affects the integration over z' at constant χ_s. Finally, eq 23 includes the contribution of free chains, which should not be affected by C or χ_s. On the other hand, the lattice model has the limitation of being discrete in spatial position. As a result of these approximations, small differences between the lattice and continuum results are likely to occur. It would be interesting to investigate whether a chain-length-dependent adsorption/depletion transition is found also in other theoretical models, such as the freely jointed discrete ideal chain model.

We should, however, not overemphasize these small differences. The overall agreement between lattice and continuum descriptions based upon eq 25 is quite good, giving nearly the same values for the two contributions $Y(-\gamma) - 1$ (adsorbed chains) and $-2\gamma/\sqrt{\pi}$ (free chains) in eq 21. The differences occur only in the sum, which constitutes a small difference between two relatively large numbers. Hence, in first order the agreement is quite satisfactory, and only in second-order contributions some (minor) differences show up.

4. Chemically Different End Segments

So far, we have considered only chains in which all segments are identical. In most polymers used in practice, however, the end segments are chemically different from the segments in the middle of the chain, for example because they carry a residual group from a polymerization initiator. These different end segments may have a different interaction with the surface than the other segments. The relative importance of a chemically different end segment becomes larger with decreasing chain length. As a result, we may expect the chain-length dependence of the adsorption/depletion transition to change.

The lattice model can be extended to include different types of segments.[1,15] An extra segment type is defined with a potential which may be different from the potential of the middle segments. We consider only differences in the adsorption energy χ_s of the end segments. First, we give one of both end segments a different adsorption energy. The other end is the same as the middle segments. The extra affinity that the modified end segment has as compared to middle segments is $\Delta\chi_s$. For $\Delta\chi_s > 0$, the end segment is preferentially adsorbed. For $\Delta\chi_s < 0$, the end segment has a lower affinity for the surface.

A positive $\Delta\chi_s$ results in an increase of θ^{ex}, because conformations with the end segment adsorbed are favored. A careful examination of the numerical results suggests that the excess amount of polymers at $\chi_s \approx \chi_{sc}^{\infty}$ is now very accurately described by (compare eq 9)

$$\frac{\theta^{ex}}{\phi^b} = A(B + (\chi_s - \chi_{sc}^{\infty})N) + e^{\Delta\chi_s} - 1 \tag{27}$$

with again $A \approx {}^5/_6$ in a cubic lattice and $B \approx {}^1/_5$. Hence, as a result of the different end segments, the curves are shifted up or down by an amount $e^{\Delta\chi_s} - 1$, but the slope of the lines does not change.

Equation 27 can be easily understood in terms of the continuum model. The distribution of end segments for ideal chains in a continuum description was given by eq 17. This distribution function is modified because of the different end segments. If the end segments are preferentially adsorbed ($\Delta\chi_s > 0$), conformations with the end segment on the surface will have a higher statistical weight. For $\Delta\chi_s < 0$ these conformations will have a lower weight. The new weights are found by multiplication of $G(0,N)$ by a Boltzmann factor $e^{\Delta\chi_s}$. Conformations with the end segment at $z > 0$ are not affected. The new end-point distribution $G'(z,N)$ thus becomes

$$G'(z,N) = G(z,N)[1 + \delta(z)(e^{\Delta\chi_s} - 1)] \qquad (28)$$

with $G(z,N)$ the end-point distribution of ideal chains as given by eq 17 and where the delta function $\delta(z)$ is unity for $z = 0$ and zero elsewhere. The excess amount follows again from integration of eq 28 (see eq 20). The integration yields

$$\frac{\theta^{ex}}{\phi^b} = \frac{1}{C\sqrt{6}}\left[Y(-\gamma) - 1 - \frac{2\gamma}{\sqrt{\pi}}\right] + (e^{\Delta\chi_s} - 1)Y(-\gamma) \qquad (29)$$

The first term in this expression is the same as for ideal chains (eq 21), and the last term is the extra contribution of the chains having their end segment on the surface. Expanding this expression for $|\gamma| \ll 1$ and with C given by eq 25 yields eq 27, but without the term $AB = {}^1/_6$. This discrepancy was discussed at some length in section 3.

From eq 27 we find for the adsorption/depletion transition

$$\chi_{sc}^N = \chi_{sc}^\infty - \frac{AB + e^{\Delta\chi_s} - 1}{AN} \quad \text{or} \quad N_c = \frac{AB + e^{\Delta\chi_s} - 1}{A(\chi_{sc}^\infty - \chi_s)} \qquad (30)$$

which are generalized versions of eqs 10 and 11. We see that if $\Delta\chi_s$ is large, the adsorption/depletion transition becomes strongly dependent on the chain length. The chain length N_c for which $\theta^{ex} = 0$, at a given χ_s of the middle segments, is an exponential function of $\Delta\chi_s$. These results may have significant consequences for practical polymer systems, for example in critical chromatography.[2,3]

The modification for chains with two different end segments is straightforward. If both end segments have an extra adsorption energy $\Delta\chi_s$, the extra contribution of terminally adsorbed chains is twice as large, and there is an extra contribution of conformations with both ends on the surface (loops). The continuum expression for the surface excess becomes

$$\frac{\theta^{ex}}{\phi^b} = \frac{1}{C\sqrt{6}}\left[Y(-\gamma) - 1 - \frac{2\gamma}{\sqrt{\pi}}\right] + 2(e^{\Delta\chi_s} - 1)Y(-\gamma) + \sqrt{6}(e^{\Delta\chi_s} - 1)^2\left[\frac{1}{\sqrt{N\pi}} + CY(-\gamma)\right] \qquad (31)$$

The last term is the contribution of loops.[5,9] It is very small for small C, so that in first approximation the curves of θ^{ex}/ϕ^b vs N are shifted an amount $2(e^{\Delta\chi_s} - 1)$ with respect to the homopolymer case. The adsorption/depletion transition is found in a similar way as in eq 30.

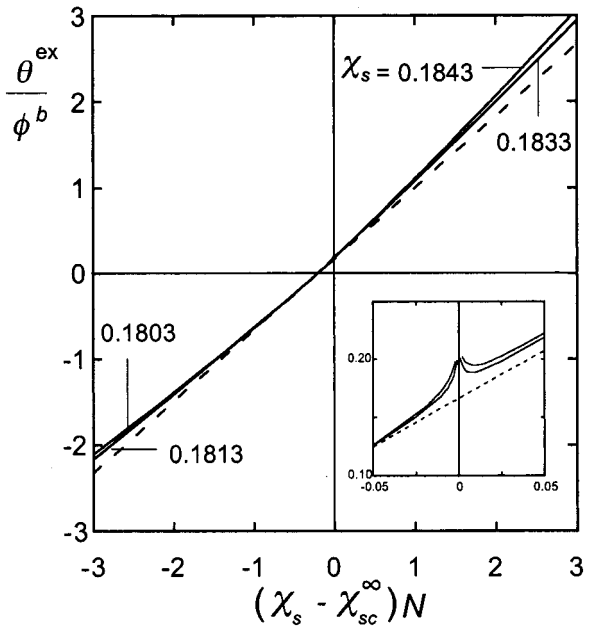

Figure 4. θ^{ex}/ϕ^b as a function of $(\chi_s - \chi_{sc}^\infty)N$ for several values of χ_s. Calculated points are connected by straight lines. Values $\chi_s > \chi_{sc}^\infty$ give the positive branches in the figure and those below χ_{sc}^∞ the negative parts. The dashed line represents eq 32. Inset: magnification for $N \leq 50$.

5. Range of Validity of the Linear Relation between θ^{ex} and N

In section 2 we have seen that close to the adsorption threshold the relation between the surface excess and the chain length can be described by the relation

$$\frac{\theta^{ex}}{\phi^b} = \frac{1}{6} + \frac{5}{6}(\chi_s - \chi_{sc}^\infty)N \qquad (32)$$

This law describes the numerical data quite well if the chain length is not too small, and the surface excess is not too large.

For small chain lengths deviations from the linear relation occur, as can be seen in the inset in Figure 3. It is not surprising that deviations occur for very short chains, since for monomers ($N = 1$) there is no adsorption threshold, and $\theta^{ex}/\phi^b = e^{\chi_s} - 1$. It is clear from Figure 3, however, that even for monomers the deviations from eq 32 are small. In the range of χ_s used in the figure, θ^{ex}/ϕ^b for $N = 1$ is around 0.20, which is not very different from the intercept 0.17 in the main figure.

Also, for large values of $|\theta^{ex}|$ deviations from eq 32 occur, as can be seen from the difference between the full and the dashed lines in Figure 3. In Figure 4 lattice results for θ^{ex}/ϕ^b are plotted as a function of $(\chi_s - \chi_{sc}^\infty)N$ for several χ_s values. The dashed line corresponds to eq 32. The inset again shows the deviations for small chain lengths. It can be seen that eq 32 gives the best description of the numerical data in the region around the adsorption threshold, where $|\theta^{ex}/\phi^b| \approx 0$ and $(\chi_s - \chi_{sc}^\infty)N \approx -{}^1/_5$. As $|\theta^{ex}/\phi^b|$ becomes larger, the deviations from eq 32 become larger. For chains of 1000 segments for example [for which $\chi_{sc}^N = \ln({}^6/_5) - 1/(5N) \approx 0.1821$] and $\chi_s = 0.1813$, the deviation from eq 32 is about 2.5%. For the same chain length and $\chi_s = 0.1803$, it is about 7%.

A similar plot as Figure 4 could be made for the continuum model (not shown). Equation 21 gives the

full expression for θ^{ex}, where C can be calculated as a function of χ_s and N by solving the implicit eq 23 iteratively. A plot of θ^{ex}/ϕ^b vs $(\chi_s - \chi_{sc}^{\infty})N$ (similar to Figure 4) goes through the origin. The linear expansion for small C ($\chi_s \approx \chi_{sc}^{\infty}$) is eq 26, which would be a straight line through the origin with slope $^5/_6$ in Figure 4. This line is shifted $^1/_5$ to the right with respect to the lattice result (the dashed line in Figure 4). The full continuum expression 21 deviates from this straight line in a similar manner as the lattice results. (The deviations are of the same order of magnitude.) Hence, a plot of θ^{ex}/ϕ^b as a function of $(\chi_s - \chi_{sc}^{\infty})N$ for the continuum model would be very similar to the results of the lattice model (Figure 3) but shifted $^1/_5$ to the right. The linear expansion in the continuum model, eq 26, is exact at $\chi_s = \chi_{sc}^{\infty}$ and deviates for larger values of $|\chi_s - \chi_{sc}^{\infty}|$.

For chains with chemically different end segments the deviations from eq 27 are of the same order of magnitude as for homopolymers for similar values of $(\chi_s - \chi_{sc}^{\infty})N$.

6. Concluding Remarks

In this paper we used a combination of a numerical lattice theory and an analytical continuum theory to investigate the relation between the surface excess and the chain length for dilute polymer solutions near the adsorption/depletion point. Under such conditions there is a very simple and very general relation between the surface excess, the bulk concentration, and the chain length of the polymer (eq 9). The adsorption/depletion point is found to be a weak function of the chain length in the lattice model. For infinitely long chains, the critical adsorption energy is given by $\chi_{sc}^{\infty} = \ln(^6/_5)$, and with decreasing chain length it is lower by an amount $1/(5N)$ (eq 10). For ideal chains the chain-length dependence of χ_{sc}^{N} is rather small. However, if the end segments are preferentially adsorbed, this dependence becomes much stronger. Such situations are likely to occur in practical situations, since, depending on the polymerization method, the end segments can have a completely different chemical structure. This may have important consequences in, for example, critical chromatography. For interpreting the data of such experiments, it is necessary to know the effect of the end groups of the polymers. In principle, an experimental validation of the theoretical predictions in this paper would be possible by means of a systematic variation of the affinity χ_s of the end groups of a given polymer.

In this paper we considered ideal chains, with no interactions between the segments. This is a very good description for dilute polymer solutions under Θ conditions. The lattice theory gives very good results for this case. A drawback of this numerical method, however, is that it does not give easy insight into the trends. Therefore, we used a continuum model, based on the Edwards equation, to investigate the same problem. The continuum model indeed predicts a linear relation between the surface excess and the chain length, with the correct slope. However, the intercept of the line predicted by the continuum model is different form that in the lattice model. As a consequence, the adsorption/depletion condition is predicted to be independent of the chain length. We have discussed several possible reasons for this discrepancy, but unfortunately we have not been able to resolve this problem. The effect of chemically different end segments is well predicted by the continuum model.

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