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# Surface Segregation in Polydisperse Polymer Melts

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ABSTRACT: The effects of polydispersity on the behavior of a polymer melt near a surface are investigated. The combined effects of the presence of a surface on the configurational freedom (entropy) of flexible chains and of the constraint that the total density is constant up to the surface yield a strikingly simple and general relation between the surface excess $\theta_N^{\mathrm{ex}}$ and the bulk volume fraction $\phi_N^b$ of a component of chain length $N$ in a polydisperse polymer melt: $\theta_N^{\mathrm{ex}}/\phi_N^b = A(1 - N/N_{\mathrm{w}})$, where $A \approx 0.195$ is a numerical prefactor and $N_{\mathrm{w}}$ the weight-averaged chain length. This relation applies *for any molecular weight distribution*. Three different methods were used to obtain this law: (i) the numerical self-consistent field model of Scheutjens and Fleer, which is exact within a mean-field assumption, (ii) an analytical approximation of this model, which gives additional physical insight, and (iii) the analogy between the surface region of a polymer melt and an ideal polymer solution close to the adsorption/depletion transition.

## 1. Introduction

The behavior of dense polymer systems near surfaces has been studied in detail before, both theoretically and experimentally. The interest in such systems derives from their relevance in practical applications. For example, many composite materials are based on polymers with filler particles dispersed in them. The mechanical properties of such composites are determined by the interplay between the particle interfaces and the polymer chains. A fundamental understanding of the factors determining the interfacial structure, such as the chain architecture, the chain length distribution, and the bulk composition, allows in principle for the controlled modification of surfaces. In this paper we investigate the influence of polydispersity.

The presence of a surface reduces the conformational entropy of a polymer coil. This entropy loss corresponds to a change in the interfacial free energy, which is important for the adhesion properties of a polymer melt. The theoretical description of the surface properties of dense polymer systems has focused mainly on monodisperse polymer systems.[1,2] Practical polymer systems, however, are always polydisperse. In such polydisperse systems, the entropy loss suffered by the long chains is larger than that by the short chains. Therefore, in a mixture of chains of high and low molecular weight with equal chemical structure, one expects the surface region to be enriched with the shorter species. Apart from differences in chain length, also differences in interaction energy with the surface,[3−5] differences in chain stiffness,[6,7] or different chain architectures[8] may drive surface segregation.

A variety of theoretical methods have been used to describe polymers near surfaces. Density functional approaches, using a square gradient approximation, have proved to give a good description of the surface segregation in blends of polymers of different chemical composition.[3,4,6] However, the correct incorporation of the chain connectivity in such models is not straightforward. Scheutjens and Fleer[9−11] developed a self-consistent-field lattice theory, which has been very successful in describing polymer adsorption and depletion. Their model uses a mean-field approximation in which correlations between the occupancy of sites within the same layer are neglected. The extension of this model to polymer melts and multicomponent systems (including block copolymers) is straightforward.[2,12]

Hariharan et al.[13] used the Scheutjens−Fleer model to study surface segregation in a bimodal polymer melt. The profiles of both components were calculated, and implications for the surface tension were discussed. In this work we do not restrict ourselves to bimodal mixtures, but we study polymer systems with an arbitrary chain length distribution.

It is known that polymer chains in a melt are effectively ideal, because excluded-volume interactions are screened.[14,15] Therefore, the analysis for a polymer melt near a surface is completely analogous to that for an ideal polymer solution near a surface. In a recent paper[16] we used a lattice model to investigate a solution of ideal polymer chains at a surface close to the adsorption/depletion transition. The effect of the chain length on the adsorption/depletion transition and on the surface excess at a certain adsorption strength was investigated. The numerical results were compared to a continuum model, and a good agreement was found. Furthermore, the effect of preferentially adsorbing end segments was investigated.

In this paper we use the Scheutjens−Fleer theory to describe a polydisperse polymer melt near a surface. We will show that the description of such a melt is almost identical to that of an ideal polymer solution at a surface close to the adsorption/depletion transition. It will be shown that there is a very simple expression that relates the surface excess of a certain component to its chain length and bulk concentration for any chain length distribution. The numerical results are compared to a simplified lattice model, for which we can obtain analytical results.

## 2. Numerical Lattice Theory

A full description of the theory can be found elsewhere in the literature.[9−11,16] Only the main features are outlined here. In the Scheutjens−Fleer theory the

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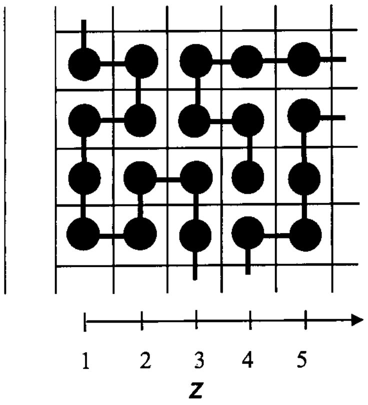

**Figure 1.** A two-dimensional schematic representation of a three-dimensional cubic lattice. Polymer segments are restricted to the layers $z \geqslant 1$.

polymer chains are described as walks upon a lattice. The space adjoining a solid surface is divided into a number of parallel lattice layers, numbered $z = 1, 2, ..., M$ (see Figure 1). The number of sites in each layer is $L$. The surface area, and hence $L$, are taken infinitely large, so that edge effects in the parallel direction can be ignored. A reflecting boundary condition is imposed at $z = M$ in this study, where $M$ is taken large enough so that near $M$ bulk properties prevail, to avoid boundary effects. The surface layer is situated at $z = 0$. Segments of the chains are restricted to layers $z \geqslant 1$. This can be considered as a model for a melt at an inert solid surface but is also a very reasonable model for the polymer/air interface of a polymer melt or for the interface between a polymer phase and a coexisting phase of a (very) poor solvent. In principle, it would be possible to allow for a gradient of air ("holes" ) or the poor solvent in the model, but we keep the system as simple as possible. The lattice properties are defined through a lattice constant $\lambda$, which is the fraction of neighboring sites that a lattice site has in an adjacent layer. The fraction of neighbors within the same layer is equal to $1 - 2\lambda$. In this paper we use a cubic lattice, with lattice coordination number $Z = 6$, and $\lambda = 1/6$. In such a cubic lattice the lattice spacing is equal to the segmental length.

We consider an athermal mixture of polymer molecules of different chain lengths $N$. The system is incompressible, so that all lattice sites are occupied by polymer segments. This implies that the following volume filling constraint must be satisfied:

$$\sum_N \phi_N(z) = 1 \tag{1}$$

for any $z$. Here $\phi_N(z)$ is the volume fraction of segments of chains of length $N$ in layer $z$. The interfacial region is in equilibrium with a bulk system of polymers. For each component we define the surface excess as

$$\theta_N^{\mathrm{ex}} = \sum_{z=1}^{M} (\phi_N(z) - \phi_N^{\mathrm{b}}) \tag{2}$$

where $\phi_N^{\mathrm{b}}$ is the bulk volume fraction of chains of length $N$. Obviously, it follows from constraint 1 that the sum of $\theta_N^{\mathrm{ex}}$ over all $N$ must be equal to zero.

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:

$$G(z) = \mathrm{e}^{-u(z)} \tag{3}$$

where $u(z)$ is the local potential of a segment, expressed in units $kT$. In the present system all segments are identical, so that we do not need an index for $G$ or $u$ to denote the segment type. The field $u(z)$ contains two contributions:

$$u(z) = u'(z) + u^a \delta_{z-1} \tag{4}$$

The first contribution $u'(z)$, which is independent of the segment type even when the segments are different, accounts for the volume-filling constraint, eq 1. It is determined self-consistently from this constraint. In the derivation it arises as a Lagrange multiplier.[9] The second contribution accounts for interactions with the surface (adsorption energy); the Kronecker delta $\delta_{z-1}$ is unity for $z = 1$ and zero elsewhere. This implies a short-ranged interaction between segments and surface ("square well" ). In the present case, there is no mixing energy, since there is only one type of segment and no solvent.

The displacement of a polymer segment in the surface layer by an other segment does not change the energy of the system, so that the adsorption energy gives a constant contribution $Lu^{\mathrm{a}}kT$ for the surface layer, regardless of the distribution of chain conformations. Hence, the only nontrivial contribution to $u(z)$ is the volume filling potential $u'(z)$.

The entropy is accounted for by assigning an end-point distribution function $G(z,s)$ to 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 segmental weighting factors $G(z)$ through the recurrence relation

$$G(z, s + 1) = G(z)\{\lambda G(z - 1, s) + (1 - 2\lambda)G(z, s) + \lambda G(z + 1, s)\} \tag{5}$$

with the initial condition $G(z, 1) = G(z)$. The distribution function of a segment $s$ in a chain of $N$ segments can be found by considering that segment $s$ joins the two chain parts $1, 2, . . ., s$ and $s, s + 1, . . ., N$. If segment $s$ is in layer $z$, the former chain part has a statistical weight $G(z, s)$ and the latter $G(z, N - s + 1)$. The statistical weight of all chains of length $N$ with segment $s$ in layer $z$ is therefore $G(z, s)G(z, N - s + 1)/G(z)$, where the division by $G(z)$ corrects for double counting of the weighting factor of segment $s$. The volume fraction of segments $s$ of chains of length $N$ in layer $z$ is proportional to this statistical weight. The total volume fraction of chains of length $N$ in layer $z$ is found by summation over all ranking numbers $s$:

$$\phi_N(z) = \frac{\phi_N^{\mathrm{b}}}{NG(z)} \sum_{s=1}^{N} G(z, s)\, G(z, N - s + 1) \tag{6}$$

The factor $\phi_N^{\mathrm{b}}/N$ is a normalization factor, ensuring $\phi_N(\infty) = \phi_N^{\mathrm{b}}$. Equations 5 and 6 with the $M$ boundary conditions 1 constitute a set of $M$ implicit equations which can be solved numerically, giving the concentration profiles $\{\phi_N(z)\}$ of all polymer chains.

The entropy $S$ of a polymer mixture near a surface, expressed in the segment concentrations, is given by[9]

$$\frac{S - S^*}{kL} = -\sum_z \sum_N \frac{\phi_N(z)}{N} \ln (\phi_N^{\mathrm{b}}) - \sum_z u(z) \qquad (7)$$

Here $S^*$ is the entropy of the reference state, for which we choose the pure, unmixed components with the same number of molecules. Since there is no mixing energy, eq 7 gives the free energy of the system, apart from the constant contribution of the adsorption energy. Subtraction of the chemical potential terms gives an expression for the surface tension $\sigma$ of a polydisperse polymer melt:[9]

$$\frac{\sigma a}{kT} = -\sum_N \frac{\theta_N^{\mathrm{ex}}}{N} - \sum_z u'(z) \qquad (8)$$

where $a$ is the area per lattice site.

For (incompressible) monomers ($N = 1$) $\phi_1(z) = 1$ for all $z > 0$, $\theta^{\mathrm{ex}} = 0$, and $u'(z) = 0$ for $z > 1$, so that eq 8 reduces to $\sigma_{\mathrm{m}}a/kT = -u'(1) = u^a$, where $\sigma_{\mathrm{m}}$ is the surface tension of pure monomer. The last equality derives from eq 4 with $u(1) = 0$. Hence, for monomers the surface tension is fully determined by the adsorption energy.

For a homodisperse melt of chains, again $\theta^{\mathrm{ex}} = 0$ and $\sigma a/kT = -\sum_z u'(z)$, where now $u'(z)$ is nonzero for $z > 1$ because of conformational contributions. When the melt is polydisperse, the Gibbs excess term $\theta_N^{\mathrm{ex}}/N$ contributes as well. With eq 4, eq 8 may now also be written as

$$\frac{(\sigma - \sigma_m)a}{kT} = -\sum_N \frac{\theta_N^{\mathrm{ex}}}{N} - \sum_z u(z) \qquad (9)$$

## 3. Numerical Results

The values of $u(z)$ in all $M$ layers are determined numerically from the $M$ self-consistent equations. These values do not depend on the value of the adsorption energy $u^a$ as they are only determined by the volume-filling constraint. The only effect of varying $u^a$ is that $u'(1)$ is changed according to $u'(1) = u(1) - u^a$, where $u(1)$ is independent of $u^a$. The resulting potential field for a mixture of three different chain lengths with equal bulk volume fractions is shown in Figure 2. The potential oscillates, because of the impenetrability of the surface and the volume-filling requirement,[9] and is very short-ranged. The range is independent of the chain length. For a melt consisting of infinitely long chains, the sum of $u(z)$ over all layers has a limiting value $-B$. For a cubic lattice $B \approx 0.1842$. For finite chain lengths the results are described very accurately by the equation

$$\sum_z u(z) = -B\left(1 - \frac{1}{N_{\mathrm{w}}}\right) \qquad (10)$$

where $N_{\mathrm{w}} = \sum_N N\phi_N^{\mathrm{b}}$ is the weight-averaged chain length. Note that eq 10 is independent of the precise chain-length distribution; only the weight-average $N_{\mathrm{w}}$ enters.

The volume fraction profiles of the components in the mixture of Figure 2 are shown in Figure 3. It is clear that the longest chains are depleted from the surface, whereas there is a net adsorption of the shortest chains. The profile of the chains of intermediate length is nonmonotonic. There is a maximum at an intermediate distance from the surface, whereas close to the surface the concentration is less than its bulk value. This nonmonotonic behavior is due to the volume-filling constraint: the chains of intermediate length fill up the holes left by the short and long chains, which have intrinsically different decay lengths for the profiles. It must be noted that the surface segregation due to differences in molecular weight is small. The enrichment or depletion near the surface is, for these chain lengths, only a few percent of the bulk concentration. The surface segregation becomes stronger if the differences in chain length are larger.

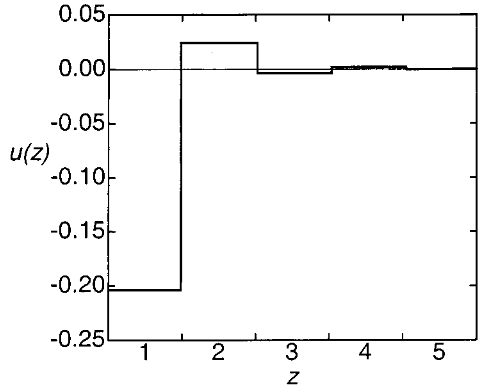

**Figure 2.** Potential profile of the polymer segments in a mixture of chains of 200, 600, and 1000 segments, all with equal bulk volume fraction ($\phi_N^{\mathrm{b}} = 1/3$).

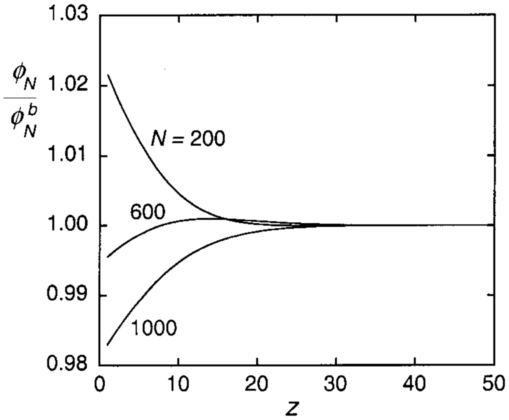

**Figure 3.** Volume fraction profiles in a mixture of chains of 200, 600, and 1000 segments, all with equal bulk volume fraction ($\phi_N^{\mathrm{b}} = 1/3$).

The surface excess can be calculated with eq 2. Figure 4 shows the surface excess relative to the bulk volume fraction as a function of the relative chain length $N/N_{\mathrm{w}}$ for several different chain length distributions, as indicated in the legend. It can be seen from this figure that the relation between $\theta_N^{\mathrm{ex}}/\phi_N^{\mathrm{b}}$ and $N$ is linear, for any distribution. Furthermore, the intercept with the vertical axis is the same for all distributions. Also, for distributions with the same weight-averaged chain length $N_{\mathrm{w}}$ but a different number-averaged chain length $N_{\mathrm{n}}$, the relation between $\theta_N^{\mathrm{ex}}$ and $N$ is identical. From the condition that the sum over all $\theta_N^{\mathrm{ex}}$ is zero, it follows immediately that the line must cross the horizontal axis at $N = N_{\mathrm{w}}$. The results in Figure 4 can thus be summarized as

$$\frac{\theta_N^{\mathrm{ex}}}{\phi_N^{\mathrm{b}}} = A\left(1 - \frac{N}{N_{\mathrm{w}}}\right) \qquad (11)$$

with $A \approx 0.195$. Only for very short chains ($N \lesssim 10$) a

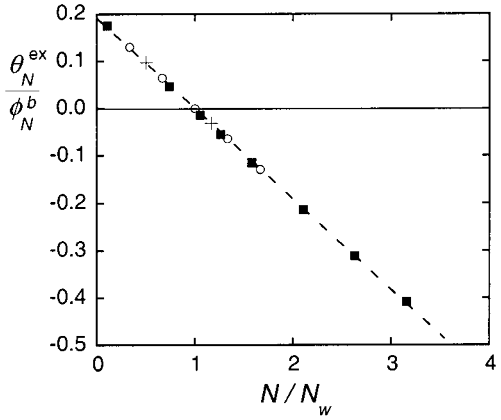

**Figure 4.** Surface segregation in a polydisperse polymer melt for several chain length distributions: crosses, bimodal distribution with $M_w = 600$, $M_n = 438$; circles, pentamodal distribution with $M_w = 600$, $M_n = 525$; squares, octamodal distribution with $M_w = 290$, $M_n = 162$. The dashed line corresponds to eq 11.

slight deviation occurs from the linear relation. We see that $\theta_N^{ex}/\phi_N^b$ depends only on $N$ and $N_w$ but not on any other aspect of the chain length distribution. This result is remarkably simple. To our knowledge, it has never been mentioned before in the literature. Remarkably, a linear $N$ dependence of $\theta_N^{ex}/\phi_N^b$ is found also for an ideal (extremely dilute) solution at an interface for which the adsorption energy is close to the adsorption/depletion threshold.[16] The reasons for this similar behavior will be explained in the next section.

Substitution of eqs 10 and 11 in eq 9 results in a very simple expression for the surface tension of a polydisperse melt:

$$\frac{(\sigma - \sigma_m)a}{kT} = B\left(1 - \frac{1}{N_w}\right) + A\left(\frac{1}{N_w} - \frac{1}{N_n}\right) \qquad (12)$$

where $N_n$ is the number-averaged chain length, defined as $1/N_n = \sum_N \phi_N^b/N$. The first term is the same as for a monodisperse melt,[2] and the second term accounts for polydispersity. Since $A$ and $B$ are nearly the same, the right-hand side is approximately $B(1 - 1/N_n)$: for a polydisperse system $\sigma$ is determined mainly by the number-averaged chain length $N_n$. In principle, eq 12 allows an experimental confirmation of the results in this paper, if it would be possible to determine the surface tension of a melt accurately enough.

Note that the results obtained in this section apply to a polymer melt at a solid surface but give also a reasonable description of the polymer/air interface of the polymer melt, since the interfacial region of a melt is usually very sharp.

## 4. Comparison to an Ideal Polymer Solution at a Surface near the Adsorption/Depletion Transition

It is well-known that chains in a polymer melt are ideal, because the excluded-volume interactions are screened.[14,15] In Figure 2 we have seen that the potential $u(z)$ in a polymer melt has an oscillatory profile, as a combined effect of the impenetrability of the surface and the volume-filling constraint. These oscillations are very short-ranged: only the first one or two layers have a potential that is significantly different from zero. We may therefore expect the surface behavior of polymer chains in a melt to be similar to the behavior of an ideal (extremely dilute) polymer solution near a surface close to the adsorption/depletion transition. In the former case the profile $u(z)$ (Figure 2) may be approximated as a square well potential: $u(z) \approx 0$ for $z > 1$ and a well depth $u(1)$ which is determined by the volume-filling constraint (and which is independent of the adsorption energy $u^a$). For the latter case, the potential $u(z)$ is again zero outside the first layer, and the well depth is determined by the interaction with the surface. The volume filling is unimportant for dilute polymer solutions.

For adsorption of polymers from a binary solution, a dimensionless adsorption energy parameter $\chi_s$ can be introduced:[17]

$$\chi_s = -(u_p^a - u_0^a) \qquad (13)$$

where $u_p^a$ is the (short-ranged) interaction energy between a polymer segment and the surface (the same as $u^a$ in eq 4) and $u_0^a$ that between a solvent molecule and the surface, both in units $kT$. The transition between positive adsorption ($\theta_N^{ex} > 0$) and negative adsorption (depletion, $\theta_N^{ex} < 0$) occurs at a threshold value of $\chi_s$, denoted as $\chi_{sc}$. A segmental adsorption energy $\chi_s = \chi_{sc}$ just compensates the conformational loss due to the presence of the surface. For $\chi_s < \chi_{sc}$ the polymer is depleted from the surface, and for $\chi_s > \chi_{sc}$ it adsorbs. In a recent paper,[16] we have investigated the behavior of ideal polymers at a surface near the adsorption/depletion transition. It was shown that $\chi_{sc}$ is a (weak) function of the chain length. For infinite chain length $\chi_{sc}$ equals the critical adsorption energy, given by[9,18]

$$\chi_{sc}^{\infty} = -\ln(1 - \lambda) \qquad (14)$$

and with decreasing chain length, the adsorption/depletion transition shifts to slightly lower $\chi_s$ values:

$$\chi_{sc}^N = \chi_{sc}^{\infty} - \frac{C}{N} \qquad (15)$$

with $C \approx {}^1/_5$. The surface excess of a polymer molecule in dilute solution at a $\chi_s$ value close to the adsorption threshold[19] was found to be a linear function of the chain length $N$:[16]

$$\frac{\theta_N^{ex}}{\phi_N^b} = \frac{5}{6}(C + (\chi_s - \chi_{sc}^{\infty})N) \qquad (16)$$

In the case of a polydisperse polymer melt there is no solvent. Since all segments are identical, there is no energetic contribution to the potential. The volume-filling potential (which has an entropic origin) now plays the role of an effective wall potential $u$. This effective wall potential $u$ may be estimated, for example, as the sum of $u(z)$ over all lattice layers. It has a small negative value (see eq 10). If $-u < \chi_{sc}^N$, the potential is too weak to compensate the loss of conformational entropy, and depletion takes place ($\theta_N^{ex} < 0$). If $-u > \chi_{sc}^N$, the chains adsorb preferentially ($\theta_N^{ex} > 0$). For chains that have a zero excess, $-u = \chi_{sc}^N$. In a polydisperse melt, this is the case for chains of length $N_w$ (see eq 11). We may conjecture that the magnitude of the effective wall potential $u$ is such that it just coincides with the adsorption/depletion point of chains of length $N_w$. For shorter chains ($N < N_w$), the wall potential is sufficient for positive adsorption ($\theta_N^{ex} > 0$), whereas for $N > N_w$ it is insufficient ($\theta_N^{ex} < 0$).

The linear relation between $\theta_N^{ex}/\phi_N^b$ and $N$ in a polydisperse polymer melt is almost the same as the one we found before for a dilute solution near the adsorption/depletion transition, eq 16.[16] For the latter case the slope of the line is determined by the difference $\chi_s - \chi_{sc}^{\infty}$, whereas in a melt it is determined by the weight-averaged chain length $N_w$, because the self-consistent potential is determined by $N_w$. The intercept ($A$ in eq 11) was found to be $^1/_6$ for the ideal solution, whereas for the melt we find $A \approx 0.195$. This difference is probably caused by the difference in the potential profile: in the ideal solution the potential is nonzero only in the first layer, while in the melt it oscillates in the first few layers.

We may quantitatively compare the conditions for which the surface excess vanishes. For the polydisperse melt we have $\theta_N^{ex} = 0$ for $N = N_w$. According to eq 10, the field is

$$\sum_z u(z) = -0.1842 + \frac{0.1842}{N_w} \tag{17}$$

For the same chain length adsorbing from dilute solution $\theta_N^{ex} = 0$ when $u(1) = \sum_z u(z)$ equals $-\chi_{sc}^N$. With eq 15

$$\sum_z u(z) = -0.1823 + \frac{0.2}{N_w} \tag{18}$$

Numerically, the results are extremely close. The minor differences are again caused by the fact that in the melt the potential oscillates.

## 5. Simplified Lattice Model

We have seen that the surface segregation in a polydisperse melt can be described by a strikingly simple law (eq 11). This law was found by careful examination of numerical results of many self-consistent-field calculations. The numerical results could be interpreted using the analogy with a dilute solution of chains near the adsorption/depletion transition.

In this section we use a simplification of the full lattice model to derive the same results analytically. For this purpose we consider a polydisperse polymer melt in a gap of $2M$ lattice layers wide between two surfaces, as in sections 2 and 3. In all layers apart from the surface layers, segments have a coordination number $Z$, as in the bulk, but segments in the surface layer have an effective coordination number $Z(1 - \lambda)$. This reduced coordination number accounts for the loss of conformational freedom of chains near the surface. (The number of possible directions for bonds to a segment in a surface layer is $Z(1 - \lambda)$ rather than $Z$.) To be able to obtain explicit analytical expressions, we assume that it is allowed to use for multilayered gaps an *averaged* coordination number for the counting of conformations. This averaged coordination number in the gap is defined as

$$\langle Z\rangle = \frac{1}{2M}[2Z(1-\lambda) + (2M-2)Z] = \left(\frac{M-\lambda}{M}\right)Z \tag{19}$$

Using an average coordination number implies that the volume fraction of polymers of length $N$ in the gap is assumed not to vary in the normal direction; i.e., $\phi_N(z)$ is constant throughout the gap. This assumption might be justified by the observation that the volume fraction does not change very much near the surface (Figure 3). Obviously, for a gap of one lattice layer ($M = {}^1/_2$), $\langle Z\rangle = Z(1 - 2\lambda) = 4$. For such a single layer the subsequent treatment is exact.

The total number of lattice sites in the gap is $V = 2ML$, with $L$ the number of lattice sites per layer. Since the whole lattice has to be filled with chains, $V = \sum_N n_N N$, with $n_N$ the number of chains of length $N$ in the gap. The partition function for a mixture of chains in a lattice of volume $V$ with coordination number $\langle Z\rangle$ has been derived by Flory:[15]

$$\Omega = V!\prod_N \frac{1}{n_N!}\left(\frac{\langle Z\rangle}{V}\right)^{n_N(N-1)} \tag{20}$$

It is convenient to evaluate $\Omega$ with respect to a reference state (which we will denote with an asterix). We choose again the pure, unmixed components with $n_N$, $n_{N'}$, ... molecules. The degeneracy for the reference state is given by[9,15]

$$\Omega^*_N = \frac{(n_N N)!}{n_N!}\left(\frac{Z}{n_N N}\right)^{n_N(N-1)} \tag{21}$$

and $\Omega^* = \prod_N \Omega^*_N$. Combination of eqs 20 and 21 gives an expression for the entropy of a polymer mixture in a gap:

$$\frac{S - S^*}{kV} = \frac{1}{V}\ln\left(\frac{\Omega}{\Omega^*}\right) = -\sum_N \frac{\phi_N}{N}\ln(\phi_N) + \left(\sum_N \frac{\phi_N}{N} - 1\right)\ln\left(\frac{Z}{\langle Z\rangle}\right) \tag{22}$$

We assume that the gap is in equilibrium with a bulk system of polymers with a certain chain length distribution. The equilibrium situation is found from a minimization of the grand potential:

$$\Psi - \Psi^* = -T(S - S^*) - \sum_N n_N(\mu_N - \mu^*_N) \tag{23}$$

where $\mu_N - \mu^*_N$ is the chemical potential difference of chains of length $N$ with respect to the reference state. This can be found from the bulk partition function $\Omega^b$ as

$$\frac{\mu_N - \mu^*_N}{kT} = -\left(\frac{\partial \ln(\Omega^b/\Omega^*)}{\partial n_N}\right)_{n_{N'\neq N},T} \tag{24}$$

where $\Omega^b$ is given by eq 20, with the bulk coordination number $Z$ instead of $\langle Z\rangle$. The result of this differentiation can be found in ref 15.

Minimization of the grand potential leads to the following chain length distribution in the gap:

$$\frac{\phi_N}{\phi_N^b} = \frac{Z}{\langle Z\rangle}e^{-\alpha N} = \left(\frac{M}{M-\lambda}\right)e^{-\alpha N} \tag{25}$$

where $\alpha$ is a Lagrange multiplier accounting for volume filling. The chain length-induced surface segregation is relatively weak, so that $\alpha$ is small. If we assume that

$\alpha \ll 1/N$, we can expand the exponential in eq 25:

$$\frac{\phi_N}{\phi_N^{\mathrm{b}}} = \left(\frac{M}{M-\lambda}\right)(1-\alpha N) \tag{26}$$

The condition that the sum of all $\phi_N$'s must be equal to unity yields $\alpha = \lambda/(N_{\mathrm{w}}M)$. It follows that the assumption of small $\alpha N$ is justified for large $M$. The excess per surface is calculated as

$$\theta_N^{\mathrm{ex}}(M) = M(\phi_N - \phi_N^{\mathrm{b}}) = \frac{\lambda M}{M-\lambda}\left(1-\frac{N}{N_{\mathrm{w}}}\right) \tag{27}$$

If now we take the limit for infinite gap width, we find an expression for the excess amount at an isolated surface. The result is

$$\frac{\theta_N^{\mathrm{ex}}}{\phi_N^{\mathrm{b}}} = \lambda\left(1-\frac{N}{N_{\mathrm{w}}}\right) \tag{28}$$

which is the same as eq 11, apart from a small deviation in the intercept: the numerical prefactor $A$ in eq 11 was found to be around 0.195 for a cubic lattice, whereas the approximate analytical treatment predicts a prefactor $\lambda = {}^1/_6$.

Using eqs 22 and 25, we can write for the entropy of the polymer mixture in the gap per surface:

$$\frac{S-S^*}{kML} = -\sum_N \frac{\phi_N}{N}\ln(\phi_N^{\mathrm{b}}) + \alpha + \ln\left(\frac{\langle Z\rangle}{Z}\right) \tag{29}$$

This expression can be compared to the expression for the entropy in the Scheutjens–Fleer theory, eq 7. The difference between the two approaches is that we used an average coordination number in this section, so that the profiles are homogeneous for each component. The Lagrange parameter $\alpha$ is related to the potential field $u(z)$ in the full lattice model of section 2. The difference is that the field $u(z)$ can vary along the $z$-axis, whereas $\alpha$ is averaged over the whole gap. If we take the average over $z$ in eq 7 and compare the result with eq 29, we find that the average potential in the SF theory $\bar{u} \equiv \sum_z u(z)/M$ is related to the Lagrange multiplier $\alpha$ as $\bar{u} = \alpha + \ln(\langle Z\rangle/Z)$. For infinite gap width this average potential goes to $M\bar{u} = -\lambda(1 - 1/N_{\mathrm{w}})$, which is almost the same result as eq 10, again with a slightly different prefactor.

Equation 25 can be interpreted as a Boltzmann distribution of chains in a gap. The exponent of the Boltzmann factor then corresponds to the free energy needed to squeeze a chain of length $N$ in the gap. This free energy is proportional to the length of the chain. This is not surprising, because chains in a melt are ideal (see section 4), and for ideal (Gaussian) chains it is well-known that the elastic free energy upon compression is proportional to $N$.[14,20] Note that eq 25 applies even if the gap is much wider than the radius of gyration of the chains. In that case, the surface affects only those chains that have their center of mass closer to the surface than their radius of gyration. These chains have a reduced conformational entropy, because they can explore a smaller volume than in the bulk due to the impenetrable surface. This entropy loss is again proportional to the chain length. The competition between the volume-filling requirement and the elastic free energy of the chains results in the simple relation for the surface segregation, eq 28.

## 6. Concluding Remarks

In this paper we have shown that there is a very simple and very general relation between the surface excess, the bulk concentration, and the chain length of a component in a polydisperse polymer mixture (eq 11). The results of the full lattice theory (section 2) are exact within the mean-field approximation. Furthermore, it is known that for concentrated polymer solutions and for melts the mean-field approximation is effectively exact. In section 4 we demonstrated the similarity between a polydisperse melt near a surface and a dilute solution of ideal chains near a surface for which the adsorption energy is close to the adsorption threshold. In section 5 we used a simplified lattice model to derive analytical expressions.

Surface segregation in a polymer melt is fully driven by entropic factors. The entropy loss of a polymer chain upon confinement next to a surface is larger for long chains than for short ones. This entropy loss determines the adsorption threshold $\chi_{\mathrm{sc}}^N$, the minimum adsorption energy for chains to adsorb from solution. In a recent paper,[16] we have shown that the adsorption/depletion transition for ideal chains is a function of the chain length. This chain-length dependence of $\chi_{\mathrm{sc}}^N$ may be interpreted as the factor driving surface segregation in a polydisperse polymer melt. The simplified lattice approach (section 5) suggests that the surface segregation is related to the compression of chains that have their center of mass closer to the surface than their radius of gyration. For ideal chains this entropy loss is proportional to the chain length.

The surface segregation of chains due to differences in molecular weight is relatively small. Depletion in dilute polymer solutions is, for example, much stronger. However, we believe that the results obtained in this paper are very interesting from a fundamental point of view, because of their simplicity and generality. For ideal chains in solution we have also investigated the effect of chemically different end-segments.[16] In practical polymer systems the end segments are usually different, for example because they carry a residual group from a polymerization initiator. It was found that the influence of the chain length is strongly enhanced if the end segments adsorb preferentially. For short chains the end segments are relatively more important than for long chains. Hence, we expect that the preferential adsorption of short chains is much larger in this case. This would result in a higher value of the prefactor $A$ in eq 11. Preliminary calculations (not shown) suggest that this is indeed the case. In practical systems, therefore, polydispersity may have a significant effect on the surface properties of a polymer melt.

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