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A Two-Dimensional Self-Consistent-Field Model for Grafted Chains: Determining the Properties of Grafted Homopolymers in Poor Solvents

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Polymers that are grafted to a solid surface display a rich variety of phase behavior.[1–5] The unique behavior arises from the fact that the grafted chain ends are immobile; thus, as environmental conditions are varied, the chains are limited in their ability to respond to these changes. This behavior is particularly interesting when adverse conditions, such as poor solvents, are introduced. It is then of particular interest to determine how opposing influences affect the properties of the grafted layer. For example, the presence of a poor solvent would normally drive the chains to associate into macroscopic aggregates. Since the ends are anchored, however, these chains cannot undergo such macroscopic phase separation. Instead, grafted homopolymers in sufficiently poor solvents are observed to form local bundles or "dimples", leading to lateral segregation within the layer.[2–5]

In order to visualize these dimpled layers, one needs to calculate the polymer density profiles at the interface. Since the layers are predicted to show unusual structure in the lateral direction, previous, one-dimensional self-consistent-field (SCF) calculations[6,7] are inadequate in capturing the features of these layers. In this paper, we develop a two-dimensional SCF model for polymers grafted onto a solid surface. In this model, the polymer density is assumed to vary in directions both perpendicular and parallel to the surface. Through this method, we can explicitly calculate the density profiles for the grafted layers in poor solvents. Furthermore, the method is sufficiently general that it can yield the polymer density profiles in a large variety of interfacial systems involving lateral inhomogeneities.

Our method is based on the one-dimensional self-consistent-field model for grafted chains developed by Cosgrove et al.[6] and Hirz.[7] The calculation is performed on a square lattice. Homopolymer chains are terminally grafted to the $z = 1$ line. The volume fractions of the homopolymer segments and solvent molecules are denoted by $\phi(x,z)$ and $\phi_0(x,z)$, respectively. In the case of an incompressible system, $\phi(x,z) + \phi_0(x,z) = 1$.

The probability of finding the grafted (first) segment of a chain i, which is grafted at $(x_i, 1)$, is given by

$$G_i(x,z) = \delta_{x,x_i}\delta_{z,1} \tag{1}$$

where δ_{x,x_i} and $\delta_{z,1}$ are Kronecker deltas.

For the nongrafted sites, $G(x,z)$ is the probability of finding a homopolymer segment at (x, z) and is given by

$$G(x,z) = \phi_0(x,z)\exp(\chi(\langle\phi(x,z)\rangle - \langle\phi_0(x,z)\rangle)) \tag{2}$$

Here, χ is the Flory–Huggins parameter and the average volume fraction of homopolymer segments at (x, z) is defined by the following:

$$\langle\phi(x,z)\rangle = \lambda_1[\phi(x-1,z) + \phi(x+1,z) + \phi(x,z-1) + \phi(x,z+1)] \tag{3}$$

where $\lambda_1 = {}^1/_4$.

Consider a terminally attached chain i, which is m segments long and has its first segment grafted at $(x_i, 1)$. The end segment probability, $G_{ta}(x,z,m;x_i,1)$, is the probability that its mth segment is at (x,z) and can be computed from the following recurrence relation:

$$G_{ta}(x,z,m;x_i,1) = G(x,z)\,\lambda_1[G_{ta}(x-1,z,m-1;x_i,1) + G_{ta}(x+1,z,m-1;x_i,1) + G_{ta}(x,z-1,m-1;x_i,1) + G_{ta}(x,z+1,m-1;x_i,1)] \tag{4}$$

This implies that a chain which arrives at site (x, z) in m (>1) steps must have been at one of the nearest neighbors of (x, z) on the $(m-1)$th step. Note that the end segment probability, G_{ta}, is calculated separately for each chain.

In a similar way, the end segment probability $G(x,z,m)$ is the probability that a chain of m segments has its first segment anywhere on the lattice and its mth segment at (x, z). This probability is given by

$$G(x,z,m) = G_m(x,z)\,\lambda_1[G(x-1,z,m-1) + G(x+1,z,m-1) + G(x,z-1,m-1) + G(x,z+1,m-1)] \tag{5}$$

where $G_m(x,z) = G_i(x,z)$ if the mth segment is grafted at $(x_i, 1)$. Otherwise, $G_m(x,z) = G(x,z)$.

The initial conditions are $G_{ta}(x,z,1;x_i,1) = G_i(x,z)$ and $G(x,z,1) = G(x,z)$. The volume fractions at grafting sites are all equal to unity. The volume fraction $\phi(x,z)$ at a site other than a grafting site can be calculated as follows:

$$\phi(x,z) = \sum_i \frac{\sum_{m=1}^{N} G(x,z,N-m+1)\,G_{ta}(x,z,m;x_i,1)}{G(x,z)\,G(x_i,1,N)} \tag{6}$$

where the sum $\sum_i$ is over all the chains in the system and N is the degree of polymerization. Using eqs 1–6 and the incompressibility condition, the density profiles can be calculated self-consistently.

In this model, the solvent quality is altered by varying the value of χ. Θ solvent conditions are modeled by setting $\chi = 0.5$. Thus, values of $\chi > 0.5$ provide poor solvent conditions, while χ values < 0.5 yield good solvent behavior. As a test of our 2D model, we first examined the properties of the grafted layer in a good solvent. In the presence of good solvents, the layer is laterally homogeneous;[5] thus, the density profile will only depend on the direction normal to the surface. Consequently, under these conditions, our polymer density profile should converge to the profile obtained from the 1D model. To perform the comparison, we calculated the average value of the polymer density along the lateral direction in the 2D model to obtain a single point for each value of Z. The resulting curve coincides with the plot obtained from the 1D model.

In carrying out the above calculations, we assumed periodic boundary conditions for our square lattice. (Periodic boundary conditions are imposed at the sides of the box and, thus, allow us to effectively model larger systems.) However, the 2D solutions can be obtained by using either periodic or "open" boundary conditions. Under the open boundary conditions, the first and last chains are both grafted 10 lattice sites away from the edge of the box, in effect creating a "box" of grafted chains within a larger, working box. Consequently, the last chain on either side is buffeted by the solvent molecules. As we will demonstrate below, both the open and periodic boundary conditions yield similar results for the behavior of the internal chains in poor solvents.

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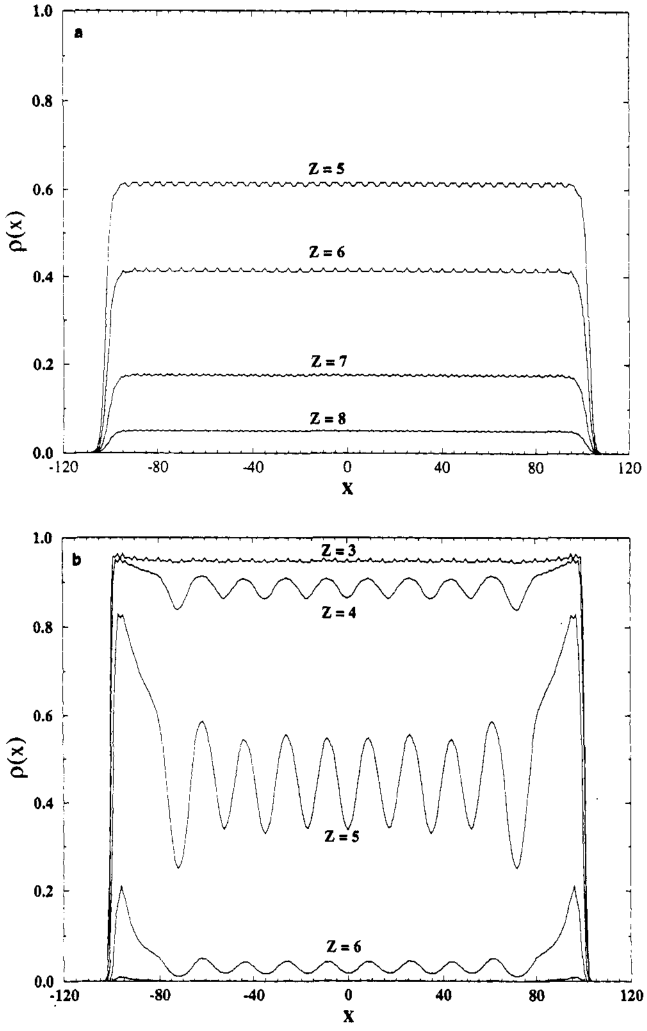

Figure 1. Grafted layer for $N = 20$ and $\sigma = 0.2$. In (a), $\chi = 1.0$, while in (b), $\chi = 2.3$. Open boundary conditions were used.

To determine the behavior of the layer in the presence of poor solvents, we varied the χ values from 0.5 to 2.3. The chain length, N, was initially fixed at 20 lattice sites, and the grafting density, σ, was set equal to 0.2. (By choosing such a high grafting density, we can make qualitative comparisons between our results and the findings obtained by Yeung et al., which yield an extensive description of this regime.) Parts a and b of Figure 1 reveal the density profiles along X for $\chi = 1.0$ and $\chi = 2.3$, respectively. At $\chi = 1.0$, the layer is still laterally homogeneous (the spikes in $Z = 5$–6 reflect the location of the grafting points). However, when χ is increased to 2.3 and the surrounding bath becomes a poorer solvent, "dimples" can clearly be seen near the top of the layer, $Z = 4$–6. The poor solvent drives the chains to aggregate; however, since the grafted ends are immobile, the chains can only respond to the solvent incompatibility by forming these local clumps. It is this clumping behavior that gives rise to the density profile in Figure 1b. (Since open boundary conditions were used in these calculations, the density profiles fall off to zero near the edges of the internal box. The larger bumps at both sides arise from lateral edge effects; namely, the chains at these edges are bordered by the poor solvent instead of other polymer chains.)

In Figure 2, the chain length was increased to $N = 30$; however, the other parameters were held fixed. By comparing Figures 1b and 2, we see that the amplitude of the dimples decreases as the chain length is increased. This implies that, for shorter chain lengths, the segments near the ends are more "pinched" than for the longer chains. The depth to which the solvent molecules penetrate the layer constitutes a greater fraction of the chain length for the shorter polymers. Thus, a higher fraction of the monomers is exposed to the poor solvent. This fact may be responsible for the more pronounced clumping in the shorter chains. We also find that the lateral spacing between the dimples increases with chain length. The later observation is in qualitative agreement with the predictions made by Yeung et al.[5]

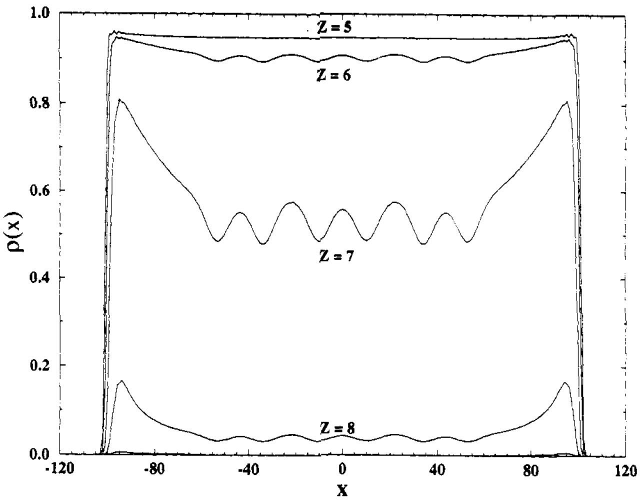

Figure 2. Grafted layer for $N = 30$, $\sigma = 0.2$, and $\chi = 2.3$. Open boundary conditions were used.

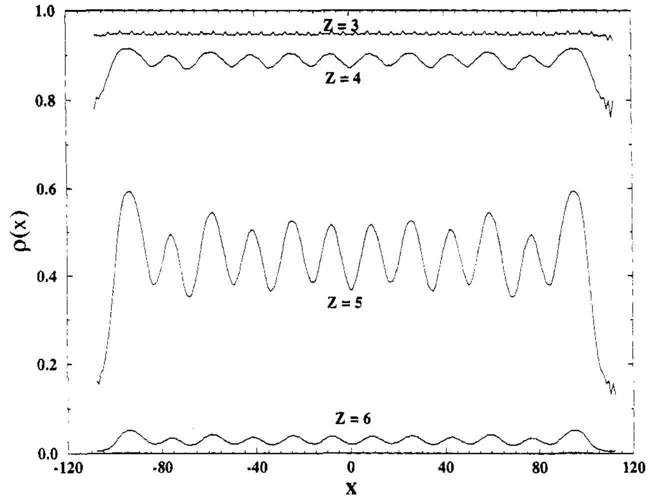

Figure 3. Grafted layer for $N = 20$, $\sigma = 0.2$, and $\chi = 2.3$. Here, periodic boundary conditions were used.

To test the effect of the different boundary conditions, we also performed the calculation for $N = 20$, $\chi = 2.3$, and $\sigma = 0.2$ with periodic conditions (see Figure 3). Under these boundary conditions, we need to break the symmetry of the system. Otherwise, all the chains are identical: there are no "central stalks" around which the other chains can aggregate. To break the symmetry in our system, we introduced a grafting dislocation in the regular grafting pattern. Specifically, the grafting distance between the last pair of chains is 6 lattice sites instead of 5. By comparing the dimples (specifically near $X = 0$) in Figures 1b and 3, we can see that the structures are comparable in their depth and lateral spacing. We believe the irregularity in the size of the dimples in Figure 3 is due to finite size effects.

The characteristics of the dimples in Figures 1b and 3 show qualitative agreement with predictions made by Yeung et al.:[5] For sufficiently poor solvents, there exists a range of chain lengths and grafting densities for which the dimples are confined to the edges of the grafted layer. Yeung et al. obtained these results by applying the random-phase approximation (RPA) to a mean-field solution. The resulting calculations provide predictions for the length scales of the dimples in 3D. However, our model describes a two-dimensional layer. Thus, we cannot make more quantitative comparisons between our findings and these earlier results. Furthermore, in our model, we assume a fairly regular distribution of grafting points. This differs from the RPA calculation, where a random distribution of grafting points is assumed. Such a difference in the distribution of grafting sites may also lead to differences in the dimpling morphology.[2]

In conclusion, we performed a 2D self-consistent-field calculation for grafted chains in poor solvents. The calculations qualitatively demonstrate the dimpling predicted by the previous RPA analysis.[5] The 2D SCF model is sufficiently general that it will be particularly useful in determining the effect of molecular architecture, solvent quality, and surface topology on the density profile for the grafted chains.

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