Adsorption of Polymers on Heterogeneous Surfaces

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ABSTRACT: An extension of a self-consistent-field lattice theory is developed to study the adsorption of polymers on energetically heterogeneous surfaces. Surface heterogeneity is modeled by introducing distinguishable surface sites which differ in their interaction energy with polymer segments and solvent molecules. The probability for the polymer segments to meet a given kind of site depends on the distribution of the surface sites. In this paper, the adsorption behavior of polymers on a surface with adsorbing and nonadsorbing surface sites is studied. For homopolymers, we find that for high chain length and adsorption energy the adsorbed amount is higher on a surface with a random distribution of adsorbing surface sites as compared to a surface with a patchwise distribution, *i.e.*, where equal surface sites are grouped together. Block copolymers can segregate strongly on a patchwise distributed surface.

Introduction

In polymer adsorption theory, the surface is usually considered to be chemically homogeneous and smooth. However, in practice surface heterogeneity can play an important role in the adsorption characteristics. Therefore, efforts have been made to incorporate the effects of surface heterogeneity into existing polymer adsorption models. Two cases can be distinguished: physically heterogeneous (*i.e.*, rough) and chemically heterogeneous surfaces. Rough surfaces have been modeled as, *e.g.*, sinusoidal surfaces,[1] fractal surfaces,[2,3] and corrugated surfaces.[4] Chemical surface heterogeneity means that some types of surface sites are preferred over others by (parts of) the adsorbing polymer. Odijk[6] and Andelman and Joanny[7] have modeled a chemically heterogeneous surface by taking the interaction between polymer and surface as a random variable. Recently, Joanny and Andelman have also considered the adsorption of polymers on soluble and insoluble surfactant monolayers and on a periodically heterogeneous surface.[8] Balazs *et al.*[5] have used Monte Carlo techniques to investigate the influence of different distributions of adsorbing patches over the surface. Huang and Balazs[9] have used two-dimensional statistics to calculate volume fraction profiles of a block copolymer on a striped surface.

In this paper we present a model that is, like the Huang and Balazs treatment, based on the self-consistent-field theory for polymer adsorption by Scheutjens and Fleer.[10,11] But in contrast to their approach we vary the average size of adsorbing patches on the surface by using neighbor probabilities for adjacent surface sites. In this way, it is possible to study the effects of site distribution on the adsorption behavior of the polymer. Most of the calculations have been performed for homopolymers on a surface where only one out of two kinds of surface sites has an attractive energetic interaction with the polymer segments. The model can be used analogously for block copolymers. One example of this type is given.

Theory

Lattice. We introduce a simple cubic lattice with a characteristic length equal to the size of a solvent molecule.

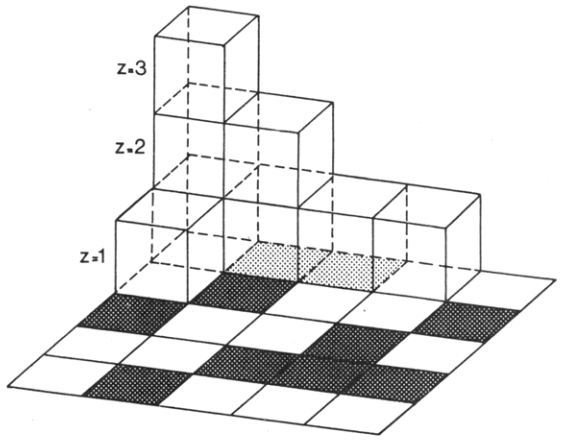

Figure 1. Schematic view of the surface and adjacent lattice. Two kinds of surface sites are indicated by white and gray squares. A small number of lattice sites is drawn in the first three layers.

The surface is modeled as a flat wall divided into squares, the surface sites. This surface may contain different kinds of surface sites, indicated by m, n, etc. The fraction of sites of type m is f_m, where $\sum_m f_m = 1$. Over the surface sites we place layers of cubes parallel to the surface, numbered 1 (at the surface) to M (in the bulk solution) (Figure 1). Each cube (lattice site) contains either a polymer segment or a solvent molecule. The volume fraction of a polymer i in layer z is denoted as $\varphi_i(z)$. If the polymer is a copolymer, $\varphi_i(z) = \sum_A \varphi_{Ai}(z)$, where $\varphi_{Ai}(z)$ is the contribution of segment type A to $\varphi_i(z)$. As surface heterogeneity can lead to an uneven distribution of polymer over the surface, we also need a separate volume fraction for every kind of site, $\varphi_A(z|m)$. The vertical bar is used because it is a conditional volume fraction: only the space above the m-sites is considered. To fill the lattice, we need to have

$$\sum_A \varphi_A(z|m) = 1 \tag{1}$$

for all z and m. In this summation the solvent is included.

Surface. We define a neighbor probability M_{mn} as the probability that, coming from a site m, the next site on the surface is of type n. As this is a probability, we have

$$0 \le M_{mn} \le 1 \tag{2}$$

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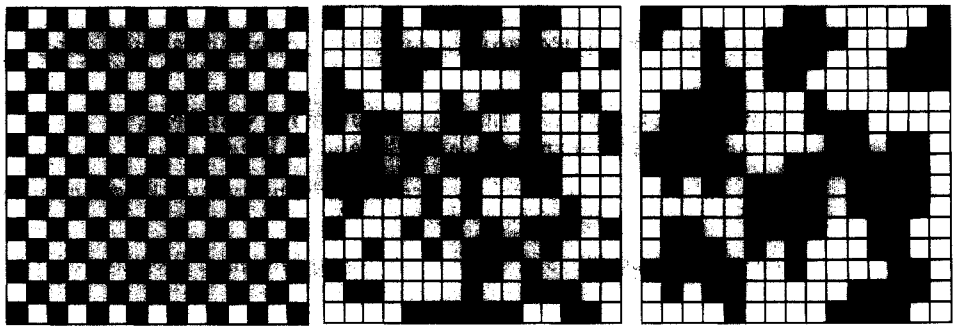

Figure 2. Schematic view of the surface with two kinds of sites: (a) alternating surface (checkerboard) ($C = -1$); (b) random surface ($C = 0$); (c) patchy surface (C positive).

and

$$\sum_n M_{mn} = 1 \tag{3}$$

The probability of finding first a site m and then a site n equals $f_m M_{mn}$. Summing over all sites m should give the *a priori* probability of finding a site n:

$$\sum_m f_m M_{mn} = f_n \tag{4}$$

Furthermore, the probability of finding a sequence mn should be equal to nm (inversion symmetry):

$$f_m M_{mn} = f_n M_{nm} \tag{5}$$

In the remainder of this section, we consider only two kinds of surface sites. In this case, eq 5 is not a new constraint, but it can be derived from eqs 3 and 4.

To describe a surface with two kinds of surface sites, a cluster parameter C is defined:

$$C = M_{mm} - M_{nm} \tag{6}$$

With eq 3 C can also be written as $1 - M_{mn} - M_{nm}$. With eq 5 we find $C = 1 - (1 + f_n/f_m)M_{nm} = 1 - (1 + f_m/f_n)M_{mn}$. Since M_{nm} and M_{mn} are in between 0 and 1, we find for C the following constraints:

$$-f_m/f_n \le C \le 1 \quad \text{and} \quad -f_n/f_m \le C \le 1 \tag{7}$$

The minimum value of C, which only occurs if $f_n = f_m$, equals -1. In this case $M_{mm} = 0$ and $M_{nm} = M_{mn} = 1$, so that with every step we change from one type of surface site to the other. In other words, we have a checkerboard distribution (Figure 2a). If C is close to unity, M_{mm} is much larger than M_{nm}, so equal surface types are grouped together (*patchwise* surface, Figure 2c). For $C = 0$, we have $M_{mm} = M_{nm} = f_m$: there is no grouping nor avoiding of equal surface sites. We call this a *random* surface (Figure 2b).

Polymer Statistics. We define a free segment distribution function $G_A(z|m)$ which gives the relative preference of a free segment of type A to be in layer z above a site m with respect to the homogeneous bulk solution. This is a Boltzmann factor:

$$G_A(z|m) = \exp\left(-\frac{u_A(z|m)}{kT}\right) \tag{8}$$

where $u_A(z|m)$ is the potential of A in layer z above a site m, k is Boltzmann's constant, and T is the absolute temperature. The potential $u_A(z|m)$ is given by

$$u_A(z|m) = u'(z|m) + kT\sum_B \chi_{AB}(\langle\varphi_B(z|m)\rangle - \varphi_B^{\text{bulk}}) \tag{9}$$

Here, $u'(z|m)$ is the so-called "hard core potential", a Lagrange parameter ensuring that eq 1 is satisfied. The second term on the right-hand side accounts for all energetic interactions. It contains the Flory–Huggins interaction parameters χ_{AB} between segment types A and B. The expression between the angular brackets is the neighbor average of $\varphi_B(z|m)$, defined as

$$\langle\varphi_B(z|m)\rangle = \frac{1}{6}\varphi_B(z-1|m) + \sum_n^4 \frac{1}{6}M_{mn}\varphi_B(z|n) + \frac{1}{6}\varphi_B(z+1|m) \tag{10}$$

Note that the choice of a cubic lattice implies that contacts with segments on a different site can only occur within a layer z: segments in layers $z-1$ or $z+1$ are automatically situated above the same site. This simplifies the equations considerably. In the two-site case, the summation in eq 10 contains only two terms: $(4/6)\{M_{mm}\varphi_B(z|m) + M_{mn}\varphi_B(z|n)\}$. For a homogeneous surface with only sites of type m, this middle term equals $(4/6)\varphi_B(z|m)$, and eq 10 reduces to the standard Scheutjens and Fleer expression for the neighbor average.

Adsorption energy is included in eq 9 provided the surface sites m [with $\varphi_m(z|m) = 1$ for $z \le 0$ and $\varphi_m(z|m) = 0$ for $z > 0$] are included in the summation over B. The adsorption energy contribution is only nonzero for $z = 1$, and equals $(1/6)kT\chi_{Am}$.

Next, we define an end segment distribution function $G_{i,m}(z,s|1)$. This is the statistical weight of all walks of molecule i that start with segment 1 somewhere in the system and end after $s-1$ steps with segment s in layer z above a site m. For $s = 1$ we get the monomer distribution function, which for monomers of type A reads

$$G_{i,m}(z,1|1) = f_m G_A(z|m) \tag{11}$$

This expression just says that the probability for a monomer A to be in layer z above a site m is f_m times the probability to be in layer z for a homogeneous surface of only sites m (*i.e.*, when $f_m = 1$). The distribution of all other segments in a chain molecule is obtained by taking into account the connectivity of the chain in a first-order Markov approximation:

$$G_{i,m}(z,s|1) = G_i(z,s|m)\left[\frac{1}{6}G_{i,m}(z-1,s-1|1) + \frac{1}{6}G_{i,m}(z+1,s-1|1) + \sum_n^4 \frac{1}{6}M_{nm}G_{i,n}(z,s-1|1)\right] \quad (12)$$

where $G_i(z,s|m) = G_A(z|m)$ if segment s in molecule i is of type A. Starting at the other end of the chain, we obtain $G_{i,m}(z,s|r)$ in a similar way:

$$G_{i,m}(z,s|r) = G_i(z,s|m)\left[\frac{1}{6}G_{i,m}(z-1,s+1|r) + \frac{1}{6}G_{i,m}(z+1,s+1|r) + \sum_n^4 \frac{1}{6}M_{nm}G_{i,n}(z,s+1|r)\right] \quad (13)$$

with the starting condition $G_{i,m}(z,r|r) = f_m G_A(z|m)$, analogous to eq 11. Combining the two end segment distribution functions computed from eqs 12 and 13 and summing over all segments s, we find the volume fraction of polymer i in layer z that is above a site m:

$$\varphi_{i,m}(z) = C_i \sum_s \frac{G_{i,m}(z,s|1)\, G_{i,m}(z,s|r)}{f_m G_i(z,s|m)} \quad (14)$$

Dividing by $f_m G_i(z,s|m)$ is necessary to correct for double counting of segment s. The normalization constant C_i can be found from the equilibrium volume fraction φ_i^{bulk} of molecules i in the bulk solution:

$$C_i = \varphi_i^{\text{bulk}}/r_i \quad (15)$$

The adsorbed amount θ^a is calculated from the volume fraction profile by considering only the polymer chains that have at least one segment in the first layer.[10] It is expressed in equivalent monolayers (=segments per site).

The free segment distribution functions $G_A(z|m)$ can be found from the volume fraction profiles using eqs 8 and 9. On the other hand, the volume fraction profiles are found from the free segment distribution functions by eqs 11–14. Also, eq 1 (volume constraint) has to be fulfilled. An iterative procedure is used to find a self-consistent solution, where the number of iteration variables equals the number of free segment distribution functions. This number is the product of the number of layers, the number of types of sites, and the number of monomer types.

Results and Discussion

Homopolymers. In this section we show results of calculations for a homopolymer adsorbing on only one out of two or three kinds of surface sites. The polymer segments are called A, and the solvent is indicated by o. We use two solvency situations: an athermal solvent (Flory–Huggins parameter $\chi_{Ao} = 0$) and a "Θ-solvent" ($\chi_{Ao} = 0.5$). The parameter χ_{om} (where o denotes the solvent) is taken to be zero as only the difference $\chi_{Am} - \chi_{om}$ is important. To facilitate the comparison with standard homopolymer theories, we use a Silberberg χ_s parameter for the adsorption energy. The χ_s parameter can be found from the Flory–Huggins parameter χ_{Am} by dividing by −6. Note that χ_s is positive if the adsorption energy is negative. The adsorption energies per site are then $\chi_{s,m}$ and $\chi_{s,n}$.

We start by taking only two kinds of surface sites. The cluster parameter C represents the distribution of lattice sites over the surface. As can be seen from eq 7, maximum variation of C is possible if we take $f_m = f_n = 0.5$. The sites of type m are taken to be repelling, those of type n adsorbing, such that the average is 0 ($\sum_m \chi_{Am} = \sum_m f_m \chi_{Am} = 0$). In Figure 3a the adsorbed amount is shown as a function of C in an athermal solvent. The polymer will try to adsorb on the adsorbing sites with as many segments as possible. On a checkered surface ($C = -1$) there is an unfavorable repelling site adjacent to each adsorbing site. For $\chi_s = \pm 1$, the energetic interaction with the adsorbing sites is not high enough to compensate for the entropy loss that accompanies adsorption: the polymer is depleted from the wall. With increasing degree of clustering, the polymer can adsorb on the favorable surface sites without having too many segments on the repelling sites, so that adsorption can occur. This effect leads to an increasing dependence of the adsorbed amount on C. For C close to unity the adsorbed amount is about half the value that is found for a homogeneous surface with an adsorption energy of 1 kT, because then the repelling sites hardly contribute to the adsorption behavior. Thus, by only changing the distribution of sites, we can change the surface from nonadsorbing to adsorbing.

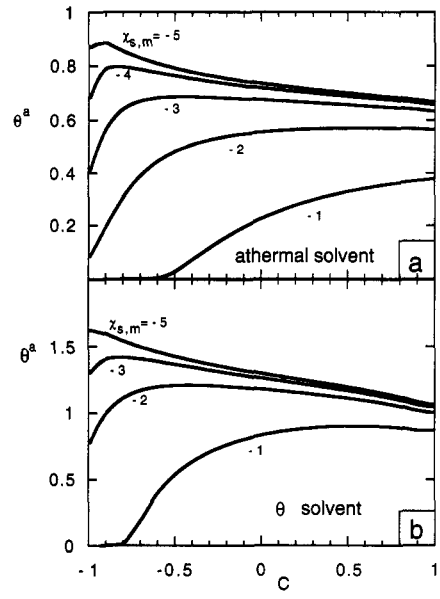

Figure 3. Adsorbed amount of a homopolymer with 1000 segments on a surface with two kinds of sites as a function of the clustering parameter C. The fraction of adsorbing sites is 0.5, and the bulk volume fraction of polymer is 0.0001. The values of χ_s on nonadsorbing sites are indicated, and χ_s on the adsorbing sites equals $-\chi_s$ on the nonadsorbing sites. Diagram a is for an athermal solvent ($\chi_{Ao} = 0$), and diagram b is for a Θ solvent ($\chi_{Ao} = 0.5$).

For higher absolute values of the adsorption energies, adsorption even occurs on an alternating surface. Here, enough energy is gained on adsorbing sites to compensate for the segments that are on the repelling sites. If the degree of clustering increases, the polymer avoids the repelling sites, so that eventually, for C close to 1, only half the surface is used. This effect leads to a decreasing dependence of the adsorbed amount on C. For intermediate values of the adsorption energy, these two compensating effects cause a maximum.

Figure 3b is similar to Figure 3a but for Θ conditions ($\chi = 0.5$). The nonadsorbing sites are now slightly less unfavorable than in the athermal case: in the first layer, the polymer has $^1/_6$ less possible unfavorable contacts with the solvent compared to the bulk solution. This causes the maximum to shift toward lower values of C. Adsorption on a heterogeneous surface without a net interaction has also been found by Odijk[6] and Andelman and Joanny.[7] The difference between adsorption on an alternating and

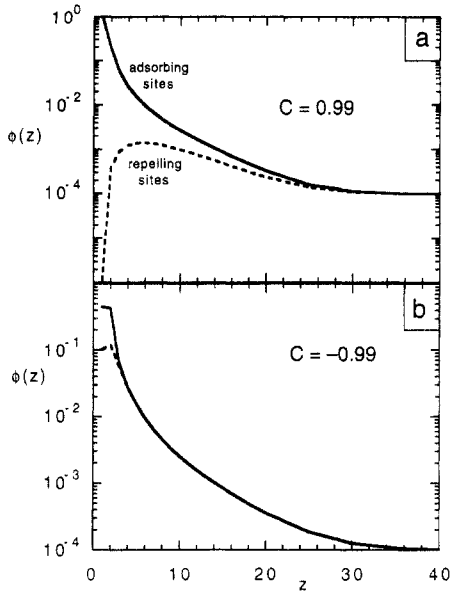

Figure 4. Volume fraction profiles taken from points in the curve in Figure 3a where χ_s (adsorbing sites) = 4 for a patchy surface with $C = 0.99$ (top) and for a checkerboard surface with $C = -0.99$ (bottom).

a patchy surface can be seen clearly in Figure 4, where the volume fraction profiles per kind of site are plotted for circumstances as in Figure 3a (athermal solvent), for the curve with $\chi_{s,n} = -\chi_{s,m} = 4$ and two widely different values of C. Figure 4a shows the volume fraction profiles on the adsorbing sites (full curve) and on the repelling sites (dotted curve) for a very "patchy" surface ($C = 0.99$). The adsorbing sites are almost completely filled with polymer ($\varphi(1) \approx 1$), whereas the repelling sites show a depletion in the first layer ($\varphi(1) < \varphi^{bulk}$). Figure 4b shows the other extreme: $C = -0.99$ or a checkerboard surface. The adsorbed amount is almost the same as in Figure 4a, but the profiles are completely different (note the different vertical scales): on the adsorbing sites the first layer is only half-filled, but the most striking difference is the significant amount of polymer that is adsorbed on the repelling sites despite the unfavorable energetic interaction.

Odijk[6] and Andelman and Joanny[7] have studied the interaction of homopolymers with a random surface, where the interaction energy between polymer segments and surface sites is a random variable with zero mean and varying standard deviation. They both find that adsorption can take place although the average interaction is too low to justify net adsorption. According to Odijk, the adsorption should decrease with increasing variance of the interaction energy, whereas Andelman and Joanny find the opposite. To model this system in our scheme, we would need a very large number of types of surface sites, which is not feasible. However, some insight can be obtained with three kinds of surface sites, where the first and third sites have an equal probability (*i.e.*, $f_1 = f_3$) but an opposite sign of the adsorption energy ($\chi_{s,1} = -\chi_{s,3} = -1$). The remaining kind of site has a χ_s of 0, so that the average adsorption energy is exactly 0 kT. Using standard statistical theory, the variance is now defined as $\sigma_2 = \sum_m(\chi_{s,m})^2 f_m$, which in this simple case reduces to $2f_1$. By plotting the adsorbed amount as a function of σ (Figure 5), we see that the adsorption increases with increasing standard deviation. If $\sigma = 0$ we have a homogeneous surface containing only sites with $\chi_s = 0$, so there can be no adsorption. By increasing σ, we create adsorbing sites. The higher σ is the higher the adsorption energy of the adsorbing sites. If the adsorption energy of the adsorbing sites is high enough, the polymer will stick. This result agrees with that of Joanny and Andelman. Although it is a rather crude approximation to model a Gaussian distribution using only three kinds of sites, there is no reason to believe that the trends will change much if more kinds of sites are taken into account.

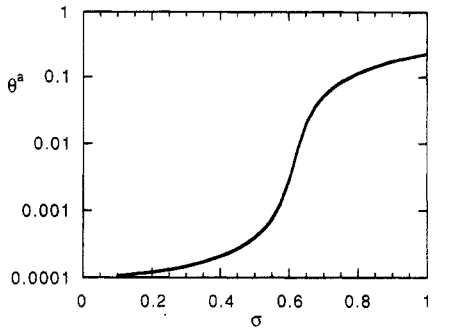

Figure 5. Adsorbed amount as a function of the width of the distribution. The surface was considered to consist of three kinds of sites, with $\chi_s = -1$, 0, and 1, respectively, and an equal fraction of adsorbing and repelling sites. The width is plotted as the standard deviation σ, where $\sigma^2 = \sum_m(f_m(\chi_{s,m})^2)$. The solvent is athermal ($\chi_{Ao} = 0$). Other parameters are as in Figure 3.

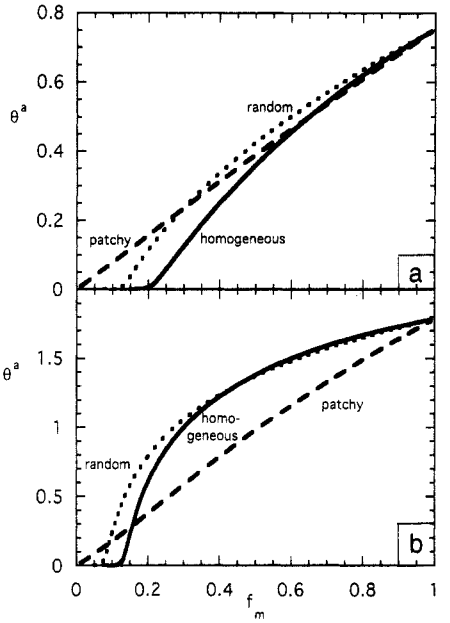

Figure 6. Adsorbed amount as a function of the fraction of adsorbing sites on a random surface (dotted curve, $C = 0$) and on a patchy surface (dashed, $C = 0.95$). On adsorbing sites $\chi_s = 1$; on nonadsorbing sites $\chi_s = 0$. A curve for a homogeneous surface is also shown for comparison (full curve). In this curve, χ_s is taken as the independent variable and equals $f_m\chi_{s,m}$. Top diagram, athermal solvent ($\chi_{Ao} = 0$); bottom diagram, Θ solvent ($\chi_{Ao} = 0.5$). The polymer has a chain length of 1000 and a bulk volume fraction of 10^{-4}.

In the remainder of this paper, we restrict ourselves to only two kinds of sites. In this case we can describe the distribution of surface sites by the cluster parameter C. The more extreme the ratio between the sites is, the smaller the possible range for C. However, any value for $0 \le C \le 1$ is always possible. We have taken two values for C: $C = 0$, a random surface, and $C = 0.95$, a patchy surface. The results are compared with those for a homogeneous surface. A homogeneous surface is defined as a smooth surface with only one kind of surface site. The value of χ_s is taken as a weighted average of the adsorption energy on the surface sites in the heterogeneous case; *i.e.*, $\chi_s = \sum_m f_m\chi_{s,m}$. Figure 6 shows the adsorbed amount as a function of the fraction of adsorbing sites f_m. We see that for a patchy surface the adsorption is almost proportional

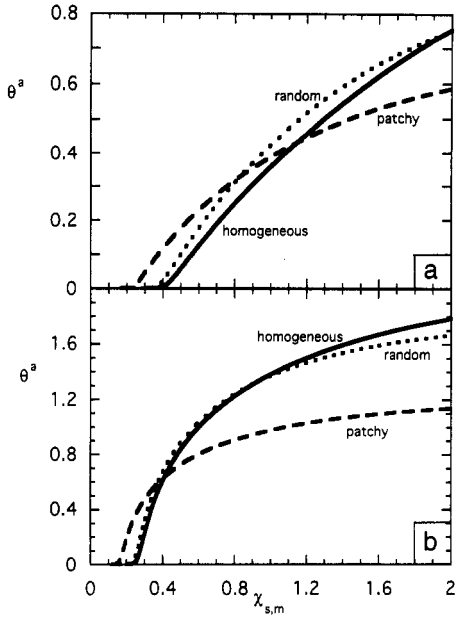

Figure 7. Adsorbed amount as a function of the adsorption energy of the adsorbing sites. The fraction of adsorbing sites is 0.5. The dotted curves are for a random surface ($C = 0$), the dashed curves are for a patchy surface, and the full curves apply to a homogeneous surface with $\chi_s = f_m\chi_{s,m}$. Other parameters are as in Figure 6.

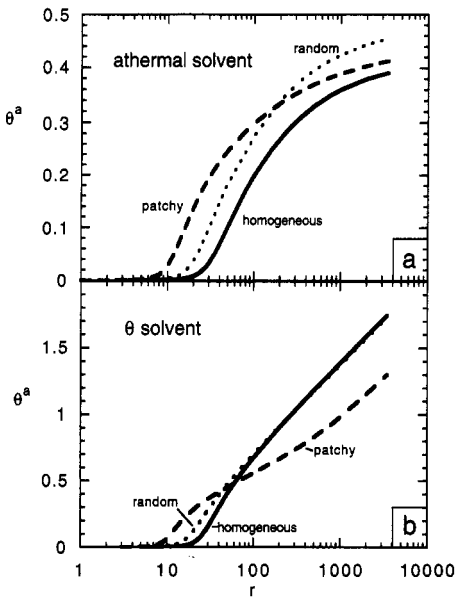

Figure 8. Adsorbed amount as a function of the chain length r of the polymer. The fraction of adsorbing sites is 0.5; the other parameters are the same as in Figure 6.

to the fraction of adsorbing sites (for $C = 1$ the plot would be linear). For a random surface there is no adsorption for small values of f_m. In this case the polymer is depleted for $f_m < 0.12$ because the entropy loss is greater than the energy gain upon adsorption. Note that, like in Figures 3 and 5, adsorption can take place on a heterogeneous surface before the average adsorption energy exceeds the critical value, which is 0.182 kT for a cubic lattice.[10] For a Θ-solvent (Figure 6b) the adsorption on a patchy surface is in most cases even less than on a corresponding homogeneous surface. All other trends are the same as in the athermal case.

Figure 7 shows the dependence of the adsorbed amount on the adsorption energy χ_s for a good solvent (a) and a Θ-solvent (b). It shows the same trend as in Figure 6: adsorption occurs first on a patchy surface, because the polymer can use the adsorbing sites more effectively. With increasing adsorption energy, adsorption will also take place on a random surface as soon as the energy gained on the adsorbing sites is enough to compensate the entropy loss on the adsorbing as well as on the nonadsorbing sites. For high adsorption energies, there will be more polymer on a random surface because the nonadsorbing sites are occupied to a greater extent than on a patchy surface. For even higher values of χ_s, the curves for a random heterogeneous surface and a homogeneous surface intersect: less polymer is adsorbed on the heterogeneous surface because of the unfavorable interaction with nonadsorbing sites so that the first layer is less filled.

For chains of increasing length one could expect surface heterogeneity to be averaged out so that the curves for a random surface and a homogeneous surface would coincide for a long enough chain. However, for a homogeneous surface it has been shown[10] that for a chain length more than, say, 100, the occupation of the first layer does not increase any more. Any increase in the adsorbed amount is then purely due to the formation of longer loops and tails. The chain length dependence is plotted in Figure 8: for short chains we see that, like in Figures 6 and 7, adsorption occurs first on a patchy surface, then on a random surface, and finally on a homogeneous surface. At high molecular weight the curve for a patchy and a random surface cross (in both Figure 8a and Figure 8b) because of the smaller useful surface area in the former case. Under the circumstances of Figure 8a (good solvent) the curves for a random surface and for a homogeneous surface do not meet: the difference in adsorbed amount (~0.06 monolayers for $r > 1000$) is situated in the layers closest to the wall, and this will not be altered with increasing chain length. However, for a Θ-solvent (Figure 8b), where the occupation in the first layer is much higher, the influence of the surface is already smoothed out at relatively small chain length so that the curves coincide for longer chain lengths.

As a last example for homopolymer adsorption, we calculate a displacement isotherm, like the ones calculated by Van der Beek *et al.*[12] In a displacement isotherm, the polymer is dissolved in a binary mixture of solvent and displacer (a component which adsorbs more strongly than the polymer). If the displacer concentration is high enough, the polymer is desorbed from the surface. The point where the polymer is fully desorbed is called the critical displacer concentration or critical solvent strength. This concentration can be used to determine the difference in adsorption energy of a polymer segment and a solvent molecule, *i.e.*, χ_s. In the paper referred to above, the authors raise the question whether the method is justified in the case of surface heterogeneity. As can be seen from Figure 9, the influence of surface heterogeneity is not very large: the shift in the critical displacer concentration is <1 vol %, which is less than the experimental error. However, from this plot we can conclude that the polymer is more weakly attached on a random surface than on a homogeneous surface (less displacer is needed to displace the polymer) but more strongly on a patchy surface. Hence, surface heterogeneity can give a higher value than a homogeneous surface, as well as a lower one.

Copolymers. For copolymers, the number of parameters increases drastically, which makes the choice for a representative system difficult. As an example, we first reproduce the results for one of the systems Huang and Balazs used in their paper in ref 9 and then compare it with our model. As stated before, the Huang and Balazs model is two-dimensional: the sites are grouped in stripes on the surface, so that the volume fraction is now a function

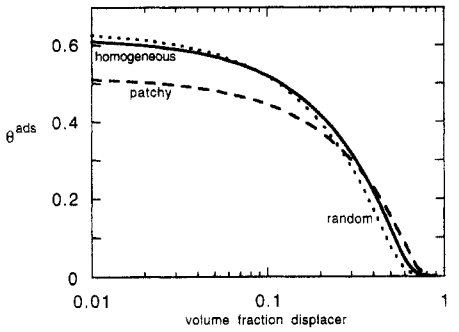

Figure 9. Displacement isotherm for a polymer on a random heterogeneous surface ($C = 0$, dotted curve), on a patchy surface ($C = 0.95$, dashed), and on a homogeneous surface (full curve). The displacer d is monomeric ($r_d = 1$). The polymer has 100 segments, and the equilibrium volume fraction in the bulk $\varphi_A^{bulk} = 0.001$. The mixture is athermal ($\chi_{Ao} = \chi_{Ad} = \chi_{do} = 0$). The fraction of adsorbing sites is 0.5. The adsorption energies on adsorbing sites are 1.9 kT for the polymer and 1.88 kT for the displacer. On the nonadsorbing sites all adsorption energies are zero. For the homogeneous surface $\chi_s = 0.95$ for the polymer and $\chi_s = 0.94$ for the displacer.

of position x on the surface as well as of the distance from the surface z. For $x = 1$–4 we have sites m, and for $x = 5$–8 sites n. By placing a reflecting boundary between $x = 0$ and 1 and between $x = 8$ and 9, we only need to calculate 8 x-values for every layer z. For periodic boundaries 16 x-values would have been necessary. In this way, we model a system with stripes of 8 consecutive lattice sites of the same kind: sites m for $x = -3$ to +4, sites n for $x = 5$–12. In the y-direction a mean-field approximation is used.

In the system, we have an $A_{25}B_{25}$ copolymer in solvent o. The interaction parameters are $\chi_{AB} = 0.5$, $\chi_{Ao} = 0.5$, and $\chi_{Bo} = 0$. These values are too low to give micelles in solution. We took the bulk volume fraction of the polymer to be 10^{-4}. The A blocks adsorb on the sites m, and the B's on the sites n: $\chi_{Am} = \chi_{Bn} = -10$, $\chi_{An} = \chi_{Bm} = 0$.

A view of the volume fraction profile distribution is shown in Figure 10, where the A segments are plotted in Figure 10a and the B segments in Figure 10b. It can be seen that the volume fractions show a gradual transition at the boundary between the sites of type m or n (*i.e.*, between $x = 4$ and $x = 5$).

In Figure 11 we compare the profiles in the middle of the stripes (*i.e.*, in layer 1 for the sites of type m and in layer 8 for the sites n, triangles) with our model for a patchy surface ($C = 0.95$, squares). The profiles on the sites m are shown in open symbols, and those on the sites n in filled symbols. The two profiles for A segments on sites m coincide, but on the sites n our model tends to show less depletion. The profiles for the B segments are in good agreement with the two-dimensional model (note the logarithmic scale).

The advantage of the two-dimensional model is that information can be gained on the interface between the two kinds of sites, which is impossible in our model. However, the geometry is limited: only stripes can be modeled (or, in a cylindrical lattice, circles), which does not seem very realistic on this scale. A random surface cannot be dealt with in this way. Furthermore, only small systems can be modeled as the number of iteration variables increases as the number of layers in the x-direction times the number of layers in the z-direction times the number of monomer types. Our model uses a separate mean-field potential for every kind of lattice site in every layer. This can be further reduced by taking only one mean-field potential per layer for $z > z'$, where z' is not too large. As the potentials above different kinds of sites converge for much smaller z than the end segment distribution functions, this is not a severe approximation.

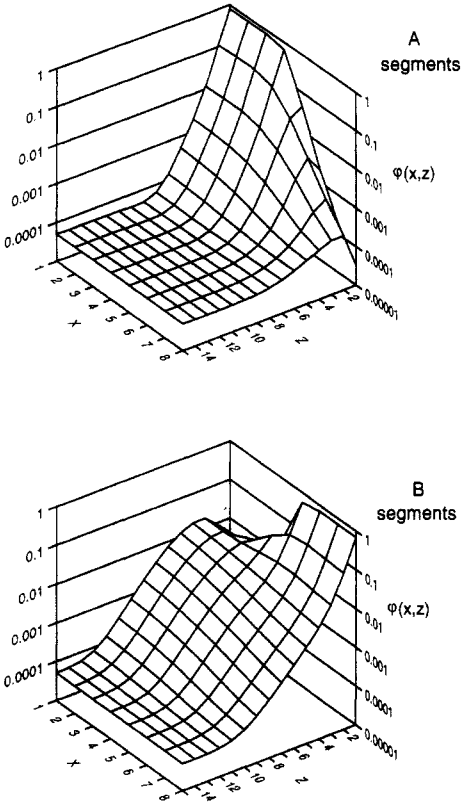

Figure 10. Volume fraction profiles calculated for a copolymer $A_{25}B_{25}$, $\varphi^{bulk} = 10^{-4}$ in solvent o with the Huang and Balazs method[9] using a two-dimensional striped surface. The top diagram gives the results for the A segments, and the bottom one is for the B segments. The wall is located at $z = 0$. For $x = 1$–4 we have sites m, and for $x = 5$–8 sites n. A reflecting boundary is placed between $x = 0$ and $x = 1$, and between $x = 8$ and $x = 9$. A mean field approximation is applied in the y-direction. Flory–Huggins parameters: $\chi_{AB} = \chi_{Ao} = 0.5$, $\chi_{Bo} = 0$; with the surface: $\chi_{Am} = \chi_{Bn} = -10$, $\chi_{An} = \chi_{Bm} = 0$.

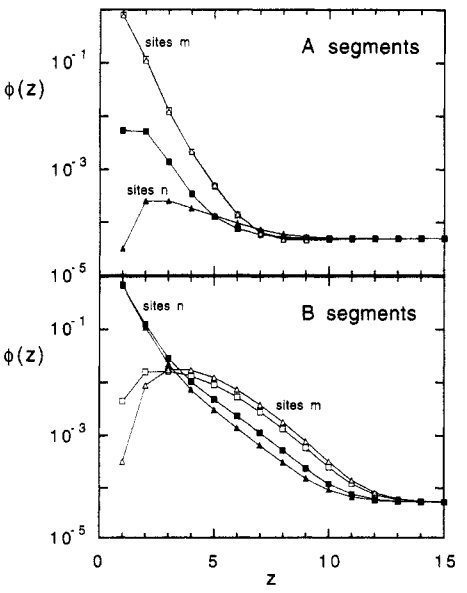

Figure 11. Comparison of volume fraction profiles calculated using the Huang and Balazs model (triangles) and our model (squares). The open triangles are for $x = 1$ (middle of the stripes with sites m), and the closed triangles are for $x = 8$ (middle of the stripes with sites n). For our model, we used the same interaction parameters as in Figure 10, fraction m-sites 0.5, cluster parameter $C = 0.95$. Open squares, on sites m; closed squares, on sites n.

The use of the proper chain statistics ensures that the information about the surface structure is passed on into the solution. This leads to a significant reduction of the number of iteration variables, thus facilitating the calculation on longer chains or a broader distribution of surface sites.

Conclusions

It is possible to model chemical surface heterogeneity even using a mean-field approximation. Homopolymers can adsorb on a heterogeneous surface if the average energetic interaction with the surface is below the critical adsorption energy. This can happen more easily if the heterogeneity is distributed patchwise than when its distribution is more random. Long polymer chains do not necessarily average out all surface heterogeneity. Adsorption is usually higher on a patchy surface than on a randomly distributed surface if the adsorption energy or chain length is low, but the opposite holds for high adsorption energy on chain length. For a patchy surface, adsorption is limited to the adsorbing patches. Displacement isotherms for homopolymers are not shifted dramatically by surface heterogeneity, regardless of distribution. The model can also be used for block copolymers on heterogeneous surfaces. Here, strong segregation can occur.

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