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End-Adsorbed Polymer Brushes in High- and Low-Molecular-Weight Matrices

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ABSTRACT: Numerical self-consistent-field theory (Scheutjens−Fleer theory) is used to describe the crossover from “dry” brush behavior, where the matrix from which the polymers adsorb is itself a high-molecular-weight polymer, to “wet” brush behavior, where the matrix is a small-molecule solvent. The free energy, f^*, required to add an additional chain to an existing brush is calculated for different values of N_a, N_b, χ, and z^*, where N_b and N_a are the respective degrees of polymerization of the adsorbing and nonadsorbing molecules, χ is the Flory interaction parameter between different segment types, and z^* is the integrated volume fraction of adsorbing chains. In situations where the adsorbing and nonadsorbing molecules have the same statistical segment length, f^* is completely specified by N_b/N_a, χN_a, and z^*/R_g, where R_g is the unperturbed radius of gyration of the adsorbing molecules. For a large range of these parameters, results for f^*, and the closely related adsorption isotherms, are in good agreement with analytic predictions from a simple scaling argument.

I. Introduction

The properties of polymer “brushes”, collections of polymer molecules which are attached by one of their ends to a surface or interface, have been studied in considerable detail in recent years.[1,2] Most of these studies have dealt with so-called “wet” brushes, where the matrix phase with which the brush is in contact is a small-molecule solvent which swells the brush. Some work has also been done on “dry” brushes, where the matrix phase is a high-molecular-weight polymer melt which is excluded from the brush. Both types of brushes have been treated by scaling theories and more complex self-consistent-field theories, all of which describe the brushes to a varying degree of approximation. Because the crossover from dry brush behavior to wet brush behavior involves the interplay between effects which are quite subtle, the scaling theories are not easily applied to these crossover situations. In addition, the practitioners of self-consistent-field theory have generally been interested in one extreme or the other, so there has been very little work describing features which both unify and distinguish between the two types of brushes. The purpose of this paper is to describe some of the important features of this crossover, using a numerical self-consistent-field treatment similar to that developed by Scheutjens and Fleer.[3]

We consider a binary blend of A and B molecules, with respective degrees of polymerization of N_a and N_b. Each of the B molecules has one end which adsorbs to the surface of the bulk melt, thereby creating an adsorbed layer as illustrated in Figure 1. Two related quantities are traditionally used to characterize the number of molecules in the adsorbed layer. The first of these is the interfacial excess z^*, defined in terms of the integral of the brush volume fraction:

$$z^* = \int_0^\infty [\phi_b(z) - \phi_\infty]\, dz \tag{1}$$

where $\phi_b(z)$ is the brush volume fraction at a distance z from the grafting surface, and ϕ_∞ is the equilibrium volume fraction of B chains in the bulk matrix phase ($\phi_\infty = \phi_b(\infty)$). Our interest here is primarily in cases of strong adsorption where ϕ_∞ is very small, in which case z^* can be viewed as the integral of the brush volume fraction profile. One can also define the interfacial excess in terms of Σ, an areal density of polymer molecules, obtained by dividing z^* by the volume of an adsorbing molecule:

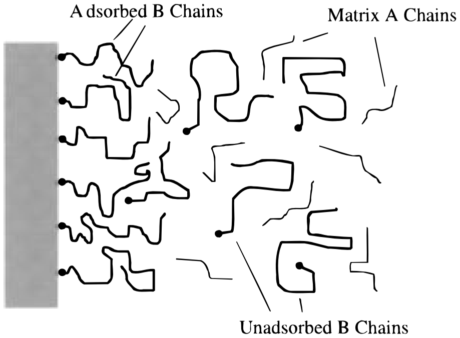

Figure 1. Schematic illustration of the formation of an end-adsorbed polymer layer.

$$\Sigma = z^*/N_b v_0, \tag{2}$$

where v_0 is the segmental volume, used to define the degrees of polymerization of the A and B molecules. A dimensionless surface coverage, σ, is defined by dividing Σ by some effective cross-sectional area of a polymer molecule. The appropriate normalization can be obtained by consideration of a lattice model. The volume of a lattice site is a^3, and the cross-sectional area of a lattice site is a^2. The unperturbed radius of gyration, R_g, of a polymer with N_b repeat units is given by

$$R_g = a(N_b/6)^{1/2} \tag{3}$$

In this case, we define $\sigma = a^2\Sigma$, so that σ corresponds to the fraction of surface sites which are occupied by the adsorbing end of the B molecules. These assumptions lead to the following relationship between z^* and σ:

$$\sigma = z^*/N_b a \tag{4}$$

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Once the repeat unit of a real polymer chain is specified, eq 3 serves as the defining relationship for the statistical segment length, a. For any flexible polymer, it will be possible to specify a repeat unit so that $v_0 = a^3$. A repeat unit specified in this way will, in general, correspond to a nonintegral multiple of actual monomeric units. For this reason, we do not require that $v_0 = a^3$ in our treatment, and we use z^* to define the surface coverage. Comparison to results expressed in terms of σ (where v_0 is implicitly assumed to be equal to a^3) can be obtained by using eq 4. Also, z^* is a more convenient measure of surface coverage when comparing to experimental results where surface coverages are expressed in units of mg/m^2. As a point of reference, for a polymer with a density of 1 g/cm^3, $z^* = 1$ nm corresponds to a surface coverage of 1 mg/m^2.

While the focus of this paper is on the results obtained from numerical self-consistent-field (SCF) theory, we begin in the following section with simple scaling theories of the wet brush and dry brush regimes. These theories give an understanding of the underlying physics and are in quantitative agreement with the SCF predictions for a certain range of parameters. The numerical SCF treatment is reviewed in section III, and results from both theoretical treatments are given in section IV. We finish with some concluding statements on the general suitability of SCF theory for studies of equilibrium and nonequilibrium properties of polymer interfaces.

II. Scaling Theory

In order to put the results of subsequent sections in the context of more readily comprehensible results, we begin here with a brief review of some scaling arguments based largely on the work of de Gennes.[4] In our terminology, the free energy per chain, k_BTf_{wet}, of a highly stretched wet brush is written as follows:

$$f_{wet} = \frac{h^2}{4R_g^{\ 2}} + \frac{N_b}{\phi_{av}}\left\{\frac{(1-\phi_{av})}{N_a}\ln(1-\phi_{av}) + \chi\phi_{av}(1-\phi_{av})\right\} \quad (5)$$

The first term in this expression is the stretching free energy of the adsorbed chains and is valid when the brush height, h, is significantly larger than R_g. The term in brackets is the interaction free energy per reference volume, v_0, in the grafted layer, which has an average polymer volume fraction of ϕ_{av} ($\phi_{av} = z^*/h$). The first of the two terms within these brackets represents the translational entropy of the matrix chains which are dissolved in the brush. The second of these terms involves the Flory interaction parameter, χ, and describes the enthalpy and nonideal entropy of the system.

By expanding for small ϕ_{av} and by neglecting terms which are constant or of higher order in ϕ_{av}, we can rewrite eq 5 as follows:

$$f_{wet} = \frac{h^2}{4R_g^{\ 2}} + \left(\frac{N_b}{2N_a} - \chi N_b\right)\phi_{av} + \frac{N_b}{6N_a}\phi_{av}^{\ 2} \quad (6)$$

Minimization of f_{wet} gives the following expressions for the equilibrium brush height, h_{wet}^{eq}:

$$\frac{h_{wet}^{eq}}{R_g} = \begin{cases} 2^{1/3}\left(\dfrac{N_b}{2N_a} - \chi N_b\right)^{1/3}\left(\dfrac{z^*}{R_g}\right)^{1/3} & (\chi N_a \ll 0.5) \\ (2/3)^{1/4}\left(\dfrac{N_b}{N_a}\right)^{1/4}\left(\dfrac{z^*}{R_g}\right)^{1/2} & (\chi N_a = 0.5) \end{cases} \quad (7)$$

The equilibrium free energy per chain in the polymer brush, f_{wet}^{eq}, is then obtained by combining eqs 6 and 7:

$$f_{wet}^{eq} = \begin{cases} 1.19\left(\dfrac{N_b}{2N_a} - \chi N_b\right)^{2/3}\left(\dfrac{z^*}{R_g}\right)^{2/3} & (\chi N_a \ll 0.5) \\ 0.408\left(\dfrac{N_b}{N_a}\right)^{1/2}\left(\dfrac{z^*}{R_g}\right) & (\chi N_a = 0.5) \end{cases} \quad (8)$$

The quantity $k_BTf_{wet}^{eq}$ is the overall free energy per chain in the adsorbed polymer layer. Because polymer brushes must necessarily exist at interfaces, the free energy per chain is these brushes also includes a contribution from the interfacial free energy. Adsorption of polymer molecules is accompanied by a decrease in the interfacial free energy, and this decreased free energy is included in f_{wet}^{eq}. The chemical potential of adsorbed molecules will therefore be larger than f_{wet}^{eq}. This chemical potential, which we define as $k_BTf_{wet}^*$, is the quantity of interest because it represents the free energy required to place a single molecule into the polymer brush. It is obtained from f_{wet}^{eq} as follows:

$$f_{wet}^* = \left.\frac{\phi(Qf_{wet}^{eq})}{\partial Q}\right|_A = \frac{\partial(z^*f_{wet}^{eq})}{\partial z^*} \quad (9)$$

where Q is the number of molecules in the adsorbed layer and A is the area of the layer. The right-hand part of eq 9 follows because, at fixed area, Q is proportional to z^*. Inspection of eq 8 indicates that f_{wet}^* is obtained from f_{wet}^{eq} by multiplying by $^5/_3$ for $\chi N_a \ll 0.5$ and by 2 for $\chi N_a = 0.5$:

$$f_{wet}^* = \begin{cases} 1.77\left(\dfrac{N_b}{2N_a} - \chi N_b\right)^{2/3}\left(\dfrac{z^*}{R_g}\right)^{2/3} & (\chi N_a \ll 0.5) \\ 0.726\left(\dfrac{N_b}{N_a}\right)^{1/2}\left(\dfrac{z^*}{R_g}\right) & (\chi N_a = 0.5) \end{cases} \quad (10)$$

where we have multiplied by an additional factor of 0.89 to take into account the decrease in brush free energy obtained by consideration of the true parabolic profile for wet brushes, as described by Milner, Witten, and Cates.[5] Equation 10 is valid for wet brushes with high values of N_b/N_a. Matrix chains with $N_a > N_b$ will be excluded from the brush entirely. In this dry brush limit, one can obtain estimates for f_{dry}^* by considering only the stretching contribution to the free energy:

$$f_{dry}^* = \frac{3}{4}\left(\frac{z^*}{R_g}\right)^2 \quad (11)$$

As described previously by Ligoure and Leibler, f^* is related to the equilibrium adsorption isotherm and also to the activation free energy for the addition of a polymer molecule to an existing brush.[6,7] Consider, for example, the buildup of the polymer layer during the adsorption process. As additional chains are added to the brush, z^*/R_g increases, and f^*, the activation free energy for the adsorption of additional chains, increases.

Note that the mean-field treatment here (and in the full SCF treatment) fails to recognize that at very low coverages, adsorbed polymer molecules are isolated from one another, giving a nonuniform lateral coverage. In this so-called "mushroom" regime, f^* will actually be independent of z^*.[6]

The beauty of the scaling treatment described above is that it gives simple relationships between f^* and the parameters χN_a, N_b/N_a, and z^*/R_g which define the system. Our aim in the current paper is to move beyond the simplistic approximations used to develop eqs 10 and 11 and to study the relationship between f^* and matrix molecular weight in detail, emphasizing the qualitative differences between "wet" brushes with $N_b/N_a \gg 1$, and "dry" brushes with $N_b/N_a < 1$. The crossover between these two regimes occurs as the spatial extent of the matrix molecules becomes significant in comparison to the dimensions of the brush chains themselves. It is impossible to describe these effects in terms of a single excluded volume parameter. One must instead resort to a much more detailed treatment, such as the numerical self-consistent-field treatment described in the following section.

III. Self-Consistent-Field Theory

As described by Scheutjens and Fleer, the treatment used here is equivalent to a calculation of the partition function via an enumeration of all possible random-coil configurations of the polymer chains.[3] The central quantities in the theory are chain end distribution functions, $q(i,j)$, which give the probability that the jth segment of a polymer chain exists in the ith layer of a discrete lattice. We consider the case where "B" molecules possessing "stickers" at one end are immersed in a matrix of "A" molecules. There are two different distribution functions for B molecules, $q_{b1}(i,j)$ and $q_{b2}(i,j)$, corresponding to the two distinct chain ends for these polymers. Because both ends of an A polymer molecule are identical, it is completely specified by a single distribution function. The three distribution functions obey recursion relationships of the following form:

$$q_{b1}(i,j) = \left\{\frac{1}{6}q_{b1}(i-1,j-1) + \frac{1}{6}q_{b1}(i+1,j-1) + \frac{4}{6}q_{b1}(i,j-1)\right\} \exp\{-w_b(i)\} \quad (12)$$

where in this case w_b is the mean field for B polymer segments. The same expression holds for q_{b2}, and q_a obeys eq 12 if w_b is replaced by w_a. The mean field is the free energy required to place a segment of volume v_0 into its surroundings. For B segments this mean field is given by the following expression:

$$w_b(i) = \frac{\mu_b'(i) - \ln\phi_b(i)}{N_b} + \Pi v_0 \quad (13)$$

where ϕ_b is the local volume fraction of B repeat units and Π is an osmotic pressure term arising from the incompressibility constraint. The quantity $\mu_b'(i)$ is related to $\phi_b(i)$ by the chemical potential expression. We use the following regular solution relationship:

$$\frac{\mu_b'(i)}{k_B T} = \ln \phi_b(i) + \phi_a(i)\left\{1 - \frac{N_b}{N_a}\right\} + \chi N_b \phi_a^{\,2}(i) \quad (14)$$

The volume fractions are related to the distribution functions as follows:

$$\phi_b(i) = \frac{1}{N_b} \exp\left\{\frac{\mu_b}{k_B T}\right\} \sum_{j=1}^{N_b} q_{b1}(i,j) q_{b2}(i,N_b-j) \quad (15)$$

Here μ_b is the actual chemical potential of B molecules, obtained from the composition of the bulk phase. For small ϕ_∞ we have

$$\frac{\mu_b}{k_B T} = \ln \phi_\infty + \left\{1 - \frac{N_b}{N_a}\right\} + \chi N_b + \chi_e^{\,b} \quad (16)$$

where $k_B T \chi_e^{\,b}$ is the free energy associated with the placement of a polymer end group in the bulk polymer. A similar quantity, $k_B T \chi_e^{\,s}$, is used to define the free energy associated with the placement of the end group at the surface with which it interacts. The above equations are solved self-consistently, in conjunction with the corresponding equations for the A molecules,[8] using a relaxation method which has been described previously.[9] Interactions between the polymer end groups and their environment are accounted for in the initial conditions for the distribution functions: $q_{b2}(i,0) = q_a(i,0) = 1$ for all i, $q_{b1}(1,0) = \exp(-\chi_e^{\,s})$, and $q_{b1}(1,i) = \exp(-\chi_e^{\,b})$ for $i > 1$. The boundary conditions are obtained from the requirements that the distribution functions vanish at the wall ($q(0,j) = 0$) and that the excess osmotic pressure associated with the incompressibility constraint vanishes in the bulk phase ($\Pi(\infty) = 0$).

One quantity which is very important with regard to the kinetics of polymer adsorption is the free energy required to move the adsorbing end of the chain to a certain distance from the adsorbing surface. The attractive interaction with the wall typically operates over a very short range, characteristic of hydrogen bond formation, for example. In order for the end to approach the wall, however, the adsorbing molecule must penetrate the layer of chains which have already been attracted to the surface. The situation is as illustrated in Figure 1. The free energy barrier which must be overcome in order for the end group to interact with the surface can be calculated by considering the partition function for polymer chains which have the adsorbing end group in the ith lattice layer. The spatial dependence of this partition function is related to the equilibrium volume fraction profile of adsorbing end groups, $\phi_{end}(i)$, according to the following expression:

$$\phi_{end}(i) = \frac{1}{N_b} \exp\left(\frac{\mu_b}{k_B T}\right) q_{b2}(i,N_b) \quad (17)$$

The free energy barrier, $k_B T \Delta f(i)$ is then given by

$$\Delta f(i) = -\ln \frac{\phi_{end}(i)}{\phi_{end}(\infty)} = -\ln q_{b2}(i,N_b) - \mu_b/k_B T + \ln \phi_\infty \quad (18)$$

We assume that the free energy of the polymer chain decreases by $k_B T \Delta$ when the end group reaches the first lattice layer, giving $\Delta f(1) = f^* - \Delta$, with $\Delta = \chi_e^{\,b} - \chi_e^{\,s}$. The quantity $k_B T \Delta$ can be viewed as the depth of the short-range potential minimum responsible for the adsorption, with $k_B T f^*$ representing the height of the free energy barrier which must be overcome in order for this attractive potential to be felt.[6,7]

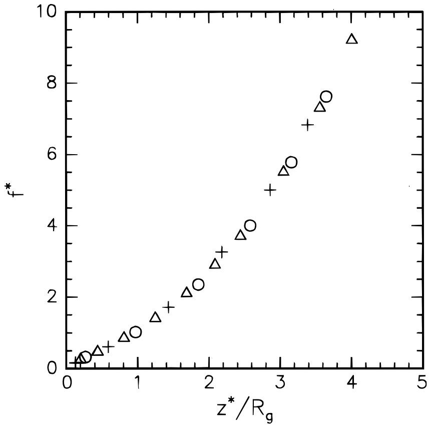

Figure 2. Activation free energy (normalized by k_BT) for insertion of a polymer chain into a polymer brush as a function of the brush coverage for $N_a = N_b = N$. Data for $N = 50$ (○), $N = 100$ (△), and $N = 300$ (+) all superpose on the same curve, indicating that z^*/R_g is the appropriate variable which determines f^*.

A useful relationship between z^*, ϕ_∞, f^*, and Δ can be obtained by realizing that $z^* = N_b a\phi_{\text{end}}(1)$ ($\sigma = \phi_{\text{end}}(1)$) and that $\phi_\infty = N_b\phi_{\text{end}}(\infty)$. These relationships can be substituted into eq 17, which, in conjunction with the definition for f^* and some rearrangement, gives

$$f^* = \ln \phi_\infty + \Delta - \ln(z^*/a) \tag{19}$$

One must also include a correction which includes information about the width of the potential felt by the end group. Very narrow potentials confine the end group to a narrow interfacial region, resulting in a correspondingly large entropic penalty. The width of the potential in our calculations corresponds to a single lattice layer. Previously, it has been shown that the free energy penalty associated with the confinement of the end group to a layer of width **a** is $\ln(R_g/\mathbf{a})$.[10,11] The quantity $k_BT\beta$ represents the net driving force for polymer adsorption and is obtained from Δ by subtracting this entropic penalty:

$$\beta = \Delta - \ln(R_g/\mathbf{a}) = \chi_e^b - \chi_e^s - \ln(R_g/\mathbf{a}) \tag{20}$$

With $R_g = (N_b/6)^{1/2}\mathbf{a}$, we can rewrite eq 19 in the following form:

$$f^* = \beta + \ln \phi_\infty - \ln\left(\frac{z^*}{R_g}\right) \tag{21}$$

One should keep in mind that β is an experimentally accessible quantity which can be obtained by comparing measured adsorption isotherms to results from numerical SCF calculations.[12,13] Values of β determined in this way are expected to be valid for coverages which are high enough so that the mean-field treatment is appropriate, i.e., where there is significant overlap between molecules in the adsorbed layer. In this case, β should be viewed as an effective, smeared interaction between the end group and the surface.

Finally, because z^*/R_g is a function only of $\beta + \ln \phi_\infty$ within the mean-field treatment,[10] eq 21 predicts that f^* itself is only a function of z^*/R_g. This prediction is confirmed by the data shown in Figure 2, where f^*, as calculated from the self-consistent-field theory, is plotted for dry brushes ($N_a = N_b$) with $N_b = 50$, $N_b = 100$, and $N_b = 300$. We are therefore able to express all of our results for f^* in terms of the single reduced variable z^*/R_g.

IV. Results

Equation 21 is valid for any equilibrium situation of strong adsorption, since the only assumption made in its derivation was that ϕ_∞ is small. These relationships are therefore equally valid for all values of N_b/N_a and χN_a. One must remember, however, that for equilibrium conditions, β, ϕ_∞, and z^*/R_g cannot all be adjusted independently. Additional relationships between these quantities exist which depend on the specific system of interest. For example, at a fixed value of β and for specified values of N_b/N_a and χN_a, there will be a one to one correspondence between z^*/R_g and ϕ_∞ which defines the adsorption isotherm. Once this relationship is known, eq 21 can be used to develop the correspondence between f^* and z^*/R_g, and *vice versa*. If, for example, it is determined that eqs 10 and 11 are an adequate representation for f^*, then we can neglect the logarithmic term in eq 21 to obtain the following for z^*/R_g:

$$\frac{z^*_{\text{wet}}}{R_g} = \begin{cases} 0.42\left(\dfrac{N_b}{2N_a} - \chi N_b\right)^{-1}(\ln \phi_\infty + \beta)^{3/2} & (\chi N_a \ll 0.5) \\ 1.38\left(\dfrac{N_a}{N_b}\right)^{1/2}(\ln \phi_\infty + \beta) & (\chi N_a = 0.5) \end{cases} \tag{22}$$

$$\frac{z^*_{\text{dry}}}{R_g} = 1.15(\ln \phi_\infty + \beta)^{1/2} \tag{23}$$

Again, it should be emphasized that these are equilibrium values of z^*. The relationships between f^* and z^* given by eqs 10 and 11, or determined from SCF theory, do not require that these z^* values correspond to equilibrium. All that is required in this case is that the structure of the brush be equilibrated locally.

For comparison to real systems involving wet brushes, it is most convenient to take $N_a = 1$, with N_b given by the molar volume of the adsorbing molecules divided by the molar volume of the matrix molecules. The spacing between lattice layers is generally defined as **a**, the statistical segment length of a repeat unit. This quantity is more ambiguous in the wet brush case than it is in the dry brush case, because of the concentration dependence of the chain dimensions. The concentration dependence is relatively weak, however, scaling as $\phi_b^{-1/8}$.[14] We neglect this concentration dependence here, and assume that **a** is a constant, independent of N_b/N_a and ϕ_b. We begin by discussing some of the qualitative features of the concentration profiles for dry brushes and wet brushes within the context of previous investigations of these profiles. We then turn our attention to the detailed adsorption isotherms and activation energies for brush formation.

Concentration Profiles. Figure 3 is a comparison of concentration profiles for a dry brush ($N_b/N_a = 1$, $\chi N_a = 0$) and a wet brush ($N_b/N_a = 300$, $\chi N_a = 0.3$), each with $z^*/R_g = 2.86$. The wet brush profile can be

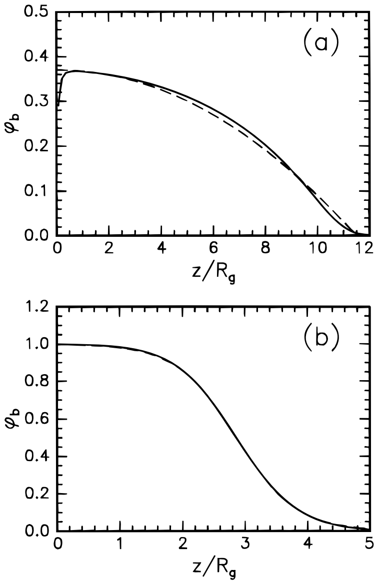

Figure 3. Comparison of characteristic concentration profiles for wet brushes and dry brushes with $z^*/R_g = 2.86$. (a) Solvent brush with $N_b/N_a = 100$ and $\chi N_a = 0.3$. The solid line is the numerical SCF result, and the dashed line is the parabolic form of eq 24, with $\phi_0 = 0.37$ and $h = 11.5R_g$. (b) Dry brush with $N_b/N_a = 1$ and $\chi N_a = 0$. The numerical SCF result is virtually indistinguishable from the hyperbolic tangent profile of eq 26, with $w = 1.9R_g$.

compared to the well-known parabolic form:[5]

$$\phi_b(z) = \phi_0\left\{1 - \left(\frac{z}{h}\right)^2\right\} \tag{24}$$

with

$$z^* = 2\phi_0 h/3 \tag{25}$$

The dashed line of Figure 3a represents the parabolic profile of eq 24, with best-fit values for ϕ_0 and h. This parabolic profile is obtained for large values of N_b/N_a and in situations where the polymer volume fraction is low enough so that the linear term in the expansion of w_b in powers of ϕ_b is dominant. As illustrated in Figure 3b, dry brush profiles for $z^*/R_g > 1.6$ are more appropriately approximated by a hyperbolic tangent form:[12]

$$\phi_b(z) = 0.5 + 0.5 \tanh\left\{\frac{2(z^* - z)}{w}\right\} \tag{26}$$

where w is a width parameter describing the region of overlap between the brush and the surrounding matrix polymer.

Wijmans, Scheutjens, and Zhulina have presented an excellent comparison of numerical and analytic treatments for wet brushes, using a form of the mean field which is identical to that described here.[15] For wet brushes with $N_a = 1$, Π represents the increased osmotic pressure of the brush, which can be expressed directly in terms of the polymer volume fraction. In this case, w_b is given by the following expression:

$$w_b = -2\chi\phi_b - \ln(1 - \phi_b) + C \tag{27}$$

where C is a constant. In this case, there are just three equations which must be solved self-consistently, *i.e.*, eq 15 for ϕ_b in terms of q_{b1} and q_{b2}, and two versions of eq 12 for q_{b1} and q_{b2} in terms of ϕ_b. The problem is simplified even further for small polymer volume fractions, where the logarithmic term in eq 27 can be expanded to give the following approximate expression for w_b:

$$w_b = \phi_b(1 - 2\chi) + C \tag{28}$$

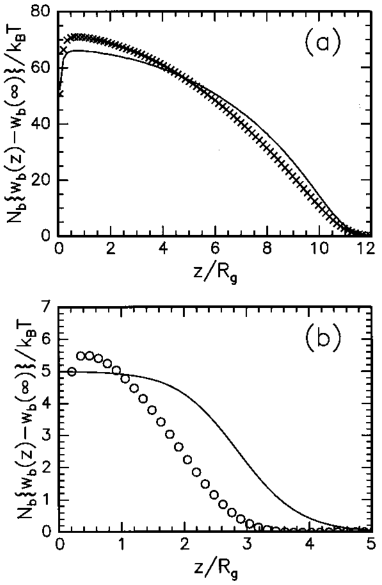

Figure 4. Comparison of mean-field and concentration profiles for the wet and dry brushes from Figure 3. In each case, symbols represent the mean-field profile, and the solid lines are proportional to the actual SCF volume fractions. (a) Wet brush data ($N_b/N_a = 100$ and $\chi N_a = 0.3$); (b) dry brush data ($N_b/N_a = 1$ and $\chi N_a = 0$).

Milner has shown that when eq 28 is valid, the parabolic volume fraction profile is virtually indistinguishable from the profile given by the full numerical SCF treatment, with the exception of a "foot" at the end of the brush profile and for a thin depletion layer near the grafting surface.[16] The factor which most complicates the analysis for dry brushes is that the "solvent" is itself a polymer, with a spatial extent extending well beyond a single lattice layer. It is therefore not possible to write a simple expression for Π in terms of the local volume fractions. In this case, the self-consistent-field equations need to be solved independently for the matrix polymer component in order to obtain accurate volume fraction profiles.

Some important qualitative differences between dry brushes and wet brushes can be illustrated by comparing the pressure profiles obtained in the two cases. Figure 4 is a comparison of the spatial dependence of the mean field, for the brushes from Figure 3. For the wet brush, the mean field is reasonably approximated by eq 28, indicating that the use of this equation is quite appropriate for $N_b/N_a = 300$, $\chi N_a = 0.3$, and $\phi_0 = 0.37$. A simple analytic treatment assuming that w_b is proportional to ϕ_b works well in this case, and the concentration profile and the mean-field profile have similar parabolic forms. For dry brushes, however, there is clearly no simple relationship between these two profiles. In addition, there is a large negative pressure in the first layer which draws polymeric material into what would otherwise be a depletion layer. This attractive force is confined to the first lattice layer and has a magnitude of approximately 0.18 k_BT per repeat unit.[2] Finally, the crossover from parabolic profiles to hyperbolic tangent profiles as N_b/N_a is decreased is illustrated by the profiles plotted in Figure 5.

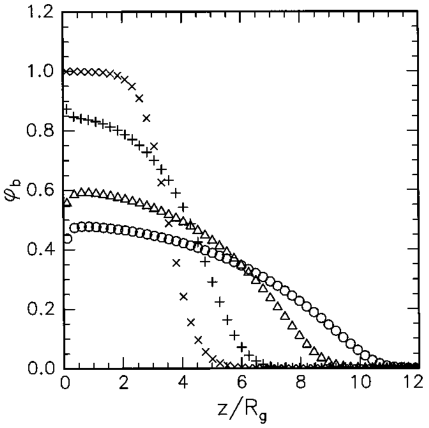

Figure 5. Volume fraction profiles illustrating the crossover from wet brush to dry brush behavior for a series of brushes with $z^*/R_g \approx 3.5$ and $\chi N_a = 0$. The different profiles have $N_b/N_a = 100$ (○), $N_b/N_a = 10$ (△), $N_b/N_a = 2$ (+), and $N_b/N_a = 1$ (×).

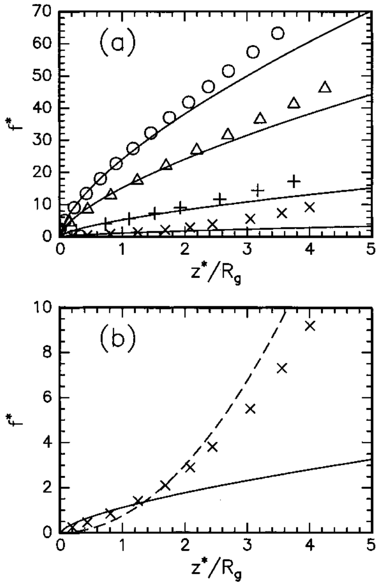

Figure 6. Numerical SCF data showing f^* as a function of coverage for a series of brushes with $\chi N_a = 0$. The different data sets in (a) correspond to $N_b/N_a = 100$ (○), $N_b/N_a = 10$ (△), $N_b/N_a = 2$ (+), and $N_b/N_a = 1$ (×). The solid lines are predictions from the wet brush scaling theory (eq 10). Part b shows the dry brush data with scaling predictions from the wet brush (eq. 10, —) and dry brush (eq 11, - - -) theories.

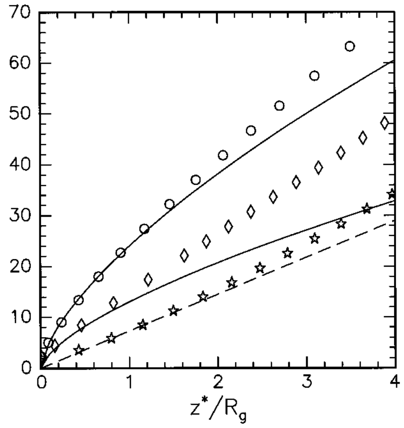

Figure 7. Free energy required to add a polymer chain to an existing wet brush as a function of the brush coverage. Symbols represent SCF values for $N_b/N_a = 100$, with $\chi N_a = 0$ (○), $\chi N_a = 0.3$ (◊), and $\chi N_a = 0.5$ (stars). The solid lines represent the corresponding wet brush scaling predictions (eq 10) for $\chi N_a \ll 0.5$. The dashed line represents the wet brush scaling relationship of eq 10 for $\chi N_a = 0.5$.

Adsorption Isotherms and Brush Free Energy. Figure 6 is a set of plots of f^* as a function of coverage for varying values of N_b/N_a, showing the continuous crossover from dry brush behavior to wet brush behavior. The interaction parameter, χ, is equal to zero in each case. The increase in the brush free energy with decreasing matrix molecular weight is a simple consequence of the increased osmotic pressure associated with the exclusion of low-molecular-weight components from the polymer brush. Equation 10 gives a surprisingly accurate description of the crossover from dry brush behavior to wet brush behavior. Agreement between eq 10 and the full SCF treatment for dry brushes is the least satisfactory, as one would expect. The discrepancy is particularly large for values of z^*/R_g which exceed 1.5, roughly the point at which the brush volume fraction begins to saturate at one. For larger values of z^*/R_g, the qualitative relationship between f^* and the brush coverage is more accurately represented by eq 11.

Inclusion of unfavorable polymer/solvent interactions also affects the equilibrium coverage, as shown in Figure 7. Here again, we see that eq 10 accurately predicts the behavior of f^* for a wide range of parameters. Agreement is particularly good at the limiting extremes of $\chi N_a = 0$ and $\chi N_a = 0.5$, where the expansion of the free energy in terms of the volume fractions is the most straightforward. The largest difficulty is for intermediate values of χN_a, which, unfortunately, are characteristic of most good solvents. In general, one sees that increasing the χ parameter has the same qualitative effect as increasing the solvent molecular weight. However, f^* for a dry brush is much less than f^* for a wet brush, even for $\chi N_a = 0.5$. The net favorable polymer self-interaction introduced by a positive χ parameter is simply not enough to offset the osmotic forces arising from the translational degrees of freedom of a small-molecule solvent. Finally, note that the SCF data from Figures 6 and 7 are listed in Table 1 in order to make them more accessible to experiments and to those interested in comparing the SCF results to results obtained by other theoretical approaches.

Equation 21 indicates that the free energy required to add a polymer chain to a brush which is at complete equilibrium with the bulk matrix phase is approximately equal to $k_BT(\ln \phi_\infty + \beta)$. This point is further emphasized in Figure 8, where f^* is plotted as a function of $\ln \phi_\infty + \beta$ for all of the systems from Figures 6 and 7. The difference between the solid line (drawn through the origin with a slope of one) and the actual data points is equal to $\ln(z^*/R_g)$. For this reason, the accuracy of the scaling predictions for z^* (eqs 22 and 23) is similar to the accuracy of the scaling predictions for f^* (eqs 10 and 11). This point is illustrated in Figure 9, where the adsorption isotherms obtained from the SCF and scaling theories are compared.

So far we have been concerned primarily with the height of the activation barrier for the attachment of additional chains to an existing brush. In a dynamic situation where chains are actively moving in and out of the brush, the shape of this barrier will also be important.[6,17] In this case, the full $\Delta f(z)$ profile needs to be determined, as opposed to just its maximum value.

Table 1. Values of f^* As Calculated by the Numerical SCF Theory (Values Accurate to within 0.1)

	$N_b/N_a = 1$	$N_b/N_a = 10$	$N_b/N_a = 50$	$N_b/N_a = 100$	$N_b/N_a = 100$	$N_b/N_a = 100$
	$\chi N_a = 0$	$\chi N_a = 0$	$\chi N_a = 0$	$\chi N_a = 0$	$\chi N_a = 0.3$	$\chi N_a = 0.5$
z^*/R_g	f^*	f^*	f^*	f^*	f^*	f^*
0.00	0.09	0.70	1.83	1.95	2.03	2.00
0.25	0.29	1.81	5.72	9.34	5.64	2.67
0.50	0.52	2.91	9.03	14.9	8.92	3.90
0.75	0.79	3.98	12.0	19.9	12.0	5.49
1.00	1.08	5.04	14.8	24.4	14.9	7.25
1.25	1.40	6.08	17.5	28.7	17.8	9.17
1.50	1.79	7.12	20.0	32.9	20.7	11.2
1.75	2.22	8.15	22.5	36.9	23.5	13.3
2.00	2.71	9.19	25.0	40.8	26.4	15.4
2.25	3.30	10.3	27.4	44.6	29.3	17.5
2.50	3.95	11.3	29.7	48.4	32.1	19.8
2.75	4.62	12.4	32.1	52.2	35.0	22.2
3.00	5.35	13.6	34.4	56.0	37.8	24.6
3.25	6.16	14.8	36.7	59.7	40.7	26.9
3.50	7.07	16.0	39.0	63.3	43.6	29.4

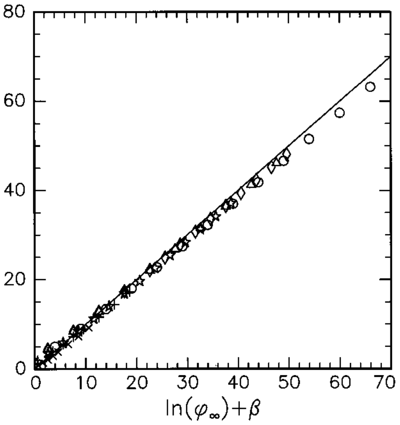

Figure 8. SCF data for f^* replotted in terms of the equilibrium volume fraction of brush chains in the bulk phase. The solid line has a slope of one and illustrates the approximate equivalence of f^* and $\ln(\phi_\infty) + \beta$ for all brushes.

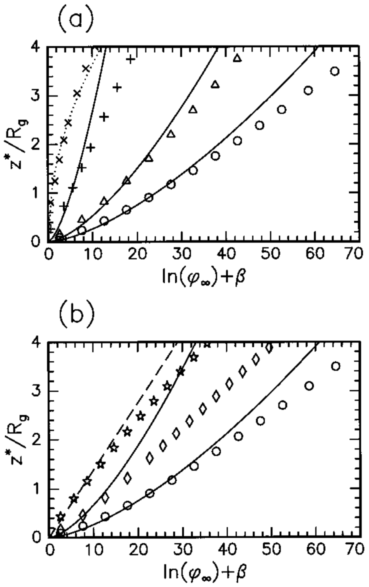

Figure 9. Adsorption isotherms for a variety of dry and wet brushes: (a) dry brush to wet brush transition for $\chi N_a = 0$, with $N_b/N_a = 100$ (○), $N_b/N_a = 10$ (△), $N_b/N_a = 2$ (+), and $N_b/N_a = 1$ (×); (b) wet brush behavior for $N_b/N_a = 100$, with $\chi N_a = 0$ (○), $\chi N_a = 0.3$ (◇), and $\chi N_a = 0.5$. Solid and dashed lines represent the wet brush prediction of eq 22 for $\chi N_a \ll 0.5$ and $\chi N_a = 0.5$, respectively. The dotted line represents the dry brush prediction of eq 23.

Milner has given the following analytic expression for this profile which provides a useful basis for comparison:[7]

$$\Delta f(z) = \frac{2f^*}{\pi}[\arccos(z/h_{\mathrm{eff}}) - (z/h_{\mathrm{eff}})\{1 - (z/h_{\mathrm{eff}})^2\}^{1/2}] \tag{29}$$

In our case, h_{eff} is an effective brush height which can be obtained by fitting eq 29 to $\Delta f(z)$ as determined from the numerical SCF treatment. Equation 29 is valid for $0 < z < h$, giving $\Delta f(0) = f^*$ and $\Delta f(h_{\mathrm{eff}}) = 0$. (It does not include the attractive interaction of depth Δ between the adsorbing group and the wall.) The quantity h_{eff} is somewhat larger than the characteristic width of the polymer brush, *i.e.*, h for wet brushes and z^* for dry brushes. For example, the wet brush in Figure 10 has $h_{\mathrm{eff}} = 12R_g$ and $h = 11.5R_g$, whereas the dry brush has $h_{\mathrm{eff}} = 4R_g$ and $z^* = 2.86R_g$. Equation 29 was derived for high values of N_b/N_a and h/R_g, so it is not at all surprising to find relatively good agreement between h and h_{eff} for the wet brush case in Figure 10.

By inspection of the curves shown in Figure 10, we see that k_BTf^*/h^{eq} is a good approximation for the free energy gradient at the grafting surface. This gradient represents the force, t, acting on the grafting point. Combination of the scaling expressions for h^{eq} (given by eq 7 for wet brushes, and equal to z^* for dry brushes) and f^* (from eqs 10 and 11) gives

$$t_{\mathrm{wet}} = \begin{cases} \dfrac{1.40k_BT}{R_g}\left(\dfrac{N_b}{2N_a} - \chi N_b\right)^{1/3}\left(\dfrac{z^*}{R_g}\right)^{1/3} & (\chi N_a \ll 0.5) \\[2ex] \dfrac{0.81k_BT}{R_g}\left(\dfrac{N_b}{N_a}\right)^{1/4}\left(\dfrac{z^*}{R_g}\right)^{1/2} & (\chi N_a = 0.5) \end{cases} \tag{30}$$

$$t_{\mathrm{dry}} = \frac{0.75k_BT}{R_g}\left(\frac{z^*}{R_g}\right) \tag{31}$$

The power laws relating the force at the anchoring point to z^*/R_g and N_b/N_a are relatively weak, so that this force is never far from the characteristic value of k_BT/R_g, which for typical high polymers is of the order 10^{-12} N. Nevertheless, a more detailed understanding of the specific value of this force is often important. Suppose, for example, that a very thin layer of an A/B diblock copolymer is placed on top of a high molecular weight homopolymer of B and annealed in the melt state

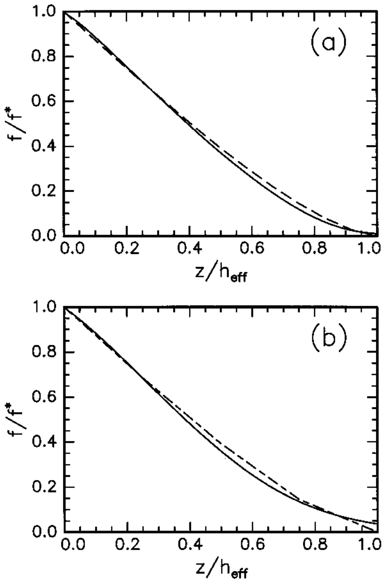

Figure 10. Normalized free energy required to bring the adsorbing group of a polymer chain to a distance z/h_{eff} from the adsorbing wall. Data for the wet and dry brushes of Figure 3 ($z^*/R_g = 2.86$) are included. The solid lines in each case represent the best fit to eq 16. (a) Wet brush with $N_b/N_a = 100$ and $\chi N_a = 0.3$ ($f^* = 70$ and $h_{\mathrm{eff}} = 12R_g$); (b) dry brush with $N_b/N_a = 1$ and $\chi N_a = 0$ ($f^* = 5.1$ and $h_{\mathrm{eff}} = 4R_g$).

to the equilibrium condition. If the surface energy of A is lower than the surface energy of B by a sufficient amount, then the block copolymer will spread on the surface to form a monolayer. The A block forms a dry brush extending away from the surface, and the B block forms a dry brush extending into the homopolymer layer. The two brushes exert forces on the junction point which are equal in magnitude but act in opposite directions. Suppose now that the layer is dipped into a solvent which is a good or marginal solvent for A but a very poor solvent for B. In this case, the force acting on the wet brush exceeds the force acting on the dry brush, and the copolymers tend to be pulled out into the solvent, thereby decreasing the coverage. In essence, the system is no longer at a local free energy minimum, but is supersaturated with copolymer. The SCF (or scaling) calculations relating free energy changes to motions of individual molecules can be used to determine the driving forces for desorption. The situation is similar for an A/B diblock copolymer confined between A and B homopolymer layers. In this case, the net tension at the junction point is zero, corresponding to a local minimum in the free energy. Exchange of copolymer chains in and out of the layer in this case is a thermally activated process, just as the formation of a polymer brush by addition of free chains to an existing adsorbed layer is an activated process. In situations where the exchange of molecules in and out of a layer is slow compared to the equilibration time for the local brush structure, the SCF calculations of the relevant forces and activation energies can be quite useful in developing theories of polymer adsorption and desorption kinetics. The recent analysis by Kramer of grafting kinetics in a pure melt of end-functionalized polymer molecules is a good example of this type of approach.[18]

V. Summary

Numerical self-consistent-field theory is clearly a very powerful technique for describing the interfacial properties of polymeric systems. With regard to the properties of end-adsorbed polymer brushes, we can make the following conclusions:

1. The activation free energy f^*, describing the free energy barrier for penetration of an adsorbing chain into a preexisting brush, is uniquely determined by N_b/N_a, χN_a, and z^*/R_g.

2. A scaling argument based on the simplest possible description of the free energy of a polymer brush gives values for f^* which are in good agreement with the numerical SCF predictions in certain regimes. In particular, good agreement is obtained for solvent brushes with $\chi N_a = 0.5$ or $\chi = 0$, provided that z^*/R_g is less than about two.

3. Relationships between f^* and z^* are valid even when z^* is not at complete equilibrium with the surrounding matrix. When full equilibrium is achieved, f^* is nearly equal to $\ln(\phi_\infty) + \beta$, where ϕ_∞ is the equilibrium volume fraction of adsorbing chains in the bulk phase, and β describes the net interaction between the end group and the surface.

4. The shape of the activation barrier is well described by an analytic form, provided that actual values for the height and width of the barrier are used.

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