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# Brush Theory of Tethered Chains with a Charged Group at the Free End

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ABSTRACT: We consider the problem of end-grafted polymer molecules with a charged group attached to the free end both by an analytical and a numerical method. In the analytical approach the Gaussian model for the polymer chains is used. In this model volume interactions are ignored and analytical solutions for special type of boundary conditions are found. We consider both a repulsive surface, and a critical adsorption energy surface. The complete Poisson−Boltzmann equation is used and deviations from local electroneutrality are considered in a perturbation method scheme. It is found that deviations of local electroneutrality both scale inversely with the chain length ($N^{-1}$) and inversely with the ionic strength ($\Phi_s^{-1}$). In the numerical method we apply a self-consistent-field scheme of freely jointed chains in Θ conditions. Results of the analytical model compare favorably to those obtained by the numerical method.

## Introduction

Polymer brushes have received much attention in recent years. The popularity finds it origin in the fact that in many limiting cases analytical solutions can be obtained for physically relevant problems. Polymer brushes are found in block copolymer systems, where the two blocks are rather different. Typically, block copolymers in selective solvents aggregate into so-called micelles of which one block forms the core of the micelle and the other one the corona. Both regions in these micelles are examples of brushes. The first one is a brush in nonsolvent conditions (core) and the other one is an example of a brush in a relatively good solvent (corona). Alternatively, block copolymers may adsorb with one segment type preferentially on particles or on the air−solution interface. At high enough coverage the block with lowest surface affinity will be displaced away from the interface. This displaced chain fragment then stretches and forms the brush. Polymer brushes can also be created by linking (grafting) chemically one chain end to a substrate. Brushes may be important for surface modification and there are applications in, e.g., drug delivery devices, pigment stabilization, and food technology.

Neutral polymer brushes have been analyzed by several groups approximately simultaneously. For a historical review see ref 1. Cosgrove and co-workers,[2] Hirz,[3] and Skvortsov et al.[4] were the first to apply a numerical self-consistent field (SCF) method. Others, Pryamitsyn and Zhulina and Borisov,[5−8] and Milner Witten and Cates[9−12] worked on it analytically following the pioneering work of Semenov.[13] Chains were, in these analytical treatments, considered as Gaussian springs and most likely trajectories were included in the model. At present the behavior of many type of polymer brushes is well documented. It is possible to go beyond the Gaussian model as has been shown recently.[14] Several simulations were performed on polymer brushes.[15] The syntheses of simulations, numerical SCF calculations, and analytical work give now a complete picture of these systems. It is noteworthy that only few experimental tests of the theoretical picture are available.[16−19]

Polymer brushes composed of macromolecules that carry electric charges along the chain are now popular objects for polymer physicists, see e.g., refs 20−31. Both annealed and quenched polyelectrolyte brushes have been studied. Again two approaches are applied successfully. The numerical SCF model has been used which features the full Poisson−Boltzmann equation for the electrostatics. Predictions for these systems with the analytical approach are based upon the usual parabolic potential profile and the so-called local electroneutrality condition. This last assumption corresponds to the Donnan equilibrium for the polyelectrolyte brush, for which also a scaling approach is available. For not too short chains good correspondence between the two approaches was obtained. This indicated that the local electroneutrality assumption is a good approximation for long chains. In this paper we consider a charged brush within an analytical approach which goes beyond the electroneutrality ansatz. This is possible in a perturbation method for a special class of problems, namely for end-tethered chains which have a charged group at the free end of the tail. We compare the analytical predictions with full numerical SCF analysis and find that deviations of the electroneutrality are significant especially for short chains.

Polymers with a charged end group can occur, e.g., as a left over of the polymerization reaction, or by tailor-made design. In this last case one can consider a short

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charged block of segments to be the end group. Thus the end group can, in the general case, carry more than one charge. The modeling of these systems must in the general case be done with numerical methods, e.g. with the SCF approach. The special case considered in this paper serves two goals. The first one is to show that analytical solutions exist also for nonneutral (no local electroneutrality assumption) brushes. The second goal is to investigate how a charged end group can modify the brush characteristics.

The remainder of this paper is organized as follows. First we will give details of the analytical theory, and then both analytical and numerical results will be discussed. Some details are given in the Appendix.

## Theory

Let us consider a system of polymer chains $-A_{N'}B_m$ with segments of length $a$. In this molecule the A units are uncharged and the B units carry a charge $-e$ (where $e$ is the elementary charge). When $m << N'$, one can approximate the block copolymer with a chain of $N$ beats of which the last segment carries $-me$ charges. This end-functionalized chain is grafted with the A end to a surface with a grafting density $\sigma$ and is in contact with an electrolyte solution. The free positive counterions with a charge $e$ and the negative co-ions with a charge $-ne$ are dissolved in the solution. Typically, $n$ will assume the values 1 or 2, e.g., $Cl^-$ or $SO_4^{2-}$, respectively. For the counterion one can take, e.g., $Na^+$.

In the analytical model the brush is composed of ideal Gaussian chains for which all volume interactions can be ignored. Only electrostatic interactions between ions and interaction between the surface and the polymer are taken into account. We will assume that the system remains laterally homogeneous so that a (one-dimensional) self-consistent field method can be applied. For the Gaussian model the distribution function of the free end is given by

$$g(x,\psi(x)) = C'\, g'(x) e^{me\psi(x)/kT} \tag{1}$$

where $\psi(x)$ is the electrostatic potential at distance $x$ from the surface, $kT$ the thermal energy, $C'$ a normalization constant and $g'(x)$ the unperturbed distribution function of the free end, which is proportional to the number of conformations of a grafted polymer chain with the free end fixed at the distance $x$ from the grafting surface. We will consider two type of surfaces. The first one is a repulsive surface, indicated by the subindex, r. In this case the segments experience conformational entropy loss near the surface, and because no adsorption energy is present the chains will avoid contact with the surface. The second case is a weakly adsorbing surface of which the attractive potential just cancels the conformational entropy loss. This so-called critical adsorption point (CAP) surface[32] will be indicated by the sub index, c. In this case the end-point distribution has the property that it levels off at the interface. In these two cases rather simple expressions are available for $g'(x)$ (see Appendix[32]):

$$\begin{aligned} g'_{\mathrm{r}}(x) &= \frac{3x}{Na^2} e^{-(3x^2/2Na^2)} \\ g'_{\mathrm{c}}(x) &= \frac{\sqrt{6}}{a\sqrt{\pi N}} e^{-(3x^2/2Na^2)} \end{aligned} \tag{2}$$

Note that both distribution functions of eq 2 are normalized to unity. In combination with the electrostatic potential profile, we now can rewrite eq 1:

$$\begin{aligned} g_{\mathrm{r}}(x) &= C_{\mathrm{r}} x \cdot [e^{-(3x^2/2Na^2)}/y(x)^m] \\ g_{\mathrm{c}}(x) &= C_{\mathrm{c}} [e^{-(3x^2/2Na^2)}/y(x)^m] \end{aligned} \tag{3}$$

where $y = \exp(-e\psi(x)/kT)$ and the normalization constants $C_{\mathrm{r}}$ and $C_{\mathrm{c}}$ follow when the electrostatic potential profile is known. Below, unless specified otherwise, we will consider the CAP condition and omit the index c.

The distribution of the co-ions and counterions follow from the Boltzmann law:

$$\begin{aligned} \rho^-(x) &= \frac{\Phi}{\mathrm{n}} e^{[ne\psi(x)]/kT} = \frac{\Phi}{n\, y(x)^n} \\ \rho^+(x) &= \Phi e^{-[e\psi(x)/kT]} = \Phi y \end{aligned} \tag{4}$$

where $\Phi$ is the concentration of positive ions (counterions) in the bulk of the solution.

The Poisson equation for the system of grafted polymer chains and free ions is given by

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{e}{\epsilon_0 \epsilon_{\mathrm{r}}}[m\sigma\, g(x) - \rho^+(x) + n\, \rho^-(x)] \tag{5}$$

In eq 5 $\epsilon_0$ is the dielectric permittivity of vacuum and $\epsilon_{\mathrm{r}}$ is the relative dielectric constant of the medium. It is useful to introduce dimensionless variables:

$$\begin{aligned} \epsilon &= \frac{3}{2a^2N} \frac{kT}{e} \frac{\epsilon_0 \epsilon_{\mathrm{r}}}{e} \frac{m}{\Phi} \\ z &= x\sqrt{\frac{3}{2a^2N}} \end{aligned} \tag{6}$$

The parameter $\epsilon$ is the square of the two length scales of the system: the Debye screening length and the size of the unperturbed polymer.

It is possible to substitute eqs 3 and 4 in eq 5 to arrive at the Poisson–Boltzmann equation in dimensionless units:

$$-\epsilon \frac{\partial^2 \ln y(z)}{\partial z^2} = C e^{-z^2} y(z)^{-m} - (y(z) - y(z)^{-n}) \tag{7}$$

with

$$C^{-1} = \sqrt{\frac{2a^2N}{3}} \frac{\Phi}{m\sigma} \int_0^\infty e^{-z^2} y(z)^{-m}\, \mathrm{d}z \tag{7'}$$

The corresponding boundary conditions are

$$\begin{aligned} y(\infty) &= 1 \\ -\left(y^{-1} \frac{\partial y}{\partial z}\right)_{z=0} &= \frac{Q}{\epsilon_0 \epsilon_{\mathrm{r}}} \frac{e}{kT} \sqrt{\frac{2a^2N}{3}} \end{aligned} \tag{8}$$

where $Q$ is the surface charge per unit area, which takes the value such that the total system remains electroneutral. Alternatively we can write

$$-\int_0^\infty C e^{-z^2} y(z)^{-m} - (y(z) - y(z)^{-n})\, \mathrm{d}z = \frac{Qm}{e\Phi} \sqrt{\frac{3}{2a^2N}} \tag{9}$$

Below we will discuss only the case of an uncharged surface, Q = 0, and thus the boundary condition near the surface reduces to $(\partial y/\partial z)_{z=0} = 0$.

**Local Neutrality Approximation.** Equation 7 with boundary conditions (eq 8) can be solved in the limit that $\epsilon$ tends to zero in such a way that $C$ remains finite. It is easy to see that this limit corresponds to a local electroneutrality condition. Until now analytical treatments of the polyelectrolyte brush make use of this local electroneutrality approximation. In such a treatment it is assumed that everywhere in the brush the charges exactly cancel each other. This does not mean that the electrostatics are unimportant. Thus, in the limit of $N \to \infty$, but when $(\Phi\sqrt{N})/(a\sigma)$ remains constant the left side of eq 7 goes to zero and eq 7 converts into an algebraic equation applicable for local electroneutral systems:

$$C\frac{e^{-z^2}}{y(z)^m} = y(z) - y(z)^{-n} \tag{10}$$

This equation can be solved for various values of $m$ and $n$. For the case that $m = n = 1$ we find

$$\begin{aligned} y_0(z) &= e^{-(z^2/2)}\sqrt{C + e^{z^2}} \\ g_0(z) &= C\frac{e^{-(z^2/2)}}{\sqrt{C + e^{z^2}}} \end{aligned} \tag{11}$$

The subindex 0 indicates that this is the zeroth-order solution of the original differential equation eq 7. For $m = 2n + 1$ under the condition that $n \geq 1$ we find

$$\begin{aligned} y_0(z,m) &= \left({}^1\!/_2 + \sqrt{{}^1\!/_4 + Ce^{-z^2}}\right)^{2/(m+1)} \\ g_0(z,m) &= C\frac{e^{-z^2}}{\left({}^1\!/_2 + \sqrt{{}^1\!/_4 + Ce^{-z^2}}\right)^{2m/(m+1)}} \end{aligned} \tag{12}$$

In the limit of $Ce^{-z^2} \gg 1$ we have intermediate asymptotes (i.e., in the central part of the brush) of eq 12:

$$m\ g_c(z,m) \cong y_c(z,m) \cong C^{1/(m+1)}e^{-z^2/(m+1)} \tag{13}$$

and a similar result can be obtained for the repulsive boundary condition case

$$m\ g_r(z,m) \cong y_r(z,m) \cong C^{1/(m+1)}\sqrt{z}e^{-[z^2/(m+1)]} \tag{14}$$

In eqn 13 and 14 we notice that the ionic strength drops out of the equation. This means that the electrostatic potential in the intermediate zone of the brush is independent of the ionic strength in the limit of low ionic strength $\Phi$, high $N$ and relatively high $\sigma$. From the exponents in eqns 13 and 14 a scaling result for the height of the brush can easily be derived. We find that $H = \int_0^\infty x\ g(x)\ dx/\int_0^\infty g(x)\ dx$ should scale as $H \propto \sqrt{N(m+1)}$ in the specified conditions. It should be noted that it is difficult to enter the intermediate asymptote conditions. In order to keep $C$ large with respect to $e^{z^2}$ it is needed that the local density of charges of the brush is much higher than the value of the ionic strength (and that $z$ is not very large). The ionic strength cannot be arbitrarily low and therefore the brush density cannot easily be small enough to make polymer–solvent interactions unimportant. The intermediate asymptote analysis is useful for an estimation of, e.g., the end-point distribution or the electrostatic potential, but a full analysis is still needed.

In the CAP boundary condition in the limit $Ce^{-z^2} \gg 1$, Eqn (13) applies. In this case we can estimate the local excess charge in the brush to be proportional to $q \propto [(m+1)N]^{-1}$.

Analytical solutions of eq 10 may also exist for other values of $m$ and $n$. For example it is possible to solve for the case $m = 2$ and $n = 1$, but the final equations become too long to be presented in this paper.

**First Correction on the Local Electroneutrality Approximation.** From the above it is clear that $\epsilon$ controls the electroneutrality in the system. When it is zero, the system is locally neutral. When it is finite, the Poisson–Boltzmann equation becomes more difficult to solve. It is possible to use $\epsilon$ as a small parameter and use eqn 11 and 12 as zeroth-order approximations to solve eq 7 by a perturbation method. To do this we express the distribution function for the density of the free ions, $y$, as a power series in $\epsilon$:

$$y(z) = y_0(z) + \sum_{i=0}^{\infty}\epsilon^i y_i(z) \tag{15}$$

Equation 15 is now substituted in eq 7. Analyzing all terms with the same power of $\epsilon$ results in an infinite system of recurrent equations for $y_i$. Here we are only interested in the first-order correction on the local electroneutrality approximation. Thus, only the solutions in the first order of $\epsilon$ are kept. We can write

$$\ln y \cong \ln\left(y_0\left(1 + \epsilon\frac{y_1}{y_0}\right)\right) \cong \ln y_0$$

and

$$\frac{1}{y} \cong \frac{1}{y_0}\left(1 - \epsilon\frac{y_1}{y_0}\right)$$

For $m = n = 1$ we find that

$$y_1(z) = \frac{1}{2}\frac{\partial^2 \ln y_0(z)}{\partial z^2}$$

and thus

$$\begin{aligned} y(z) &= y_0(z) - \epsilon C\left[\frac{C + e^{z^2} - 2z^2e^{z^2}}{2(C + e^{z^2})^2}\right] + O(\epsilon^2) \\ g(z) &= \frac{Ce^{-z^2/2}}{\left[\sqrt{C + e^{z^2}} - \epsilon C\left[\frac{e^{z^2/2}(C + e^{z^2} - 2z^2e^{z^2})}{2(C + e^{z^2})^2}\right]\right]} + O(\epsilon^2) \end{aligned} \tag{16}$$

and similar considerations for the case that $m = 2n + 1$ ($n \geq 1$) lead to

$$y(z,m) = y_0(z,m) + \epsilon Ce^{-z^2}\left[\frac{z^2\sqrt{Ce^{-z^2} + \frac{1}{4}} - 2Ce^{-z^2} - \frac{1 - z^2}{2}}{\left(Ce^{-z^2} + \frac{1}{4}\right)^2(1+m)^2}\right] + O(\epsilon^2)$$

$$g(z,m) = \frac{Ce^{-z^2}}{\left[\left(\frac{1}{2} + \sqrt{Ce^{-z^2} + \frac{1}{4}}\right)^{2/(1+m)} + \epsilon Ce^{-z^2}\left[\frac{z^2\sqrt{Ce^{-z^2} + \frac{1}{4}} - 2Ce^{-z^2} - \frac{1 - z^2}{2}}{\left(Ce^{-z^2} + \frac{1}{4}\right)^2(1+m)^2}\right]\right]^m} + O(\epsilon^2) \quad (17)$$

In the limit of large $N$ we expect that the first-order perturbation theory is correct, which means that the amount of nonelectroneutrality in the brush should be proportional to $\epsilon$. This means that the local charge in the brush should scale with $(\Phi_s N)^{-1}$.

**Parameters for Numerical Self-Consistent Field Method.** In the analytical model Gaussian chains were used without volume interactions. This analytical model will be compared to full numerical SCF calculations. The parameters used in these SCF calculations will be discussed next; for details we refer to the literature.[33,34] We use the Scheutjens−Fleer method which employs freely jointed chains (first order Markov chains) on a (cubic) lattice next to an impenetrable surface. In the numerical SCF calculations the system is less ideal, but more realistic. As the molecules are modeled as freely jointed chains volume interactions should be minimized to make the comparison possible. This is done to work in so-called Θ-conditions. In this case the second virial coefficient, $\nu = 1 - 2\chi$, is zero. The second problem is that CAP boundary conditions are not easily realised. It is possible to come reasonably close. For the present systems we fix the Silberberg adsorption energy parameter[34] for the segments to $\chi_s = 2/3$. The exact CAP boundary conditions will be a function of the chain length, the grafting density, and the solvency parameter. For the numerical SCF calculations only finite chain lengths can be used. Typically $N$ is of order 1000. The chains are grafted with a grafting density of $\sigma = 0.005$. This value is on the edge of the overlap region. We kept this value as low as possible to minimize three-particle interactions. Electrostatic interactions are included by a full Poisson−Boltzmann approach.[24] All polymer segments as well as the charged groups, including the ions, have the volume of $a^3$ ($a = 0.3$ nm). Nonelectrostatic interactions of the ions are taken to be identical to those of water molecules, and ions as well as polymer units and water molecules are restricted to take positions defined by the lattice sites. The charge of the polymer end group is fixed. For the numerical results we use a value of $m = 5$. The volume fraction of counterions in the bulk is equal to twice that of the co-ions ($n = 2$) and is kept unless specified otherwise to $\Phi = 0.0002$. The ions can penetrate the brush freely. The relative dielectric constant was set to 80 throughout the system. The charge on the solid interface was kept to zero.

## Results

Typical numerical results for end-functionalized polymer brushes, with parameters given above, are presented in Figure 1. The polymer segment density as well as the overall charge are given as a function of the dimensionless distance $z$. It is obvious from this figure that the CAP conditions are not exactly met, although we are not very far from it. Near the surface, it is noticed that the distribution of polymer units is bending upward. Thus, the adsorption energy was slightly too high. For the CAP condition the end segment distribution (shown in Figure 3) should level off horizontally.

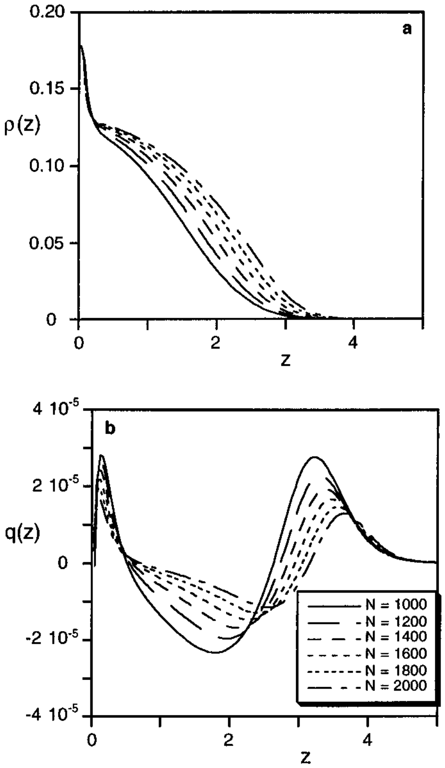

**Figure 1.** (a) Density distribution of the tethered chains as function of the dimensionless distance z of brushes of end-functionalized ($m = 5$, $n = 2$) polymer chains with length $N$. (b) Corresponding overall charge distributions. For parameters see text. The legend applies to both view graphs.

As is seen in Figure 1a the profiles extend far beyond $z = 1$, which indicates that the molecules are stretched. This stretching is due to volume interactions and the relatively high grafting density. It is noticed that longer chains stretch slightly more than the shorter ones. This is because the grafting density is kept constant. The longer molecules form tethered layers which are closer to the brush limit.

The deviations from charge compensation inside the brush are not constant as is seen in Figure 1b. Such a constant deviation from electroneutrality is predicted by the analytical model (see Figure 3), but due to the small chain lengths the deviations from electroneutrality vary throughout the profile. It is obvious from the result that the brush remains charged in the SCF calculations. Both near the surface and at the outer edge of the brush the charge distribution is complicated. The positive value of the excess charge on the outside of the brush is expected. It is analogous to the standard electric double layer. The diffuse part of the double layer is opposite of charge of the "surface" (in this case the brush takes the function of the surface). The positive excess of charges near $z = 0$ is due to the abrupt changes in polymer density near the surface and will be discussed in more detail near Figure 3.

To test the perturbation method we have to quantify the deviations from electroneutrality in the brush in some way. We have chosen to take the charge at the minimum in the curve of Figure 1b to be representative for this. In Figure 2a this minimum is plotted as a function of the inverse degree of polymerization for an ionic strength of $\Phi_s = 0.0002$. In Figure 2b the same is plotted as a function of the ionic strength for $N = 2000$. If the first-order perturbation result is good, the point should all be on a straight line through the origin. We

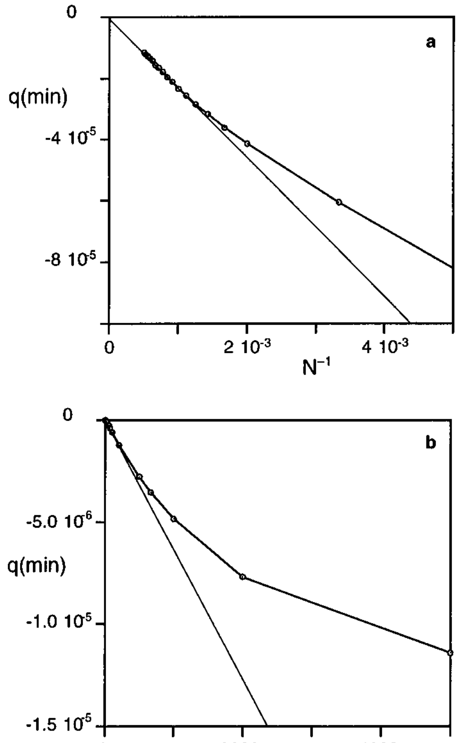

**Figure 2.** (a) The minimum in the charge distribution in the polymer brush as a function of the inverse chain length. (b) The minimum in the charge distribution in the polymer brush as a function of the inverse of the bulk volume fraction of the co-ions. The straight lines are the scaling predictions by the analytical model.

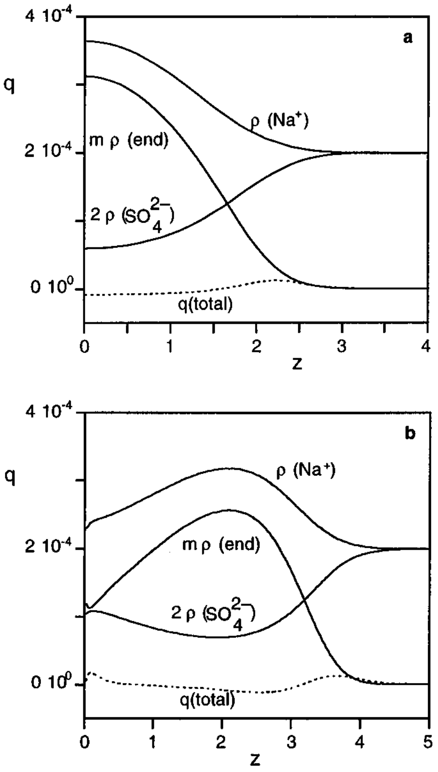

**Figure 3.** Density of charges of co-ions, counterions ($n = 2$), charged end groups ($m = 5$) and the overall charge, $q$, as a function of the normalized distance $z$. $N = 2000$, $\Phi_s = 0.0002$. Other parameters as in Figures 1 and 2: (a) analytical model of Gaussian chains and (b) numerical SCF results.

find in Figure 2a that for $N < 1000$ deviations from linearity are significant, indicating that a higher order perturbation scheme should be used. For $N > 1000$ the present approximation scheme works well and we conclude that deviations from the electroneutrality condition in the brush are indeed proportional to $N^{-1}$ for not too small chains. In Figure 2b we see that for not too small ionic strength conditions the results follow the scaling prediction, $\Phi_s{}^{-1}$. In the limit of low ionic stength, where the perturbation theory does not strictly hold, we have derived above intermediate assymptotics. These show that the electrostatic potential in the central region in the brush becomes independent of ionic strength and the local charge in the brush goes to a limiting value given by the chain length $N$ and then number of charges at the end $m$. In Figure 2b we do not reach this limit, but we see a leveling off of the charge for low ionic strength.

Finally, a detailed comparison between predictions of the brush structure obtained by the analytical model (Gaussian chains) and the numerical SCF theory is presented in Figure 3. From Figure 3 it is obvious that the chains in the SCF model are more stretched than in the Gaussian model. This is due to the complete neglecting of interactions in the Gaussian model. The grafting density is not extremely low, the chains stretch in the SCF approach by almost a factor of 2 with respect to the Gaussian model. Note that there is also a significant stretching in the Gaussian model due to the $m$ charges at the end of each chain. The overall charge profile, $q$, of both models is very similar. The positive values of the maxima on the outside of the brush are almost equally high. Further, the minimum in the curve in the SCF result is of the same size as the negative value of $q$ near $z = 0$ in the analytical model. The end groups have a good behaving Gaussian distribution for the analytical model (CAP boundary conditions). In the SCF model the CAP boundary conditions are not exactly obtained. Here the end-group profile has a maximum near $z = 2$. For a real brush in Θ-conditions the end-point distribution is expected to peak at the outer edge of the brush. The fact that the maximum is weak shows that we are not very far from the CAP condition (see also Figure 1). Also, for very small $z$ values (near the surface) the end point density shows a very small local minimum. This indicates that the $g$ profile almost levels off, which is also an indication that the system is near the CAP condition. The intricacies near $z = 0$ cause $q$ to become slightly positive. The positive counterions have accumulated in the brush in both models and the negative counterions show a depletion as expected. In the SCF result the distributions show an extreme at the same point where the end points have a maximum. This makes the exact features of Figure 3b to be different from those in Figure 3a. Apart from this it is clear that the Gaussian model features the correct trends near the CAP conditions.

In the present paper we have discussed polymer brushes in Θ-solvents or under the conditions that volume interactions could be ignored. Usually, however, these conditions are hard to realize. In the other extreme we have polymer brushes in nonsolvents. The polyacid brush in nonsolvents can be treated both by (semi) analytical methods, on the basis of the local electroneutrality conditions and with the numerical SCF model. It was shown recently that this brush can undergo a first-order structural phase transition for finite chain lengths.[35] The modeling of the brush system composed of neutral chains with a charge on its free end in bad (non) solvents will lead to a model for latex particles. This is left for future work.

## Conclusions

We have shown that it possible to model the polymer brush with a charged group at the free end. A first-order perturbation scheme shows that deviations from electroneutrality scale with the inverse of the chain length. This result is already obtained for chains with a chain length of $N = 1000$. In the limit of infinitely large chains the local electroneutrality conditions is expected to hold. We further have shown that the deviations from electroneutrality increase with decreasing ionic strength. The $q \propto \phi_s^{-1}$ scaling is best for relatively high ionic strength conditions. Self-consistent field calculations agree reasonably well with the analytical predictions, although it is not possible to reach identical conditions in the two approaches.

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## Appendix

According to the Gaussian model for polymer chains,[32,36] the partition function of polymer chains of length $N$ with the ends placed at the layers $x$ and $x'$ is a Green function obeying the diffusion equation:

$$\left(\frac{\partial}{\partial N} - \frac{a^2}{6}\frac{\partial^2}{\partial x^2}\right)G_N(x,x') = \delta(N)\,\delta(x - x') \qquad [A1]$$

The solution of these equations in free space is

$$G_N(x,x') = \frac{\sqrt{6}}{\mathrm{a}\sqrt{\pi N}}\mathrm{e}^{-[3(x-x')^2/2Na^2]} \qquad [A2]$$

The interaction of the chain with the interface, positioned at layer $x = 0$, can be introduced by the boundary conditions for eq A1. According to de Gennes[32] the weak adsorption can be described by the boundary condition

$$\left(\frac{\partial \ln G_N(x,x')}{\partial x}\right)_{x=0} = -b \qquad [A3]$$

where $b$ is a parameter with a dimension length$^{-1}$, which must be positive when the attraction dominates and negative for repulsive conditions. The case of $b = 0$ is usually called the critical adsorption point (CAP). In this case $[\partial \ln G_N(x,x')/\mathrm{d}x]_{x=0} = 0$. For the repulsive boundary condition $b = -\infty$ and $G_N(x,x')_{x=0} = 0$. The solution of eq A1 for these two cases can be obtained by the reflection method:

$$G_N(x,x') = \frac{\sqrt{6}}{\mathrm{a}\sqrt{\pi N}}\left(\mathrm{e}^{-[3(x-x')^2/2\mathrm{Na}^2]} - \mathrm{e}^{-[3(x+x')^2/2\mathrm{Na}^2]}\right) \qquad b = -\infty$$

$$G_N(x,x') = \frac{\sqrt{6}}{a\sqrt{\pi N}}\left(\mathrm{e}^{-[3(x-x')^2/2\mathrm{Na}^2]} + \mathrm{e}^{-[3(x+x')^2/2\mathrm{Na}^2]}\right) \qquad b = 0 \qquad [A4]$$

The functions $g'_\mathrm{r}(x)$ and $g'_\mathrm{c}(x)$ mentioned in the text can be obtained from eq A4 by taking the limit for $x'$ to zero.

$$g'(x) = \lim_{x'\to 0}\left[\frac{G_N(x,x')}{\int_0^\infty G_N(x,x')\,\mathrm{d}x}\right] \qquad [A5]$$

## References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1991**, *100*, 31.

(2) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F. A. M.; Scheutjens, J. M. H. M. *Macromolecules* **1987**, *20*, 1692−1696.

(3) Hirz, S. M.S. Thesis, University of Minnesota, 1987.

(4) Skvortsov, A. M.; Gorbunov, A. A.; Pavlushkov, I. V.; Zhulina, E. B.; Borisov, O.V.; Pryamitsyn, V. A. *Polym. Sci. USSR* **1988**, *30*, 1706.

(5) Pryamitsyn, V. A.; Ph.D. Thesis, Inst. Macromolecular Compounds, Academy of Science USSR, Leningrad, 1987.

(6) Zhulina, E. B.; Pryamitsyn, V. A.; Borisov, O. V. *Polym. Sci. USSR* **1989**, *31*, 205.

(7) Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A. *J. Colloid Interface Sci.* **1990**, *137*, 495.

(8) Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A.; Birshtein, T. M. *Macromolecules* **1991**, *24*, 140.

(9) Milner, S. T.; Witten, T. A. *J. Phys.* **1988**, *49*, 1951.

(10) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.

(11) Milner, S. T.; Witten, T. A. *J. Phys. (France)* **1988**, *49*, 1951.

(12) Milner, S. T. *Science* **1991**, *251*, 905.

(13) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.

(14) Amoskov, V. M.; Pryamitsyn, V. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 889−893.

(15) Grest, G. S.; Murat, M. In *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Binder, K., Eds.; Oxford University Press: New York, 1995; pp 476.

(16) Hair, M. L.; Guzonas, D.; Boils, D.; Tripp, C. *Macromolecules* **1992**, *24*, 2434.

(17) Auroy, P.; Auvray, L.; Léger, L. *Phys. Rev. Lett.* **1991**, *66*, 719.

(18) Mansfield, T. L.; Iyengar, D. R.; Beaucage, G.; McCarthy, T. J.; Stein, R. S. *Macromolecules* **1995**, *28*, 492.

(19) Bijsterbosch, H. D.; De Haan, V. O.; De Graaf, W. W.; Mellema, M.; Leermakers, F. A. M.; Cohen Stuart, M. A.; Van Well, A. A. *Langmuir* **1995**, *11*, 4467−4473.

(20) Misra, S.; Varanasi, S. *Macromolecules* **1991**, *24*, 322.

(21) Misra, S.; Varanasi, S. *J. Chem. Phys.* **1991**, *95*, 2183.

(22) Misra, S.; Varanasi, S.; Varanasi, P. *Macromolecules* **1989**, *22*, 4173.

(23) Miklavic, S. J.; Marcelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.

(24) Israëls, R.; Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1993**, *26*, 5405−5413.

(25) Israëls, R.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249.

(26) Lyatskaya, Y. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562−3569.

(27) Pincus, P. *Macromolecules* **1991**, *24*, 2912.

(28) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. *Macromolecules* **1995**, *28*, 1491−1499.

(29) Zhulina, E. B.; Borisov, O. V.; Birshtein, T. M. *J. Phys. II.* **1992**, *2*, 63.

(30) Borisov, O. V.; Birshtein, T. M.; Zhulina, E. B. *J. Phys. II.* **1991**, *1*, 521.

(31) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.

(32) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(33) Evers, O. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *Macromolecules* **1990**, *23*, 5221.

(34) Fleer, G. J.; Scheutjens, J. M. H. M.; Cohen Stuart, M. A.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall: London, 1993.

(35) Pryamitsyn, V. A.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; *Macromolecules* **1996**, *29*, 8260.

(36) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*, Clarendon Press: Oxford, 1986.

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