# Statistical Thermodynamics of Block Copolymer Adsorption. 1. Formulation of the Model and Results for the Adsorbed Layer Structure

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ABSTRACT: A generalization of the self-consistent-field theory of Scheutjens and Fleer for adsorption of homopolymer from a binary solution toward a theory for adsorption of block copolymers from a multicomponent mixture is presented. No a priori assumptions about the conformations of the adsorbed molecules are made. Equations for the conformation probabilities, the segment density profiles, and the free energy are derived. Results on the segment density distribution in adsorbed layers of diblock and triblock copolymers are given. We find that diblock copolymers tend to adsorb with the adsorbing block rather flat on the surface and the less adsorbing or nonadsorbing block in one dangling tail protruding far into the solution. We compare these predictions with those for terminally anchored chains and find overall agreement but also typical differences. The effect of the surface affinity and the solvent quality on the structure of adsorbed diblock copolymers is discussed.

## 1. Introduction

Block copolymers play an important role as additives in many industrial products like inks, paints, lubricants, coatings, etc. In these systems block copolymers are used since they are very effective in stabilizing colloidal suspensions. This property finds its origin in the way block copolymers adsorb. An adsorbed diblock copolymer has usually one block adsorbed on the surface in a rather flat conformation, whereas the other block, having a lower surface affinity, forms a dangling tail. This has important consequences for the interaction between two layers of adsorbed diblock copolymers, since formation of bridges in this situation is unlikely. Hence, block copolymers are better stabilizers than homopolymers. Because of their freely dangling blocks, adsorbed diblock copolymers are often interpreted and theoretically modeled as terminally anchored chains. For example, Hadziioannou et al.[1] applied the Alexander–de Gennes analysis[2,3] for anchored chains to adsorption of diblock copolymers.

In this article we present a self-consistent-field theory for the adsorption of block copolymers of any block sequence without making a priori assumptions about the conformations of the adsorbed molecules. The theory is a generalization of the Scheutjens and Fleer theory[4–6] for the adsorption of homopolymers from a binary mixture. For binary mixtures containing a solvent monomer, the extension of the Scheutjens and Fleer theory to diblock copolymers is straightforward as has been shown by Leermakers et al.,[7] who modeled the self-association of small surfactant molecules. Here we will extend the Scheutjens and Fleer theory to the case of adsorption of block copolymers from a multicomponent mixture of arbitrary composition, including the case that no monomeric solvent is present.

Scheutjens and Fleer use a lattice model to achieve a finite number of different conformations of adsorbed molecules. The distribution of molecules over the various possible conformations is found by minimization of the free energy, subject to the packing constraint that every lattice layer has to be filled completely. The minimum of the free energy is obtained by differentiating the logarithm of the canonical partition function, $Q$, with respect to the number of polymer molecules in a given conformation. In order to satisfy the constraint of a filled lattice Scheutjens and Fleer perform the differentiation of ln $Q$ by adding a polymer chain of $r$ segments long in a given conformation and at the same time subtracting $r$ solvent monomers. This method works only if a monomer solvent is present in the mixture. In this article the Lagrange multiplier method for obtaining a constrained extremum of a function is applied to the Scheutjens and Fleer formalism in such a way that no solvent monomers need be present in the mixture. Similar procedures have been used by other authors.[8–13]

After the description of the theory, we present some typical results on the segment distribution in adsorbed layers of block copolymers. In a subsequent publication[14] we report more systematic results of the dependence of the adsorbed amount and the hydrodynamic layer thickness on the internal composition of block copolymers.

## 2. Theory

**2.1. Model.** Consider a lattice between two parallel plates (see Figure 1). The lattice layers parallel to the surface are numbered from one surface to the other ($z$ = 1, 2, ..., $M$) and have $L$ lattice sites each. Every lattice site has $Z$ neighboring sites, a fraction $\lambda_0$ of which is in the same layer and fractions $\lambda_1$ of which are in each of the adjacent layers. For example, in a hexagonal lattice ($Z$ = 12) $\lambda_0$ = $^6/_{12}$ and $\lambda_1$ = $^3/_{12}$. Each lattice site is assumed to be occupied by some segment. In this context, a solvent molecule (if present) contains usually one, but sometimes more, segments. Segments in the layers adjacent to the surfaces are considered to be adsorbed.

A polymer molecule is represented by a chain of $r_i$ connected segments numbered $s$ = 1, 2, ..., $r_i$. We adopt the index $i$ to denote the type of molecule. For copolymers it is necessary to know the chemical nature of each segment $s$. The segment types are denoted by A, B, C, .... For example, in the block copolymer AAABBBB segments $s$ = 1–3 are of type A and $s$ = 4–7 of type B. Solvent molecules and homopolymers are considered as special types of block copolymers. Therefore, we will use the general word molecule.

In equilibrium, the molecules are distributed over the various possible conformations in the lattice in such a way that the free energy is at its minimum. We will adopt a mean-field approximation within each lattice layer; i.e.,

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density fluctuations within each layer are neglected, and only the distance to either surface is relevant. Therefore, to characterize the energy of a molecule of type $i$ in a certain conformation $c$, it is sufficient to specify the number $r_{Ai}^c(z)$ of segments of each segment type (A) that this conformation has in layer $z$. Thus, a conformation is uniquely defined by specifying the layer number of every segment $s$. The number of molecules $i$ in conformation $c$ is indicated as $n_i^c$. The conformation distribution of all molecules $i$ between the two surfaces is denoted by $\{n_i^c\}$. The various possible conformations are not equally probable: their frequency depends on the interaction energies, which are a function of the local concentrations of segments. Since we consider only density gradients perpendicular to the surfaces, we use average volume fractions in each lattice layer. The volume fractions are as follows: $\phi_{Ai}(z)$ for segments A of molecules $i$ in layer $z$, $\phi_i(z)$ for all segments belonging to molecules $i$, and $\phi_A(z)$ for all segments of type A, irrespective of the type of molecule. Obviously, $\phi_i(z) = \sum_A \phi_{Ai}(z)$ and $\phi_A(z) = \sum_i \phi_{Ai}(z)$. If molecules $i$ have no segment of type A, then $\phi_{Ai}(z)$ is zero. The total number of molecules $i$ between the two surfaces is denoted by $n_i$, with $n_i = \sum_c n_i^c$. Since all lattice sites are occupied, $\sum_i r_i n_i = ML$.

**2.2. Partition Function.** The grand canonical partition function, $\Xi$, of the system is given by a summation of canonical partition functions $Q$, weighted with their appropriate Boltzmann factors

$$\Xi(\{\mu_i\},M,L,T) = \sum_{\text{all } \{n_i^c\}} Q(\{n_i^c\},M,L,T) \exp[\sum_i n_i\mu_i/kT] \quad (1)$$

where $\mu_i$ is the chemical potential of molecules $i$. The summation on the right-hand side of eq 1 is taken over all possible distributions of all molecules over the various conformations. Each set $\{n_i^c\}$ represents a single distribution that fills each lattice layer exactly.

We derive an expression for the canonical partition function, $Q$, which equals $\Omega \exp(-U/kT)$, where $\Omega(\{n_i^c\},M,L)$ is the degeneracy. Because of the mean-field approximation, the total energy, $U$, is constant for a given concentration profile and, consequently, for a given set $\{n_i^c\}$. If we define $Q^* = \prod_i Q_i^*$, where $Q_i^* = \Omega_i^* \exp(-U_i^*/kT)$ is the canonical partition function of $n_i$ molecules $i$ in pure amorphous bulk state, we can write

$$Q = Q^*\left(\frac{\Omega}{\Omega^*}\right) \exp[-(U - U^*)/kT] \quad (2)$$

where $\Omega^* = \prod_i \Omega_i^*$ and $U^* = \sum_i U_i^*$.

The exponential in eq 2 contains the energy difference between the system and the reference state. The combinatory factor $\Omega_i^*(n_i)$ is the number of ways to arrange $n_i$ molecules $i$ over $r_i n_i$ lattice sites in a pure phase of liquid molecules $i$. An expression for $\Omega_i^*$ has been derived by Flory:[15]

$$\Omega_i^* = \frac{(r_i n_i)!}{n_i!}\left(\frac{Z}{r_i n_i}\right)^{(r_i-1)n_i} \quad (3)$$

The factorial $(r_i n_i)!$ accounts for the number of ways to place $r_i n_i$ distinguishable monomers over $r_i n_i$ lattice sites. A correction factor $Z/(r_i n_i)$ comes in for each of the $(r_i - 1)n_i$ monomers linked to a previous monomer. These monomers have only $Z$ instead of $r_i n_i$ possible locations (if internal overlap of segments is allowed). Finally, a factor $n_i!$ corrects for the fact that the $n_i$ molecules are mutually indistinguishable.

Scheutjens and Fleer[4] have derived an expression for $\Omega$ for the case of a binary mixture of a polymer and a solvent in a density gradient. It is easy to extend their equation so that it applies to a multicomponent mixture in a density gradient. The result is

$$\Omega = (L!)^M \prod_{i,c} [\lambda^c (Z/L)^{r_i-1}]^{n_i^c}/n_i^c! \quad (4)$$

where $\lambda^c$ is a multiple product of $r_i - 1$ bond weighting factors $\lambda_0$ and/or $\lambda_1$; see eq 5 below.

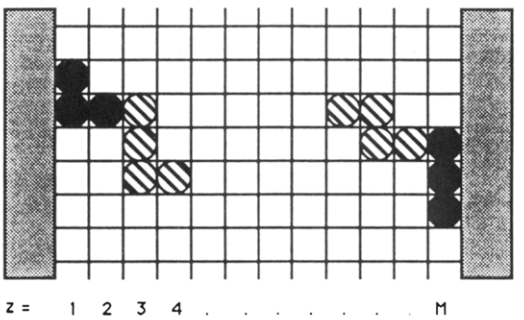


**Figure 1.** Two chains AAABBBB in a lattice between two surfaces.

There is a close analogy between eqs 3 and 4. The $M$ factorials $L!$ account for the number of ways of placing $LM$ distinguishable monomers over the $M$ distinguishable layers with $L$ sites each and replace the factorial $(r_i n_i)!$ in eq 3. The factor $\lambda^c(Z/L)^{r_i-1}$ corrects for the $r_i - 1$ segments per chain $i$ in conformation $c$ that are linked to a previous one. This correction factor can be illustrated as follows.

As defined before, a conformation is characterized by specifying the layer number for each segment. For the first segment of a molecule in conformation $c$ (which is to be placed in a specific layer) there are $L$ possible locations. For the second segment there are $\lambda^c(2|1)Z$ possible locations, where $\lambda^c(2|1)$ is the fraction of nearest neighbors that segment 1 has in the layer where segment 2 is found. Clearly, $\lambda^c(2|1)$ is either $\lambda_0$ (if segments 1 and 2 are in the same layer) or $\lambda_1$ (if they are in adjacent layers). The number of arrangements within conformation $c$ is then given by $L\lambda^c Z^{r_i-1}$ where $\lambda^c$ is defined as

$$\lambda^c = \lambda^c(r_i|1) = \prod_{s=2}^{r_i} \lambda^c(s|s-1) \quad (5)$$

For each of the $n_i^c$ chains in conformation $c$ the correction factor is the ratio between $L\lambda^c Z^{r_i-1}$ and $L^{r_i}$, which is the number of possibilities for $r_i$ independent segments. Finally, the factorial $n_i^c!$ in eq 4 corrects for the fact that the $n_i^c$ molecules $i$ in conformation $c$ are indistinguishable.

Equation 5 gives the multiple product of $r_i - 1$ bond weighting factors for a complete chain. It is sometimes convenient to consider only part of a chain, from segment $s'$ to $s''$. Therefore, we define $\lambda^c(s''|s')$ as

$$\lambda^c(s''|s') = \prod_{s=s'+1}^{s''} \lambda^c(s|s-1) \quad (6)$$

The logarithm of $\Omega/\Omega^*$ can be approximated by applying Stirling's formula, $\ln N! = N \ln N - N$. From eqs 3 and 4 we find the relatively simple expression

$$\ln \frac{\Omega}{\Omega^*} = \sum_{i,c} n_i^c \ln\left(\frac{L\lambda^c}{r_i n_i^c}\right) \quad (7)$$

Substitution of eq 7 in eq 2 leads to the following expression for the logarithm of the canonical partition function, $Q$:

$$\ln Q = \sum_{i,c} n_i^c \ln\left(\frac{L\lambda^c}{r_i n_i^c}\right) - (U - U^*)/kT + \ln Q^* \quad (8)$$

**2.3. Equilibrium Distribution.** We will make the usual assumption of replacing the sum in the right-hand side of eq 1 by its maximum term. The maximum term of the sum is determined by that set of conformations $\{n_i^c\}$ that satisfies the total differential

$$\sum_{i,c}\left[\left(\frac{\partial \ln Q}{\partial n_i^c}\right)_{M,L,T} + \frac{\mu_i}{kT}\right] dn_i^c = 0 \quad (9)$$

The variables $n_i^c$ are subject to the constraints

$$L - \sum_{i,c} n_i^c r_i^c(z) = 0, \quad \text{for } z = 1, 2, ..., M \quad (10)$$

where $r_i^c(z)$ is the number of segments that a molecule $i$ in conformation $c$ has in layer $z$. Obviously, $\sum_z r_i^c(z) = r_i$. Physically, eq 10 means only that each lattice site in any layer $z$ must be occupied.

It is convenient to use the multiplier method of Lagrange to obtain a constrained extreme of a function. In this method a set of multipliers, $\alpha(z)$, one for each constraint, is introduced and a new unconstrained function, $f$, is defined by adding to $\ln \Xi$, for each layer, a term $\alpha(z)$ times the constraint:

$$f = \ln Q + \sum_i \frac{\mu_i n_i}{kT} + \sum_z \alpha(z)[L - \sum_{i,c} n_i^c r_i^c(z)] \quad (11)$$

The unconstrained function, $f$, has a saddle point in the $(\{n_i^c\},\{\alpha(z)\})$ space, i.e., a maximum on $\{n_i^c\}$ combined with a minimum on $\{\alpha(z)\}$. Moreover, in this saddle point $f$ satisfies the constraining relations, so that the added terms are zero. Hence, in this point the function $f$ equals the maximum term of $\ln \Xi$ for the equilibrium set $\{n_i^c\}$.

The equilibrium set $\{n_i^c\}$ and the $M$ multipliers $\alpha(z)$ are given by the set of equations

$$\frac{\partial f}{\partial n_j^d} = \frac{\partial \ln Q}{\partial n_j^d} + \frac{\mu_j}{kT} - \sum_z \alpha(z)\, r_j^d(z) = 0, \quad \text{for all } n_j^d \in \{n_j^c\}$$

$$\frac{\partial f}{\partial \alpha(z)} = 0, \quad z = 1, 2, ..., M \quad (12)$$

For the derivative $\partial \ln Q/\partial n_j^d$ we use eq 8. The differential of $-kT \ln Q^*$ with respect to $n_j^d$ gives the chemical potential $\mu_j^*$ of a molecule $j$ in the pure amorphous state. Hence, the first term of $\partial f/\partial n_j^d$ in eq 12 is

$$\frac{\partial \ln Q}{\partial n_j^d} = \ln \frac{L\lambda^d}{r_j n_j^d} - 1 - \frac{\partial (U - U^*)/kT}{\partial n_j^d} - \mu_j^*/kT \quad (13)$$

We assume the energy $U - U^*$ to depend only on the segment density distribution of every segment type, irrespective of the type of molecule or conformation to which it belongs. The third term on the right-hand side of eq 13 then becomes

$$\frac{\partial (U - U^*)/kT}{\partial n_j^d} = -\frac{\partial U^*/kT}{\partial n_j} + \sum_{z,A} \frac{\partial U/LkT}{\partial \phi_A(z)} \frac{\partial L\phi_A(z)}{\partial n_j^d} \quad (14)$$

Differentiating $U^*$ with respect to $n_j^d$ is the same as differentiating $U^*$ with respect to $n_j$, since $U^*$ does not depend on the conformation of the molecules but only on the number of molecules of each type. The differential $\partial L\phi_A(z)/\partial n_j^d$ can be written as $r_{Aj}^d(z)$, the number of segments A in layer $z$ originating from a molecule $j$ in conformation $d$. In order to find the equilibrium set of conformations $\{n_i^c\}$, we substitute eqs 13 and 14 into eq 12 and obtain the following set of equations:

$$\ln \frac{L\lambda^d}{r_j n_j^d} - 1 + (\mu_j - \mu_j^*)/kT + \frac{\partial U^*/kT}{\partial n_j} - \sum_{z,A} r_{Aj}^d(z)\left[\alpha(z) + \frac{\partial U/LkT}{\partial \phi_A(z)}\right] = 0, \quad \text{for all } n_j^d \in \{n_i^c\}$$

$$L - \sum_{i,c} r_i^c(z)\, n_i^c = 0, \quad z = 1, 2, ..., M \quad (15)$$

Equation 15 gives the number $n_j^d$ of molecules $j$ in conformation $d$, i.e., the equilibrium distribution of conformations. From this distribution all the equilibrium properties of the system can be derived, as will be shown in the following sections.

**2.4. Segment Potential and Segment Weighting Factor.** Equation 15 constitutes our central result for the equilibrium situation. Upon closer inspection, the term in between the square brackets can be interpreted as $1/kT$ times the potential $u_A(z)$ of a segment A in layer $z$ with respect to an arbitrary reference potential $u_A^{ref}$. Hence, we define $u_A(z)$ as

$$u_A(z) = kT\alpha(z) + \frac{\partial U/L}{\partial \phi_A(z)} + u_A^{ref} \quad (16)$$

The segment potential, $u_A(z)$, depends only on the type of segment and not on the type of molecule or conformation to which it belongs. In section 2.8 we will discuss the physical meaning of the terms on the right-hand side of eq 16.

From the definition of the segment potential, $u_A(z)$, and eq 15 the number of molecules $i$ in conformation $c$ per surface site, $n_i^c/L$, is easily found. The result is

$$\frac{n_i^c}{L} = C_i \lambda^c \prod_{z,A} G_A(z)^{r_{Ai}^c(z)} \quad (17)$$

where the segment weighting factor, $G_A(z)$, for a segment of type A in layer $z$ is defined as

$$G_A(z) = \exp[-u_A(z)/kT] \quad (18)$$

and the normalization constant $C_i$, which depends only on the type of molecule, is given by

$$\ln C_i = (\mu_i - \mu_i^*)/kT - 1 + \sum_A \frac{r_{Ai} u_A^{ref}}{kT} + \frac{\partial U_i^*/kT}{\partial n_i} - \ln r_i \quad (19)$$

where $r_{Ai}$ is the number of A segments in one molecule of type $i$. In fact, $G_A(z)$ is a Boltzmann factor depending on the segment type and the layer number but not on the molecule type. It gives the statistical weight to find a detached segment of type A in layer $z$, according to its local potential $u_A(z)$. That is the reason for calling $G_A(z)$ the segment weighting factor.

If we denote the segment weighting factor of segment $s$ of a molecule $i$ in conformation $c$ by $G_i^c(s)$, we can rewrite eq 17 as

$$\frac{n_i^c}{L} = C_i \lambda^c G_i^c \quad (20)$$

where $G_i^c$ is a product of $r_i$ segment weighting factors:

$$G_i^c = \prod_{s=1}^{r_i} G_i^c(s) \tag{21}$$

If segment $s$ of molecule $i$ in conformation $c$ is of type A, and finds itself in layer $z$, then $G_i^c(s)$ equals $G_A(z)$. The number $n_i^c/L$ of molecules $i$ per surface site in conformation $c$ is given by the product of a normalization factor $C_i$, a weighting factor $\lambda^c$ (i.e., $r_i - 1$ bond weighting factors $\lambda_0$ or $\lambda_1$) for performing a walk over an empty lattice according to conformation $c$, and a multiple product of $r_i$ segment weighting factors $G_i^c(s)$, one for each segment according to its type and layer number.

**2.5. Segment Density Distributions.** In this section we describe how the segment density distributions $\phi_i(z)$, $\phi_{Ai}(z)$, and $\phi_A(z)$ are found from the set $G_A(z)$ of segment weighting factors using eq 20, but without the need to generate all the configurations separately.

We start our derivation by introducing a chain end distribution function, $G_i(z,s|1)$, for a chain part consisting of the segments 1, ..., $s$ of a molecule $i$. This distribution function gives the statistical weight of all possible walks starting from segment 1, which may be located anywhere in the lattice, and ending at segment $s$ in layer $z$. In other words, $G_i(z,s|1)$ is the statistical weight of $s$-mers (of the same composition as the first $s$ segments of a molecule $i$) with the end segment $s$ in layer $z$. We denote the segment weighting factor for segment $s$ of molecule $i$ in layer $z$ by $G_i(z,s)$. The difference with $G_i^c(s)$ as given above is that in the latter case the layer number need not be specified because it is fully defined by the conformation $c$. The factor $G_i(z,s)$ equals $G_A(z)$ if segment $s$ of molecule $i$ is of type A and in layer $z$, whereas $G_i^c(s)$ equals $G_A(z)$ if $s$ is of type A and if conformation $c$ prescribes that $s$ is in $z$.

Our aim is to express the chain end distribution function in the segment weighting factors, $G_i(z,s)$. According to its definition, $G_i(z,r_i|1)$ is the statistical weight of molecules $i$ ending with the last segment $r_i$ in layer $z$. Summation over all $z$ gives the statistical weight of all chains $i$, the chain weighting factor, $G_i(r_i|1)$. In $G_i(r_i|1)$ all possible conformations of the chains $i$ in the system are included. The same total weight is obtained by summing $\lambda^c G_i^c$, the weight of chains $i$ in one particular conformation $c$, over all $c$. Hence

$$G_i(r_i|1) = \sum_z G_i(z,r_i|1) = \sum_c \lambda^c G_i^c = \frac{n_i}{C_i L} \tag{22}$$

The last identity in this equation follows from eq 20.

In order to obtain the chain end distribution function, $G_i(z,r_i|1)$, itself, we sum only over those conformations $c$ having the $r_i$th segment located in layer $z$. We denote these conformations by $c(z,r_i)$

$$G_i(z,r_i|1) = \sum_{c(z,r_i)} \lambda^c G_i^c \tag{23}$$

which is part of the statistical weight $G_i(r_i|1)$ given in eq 22. For all conformations $c(z,r_i)$ the segment weighting factor, $G_i^c(r_i)$, for segment $r_i$ equals $G_i(z,r_i)$, and this factor may be taken outside the summation. Moreover, $\lambda^c$ may be separated in the bond weighting factor $\lambda^c(r_i|r_i-1)$ for the last bond and the product of the first $r_i - 2$ bond weighting factors; see eqs 5 and 6:

$$G_i(z,r_i|1) = G_i(z,r_i) \sum_{c(z,r_i)} [\lambda^c(r_i|r_i-1)\ \lambda^c(r_i-1|1)\ G_i^c(r_i-1|1)] \tag{24}$$

Because segment $r_i$ is found in layer $z$ there are only three possible locations for segment $r_i - 1$: $z - 1$, $z$, and $z + 1$. If we allow for backfolding we can replace the sum in eq 24 by three terms, using eq 5: $\lambda_1 G_i(z-1,r_i-1|1)$, $\lambda_0 G_i(z,r_i-1|1)$, and $\lambda_1 G_i(z+1,r_i-1|1)$. Backfolding is included because the chain end distribution functions $G_i(z,r_i-1|1)$, $G_i(z-1,r_i-1|1)$, and $G_i(z+1,r_i-1|1)$ contain a few conformations other than $c(z,r_i)$, namely those in which one or more of the first $r_i-2$ segments occupy the same lattice site as segment $r_i$. We rewrite eq 24 by introducing an abbreviated notation $\langle ... \rangle$ for a weighted average over three layers:

$$\langle G_i(z,s|1) \rangle = \lambda_1 G_i(z+1,s|1) + \lambda_0 G_i(z,s|1) + \lambda_1 G_i(z-1,s|1) \tag{25}$$

This average expresses the average weight of an $s$-mer with segment $s$ adjacent to a site in layer $z$. Now eq 24 becomes simply

$$G_i(z,r_i|1) = G_i(z,r_i) \langle G_i(z,r_i-1|1) \rangle \tag{26}$$

According to eq 26 the chain distribution function for an $r$-mer of molecule type $i$ can be expressed in terms of the distribution function of an $(r - 1)$-mer. The same arguments can be used to obtain the following recurrence relations

$$G_i(z,s|1) = G_i(z,s) \langle G_i(z,s-1|1) \rangle \tag{27}$$

$$G_i(z,s|r_i) = G_i(z,s) \langle G_i(z,s+1|r_i) \rangle \tag{28}$$

Starting at the first segment ($s = 1$) of a molecule of type $i$, for which $G_i(z,1|1) = G_i(z,1)$, the chain end distribution functions $G_i(z,s|1)$ are calculated by applying eq 27. The chain end distribution functions $G_i(z,s|r_i)$ are calculated starting at the other end of the chain ($s = r_i$).

For the distribution functions of inner segments of chains $i$ we use the connectivity law, also known as the composition law. Segment $s$ joints the chain parts 1, 2, ..., $s$ and $s$, $s + 1$, ..., $r_i$. If segment $s$ is in layer $z$ the first chain part has a statistical weight $G_i(z,s|1)$, and the other $G_i(z,s|r_i)$. The statistical weight of all chains $i$ with segment $s$ in layer $z$ becomes $G_i(z,s|1)\ G_i(z,s|r_i)/G_i(z,s)$, where the factor $G_i(z,s)$ comes in to correct for double counting of the weighting factor of segment $s$. The volume fraction $\phi_i(z,s)$ due to segments $s$ of molecules $i$ in layer $z$ is proportional to this. With $\phi_i(z) = \sum_s \phi_i(z,s)$ we obtain

$$\phi_i(z) = C_i \sum_{s=1}^{r_i} G_i(z,s|1)\ G_i(z,s|r_i)/G_i(z,s) \tag{29}$$

If $\partial U_i^*/\partial n_i$ and the chemical potential of molecules $i$ in the mixture between the two plates are known, the normalization constant $C_i$ is directly obtained from eq 19. The choice of the reference potential $u_A^{ref}$ in eqs 16 and 19 is arbitrary, as it cancels in eq 29. Alternatively, if the total amount $\theta_i$ of molecules $i$ is known, the normalization constant is directly obtained from eq 22

$$C_i = \frac{\theta_i}{r_i G_i(r_i|1)} \tag{30}$$

where we have defined $\theta_i$ as the total number of segments of molecules $i$ per surface site present between the two plates, which equals the number of equivalent monolayers of molecules $i$:

$$\theta_i = \sum_z \phi_i(z) = r_i n_i / L \tag{31}$$

The expression for the volume fraction given in eq 29 is a straightforward generalization of that given by Scheutjens and Fleer, which only applies to chains with inversion symmetry. If we want to obtain $\phi_{Ai}(z)$, we should include in the summation over $s$ in eq 29 only those segments which are of type A.

**2.6. Adsorbing, Bridging, and Free Molecules.** Scheutjens and Fleer[6] have shown how to obtain detailed information on adsorbing, bridging, and free polymers between two plates in case of a mixture of homopolymer and solvent, once the segment weighting factors $\{G_A(z)\}$ are known. Their equations can easily be extended to the case of a multicomponent mixture containing block copolymers.

The amount $\theta_i$ of molecules $i$ can be subdivided into five groups: $\theta_i^{a'}$ of molecules $i$ adsorbed on the first plate; $\theta_i^{a''}$ of molecules $i$ adsorbed on the second plate; $\theta_i^{f}$ of nonadsorbed (free) molecules $i$ having no segments in layers 1 and $M$; $\theta_i^{b'}$ of bridging molecules $i$ with the last chain end leaving from the first plate, and $\theta_i^{b''}$ of bridging molecules $i$ with the last chain end leaving from the second plate. Obviously

$$\sum_g \theta_i^g = \theta_i \tag{32}$$

where $g$ denotes f, a′, a″, b′, or b″. For each group we can define a chain weighting factor $G_i^g(r_i|1)$, so that

$$\sum_g G_i^g(r_i|1) = G_i(r_i|1) \tag{33}$$

From the conditions that $G_i(z,s|1) = \sum_g G_i^g(z,s|1)$ and $G_i(z,s|r_i) = \sum_g G_i^g(z,s|r_i)$, and the recurrence relations 27 and 28, we can calculate the chain end distribution functions $G_i^g(z,s|1)$ and $G_i^g(z,s|r_i)$ for every group using eqs 36–43 of ref 6. If all $G_i^g(z,s|1)$ and $G_i^g(z,s|r_i)$ are known, the volume fraction profiles of segments in trains, loops, and tails of adsorbing and bridging molecules can be calculated, as well as their size distributions. Since we are dealing with block copolymers, which, in general, show no inversion symmetry, the equations for the volume fraction profiles and for the average number of trains, loops, tails, etc., will be slightly different from those derived by Scheutjens and Fleer for homopolymers. Substitution of $\sum_g G_i^g(z,s|1)$ for $G_i(z,s|1)$ and $\sum_g G_i^g(z,s|r_i)$ for $G_i(z,s|r_i)$ into eq 29 and performing the multiplication $[\sum_g G_i^g(z,s|1)][\sum_g G_i^g(z,s|r_i)]/G_i(z,s)$ gives 25 terms which contribute to $\phi_i(z)$. These 25 terms can be recognized as the distribution of segments $s$ in free chains, in trains (or loops) on each of the surfaces, in tails of bridging or nonbridging chains, etc. For more details we refer to Table I of ref 6. From these 25 terms we can calculate the volume fraction profiles of free chains, trains, loops, tails, etc. The complete equations are given in Appendix II.

**2.7. Flory–Huggins Approximation.** In order to derive the potential $u_A(z)$ of segment A in layer $z$ and the differential of $U_i^*$ with respect to $n_i$ (see eqs 16 and 19), we have to find expressions for the total energy, $U$, of the mixture and the energies, $U_i^*$, of the reference states.

For the energy of mixing we use the familiar Flory–Huggins[15] interaction parameter $\chi_{AB}$, defined as the energy change (in units of $kT$) associated with the transfer of a segment of type A from a solution of pure A to a solution of pure B. For segments of equal size, the same energy effect occurs upon the transfer of a segment B from pure B to a solution of pure A, so that $\chi_{AB} = \chi_{BA}$ and $\chi_{AA} = 0$. In this paper, we will only account for nearest-neighbor interactions, although the incorporation of long-range interactions is straightforward. If a segment is located in layer $z$, it can only be in contact with segments in the layers $z+1$, $z$, and $z-1$. Since we are using a mean-field approximation within each layer, we need only the average number of contacts a segment in layer $z$ will have with, for instance, segments of type B. This average number of contacts with B segments is given by $\lambda_1 Z\phi_B(z-1) + \lambda_0 Z\phi_B(z) + \lambda_1 Z\phi_B(z+1) \equiv Z\langle\phi_B\rangle$. The use of the angular brackets is the same as in eq 25. If A would be fully surrounded by B segments, the energy contribution to the system would be $\chi_{AB}$. Hence, the contact energy of segments A in layer $z$ with B segments is $L\phi_A(z)\,\chi_{AB}\langle\phi_B(z)\rangle$, and the total energy of mixing, $U$, can be written as

$$U/kT = \frac{L}{2}\sum_{z,A,B} \phi_A(z)\,\chi_{AB}\langle\phi_B(z)\rangle \tag{34}$$

where $\langle\phi_B(z)\rangle$ is called the contact fraction with B segments for a segment in layer $z$ and is given by

$$\langle\phi_B(z)\rangle = \lambda_1\phi_B(z-1) + \lambda_0\phi_B(z) + \lambda_1\phi_B(z+1) \tag{35}$$

The factor $^1/_2$ in eq 34 corrects for double counting, because in the double summation over A and B each type of contact occurs twice. Note that the total number of contacts A–B in the system is

$$L\sum_z \phi_A(z)\,\langle\phi_B(z)\rangle = L\sum_z \phi_B(z)\langle\phi_A(z)\rangle \tag{36}$$

Equation 34 includes the energy of adsorption, $U^a$, provided that the solid $S$ is included in the summation over A and B. To show this, we define a Flory–Huggins parameter $\chi_{AS}$ for the interaction between a segment A and a surface site. (Scheutjens and Fleer, following Silberberg,[16] use an adsorption energy parameter $\chi_s$, which is defined as the dimensionless difference $-(u_A^a - u_O^a)/kT$, where $u_A^a$ is the adsorption energy of a polymer segment A and $u_O^a$ that of a solvent molecule. Thus, $\chi_s$ is positive if A adsorbs preferentially from the solvent. Since in the adsorption process only $\lambda_1 Z$ instead of $Z$ contacts are formed, $u_A^a/kT = \lambda_1\chi_{AS}$ and $u_O^a/kT = \lambda_1\chi_{OS}$. Therefore, $\chi_s = -\lambda_1(\chi_{AS} - \chi_{OS})$.) The energy change (in units of $kT$) resulting from bringing a segment A from pure A into an environment of pure S is given by $\chi_{AS}$. Now the adsorption energy follows directly from eq 34. In this equation, both A and B may refer to the two solid surfaces S and S′. The four terms containing S and S′ combine pairwise so that the factor $^1/_2$ cancels:

$$U^a/kT = L\sum_{z,A}[\phi_A(z)\,\chi_{AS}\langle\phi_S(z)\rangle + \phi_A(z)\,\chi_{AS'}\langle\phi_{S'}(z)\rangle] \tag{37}$$

For the remainder of this article we adopt the convention that, unless stated otherwise, the surfaces S and S′ are included whenever a summation over segment types is taken. For S we assume that $\phi_S(z)$ is unity for $z \le 0$ and zero for $z > 0$, so that $\langle\phi_S(1)\rangle = \lambda_1$ and $\langle\phi_S(z)\rangle = 0$ for $z > 1$. Similarly, $\phi_{S'}(z)$ is zero for $z \le M$ and unity for $z > M$, and $\langle\phi_{S'}(M)\rangle = \lambda_1$ and $\langle\phi_{S'}(z)\rangle = 0$ for $z < M$. Equation 37 can thus also be written in the form

$$U^a/kT = L\sum_A[\phi_A(1)\,\chi_{AS}\lambda_1 + \phi_A(M)\,\chi_{AS'}\lambda_1] \tag{38}$$

To obtain the differential of $U/LkT$ with respect to $\phi_A(z)$, needed in eq 16, we differentiate the right-hand side of eq 34. Since the volume fraction of type A segments is contained in both summations (over A and B) the factor $^1/_2$ drops out.

$$\frac{\partial U/L}{\partial\phi_A(z)} = kT\sum_B \chi_{AB}\langle\phi_B(z)\rangle \tag{39}$$

For the fourth term of eq 19 we need an expression for the energy $U_i^*$ of $n_i$ molecules in the pure amorphous state, which may contain various segment types. This energy follows from eq 34 as

$$U_i^*/kT = \frac{L}{2}\sum_{z,A,B}\phi_{Ai}(z)\chi_{AB}\phi_{Bi}^* \tag{40}$$

where $\phi_{Bi}^*$ is the volume fraction of segments B in pure amorphous $i$, or

$$\phi_{Ai}^* = \frac{r_{Ai}}{r_i} \tag{41}$$

When differentiating the right-hand side of eq 40 with respect to $n_i$, we should note that $L\sum_z\phi_{Ai}(z) = r_i n_i \phi_{Ai}^*$ and that $\phi_{Ai}^*$ is independent of $n_i$:

$$\frac{\partial U_i^*/kT}{\partial n_i} = \frac{r_i}{2}\sum_{A,B}\phi_{Ai}^*\chi_{AB}\phi_{Bi}^* \tag{42}$$

In order to choose a proper reference potential, we consider a homogeneous bulk solution, which is in equilibrium with the mixture between the two plates; i.e., for every molecule type the chemical potential in the bulk solution and in the mixture between the two plates are equal. The volume fraction of molecules $i$ in this bulk solution is denoted as $\phi_i^b$. An obvious choice for the reference potential would be such that $u_A^b$ becomes zero; i.e., all $G$'s will be unity in the bulk solution. From the condition that all $G$'s are unity and eq 29 we can express the normalization constant, $C_i$, in the bulk solution volume fraction $\phi_i^b$:

$$C_i = \phi_i^b/r_i \tag{43}$$

In Appendix I we have derived an expression for the chemical potential $\mu_i - \mu_i^*$ of molecules $i$ in a homogeneous mixture, which is a generalization of the Flory–Huggins expression. The reference potential corresponding to the condition that all $G$'s are unity in the bulk solution is found from substitution of eq 42, 43, and I.8 of Appendix I into eq 19:

$$u_A^{ref}/kT = \sum_j\frac{\phi_j^b}{r_j} + \frac{1}{2}\sum_{B,C}\phi_B^b\chi_{BC}\phi_C^b - \sum_B\chi_{AB}\phi_B^b \tag{44}$$

Since the choice of the reference potential $u_A^{ref}$ is arbitrary, we can still use eq 44 for $u_A^{ref}$ when applying it to an arbitrary chosen homogeneous bulk solution. However, if the chosen bulk solution is not in full equilibrium with the mixture between the two plates, then eq 43 will no longer hold. Using this reference potential (eq 44) and eq 42, we can rewrite the expression for the normalization constant, $C_i$, given in eq 19 as

$$\ln C_i = (\mu_i - \mu_i^*)/kT - 1 + r_i\sum_j\frac{\phi_j^b}{r_j} - \ln r_i + \frac{r_i}{2}\sum_{A,B}(\phi_A^b - \phi_{Ai}^*)\chi_{AB}(\phi_B^b - \phi_{Bi}^*) \tag{45}$$

This equation for the normalization constant is, like eq 30, generally valid. For the case of full equilibrium eq 45 reduces to the simple form of eq 43, which can be seen by substituting eq I.8 of Appendix I into eq 45.

**2.8. Hard-Core Potential and Interaction Potential.** Generally, the segment potential, $u_A(z)$, of segment A in layer $z$ can be expressed as

$$u_A(z) = u'(z) + u_A^{int}(z) \tag{46}$$

where both $u'(z)$ and $u_A^{int}(z)$ can be defined with respect to the bulk solution by a suitable choice of the reference potential, so that $u_A^b = u'^b = 0$. For example, substituting eq 44 for the reference potential $u_A^{ref}$ and eq 39 into eq 16 results in the following expression for the potential $u'(z)$ in the Flory–Huggins approximation

$$u'(z)/kT = \alpha(z) + \sum_j\frac{\phi_j^b}{r_j} + \frac{1}{2}\sum_{A,B}\phi_A^b\chi_{AB}\phi_B^b \tag{47}$$

and similarly, the potential $u_A^{int}(z)$ is given by

$$u_A^{int}(z)/kT = \sum_B\chi_{AB}(\langle\phi_B(z)\rangle - \phi_B^b) \tag{48}$$

As can be seen from eqs 46–48, $u_A(z)$ contains a part $u'(z)$, which is independent of the segment type, and a mixing contribution $u_A^{int}(z)$, which, obviously, depends on the type of segment. The potential $u'(z)$ may be identified as the "hard-core" potential. If there is no mixing energy (i.e., if all $\chi_{AB}$ are zero), only $u'(z)$ remains. This is, for instance, the case in a polymer melt containing only one segment type. Now $u'(z)$ is the potential in each layer that must be applied to ensure complete occupancy of the lattice. Without this potential, the surface region of a polymer melt would be depleted because of entropic restrictions. The hard-core potential $u'(z)$ prevents this depletion and makes $\sum_i\phi_i(z) = 1$ for any $z$. In fact, $u'(z)$ gives, through eq 47, the physical meaning of the Lagrange multipliers, $\alpha(z)$, that were introduced precisely to satisfy the volume-filling constraint 10. The potential $u'(z)$ is the same for any segment type. In Appendix III it will be shown how $u'(z)$ can be found self-consistently.

A similar hard-core potential occurs also in other theories. For example, Helfand and Tagami[8] and Hong and Noolandi[9] define a compresibility parameter $\omega(z)$, and Gruen and De Lacey[10] introduce a lateral pressure $\pi(z)$. Marqusee and Dill[11] use parameters $\ln q(z)$, and Theodorou[12,13] arrives at $\xi(z)$ as Lagrange parameters. All these parameters have a similar physical meaning as our $u'(z)$.

The second part of $u_A(z)$, the interaction potential $u_A^{int}(z)$, corresponds to the energy of mixing. In the Flory–Huggins approximation it represents the energy associated with the transfer of a segment A from the bulk solution, with contact fractions $\phi_B^b$, $\phi_C^b$, ..., to layer $z$ where the contact fractions are $\langle\phi_B(z)\rangle$, $\langle\phi_C(z)\rangle$, ...; see eq 48. Clearly, this mixing energy term depends on the segment type and on the actual model used for the interaction energies.

**2.9. Free Energy and Surface Tension.** The free energy, $A - A^*$, of the mixture between the two surfaces with respect to the reference state is, according to standard statistical thermodynamics, given by

$$A - A^* = -kT\ln(Q/Q^*) \tag{49}$$

The logarithm of the canonical partition function is given by eq 8. Let us rewrite the first term on the right-hand side of eq 8, i.e., the entropic part of $Q$, using eqs 17 and 18. Taking the logarithm of the former equation, multiplying by $n_i^c$, and summing over $i$ and $c$ gives after some rearrangement

$$\sum_{i,c}n_i^c\ln\frac{L\lambda^c}{r_i n_i^c} = -L\sum_i\frac{\theta_i}{r_i}\ln r_i C_i + L\sum_{z,A'}\phi_{A'}(z)\,u_{A'}(z)/kT \tag{50}$$

In the summation over A′ the surfaces S and S′ are *not*

included. Substitution of eq 8 into eq 49, using eqs 34, 40, and 50, results in the following expression for the free energy $A - A^*$:

$$\frac{A - A^*}{LkT} = \sum_i \frac{\theta_i}{r_i} \ln r_i C_i - \sum_{z,A'} \phi_{A'}(z)\, u_{A'}(z)/kT + \frac{1}{2}\sum_{z,A,B} \phi_A(z)\, \chi_{AB} \langle \phi_B(z) \rangle - \frac{1}{2}\sum_i (\theta_i \sum_{A,B} \phi_{Ai}{}^* \chi_{AB} \phi_{Bi}{}^*) \quad (51)$$

For the normalization constant $C_i$ we can substitute $\theta_i / r_i G_i(r_i|1)$, according to eq 30, so that the free energy is written in terms of the segment potentials and segment densities only.

We can also express the free energy in terms of hard-core potentials, chemical potentials, and segment densities, by substituting eqs 45, 46, and 48 into eq 51

$$\frac{A - A^*}{LkT} = -\sum_i \frac{\theta_i^{ex}}{r_i} - \sum_z u'(z)/kT - \frac{1}{2}\sum_{z,A',B'} \chi_{A'B'} \times (\phi_{A'}(z) \langle \phi_{B'}(z) \rangle - \phi_{A'}{}^b \phi_{B'}{}^b) + \sum_i \frac{\theta_i}{r_i kT} (\mu_i - \mu_i{}^*) \quad (52)$$

where $\theta_i^{ex}$ is, analogous to eq 31, the excess amount of molecules $i$, expressed as equivalent monolayers:

$$\theta_i^{ex} = \sum_z (\phi_i(z) - \phi_i{}^b) \quad (53)$$

Again, the primes in the third term on the right-hand side of eq 52 indicate that the surfaces S and S′ are *not* included in the double summation.

The surface tensions $\gamma_S$ and $\gamma_{S'}$ are the excess surface free energies per unit area for the two surfaces. At constant volume $V = ML$ and surface areas $A_S$ and $A_{S'}$, standard thermodynamics gives $-pV + \gamma_S A_S + \gamma_{S'} A_{S'} = -kT \ln \Xi(\{\mu_i\},M,L,T)$, where $p$ is the pressure. In the reference state, containing only bulk phases, we have $-p\sum_i V_i = -kT\sum_i \ln \Xi_i{}^*$. Hence

$$\gamma_S A_S + \gamma_{S'} A_{S'} = -kT \ln(\Xi/\Xi^*) = A - A^* - \sum_i n_i(\mu_i - \mu_i{}^*) \quad (54)$$

Substituting eq 52 into eq 54 gives the following result for the excess surface free energy per surface site:

$$\frac{\gamma_S A_S + \gamma_{S'} A_{S'}}{LkT} = -\sum_i \frac{\theta_i^{ex}}{r_i} - \sum_z u'(z)/kT - \frac{1}{2}\sum_{z,A',B'} \chi_{A'B'}(\phi_{A'}(z)\, \langle \phi_{B'}(z) \rangle - \phi_{A'}{}^b \phi_{B'}{}^b) \quad (55)$$

Obviously, the value of $\gamma_S A_S + \gamma_{S'} A_{S'}$ depends on the plate separation $M$. In the case of two equal surfaces, the excess surface free energy can be written as $2\gamma_S A_S$. If the volume fractions in each layer are the same as in the bulk solution, eq 55 reduces to $\gamma_S A_S + \gamma_{S'} A_{S'} = -L\sum_z u'(z)$. This implies, e.g., to a one-component system, for which the volume fraction at any $z$ is unity.

## 3. Results and Discussion

In this section we present a selection of numerical results on the segment distributions of adsorbed block copolymers in relation to parameters like solvent quality, surface affinity, and bulk concentration. In another publication[14] we will give detailed and systematic results on the effect of the chain composition of block copolymers on the adsorbed amount and the hydrodynamic layer thickness.

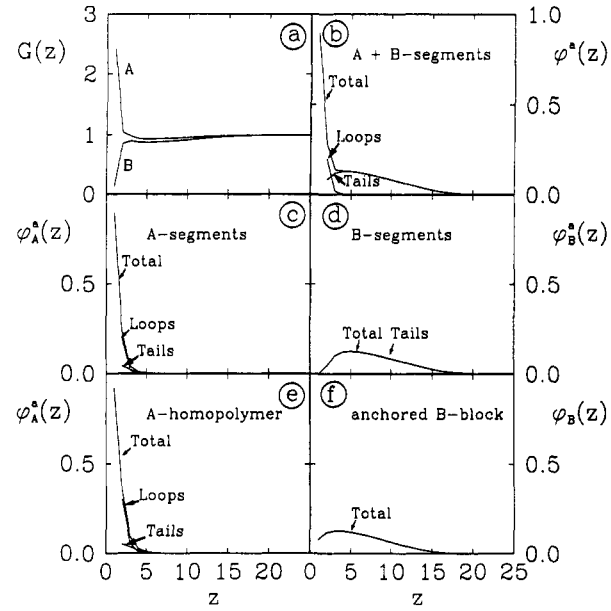


**Figure 2.** Segment weighting factor profiles of the A and B segments for an $A_{50}B_{50}$ diblock copolymer (a), the corresponding (total) segment density profile for the copolymer (b), and the separate segment density profiles for A and B segments (c and d). The volume fraction of polymer in the bulk solution is $10^{-4}$. The latter profiles may be compared with those of an $A_{50}$ homopolymer at the same adsorbed amount of A segments (e) and a $B_{50}$ terminally attached homopolymer (f) at the same amount of B segments. The A segments are strongly adsorbing ($\chi_{AS} = -10$), $\chi_{AO} = 0.5$; all other $\chi$ parameters are zero.

All results presented here have been calculated for a hexagonal lattice ($Z = 12$, $\lambda_0 = {}^6/_{12}$).

**3.1. Segment Density Distributions.** In order to illustrate the structure of an adsorbed layer on one surface, we examine the segment weighting factors $G_A(z)$ and $G_B(z)$, and the segment density profiles $\phi(z)$, $\phi_A(z)$, and $\phi_B(z)$ of an $A_{50}B_{50}$ diblock copolymer. The 50 A segments are given a high affinity for the surface ($\chi_{AS} = -10$) and the 50 B segments have the same affinity for the surface as the solvent O ($\chi_{BS} = \chi_{OS} = 0$). The solvent quality is taken poor for the A segments ($\chi_{AO} = 0.5$) and good for the B segments ($\chi_{BO} = 0$). Figure 2a gives the segment weighting factors $G(z)$ for the A and B segments. Near the surface $G_A(z)$ is higher than 1 since the A segments adsorb preferentially on the surface because of their high surface affinity ($\chi_{AS} = -10$). For $G_B(z)$ low values (<1) are found near the surface because B segments are displaced by the preferentially adsorbing A segments.

From the volume fraction profiles in parts b–d of Figure 2, we may conclude that the A segments are mainly found in trains and loops, whereas the B segments contribute predominantly to the density profile of tails. It is instructive to compare the density profiles of the A segments of the $A_{50}B_{50}$ diblock copolymer with those of an $A_{50}$ homopolymer (Figure 2e) at the same adsorbed amount of A segments. The (total) volume fraction profile of A segments is nearly equal for both types of molecules. However, the volume fraction of A segments in loops is slightly higher for the A homopolymer and, consequently, that of A segments in tails lower than for the $A_{50}B_{50}$ copolymer. Hence, the distribution of A segments in the homopolymer is more homogeneous (i.e., depends less on the ranking number). In the next section we will study the distribution of the individual segments of adsorbed molecules over the layers in more detail.

As adsorbed block copolymers are often treated as anchored chains, it is also interesting to compare the profile

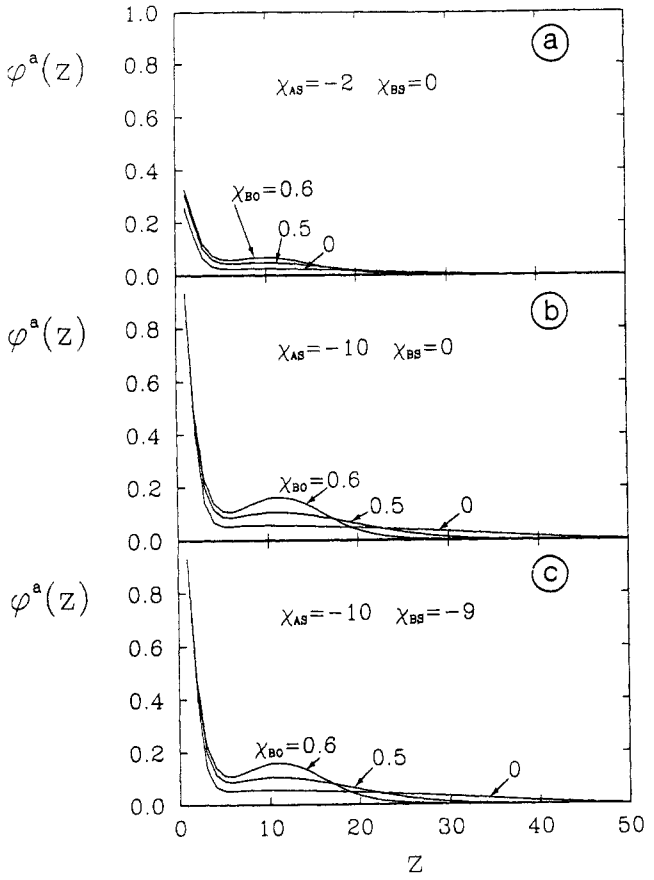


**Figure 3.** Segment density profiles of an $A_{250}B_{250}$ diblock copolymer for a low (a) and a high (b and c) surface affinity of A segments ($\chi_{AS}$ = −2 and −10, respectively) and three different solvent qualities for the B segments (indicated). The B segments are nonadsorbing ($\chi_{BS}$ = 0) in (a) and (b) and are given a surface affinity $\chi_{BS}$ = −9 in (c). Other parameters are as follows: $\chi_{OS}$ = 0, $\chi_{AO}$ = 0.5, $\chi_{AB}$ = 0.3, and $\phi^b = 10^{-4}$.

of B segments with that of an anchored B block. Cosgrove et al.[17] and Hirz[18] have extended the theory of Scheutjens and Fleer to the case of anchored tails. We used this modification of the theory to calculate the profile of a terminally attached B block (Figure 2f). The amount of anchored B blocks of 50 segments is taken equal to the adsorbed amount of B segments of the $A_{50}B_{50}$ diblock copolymers. The shape of both density profiles is essentially the same, with the profile of the B segments of the block copolymer shifted about two layers further into the solution than the profile of the anchored B block. There is a significant difference between both profiles in the first two layers since the B segments of the copolymer interpenetrate into the adsorbed layer of A segments.

The effect of the surface affinity of the A and B segments and that of the solvent quality for the B segments on the segment density profiles of an adsorbing AB block copolymer is shown in Figure 3, for a longer copolymer $A_{250}B_{250}$. In this case $\chi_{AB}$ was chosen as 0.3, the other parameters are $\chi_{OS}$ = 0, $\chi_{AO}$ = 0.5, and $\phi^b = 10^{-4}$. In Figure 3a the A segments are weakly adsorbing ($\chi_{AS}$ = −2) whereas in Figure 3b the A segments have a high surface affinity ($\chi_{AS}$ = −10); in both cases the B segments are nonadsorbing ($\chi_{BS}$ = 0). When the surface affinity is high (Figure 3b), more extended adsorbed layers than for $\chi_{AS}$ = −2 are found due to a higher adsorbed amount. This higher adsorbed amount for $\chi_{AS}$ = −10 gives also higher segment densities. If the solvent quality is good for the B segments ($\chi_{BO}$ = 0), a very extended profile is found for $\chi_{AS}$ = −10: up to 45 layers. In case of a low surface affinity for the A segments ($\chi_{AS}$ = −2), lowering the solvent quality for the B segments results primarily in higher segment densities. A poor ($\chi_{BO}$ = 0.5, Θ-solvent) or bad solvent quality for the B segments makes it less favorable for these segments to be surrounded by solvent. However, even at $\chi_{BO}$ = 0.6, just below the critical $\chi$ value where phase separation between solvent and B chains of 250 segments occurs, there is no substantial collapse of the B block because the surface affinity is too low to compensate for the loss of entropy. If the surface affinity is high for the A segments ($\chi_{AS}$ = −10), a lower solvent quality for the B segments results in less extended segment density profiles (25–30 layers) and the density in the tail region increases. In this case the loss of entropy due to the partial collapse of the B tail is compensated by the strongly adsorbing A segments. There is hardly any effect on the segment density profiles if the B segments have a surface affinity somewhat lower than the A segments ($\chi_{AS}$ = −10 and $\chi_{BS}$ = −9), as is seen from Figure 3c. Since the A and B blocks are equally long and the adsorbed amount is high because of the high surface affinity of the A segments, displacement of A segments from the surface by B segments is not likely, even if the difference in surface affinity is rather low.

**3.2. Distribution of Individual Segments.** In order to obtain more detailed information on the structure of the adsorbed layer, we present in this subsection some typical results of the distribution of individual segments of adsorbed molecules over the various layers.

For every individual segment $s$ the ratio $\phi_i^a(z,s)/\sum_z \phi_i^a(z,s)$ gives the normalized distribution of segment $s$ over the various layers. In fact, this ratio is the probability, $P_i^a(z,s)$, of finding segment $s$ of an adsorbed molecule $i$ in layer $z$.

$$P_i^a(z,s) = \frac{\phi_i^a(z,s)}{\sum_z \phi_i^a(z,s)} \tag{56}$$

For showing the dependence of $P_i^a(z,s)$ on the layer number, $z$, and the segment ranking number, $s$, we will give contour plots of $100P_i^a(z,s)$ as a function of $z$ and $s$. The curves in these contour plots represent points of equal $P_i^a(z,s)$ values.

Figure 4 gives the individual segment distributions of an $A_{100}$ homopolymer, an $A_{100}B_{100}$ diblock copolymer, and an $A_{100}B_{100}A_{100}$ triblock copolymer. The A segments are the adsorbing segments ($\chi_{AS}$ = −10), all other $\chi$ parameters are zero, and the solution concentration is $\phi^b = 10^{-4}$. From comparison of the $P_i^a(z,s)$ profile of the $A_{100}$ homopolymer with the profile of the $A_{100}$ block of the diblock copolymer, we may conclude the following.

Obviously, the segment probability profile for the $A_{100}$ homopolymer is symmetric with respect to $s$. The end segments are distributed over a larger distance from the surface than the middle segments. The average tail length of the homopolymer is found to be 6.2 segments long. The segment probability profile of the A block of the $A_{100}B_{100}$ diblock copolymer is asymmetric (Figure 4b), since the A segment with $s$ = 100 is connected to the nonadsorbing B block. The A block is closer to the surface except the A segments near $s$ = 100, and the effect of the ranking number is weaker than that in the $A_{100}$ homopolymer, in contrast to the situation in parts b and c of Figure 2. This is due to the fact that at the same equilibrium solution concentration the adsorbed amount of A segments is lower for the diblock copolymer than that for the A homopolymer, whereas in Figure 2 the comparison has been made at the same adsorbed amount of A segments. As already

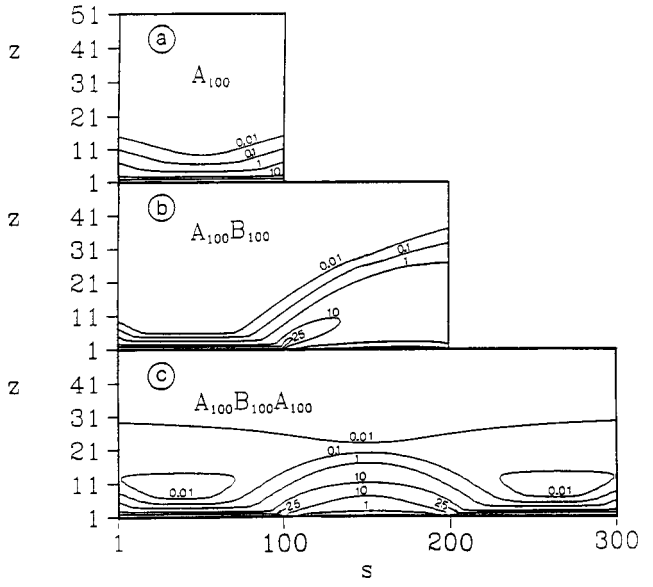


**Figure 4.** Contour plots of $100P_i^a(z,s)$ as a function of segment ranking number, $s$, and layer number, $z$, for an $A_{100}$ homopolymer (a), an $A_{100}B_{100}$ diblock copolymer (b), and an $A_{100}B_{100}A_{100}$ triblock copolymer (c). The A segments are strongly adsorbing ($\chi_{AS} = -10$), all other $\chi$ parameters are zero, and $\phi^b = 10^{-4}$.

concluded from the volume fraction profiles of the B segments in Figure 2d, the B block is found in one dangling tail, which is also seen in the segment probability profile of the B blocks. The loops in the probability curves for the B segments ($s > 100$) indicate that the distance from the surface where B segments have the highest probability increases with increasing ranking number. The strongest increase is found for the B segments near the A block.

For the $A_{100}B_{100}A_{100}$ triblock copolymer a symmetric profile is found (Figure 4c). From the profile of the B block we can conclude that most B segments are found in one loop. For the first 10 layers we obtain a profile for the A blocks very similar to that of the A blocks of the $A_{100}B_{100}$ diblock copolymer. However, at a larger distance from the surface the profile of the end segments of the copolymer shows a hump. This originates from a few chains with one A block adsorbed and a "sticky" tail containing both the B block and the other A block. A second interesting point is the extension of the profile of the A blocks into the solution as compared with the diblock copolymer. The conformation of the A blocks of the $A_{100}B_{100}A_{100}$ triblock copolymer is less "flat" than that of the A block of the $A_{100}B_{100}$ diblock copolymer, because the adsorbed amount of A segments is higher for the triblock copolymer.

The effect of surface affinity of the A segments on an $A_{100}B_{100}$ diblock copolymer is shown in parts a and b of Figure 5. The segment probability profile of the diblock copolymer is given for two different surface affinities for the A segments ($\chi_{AS} = -4$ and $-10$). When $\chi_{AS}$ becomes more negative, the A block is found closer to the surface and the B block is somewhat more stretched out. This is easily understood since a higher surface affinity gives a better compensation for the loss of entropy. Hence, more copolymers adsorb, the B blocks are in a more extended conformation because of lateral interactions, and the A blocks will be found in a more closely packed and relatively collapsed conformation on the surface.

Similarly, the effect of the surface affinity of the B segments is given in parts b and c of Figure 5. For the two $\chi_{BS}$ values used ($\chi_{BS} = 0$ and $-8$) there is hardly any effect on the profile of the A block. The profile of the B block becomes slightly less extended as $\chi_{BS}$ becomes more negative, especially for the B segments with a low

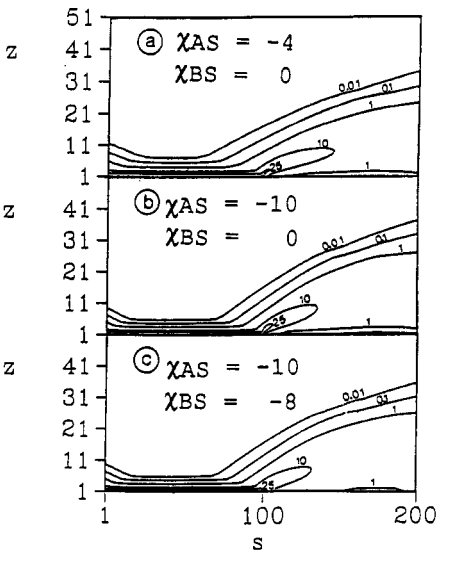


**Figure 5.** Contour plots of $100P_i^a(z,s)$ as a function of segment ranking number, $s$, and layer number, $z$, of an $A_{100}B_{100}$ diblock copolymer for two different values of $\chi_{AS}$ and $\chi_{BS}$ (indicated). As in Figure 4 all other $\chi$ parameters are zero. Figure 5b is the same as Figure 4b.

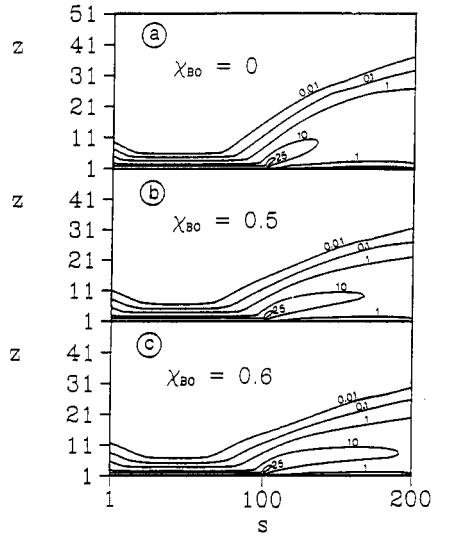


**Figure 6.** Contour plots of $100P_i^a(z,s)$ as a function of segment ranking number, $s$, and layer number, $z$, of an $A_{100}B_{100}$ diblock copolymer for three different values of $\chi_{BO}$. All other $\chi$ parameters are zero.

ranking number, i.e., close to the A block. As the difference in surface affinity between A and B segments decreases, more B segments will be found in long loops and in short trains.

The solvent quality for the B segments has a drastic effect on the conformation of the B block as is seen in Figure 6. The B segments are found closer to the surface when the solvent quality for these segments decreases. This is especially the case for the B segments with a high ranking number, near the chain end. Since the adsorbed amount increases with increasing $\chi_{BO}$, the profile for the A block becomes somewhat more extended.

## 4. Conclusions

We have shown how the self-consistent-field theory of Scheutjens and Fleer for adsorption of homopolymers from a binary mixture can be generalized to describe adsorption of block copolymers of any composition from a multicomponent mixture. Also, we have shown how the surface tension of adsorbed block copolymers in a multicompo-

nent mixture can be calculated.

Detailed information on the structure of the adsorbed layer of block copolymers has been obtained. Diblock copolymers tend to adsorb with the adsorbing block rather flat on the surface. The density profile of the adsorbing A segments is similar to that of an A homopolymer of the same length. The less adsorbing or nonadsorbing block is found in one dangling tail and protrudes far out into the solution. The segment density profile of this block resembles that found for terminally anchored chains. For high adsorbed amounts the extension of the segment density profile of the less adsorbing or nonadsorbing block depends highly on the solvent quality for the segments of this block. Triblock copolymers with adsorbing end blocks form dangling tails with "sticky" ends.

## Appendix I. Derivation of a Generalized Flory–Huggins Formula for the Chemical Potential

Flory[15] has derived a formula for the chemical potential of a homopolymer in binary and ternary mixtures. His expression for a binary mixture can be written as

$$(\mu_1 - \mu_1^*)/kT = \ln \phi_1 + 1 - r_1(\phi_1/r_1 + \phi_2/r_2) + r_1\chi_{12}\phi_2^2 \tag{I.1}$$

When the indices 1 and 2 are interchanged, $\mu_2$ is obtained.

We need a general equation for the chemical potential of a copolymer in a homogeneous multicomponent mixture. The chemical potential, $\mu_j$, of a molecule $j$ in a mixture containing $n_j$ molecules $j$ is obtained by differentiating the free energy, $A$, of the mixture with respect to $n_j$:

$$(\mu_j - \mu_j^*)/kT = \frac{\partial(A - A^*)}{\partial n_j} \tag{I.2}$$

The free energy of the pure unmixed liquid phases of the same molecules is denoted by $A^*$. The free energy difference, $A - A^*$ is simply given by

$$\frac{A - A^*}{kT} = \sum_i n_i \ln \phi_i + \frac{1}{2}\sum_{i,A,B} n_i r_{Ai}\chi_{AB}(\phi_B - \phi_{Bi}^*) \tag{I.3}$$

This equation can be derived as $A - A^* = -kT \ln (Q/Q^*) = -kT \ln (\Omega/\Omega^*) + U - U^*$, applied to a homogeneous bulk solution along the lines given in sections 2.3 and 2.8. It is easily verified that eq 7 reduces to the first term (the entropy part) of eq I.3, whereas eqs 34 and 40 give the second (energetic) term.

The physical process corresponding to the differentiation in eq I.2 is the transfer of a molecule $j$ from the reference state to the mixture. During this transfer the number of molecules of component $j$ in both phases will change. For the entropy part of the free energy difference we obtain

$$\frac{\partial \sum_i n_i \ln \phi_i}{\partial n_j} = \ln \phi_j + 1 - r_j \sum_i \frac{\phi_i}{r_i} \tag{I.4}$$

For the derivative of the energy part we make use of the expressions given in eqs I.5 and I.6. Note that $\phi_j = r_j n_j/n$, where $n$ is the total number of molecules in the mixture, and $r_{Ai}$ is the number of segments A per molecule of type $i$.

$$\frac{\partial \phi_B}{\partial n_j} = (r_{Bj} - \phi_B r_j)/\sum_i r_i n_i \tag{I.5}$$

$$\frac{\partial \phi_{Bj}^*}{\partial n_j} = 0 \tag{I.6}$$

Equation I.6 follows from the fact that the segment volume fractions of pure liquid molecules $j$ ($\phi_{Ai}^* = r_{Aj}/r_j$) are independent of the number of molecules. With eqs I.5 and I.6 we obtain

$$\frac{\partial(U - U^*)}{\partial n_j} = \frac{1}{2}kT\sum_{A,B}\chi_{AB}[r_{Aj}(\phi_B - \phi_{Bj}^*) + \phi_A(r_{Bj} - \phi_B r_j)] \tag{I.7}$$

where $\sum_i n_i r_{Ai}/\sum_i n_i r_i$ was replaced by $\phi_A$. Combining eqs I.7 and I.4, we obtain for $\mu_j - \mu_j^*$

$$\frac{\mu_j - \mu_j^*}{kT} = \ln \phi_j + 1 - r_j\sum_i \frac{\phi_i}{r_i} - \frac{r_j}{2}\sum_{A,B}(\phi_A - \phi_{Aj}^*)\chi_{AB}(\phi_B - \phi_{Bj}^*) \tag{I.8}$$

where we used the relation $r_{Aj} = r_j\phi_{Aj}^*$.

It is easily verified that eq I.8 reduces to eq I.1 for the case of a binary mixture.

## Appendix II. Adsorbing, Bridging, and Free Molecules

The equations for the chain end distribution functions of adsorbed (a), bridging (b), and free (f) chains are given below, where a prime indicates the surface adjacent to layer 1 (surface 1) and a double prime the surface adjacent to layer $M$ (surface 2). The equations are straightforward generalizations of those given in ref 6.

The chain end distribution function $G_i^f(z,s|1)$ of segment $s$ of nonadsorbed (free) molecules $i$ is given by

$$G_i^f(1,s|1) = 0$$

$$G_i^f(z,s|1) = G_i(z,s)\,\langle G_i^f(z,s-1|1)\rangle, \quad \text{for } 1 < z < M$$

$$G_i^f(M,s|1) = 0 \tag{II.1}$$

For $z = 1$ we have $G_i(1,s)\,\langle G_i^f(1,s-1|1)\rangle$, but this term contributes to adsorbing chains. The equations for the chain end distribution functions $G_i^f(z,s|r_i)$ are similar.

The chain end distribution function $G_i^{a'}(z,s|1)$ of segment $s$ of molecules $i$ adsorbed on the first surface is given by

$$G_i^{a'}(1,s|1) = G_i(1,s)\,\langle G_i^{a'}(1,s-1|1) + G_i^f(1,s-1|1)\rangle, \quad \text{for } M > 1$$

$$G_i^{a'}(z,s|1) = G_i(z,s)\,\langle G_i^{a'}(z,s-1|1)\rangle, \quad \text{for } 1 < z < M$$

$$G_i^{a'}(M,s|1) = 0 \tag{II.2}$$

The equations for the chain end distribution functions $G_i^{a'}(z,s|r_i)$ are similar.

The chain end distribution function $G_i^{a''}(z,s|1)$ of segment $s$ of molecules $i$ adsorbed on the second surface is given by

$$G_i^{a''}(1,s|1) = 0$$

$$G_i^{a''}(z,s|1) = G_i(z,s)\,\langle G_i^{a''}(z,s-1|1)\rangle, \quad \text{for } 1 < z < M$$

$$G_i^{a''}(M,s|1) = G_i(M,s)\,\langle G_i^{a''}(M,s-1|1) + G_i^f(M,s-1|1)\rangle, \quad \text{for } M > 1 \tag{II.3}$$

The equations for the chain end distribution functions $G_i^{a''}(z,s|r_i)$ are similar.

The chain end distribution function $G_i^{b'}(z,s|1)$ of segment $s$ of bridging molecules $i$ with the last chain end leaving from the first surface is given by

$$G_i^{b'}(1,s|1) = G_i(1,s)\,\langle G_i^{b'}(1,s-1|1) + G_i^{b''}(1,s-1|1) + G_i^{a''}(1,s-1|1)\rangle, \quad \text{for } M > 1$$

$$G_i^{b'}(z,s|1) = G_i(z,s)\,\langle G_i^{b'}(z,s-1|1)\rangle, \quad \text{for } 1 < z < M$$

$$G_i^{b'}(M,s|1) = 0, \quad \text{for } M > 1 \qquad \text{(II.4)}$$

The equations for the chain end distribution functions $G_i^{b'}(z,s|r_i)$ are similar.

The chain end distribution function $G_i^{b''}(z,s|1)$ of segment $s$ of bridging molecules $i$ with the last chain end leaving from the second surface is given by

$$G_i^{b''}(1,s|1) = 0, \quad \text{for } M > 1$$

$$G_i^{b''}(z,s|1) = G_i(z,s)\,\langle G_i^{b''}(z,s-1|1)\rangle, \quad \text{for } 1 < z < M$$

$$G_i^{b''}(M,s|1) = G_i(M,s)\,\langle G_i^{b'}(M,s-1|1) + G_i^{b''}(M,s-1|1) + G_i^{a'}(M,s-1|1)\rangle, \quad \text{for } M > 1 \qquad \text{(II.5)}$$

For $M = 1$ all chains are bridging:

$$G_i^{b'}(1,s|1) = G_i^{b''}(1,s|1) = G_i(1,s)\,\langle G_i^{b'}(1,s-1|1)\rangle, \quad \text{for } M = 1 \qquad \text{(II.6)}$$

The equations for the chain end distribution functions $G_i^{b''}(z,s|r_i)$ are similar.

All starting values of the various chain end distribution functions $G_i^{g}(z,1|1)$, where $g$ = a', a'', f, b', or b'', are zero except the following nonzero terms:

$$G_i^{a'}(1,1|1) = G_i(1,1), \quad \text{for } M > 1$$

$$G_i^{f}(z,1|1) = G_i(z,1), \quad \text{for } 1 < z < M$$

$$G_i^{a''}(M,1|1) = G_i(M,1), \quad \text{for } M > 1$$

$$G_i^{b'}(1,1|1) = G_i^{b''}(1,1|1) = \frac{1}{2}G_i(1,1), \quad \text{for } M = 1 \qquad \text{(II.7)}$$

For the starting values of $G_i^{g}(z,s|r_i)$ we have similar equations.

From the chain end distribution functions $G_i^{g}(z,s|1)$ and $G_i^{g}(z,s|r_i)$ the volume fractions of trains (tr), loops (lp), and tails (tl) may be calculated with the following equations. The volume fraction profile of loops of molecules adsorbed on surface 1 only is given by

$$\phi_{lp,i}^{a'}(z) = C_i\sum_{s=1}^{r_i} G_i^{a'}(z,s|1)\,G_i^{a'}(z,s|r_i)/G_i(z,s), \quad \text{for } 1 < z < M \qquad \text{(II.8)}$$

For the loops of molecules adsorbed on surface 2 only, replace a' by a'' in eq II.8. Set $z = 1$ to obtain $\phi_{tr,i}^{a'}(1)$, the volume fraction of trains of nonbridging molecules on surface 1, and replace a' by a'' and $z$ by $M$ to obtain $\phi_{tr,i}^{a''}(M)$, the volume fraction of trains of nonbridging molecules on surface 2. The volume fractions of tails of molecules adsorbed only on surface 1 consist of two contributions, one for each chain end:

$$\phi_{tl,i}^{a'}(z) = C_i\sum_{s=1}^{r_i}[G_i^{a'}(z,s|1)\,G_i^{f}(z,s|r_i) + G_i^{f}(z,s|1)\,G_i^{a'}(z,s|r_i)]/G_i(z,s), \quad \text{for } 1 < z < M \qquad \text{(II.9)}$$

Again, replace a' by a'' for the tails of chains adsorbed on surface 2 only. For the volume fractions $\phi_{br,i}(z)$ of bridges we obtain

$$\phi_{br,i}(z) = C_i\sum_{s=1}^{r_i}[(G_i^{a'}(z,s|1) + G_i^{b'}(z,s|1))(G_i^{a''}(z,s|r_i) + G_i^{b''}(z,s|r_i)) + (G_i^{a''}(z,s|1) + G_i^{b''}(z,s|1))(G_i^{a'}(z,s|r_i) + G_i^{b'}(z,s|r_i))]/G_i(z,s), \quad \text{for } 1 < z < M \qquad \text{(II.10)}$$

The volume fractions of loops, attached to surface 1, of bridging molecules are given by

$$\phi_{lp,i}^{b'}(z) = C_i\sum_{s=1}^{r_i}[G_i^{a'}(z,s|1)\,G_i^{b'}(z,s|r_i) + G_i^{b'}(z,s|1)\,G_i^{a'}(z,s|r_i) + G_i^{b'}(z,s|1)\,G_i^{b'}(z,s|r_i)]/G_i(z,s), \quad \text{for } 1 < z < M \qquad \text{(II.11)}$$

For loops attached to surface 2, replace a' by a'' and b' by b'' in eq II.11. As above, $z = 1$ gives the volume fraction of trains of these molecules on surface 1 and replacement of a' by a'' and b' by b'' with $z = M$ gives the volume fraction of their trains on surface 2. The volume fractions of their tails attached on surface 1 follow from

$$\phi_{tl,i}^{b'}(z) = C_i\sum_{s=1}^{r_i}[G_i^{b'}(z,s|1)\,G_i^{f}(z,s|r_i) + G_i^{f}(z,s|1)\,G_i^{b'}(z,s|r_i)]/G_i(z,s), \quad \text{for } 1 < z < M \qquad \text{(II.12)}$$

Replace b' by b'' for the tails of bridging molecules attached on surface 2. The volume fraction $\phi^{f}(z)$ of free molecules, for $1 < z < M$, is simply given by

$$\phi_i^{f}(z) = C_i\sum_{s=1}^{r_i} G_i^{f}(z,s|1)\,G_i^{f}(z,s|r_i)/G_i(z,s) \qquad \text{(II.13)}$$

The equation for the average number of loops per adsorbing molecule on surface 2 is

$$n_{lp,i}^{a''} = \frac{\lambda_1}{G_i^{a''}(r_i|1)}\sum_{s=2}^{r_i-1} G_i^{a''}(M-1,s|1)\,G_i^{a''}(M,s+1|r_i) \qquad \text{(II.14)}$$

For surface 1, replace a'' by a', $M - 1$ by 2, and $M$ by 1. The number of trains per adsorbing molecule $i$ is 1 more than their number of loops: $n_{tr,i}^{a'} = n_{lp,i}^{a'} + 1$ and $n_{tr,i}^{a''} = n_{lp,i}^{a''} + 1$ for surfaces 1 and 2, respectively. The number of tails per molecule is 2 minus the average number of their ends ending on the surface. For adsorbing chains on surface 2 we obtain

$$n_{tl,i}^{a''} = 2 - \frac{G_i^{a''}(M,r_i|1) + G_i^{a''}(M,1|r_i)}{G_i^{a''}(r_i|1)} \qquad \text{(II.15)}$$

and for adsorbing chains on surface 1 replace a'' by a' and $M$ by 1.

The average number of bridges per bridging molecule $i$ is given by

$$n_{br,i} = \frac{\lambda_1}{G_i^{b'}(r_i|1) + G_i^{b''}(r_i|1)}\sum_{s=1}^{r_i-1}[(G_i^{a''}(2,s|1) + G_i^{b''}(2,s|1))(G_i^{a'}(1,s+1|r_i) + G_i^{b'}(1,s+1|r_i)) + (G_i^{a'}(1,s|1) + G_i^{b'}(1,s|1))(G_i^{a''}(2,s+1|r_i) + G_i^{b''}(2,s+1|r_i))] \qquad \text{(II.16)}$$

The equations for the average number of loops, trains, and

tails per bridging molecule on surface 2 are

$$n_{lp,i}^{b''} = \frac{\lambda_1}{G_i^{b'}(r_i|1) + G_i^{b''}(r_i|1)} \sum_{s=1}^{r_i-1} [G_i^{b''}(M-1,s|1)(G_i^{a''}(M,s+1|r_i) + G_i^{b''}(M,s+1|r_i)) + G_i^{a''}(M,s|1)\, G_i^{b''}(M-1,s+1|r_i)] \quad \text{(II.17)}$$

$$n_{tr,i}^{b''} = n_{lp,i}^{b''} + \frac{n_{br,i}}{2} + \frac{G_i^{b''}(r_i|1)}{G_i^{b'}(r_i|1) + G_i^{b''}(r_i|1)} \quad \text{(II.18)}$$

$$n_{tl,i}^{b''} = \frac{G_i^{b''}(r_i|1) + G_i^{b''}(1|r_i) - G_i^{b''}(M,r_i|1) - G_i^{b''}(M,1|r_i)}{G_i^{b'}(r_i|1) + G_i^{b''}(r_i|1)} \quad \text{(II.19)}$$

Replacing $M-1$ by 2, $M$ by 1, and a'' by a' and exchanging b' and b'' in eqs II.17–19 leads to the number of loops, trains, and tails, respectively, per bridging molecule on surface 2.

The average fraction of segments, $\nu$, in trains, loops, tails, and bridges of molecule $i$ is given by

$$\nu_{sq,i}^{g} = \sum_{z=1}^{M} \frac{\phi_{sq,i}^{g}(z)}{\theta_i^{g}} \quad \text{(II.20)}$$

where $g$ (=a', a'', b) refers to one of the molecule fractions (adsorbed molecules on the first surface, adsorbed molecules on the second surface, or bridging molecules) and sq (=tr, lp, tl) denotes the sequence type (either trains, loops, or tails).

The average length, $l_{sq,i}^{g}$, for chain part sq of the molecule fractions $g$ of molecules $i$ is then given by

$$l_{sq,i}^{g} = \frac{r_i \nu_{sq,i}^{g}}{n_{sq,i}^{g}} \quad \text{(II.21)}$$

## Appendix III. Numerical Method

The segment density profiles $\{\phi_A(z)\}$ can be calculated according to eqs 18 and 29 once the potentials $\{u_A(z)\}$ are known. These potentials are given by eq 46 and depend on the segment densities and $u'(z)$. Hence, we are dealing with an implicit set of equations, which can be solved numerically, for instance with the FORTRAN program of Powell.[19]

We define a set of unconstrained variables $x_A(z)$, which we relate to the deviation of $u_A(z)$ from the average segment potential $\bar{u}$ and a term independent of A and $z$

$$x_A(z) = -\frac{u_A(z) - \bar{u}}{kT} + \frac{\sum_i \ln G_i(r_i|1)}{\sum_{z,A} 1} \quad \text{(III.1)}$$

where the average segment potential, $\bar{u}$, is defined as

$$\bar{u} = \frac{\sum_{z,A} u_A(z)}{\sum_{z,A} 1} \quad \text{(III.2)}$$

From the definition of the unconstrained variables, $x_A(z)$, in eq III.1 it follows immediately that the following relations must hold

$$\sum_{z,A} x_A(z) = \sum_i \ln G_i(r_i|1) \quad \text{(III.3)}$$

and

$$x_A(z) - \bar{x} = -\frac{u_A(z) - \bar{u}}{kT} \quad \text{(III.4)}$$

where $\bar{x}$ is the average of all $x_A(z)$ defined in the same way as $\bar{u}$. We introduce a reduced segment weighting factor, $\tilde{G}_A(z)$. It is defined as

$$\tilde{G}_A(z) = G_A(z) \exp[\bar{u}/kT] \quad \text{(III.5)}$$

With the help of eqs 18 and III.4 we can rewrite eq III.5 and express $\tilde{G}_A(z)$ in terms of the unconstrained variables $x_A(z)$.

$$\tilde{G}_A(z) = \exp[x_A(z) - \bar{x}] \quad \text{(III.6)}$$

From the set $\{x_A(z)\}$ we calculate the reduced segment weighting factors, $\tilde{G}_A(z)$, according to eq III.6, the corresponding reduced chain distribution functions, $\tilde{G}_i(z,s|1)$ and $\tilde{G}_i(z,s|r_i)$, according to the equivalents of eqs 27 and 28, and the reduced chain weighting factors, $\tilde{G}_i(r_i|1)$, according to the equivalent of eq 22. Note that $\tilde{G}_i(r_i|1) = G_i(r_i|1) \exp[r_i\bar{u}/kT]$, so that $\bar{u}/kT$ may be obtained from eq III.3 as

$$\frac{\bar{u}}{kT} = \frac{\sum_i \ln G_i(r_i|1) - \sum_{z,A} x_A(z)}{\sum_i r_i} \quad \text{(III.7)}$$

The segment densities $\phi_i(z)$ are found with the equivalent of eq 29 in reduced weighting factors

$$\phi_i(z) = \tilde{C}_i \sum_{s=1}^{r_i} \tilde{G}_i(z,s|1)\, \tilde{G}_i(z,s|r_i)/\tilde{G}_i(z,s) \quad \text{(III.8)}$$

where the reduced normalization constant, $\tilde{C}_i$, is related to $C_i$ by

$$\tilde{C}_i = \frac{C_i}{\exp[r_i\bar{u}/kT]} \quad \text{(III.9)}$$

If $\theta_i$ is given, we can substitute eq 30 into eq III.9:

$$\tilde{C}_i = \frac{\theta_i}{r_i \tilde{G}_i(r_i|1)} \quad \text{(III.10)}$$

It is easily verified that the factors $\exp[\bar{u}/kT]$ cancel out in eq III.8.

The Lagrange multipliers, $\alpha(z)$, may be calculated from eqs 16 and 39. During the iterations $\alpha(z)$ may depend on the type of segment. Therefore, we define $\alpha_A(z)$ as

$$\alpha_A(z) = u_A(z)/kT - \sum_B \chi_{AB} \frac{\langle \phi_B(z) \rangle}{\sum_C \phi_C(z)} - u_A^{ref}/kT \quad \text{(III.11)}$$

For $u_A^{ref}$ we use the expression given in eq 44. The division by $\sum_C \phi_C(z)$ damps strong fluctuations in $\alpha_A(z)$ during the iterations (when the boundary conditions $\sum_C \phi_C(z) = 1$ are not yet satisfied) and has no effect on the final result.

For every layer $z$ we have to satisfy the boundary condition $\sum_A \phi_A(z) = 1$. In addition, $\alpha(z)$ must have the same value for every type of segment in layer $z$. We have formulated the following function $f_A(z)$, which combines the boundary conditions and has turned out to be reasonably linear in $u_A(z)$ for most cases

$$f_A(z) = 1 - \frac{1}{\sum_A \phi_A(z)} + \alpha(z) - \alpha_A(z) \quad \text{(III.12)}$$

where $\alpha(z) = \sum_A \alpha_A(z)/\sum_A 1$ is the average of $\alpha_A(z)$ in layer $z$. This function $f_A(z)$ is only zero if the boundary conditions are satisfied and if $\{u_A(z)\}$ is consistent with $\{\phi_A(z)\}$.

Initial values of $\{x_A(z)\}$ are obtained as follows. The potentials $u_A(z)$ for $1 < z < M$ are set to zero. Only $u_A(1)$ and $u_A(M)$ are given a small negative value. From these initial values of $\{u_A(z)\}$ we can calculate $\{G_A(z)\}$ and, from them, $G_i(r_i|1)$ of every molecule type $i$. The corresponding initial values of $\{x_A(z)\}$ are then found from eq III.1. Then the iteration procedure is started to find the set of $\{x_A(z)\}$ for which the functions $\{f_A(z)\}$ are zero. The iteration is stopped when the tolerance $(\sum_z \sum_A [f_A(z)]^2)^{1/2}$ is typically less than $10^{-7}$.

For each component either $\theta_i$ or $\mu_i$ (or $\phi_i^b$) should be given. However, in order to avoid that the functions $f_A(z)$ become overdetermined because of $\sum_i \theta_i = \sum_{i,z} \phi_i(z)$, at least one component, e.g., a solvent, should be free to adapt its $\theta_i$ during the iterations.

## References and Notes


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