Macromolecules **2000,** *33,* 4945−4953

Screening Effects in a Polyelectrolyte Brush: Self-Consistent-Field Theory

E. B. Zhulina,[†] J. Klein Wolterink,[‡] and O. V. Borisov*[,†,§]

Institute of Macromolecular Compounds, Russian Academy of Sciences, St.Petersburg 199004, Russia; and Laboratory for Physical Chemistry and Colloid Science, Wageningen University 6703 HB Wageningen, The Netherlands

Received February 10, 1999; Revised Manuscript Received February 22, 2000

ABSTRACT: We have developed an analytical self-consistent-field (SCF) theory describing conformations of weakly charged polyelectrolyte chains tethered to the solid−liquid interface and immersed in a solution of low molecular weight salt. Depending on the density of grafting of the polyelectrolytes to the interface and on the salt concentration we distinguish three main asymptotic regimes of behavior of the grafted layer. These regimes are characterized by (i) unscreened Coulomb repulsion between polyions, (ii) screening of the interchain interactions predominantly by counterions, or (iii) screening ensured by co-ions and counterions of the salt, respectively. We have demonstrated that all the structural and thermodynamic properties of the brush are determined by two dimensionless parameters, i.e., the bare Gouy−Chapman length normalized by the characteristic brush thickness and the bulk Debye screening length, respectively. The theory describes contraction of the brush as a whole and its internal structural rearrangements with increasing salt concentration. In particular, we consider variation of the polymer density profile and distributions of the end segments and small ions with increasing salt concentration. The maximum sensitivity of the brush to the addition of salt is predicted in the intermediate range of grafting density while dense and sparse brushes are less affected by added salt.

1. Introduction

During the last two decades major efforts have been invested in theoretical, experimental, and computation studies of polymers tethered to solid−liquid interfaces (see refs 1 and 2 and references therein). Modification of interfaces by anchored or grafted long flexible chains provides an important mechanism for the manipulation of the phase behavior and rheological properties of colloidal systems.[3−6]

The properties of grafted polymer layers (referred to as polymer brushes) are determined by the interactions between the grafted polymers. If the grafting density is sufficiently high then the repulsive interactions between monomers result in the extension of grafted chains in the direction perpendicular to the interface thus inducing anisotropy of the conformational properties of tethered chains.[7,8]

There is an important distinction between polymer brushes formed by neutral and charged (polyelectrolyte) chains. In the former case the repulsion between monomers of grafted chains is of the short-range character and can be described in terms of the excluded volume interactions. The conformations of neutral polymers are perturbed and the chains get stretched only if the density of grafting is high enough to ensure strong spatial overlapping. In contrast the long-range Coulomb forces between charged monomers of polyelectrolyte chains come into play at much larger distances between the grafted polyelectrolytes. These long-range interchain electrostatic repulsions are partially screened even in a salt-free solution. The screening is ensured by the mobile counterions which are necessarily present in the system due to the condition of total electroneutrality. The extent of screening of interchain Coulomb repulsion is determined by the spatial distribution of counterions which proves to be essentially inhomogeneous.With increasing grafting density the counterions get localized preferentially inside the brush. This accumulation of counterions results in enhanced screening of the Coulomb repulsion between grafted chains and, consequently, the chain extension grows only weakly (logarithmically) with increasing grafting density.[9−12]

In realistic experimental situations (as well as in technological applications) the layer of end-grafted polyelectrolyte is immersed in the solution of low molecular weight salts. An additional screening of Coulomb interactions between charged monomers is provided by co-ions and counterions of the salts. Therefore, the controlled variation of the ionic strength of the solution via variation of the salt concentration provides an important tool for tuning of the structural properties of the grafted polyelectrolyte layers.[13−17]

The main asymptotic scaling type relations for the large-scale properties of polyelectrolyte brushes were derived on the basis of the boxlike model in refs 9−12. The asymptotic power dependences of the brush height on the grafting density, fraction of charged monomers, and ionic strength of the solution were obtained in the limits of high and low density of charge immobilized on the chains per unit area of the brush. Recent experiments with performed mostly on polystyrene sulfonate polyelectrolyte chains anchored at solid−liquid[14−16] or air−liquid interfaces[13,17] have confirmed the main theoretical predictions. The most important approximation used in these scaling-type theories as well as in later ones[18−21] whose aim was to go beyond a boxlike model and to describe the intrinsic structure of the polyelectrolyte brush is a local electroneutrality approximation (LEA). According to LEA it is pre-assumed that irrespective of the ionic strength of the solution the excess number of counterions localized inside the brush is

---

[†] Russian Academy of Sciences.

[‡] Wageningen University.

[§] Present address: BASF AG, ZDP, D-67056 Ludwigshafen, Germany.

10.1021/ma990187i CCC: $19.00

equal to the number of charges immobilized on grafted chains.

Another theoretical approach to the problem based on the numerical solution of the differential Poisson–Boltzmann equation for the system comprising grafted polyions and small mobile counterions and co-ions of salt was developed in the pioneering papers of Miklavic and Marcelja[22] and Misra et al.[23] The profiles of polymer density and distributions of small ions were obtained numerically for different ionic strengths of the solution and the contraction of the brush as a whole with increasing salt concentration was observed. In refs 24 and 25, the modified Scheutjens–Fleer numerical SCF model was applied to the study of polyelectrolyte brushes, the results obtained for the large-scale properties of the brushes were rationalized on the basis of predictions of scaling theories.[9–12]

Recently we have developed an analytical self-consistent-field (SCF) approach[26,27] for the analysis of intrinsic structural properties of polyelectrolyte brushes immersed in salt-free solutions. This approach has made possible to interpolate between the asymptotic regimes without any preassumption about the distribution of counterions, i.e., to go beyond the LEA. The approximation used in refs 26 and 27 is justified as long as Coulomb interactions predominate over short-range excluded volume interactions between grafted chains, that is the case in a wide range of grafting densities corresponding to real experimental conditions (see refs 10 and 12 for the particular discussion). As a result, we were able to derive the distribution of electrostatic potential and that of mobile counterions inside and outside the brush in the analytic form on the basis of the exact solution of the Poisson–Boltzmann equation. It was proved that if the surface charge density provided by grafted polyions is sufficiently high, then most of counterions are essentially trapped inside the brush.

The aim of the present paper is to generalize our analytical SCF approach for polyelectrolyte brushes immersed in a solution of low molecular weight salt added in arbitrary amount. We analyze the effect of screening of electrostatic interaction by added salt on the intrinsic structure of the brush and on its large-scale properties. Not only the distributions of small ions and the electrostatic potential but also the polymer density profile and the distribution of end segments of the chains are derived. Thus, a detailed description of the intrinsic structure of the polyelectrolyte brush immersed in a salt-free solution is obtained. The rest of the paper is organized as follows. In section 2 we introduce our model, in section 3 we present general formalism of the SCF-analytical approach. The results are discussed in section 4. Finally, in section 5 we summarize our conclusions.

2. Model

We consider the polymer brush formed by long weakly charged polyelectrolyte chains grafted at one end onto an impermeable planar surface and immersed in a solution, Figure 1. The grafting density $1/s$ (s is grafting area per chain) is assumed to be high enough to ensure predominance of the interchain Coulomb interactions over the intrachain ones. We remark that the latter condition does not necessarily imply the geometrical overlapping of grafted polyions.[12]

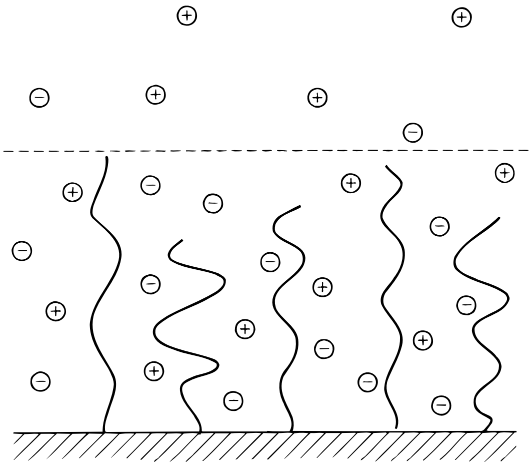

Figure 1. Layer of polyelectrolyte chains grafted to the planar surface (the polyelectrolyte brush).

Let N be the degree of polymerization of grafted chains and α be the fraction of elementary (positively) charged monomers. We assume α to be small so that locally the chains obey Gaussian statistics. The chains are assumed to be intrinsically flexible; i.e., the Kuhn segment length A is of the order of a monomer unit length, a. Then the condition of weak charging can be quantitatively formulated as

$$\alpha(l_B/a)^2 \ll 1$$

where $l_B = e^2/k_BT\epsilon$ is the Bjerrum length. Here ϵ is the dielectric constant of the solvent, k_B is the Boltzmann constant, and T is temperature. The dimensionless ratio l_B/a plays a role of a coupling constant for the Coulomb interaction in the system.

The total number of charges per polyion is $Q = \alpha N$. The ratio Q/s characterizes the average number of charges immobilized on grafted chains per unit area of the grafting surface. These charges are localized in the layer of thickness H in which all the monomers of grafted chains are found. H will be called the total thickness of the brush.

If the brush is immersed in a salt-free solution, then the solution contains Q mobile counterions per grafted chain. These counterions compensate the charge of grafted polyelectrolytes and are distributed between the interior of the brush and the bulk of the solution. We introduce the "bare" Gouy–Chapman length

$$\Lambda = \frac{s}{2\pi l_B Q} \tag{1}$$

which gives the characteristic length of decay of the density of counterions above uniformly charged planar surface with the immobilized charge Q/s per unit area.[4] We assume that in our system in addition to counterions, the low molecular weight monovalent salt is added into the solution up to the bulk concentration c_s.

We focus on the case when excluded volume interactions between uncharged monomers can be neglected. This is the case if the compensation of steric repulsions between monomers by the short-range attractions occurs, i.e., the solvent conditions are close to Θ-solvent for corresponding uncharged polymer chains. This approximation significantly simplifies the analysis (under Θ-conditions the chains obey Gaussian elasticity) and is not unrealistic for many relevant experimental systems. In fact, most of synthetic polyelectrolytes are soluble in water only due to the presence of charges on the chains (i.e., due to dissociation of counterions and corresponding gain in the translational entropy and in the solvation enthalpy) while for uncharged backbone water is only a marginally good or even a poor (like for PSS) solvent.[28] In the latter case the brush may collapse as a whole if the fraction of charge monomers is sufficiently small.[9,10] However, as we prove below, the chains in the polyelectrolyte brush are strongly extended due to the Coulomb repulsion of charged monomers. As a result, on the scale of an elastic blob[29] the intrachain short-range attraction may be not strong enough to induce even local collapse of the chain. However, this attraction is sufficient to reduce significantly the effect of excluded volume of monomers, so that the elastic response of the polymer with respect to extension is almost the same as that of a Gaussian chain. The ternary repulsive interactions involving monomers of different chains become are important and contribute to the osmotic swelling of the brush at high grafting densities, as has been discussed in refs 10 and 12. However, in our present paper we do not consider crossover to this so-called quasi-neutral regime and focus on the case when Coulomb interchain interactions predominate over the nonelectrostatic ones. This situation corresponds to experimentally available brushes formed by polyelectrolytes anchored at solid−liquid or air−liquid interfaces. Because of strong Coulomb repulsion between charged chains the high grafting density is practically hardly attainable.

3. General Formalism

Our analysis of the conformations of grafted chains in the polyelectrolyte brush is based on the direct solution of the Poisson−Boltzmann equation for the electrostatic potential $\Psi(z)$ and density distributions of co-ions and counterions inside and outside the brush, i.e., in the regions $z \leq H$ and $z \geq H$, respectively. Here z is the coordinate normal to the grafting surface.

The reduced electrostatic potential, $\psi(z) \equiv e\Psi(z)/k_BT$, obeys the Poisson equation

$$\frac{d^2\psi}{dz^2} = -4\pi l_B[\alpha c_p(z) + c_+(z) - c_-(z)], \quad z \leq H \quad (2)$$

$$\frac{d^2\psi}{dz^2} = -4\pi l_B[c_+(z) - c_-(z)], \quad z \geq H \quad (3)$$

inside and outside the brush, respectively. Here $c_p(z)$, $c_+(z)$ and $c\_(z)$ are the local concentrations of monomer units, co-ions, and counterions, respectively. We assume that all the local properties of the brush depend only on the z co-ordinate, i.e., on the distance from the grafting surface, while in the lateral direction the system is translationally invariant. The distributions of mobile co-ions and counterions obey the Boltzmann law

$$c_+(z) = c_+(H) \exp(-\psi(z)) \quad (4)$$

$$c\_(z) = c\_(H) \exp(-\psi(z)) \quad (5)$$

where the choice of the preexponential factors corresponds to the condition of vanishing of the electrostatic potential at the edge of the brush, $\psi(z = H) = 0$. The density distributions of mobile ions, as well as their derivatives, must be continuous at the brush edge, i.e., at $z = H$.

We can proceed making use of the fact, that the self-consistent molecular field $\mu(z)$ which experience each monomer unit in the brush must have a parabolic shape irrespectively of the particular form of interactions between the monomers. This is the case if the chains in the brush are grafted sufficiently densely and, as a result, are strongly extended with respect to their Gaussian dimension, i.e., $H \gg N^{1/2}a$. In the case of the strong chain extension the quasi-classical approximation leading to the parabolic form of the self-consistent molecular field in the brush

$$\mu(z)/k_BT = \text{const} - 3\pi^2z^2/8N^2a^2 \quad (6)$$

applies as has been shown in refs 30−33. If the brush consists of polyelectrolyte chains then the self-consistent field experienced by a monomer in the brush comprises the osmotic contribution (due to nonelectrostatic excluded volume interactions between the monomers) and the Coulomb potential. As the latter acts only on a fraction α of charged monomers, the *average* contribution of the electrostatic potential calculated *per monomer* should be corrected by a factor of α. If the excluded volume interaction in the brush formed by polyelectrolyte chains are negligibly week (qualitatively this condition is specified in ref 12), then the self-consistent molecular potential in the brush comprises only the electrostatic contribution. Consequently, the self-consistent potential of a monomer given by eq 6 is equal to $\alpha e\Psi(z)/k_BT$. Setting the electrostatic potential $\Psi(z)$ equal to zero at the edge of the brush, $z = H$; i.e., making the corresponding choice of the constant in eq 6, we get an explicit expression for the electrostatic potential inside the brush, i.e., at $z \leq H$

$$\psi(z) = (H^2 - z^2)/H_0^{\,2} \quad (7)$$

where

$$H_0 = \sqrt{\frac{3}{8\pi^2}}\,N\alpha^{1/2}a \quad (8)$$

is an important characteristic length scale which we discuss below. We remark that eq 7 can be obtained by direct minimization of the free energy of the system; this free energy comprises the energy of electrostatic interactions, the conformational entropy of grafted chains and the translational entropy of mobile ions[26].

Substituting eq 7 into eq 2 we get an interrelation between the distribution of polymer density and those for both types of mobile ions inside the brush

$$\alpha c_p(z) + c_+(z) - c\_(z) = \frac{1}{2\pi l_B H_0^{\,2}}, \quad z \leq H \quad (9)$$

As follows from eq 9 the net local charge density is uniform throughout the brush, i.e., does not depend on z at $z \leq H$. By integrating of eq 9 from 0 to H, we obtain the total uncompensated charge localized inside the brush. This charge is equal to the excess number of counterions which are spread in the range $z \geq H$. This excess charge (calculated per area s, i.e., per chain) equals

$$\tilde{Q} = \frac{sH}{2\pi l_B H_0^{\,2}} \quad (10)$$

and we have to use a “tilde” in order to distinguish it from the “bare” charge Q per area s arising due to grafting of polyelectrolyte chains. The distribution of mobile ions above the brush edge, i.e., at $z \geq H$, coincides with that above the charged plane with immobilized charge $\tilde{Q}/s$ per unit area and depends on the effective Gouy−Chapman length

$$\tilde{\Lambda} = \frac{s}{2\pi l_B \tilde{Q}} = \frac{{H_0}^2}{H} \tag{11}$$

(compare to eq 1) where the last equality takes into account eq 10. The explicit expression for the concentrations of co-ions and counterions at $z \geq H$ as a function the effective surface charge density (via $\tilde{\Lambda}$ and the salt concentration are derived in the Appendix.

Making use of the continuity of the electrostatic potential and, as a result, of the density profiles of co- and counterions at the brush edge, $z = H$, and taking into account eq 10 we get explicit expressions for the profiles of density of co-ions and counterions inside the brush

$$c_{\pm}(z) = \frac{1}{2\pi l_{\mathrm{B}} {H_0}^2}\left[\Phi_{\mathrm{s}} + \frac{H^2}{2{H_0}^2} \mp \frac{H}{H_0}\sqrt{\Phi_{\mathrm{s}} + \frac{H^2}{4{H_0}^2}}\right] \exp[\mp(H^2 - z^2)/{H_0}^2] \tag{12}$$

where the prefactor $^1/_{2\pi l_{\mathrm{B}} H_0}$ equals to the density of uncompensated charge inside the brush, eq 9, and we have introduced the renormalized dimensionless salt concentration in the bulk of the solution as

$$\Phi_{\mathrm{s}} = 2\pi l_{\mathrm{B}} {H_0}^2 c_{\mathrm{s}} = (\kappa H_0/2)^2 \tag{13}$$

where $\kappa^{-1} = (8\pi l_{\mathrm{B}} c_{\mathrm{s}})^{-1/2}$ is the bulk Debye screening length. At this point it is convenient to introduce the reduced variables by normalizing all the lengths to H_0 as

$$h \equiv H/H_0$$

$$\xi \equiv z/H_0$$

$$\zeta \equiv H_0/\Lambda$$

In reduced coordinates, the density profiles of the mobile ions can be represented as

$$c_{\pm}(\xi) = \frac{c_0}{\zeta}\left[\frac{h}{2} \mp \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp[\mp(h^2 - \xi^2)] \tag{14}$$

where

$$c_0 = \frac{Q}{sH_0}$$

Using eq 9 we can obtain also the explicit expression for the polymer density profile inside the brush to give

$$\alpha c_{\mathrm{p}}(\xi) = \frac{c_0}{\zeta}\left[1 + 2\left(\Phi_{\mathrm{s}} + \frac{h^2}{2}\right)\sinh(h^2 - \xi^2) + 2h\sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\cosh(h^2 - \xi^2)\right] \tag{15}$$

The distribution of the free chain ends $g(z)$ can be obtained by inverting of the equation for the monomer density[31,33]

$$c_{\mathrm{p}}(z) = \frac{2N}{s\pi}\int_z^H \frac{g(z')\,\mathrm{d}z'}{\sqrt{z'^2 - z^2}} \tag{16}$$

The result is

$$g(\xi) = \xi\zeta^{-1}\left\{\frac{1 + 2h\sqrt{\Phi_{\mathrm{s}} + h^2/4}}{\sqrt{h^2 - \xi^2}} + 2\left[\frac{h}{2} + \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(h^2 - \xi^2)\int_0^{\sqrt{h^2 - \xi^2}} \exp(-t^2)\,\mathrm{d}t + 2\left[\frac{h}{2} - \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(\xi^2 - h^2)\int_0^{\sqrt{h^2 - \xi^2}} \exp(t^2)\,\mathrm{d}t\right\} \tag{17}$$

The overall height of the brush H can be obtained from the condition of conservation of the polymer inside the brush

$$s\int_0^H c_{\mathrm{p}}(z)\,\mathrm{d}z = N$$

By substituting eq 15 into this normalization condition we obtain the equation for the reduced brush height $h \equiv H/H_0$

$$\left[\frac{h}{2} + \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(h^2)\int_0^h \exp(-t^2)\,\mathrm{d}t - \left[\frac{h}{2} - \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(-h^2)\int_0^h \exp(t^2)\,\mathrm{d}t + h = \zeta \tag{18}$$

where t is the integration variable.

Another property which characterizes the brush thickness and can be measured experimentally is the root-mean-square thickness, that is the second moment of the polymer density distribution. The equation for the reduced root-mean-square thickness of the brush, h_{rms}, reads

$${h_{\mathrm{rms}}}^2 = \zeta^{-1}\left\{\frac{1}{2}\left[\frac{h}{2} + \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(h^2)\int_0^h \exp(-t^2)\,\mathrm{d}t + \frac{1}{2}\left[\frac{h}{2} - \sqrt{\Phi_{\mathrm{s}} + \frac{h^2}{4}}\right]^2 \exp(-h^2)\int_0^h \exp(t^2)\,\mathrm{d}t - \frac{h^3}{6} - h\Phi_{\mathrm{s}}\right\} \tag{19}$$

4. Discussion

As we can see from eqs 12−19, the structural properties of the polyelectrolyte brush exhibit certain universality in properly reduced coordinates. The most important characteristic length is given by H_0 which scales as the thickness of the brush in the salt free solution in the regime of strong localization of counterions (see below). The normalized by H_0 overall thickness of the brush and the root-mean-square thickness depend only on two dimensionless parameters: (i) the normalized by H_0 bare Gouy−Chapman length, Λ, or the inverse quantity ζ which we call the localization parameter and (ii) the normalized by H_0 Debye screening length κ^{-1} in

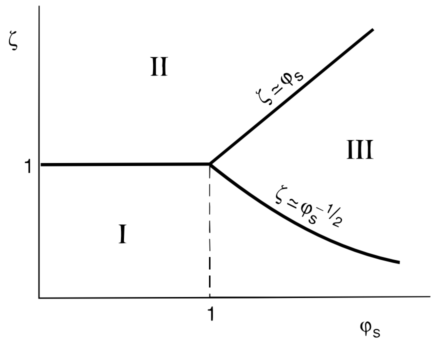

Figure 2. Asymptotic ranges for the solution of eq 18 in the ζ, Φ_s plane.

the bulk of the solution, or the reduced salt concentration Φ_s. All the density distributions of monomer units, mobile ions and end segments of the chains are universal functions of the reduced coordinate $\xi \equiv z/H_0$ and depend only on two parameters Φ_s and h or, which is the same if we take into account the $h(\zeta, \Phi_s)$ dependence, on two reduced screening lengths: κ^{-1}/H_0 and $\zeta^{-1} \equiv \Lambda/H_0$.

To get better insight in the asymptotic behavior of the solution of eqs 18 and 19 and to make links to the predictions of the earlier scaling theories[9-12] it is convenient to distinguish three main asymptotic regions in the plane of parameters (ζ,Φ_s), Figure 2. These regions correspond to physically different regimes of behavior of the brush and are characterized by (i) negligibly weak screening of the Coulomb repulsion between grafted polyions in region I, (ii) strong screening of the Coulomb repulsion predominantly by counterions localized inside the brush in region II and (iii) screening predominantly by co-and counterions of salt in region III. The latter regime can be attributed to the salt-dominance regime predicted in ref 12 on the basis of scaling-type arguments. Expansions of eqs 18 and 19 at $h \gg 1$ (for region II) and at $h \ll 1$ (for regions I and III) gives the corresponding asymptotic solutions for the reduced brush height $h(\zeta,\Phi_s)$:

$$h(\zeta,\Phi_s) \cong \begin{cases} \zeta & \zeta \ll \min\{1,\Phi_s^{-1/2}\}, \text{region I} \\ \sqrt{\ln(2\zeta/\sqrt{\pi})} & \zeta \ll \max\{1,\Phi_s\}, \text{region II} \\ (3\zeta/4\Phi_s)^{1/3} & \Phi_s^{-1/2} \ll \zeta \ll \Phi_s, \text{ region III} \end{cases} \tag{20}$$

and for the root-mean-square brush thickness $h_{\mathrm{rms}}(\zeta,\Phi_s)$- The conditions of the crossover between these asymptotic solutions determine the boundaries between the region in Figure 2.

$$h_{\mathrm{rms}}(\zeta,\Phi_s) \cong \begin{cases} \zeta/\sqrt{3} & \text{region I} \\ 1/\sqrt{2} & \text{region II} \\ (3\zeta/20\sqrt{5}\Phi_s)^{1/3} & \text{region III} \end{cases} \tag{21}$$

We remark that at low salt concentration, $\Phi_s \ll 1$, our equations recover results obtained in[26] for the polyelectrolyte brush in a salt-free solution. In the latter case the screening of Coulomb interactions between grafted polyelectrolytes is provided by counterions only. Depending on the magnitude of the localization parameter ζ the counterions are either retained inside the brush by strong Coulomb attraction to grafted polyions at $\zeta \gg 1$ (this is the case for sufficiently densely grafted charged chains) or released from the brush and spread far above the brush edge due to the entropic reasons at $\zeta \ll 1$ (sparsely grafted brushes). An increase in ζ corresponding to increasing grafting density leads to monotonic increase both in H and in H_{rms}. This increase reflects the interplay of two opposite trends: increasing density of immobilized charges in the brush and simultaneously enhancing screening of the Coulomb repulsion between these charges due to localization of growing fraction of counterions inside the brush. At $\zeta \ll 1$ (weak screening regime) both $H \sim H_{\mathrm{rms}} \sim \zeta$ in region I. At $\zeta \gg 1$, i.e., in region II, the localization of counterions gets more pronounced and results in strong screening of Coulomb repulsion between grafted polyions. As a result H continues to grow with ζ but only logarithmically while H_{rms} tends an asymptotic value proportional to H_0. Hence, H_0 defined by eq 8 gives the inherent characteristic scale for the brush thickness in the limit of strong screening of the interchain Coulomb repulsion by counterions trapped inside the brush, that was first pointed out in refs 9 and 10.

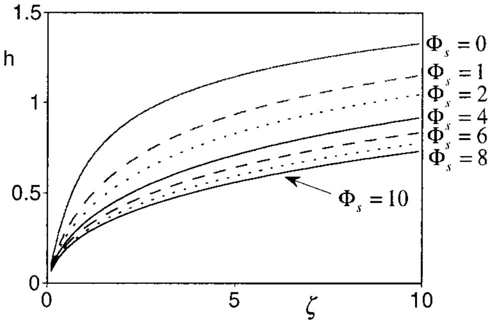

Figure 3. Dependence of the reduced brush thickness on the grafting density via parameter ζ for different salt concentrations (shown in the figure).

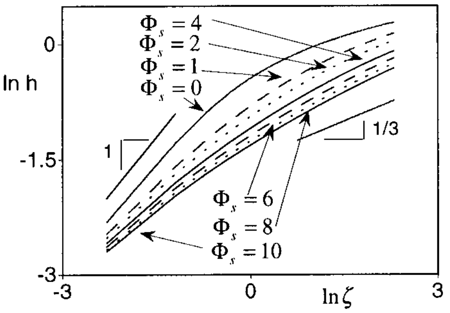

Figure 4. Same as in Figure 3, but in log–log scale.

If salt is added in the solution, then co-ions and counterions penetrate into the brush that leads to additional screening of Coulomb repulsion between polyions. The extent of these screening and, as a result, the conformation of grafted chains in the brush are now determined by the interplay of two parameters, ζ and Φ_s. For each value of ζ the brush height monotonically decreases with increasing salt concentration, i.e., increasing Φ_s, and for every salt concentration the brush height monotonically increases as a function of ζ, that is demonstrated in Figures 3–5, respectively. The asymptotic power dependence $H \sim c_s^{-1/3}$ for the brush height as a function of the salt concentration in the salt-dominance regime III as given by eqs 20, 21 is in agreement with earlier scaling predictions of refs 9, 12, and 18.

Equation 20 makes transparent the shapes of the h vs ζ and the h vs Φ_s curves presented in Figures 4 and

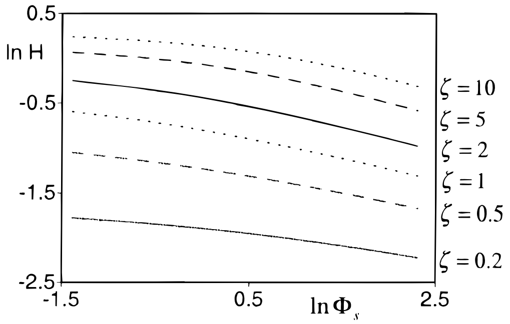

Figure 5. Dependence of the reduced brush thickness on the salt concentration via parameter Φ_s for different values of ζ in log–log scale.

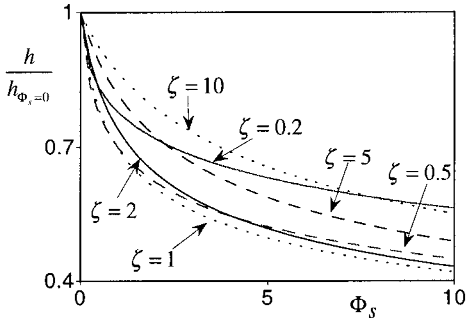

Figure 6. Relative magnitude of the salt-induced contraction of the brush $h(\Phi_s)/h(\Phi_s = 0)$ vs Φ_s for different values of parameter ζ (shown at the curves).

5 in a log–log scale. At small salt concentration, $\Phi_s \leq 1$, the initial slope of ln h vs ln ζ equals 1 (regime I), while at large ζ the curves virtually flatten off (regime II). For large salt concentration, $\Phi_s \gg 1$, an intermediate linear part with the slope $^1/_3$ appears and extends with increasing Φ_s; this range corresponds to the crossing of the dominated by salt region III of the diagram. All the ln h vs ln Φ_s curves exhibit the slope $-^1/_3$ at sufficiently large Φ_s.

It is instructive to analyze the relative magnitude of the contraction of the brush due to enhancing screening by added salt. In Figure 6 we present the salt concentration dependence of the brush height normalized to its value at zero salt, i.e., $h(\Phi_s)/h(\Phi_s = 0)$ vs Φ_s. As follows from Figure 6 the effect of added salt on the structure of the polyelectrolyte brush is more pronounced at intermediate values of $\zeta \cong 1$, while more dense ($\zeta \gg 1$) or, in contrast, more sparse ($\zeta \ll 1$) brushes are less affected by salt. This nonmonotonic dependence of the sensitivity of the brush with respect to added salt on the grafting density via ζ can be rationalized with the aid of the following simple arguments: In densely grafted brushes, i.e., at $\zeta \gg 1$, the major fraction of counterions are trapped inside the brush and ensure partial screening of the Coulomb repulsion between polyions even when the brush is in contact with a salt-free solution. The onset of the salt-induced contraction of the brush occurs when the salt concentration becomes larger than the concentration of counterions (in the salt-free case the latter is approximately equal to the concentration of charged monomers) inside the brush. This condition can be reformulated in terms of screening lengths as the following: the bulk Debye screening length must become smaller than the intrinsic screening length ensured by trapped inside the brush counterions. Therefore, the higher is the grafting density (the larger ζ), the larger bulk salt concentration is required to affect the structure of dense brushes.

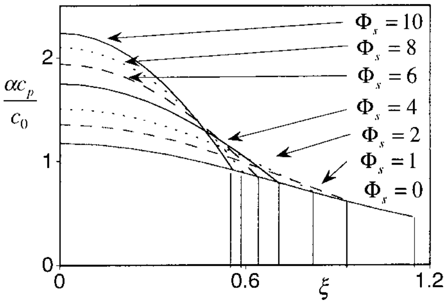

Figure 7. Normalized per one chain polymer density profiles for $\zeta = 5$ and different values of Φ_s (shown at the curves).

In contrast, at small ζ the screening of interchain repulsion in the brush immersed in the salt-free solution is weak because of low concentration of counterions inside the brush. With addition of salt the screening effect becomes significant at $\kappa H \geq 1$ or, that is the same, at $\Phi_s\zeta^2 \geq 1$, because the brush thickness H grows proportionally to ζ in the low screening regime. Therefore, the smaller is ζ, the larger salt concentration is required to provide significant screening of the Coulomb interactions on the scale of order of the brush thickness H and, consequently, to induce the brush contraction.

The evolution of the density profiles of monomers and counterions with increasing salt concentration are presented in Figures 7 and 8, respectively. With increasing salt concentration the extension of the chains in the brush decreases. As a result both the average polymer concentration in the brush and its value at $z = H$ increase. However, the relative magnitude of the contraction is larger in the central regions of the brush rather than at the periphery. As follows from eq 15 the value of the polymer concentration at the edge of the brush, $z = H$, grows with the salt concentration as

$$\alpha c_p(h)/c_0 = \zeta^{-1}(1 + 2h\sqrt{\Phi_s + h^2/4}) \cong \zeta^{-1}(1 + O(\zeta^{1/3}\Phi_s^{\ 1/6})) \quad (22)$$

while the average polymer concentration in the brush grows as

$$\alpha\bar{c}_p/c_0 = h^{-1} \sim (\Phi_s/\zeta)^{1/3} \quad (23)$$

This trend is demonstrated by Figure 7 where the polymer density profiles normalized per one chain are plotted vs the reduced coordinate $\xi \equiv z/H_0$ according to eq 15. As follows from eq 15 and is illustrated by Figure 7, the polymer density profiles acquire truncated parabolic shape in the regime III of strong screening by salt, i.e., at $\Phi_s \gg 1$, $h \ll 1$. This shape of the density profiles is also reflected by the asymptotic ratio $h_{rms}^2 = h^2/5$ between the overall and the root-mean-square brush thicknesses in the regime III given by eqs 20 and 21, respectively. The parabolic monomer density distribution is expected for the brush with short-range binary repulsion between monomers. In the limit of high salt concentration screened Coulomb interactions between charged monomers are equivalent to the binary short-range (excluded volume) repulsions that must result (asymptotically) in the parabolic distribution of the polymer density in the brush.[18] We remark that with increasing salt concentration and corresponding decrease in the extension of the chains in the brush the

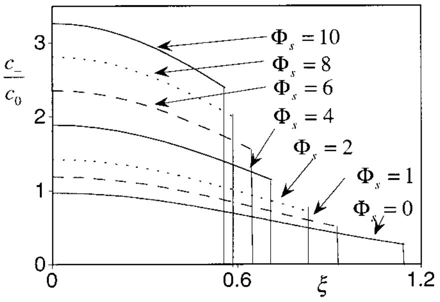

Figure 8. Normalized per one chain distributions of counterions inside the brush for $\zeta = 5$ and different values of Φ_s (shown at the curves).

jump of the polymer concentration at $z = H$ gets smoothed due to enhancing Gaussian fluctuations of nonextended terminal parts of the chains.[34,35] The latter effect is however beyond the scope of our theory.

The density profiles of counterions and co-ions given by eq 14 demonstrate their nonuniform distribution inside the brush: The local density of counterions monotonically decrease with the distance from the grafting surface; in the salt-free case ($c_+(z) \equiv 0$) the density profile of counterions follows (with the constant deviation) the distribution of charged monomers and has the truncated Gaussian shape, Figure 8. The density of co-ions in contrast increases with z. The latter ones are depleted from the presurface region. This depletion gets more pronounced with increasing grafting density, i.e with increasing ζ. As the salt concentration in the bulk of the solution increases both co-ions and counterions concentrations inside the brush increase as well, but their distribution inside the brush becomes more strongly nonuniform.

Figure 9 visualize the evolution of the distributions of the end segments of the grafted chains with increasing salt concentration as described by eq 17. In the case of small ζ (Figure 9a corresponding to relatively sparsely grafted layer) the density of the end segments is a monotonically increasing function of the distance z from the surface and diverges at the edge of the brush, $z = H$. This divergence corresponds to the sharp maximum in the distribution, if Gaussian fluctuations in the terminal parts of the chains are taken into account. This shape of the end segment distribution is preserved when the salt concentration increases while the position of the maximum gets displaced toward the surface as a result of the contraction of a brush as a whole. In contrast, in the case of large ζ an increase in the salt concentration results in significant modification of the density profile of the end segments, as demonstrated by Figure 9b. In the low salt limit $g(\xi)$ exhibits two maxima: a broad one in the central region of the brush, $\xi \le 1$, and a sharp maximum near the edge of the brush. The latter maximum is expected to be partially smoothened due to the Gaussian fluctuations in nonextended terminal parts of the chains. With increasing salt concentration these fluctuations become progressively more important due to the contraction of the brush as a whole. As the brush becomes more compact, the more chain ends appear to be localized in the periphery of the brush so that two maxima in the end segment distribution merge. At high salt concentration the end segments distributions have qualitatively similar shapes with one maximum displaced to the edge of the brush irrespectively of the value of ζ.

5. Conclusions

We have developed an analytical SCF theory of the polyelectrolyte brushes in the solutions with arbitrary concentration of salt. This theory is valid as long as the interchain Coulomb interactions in the brush (i) predominate over nonelectrostatic ones and (ii) can be treated on the level of the Poisson−Boltzmann approximation.

The evolution of the polymer density profiles, co-ions and counterions distributions with increasing salt concentration demonstrate the same trends as the corresponding distributions obtained earlier[22−25] on the basis of numerical solutions of the coupled differential Poisson−Boltzmann and SCF equations. However, in contrast to earlier works, we present all the distributions of the polymer density, end segments and small ions in closed analytical form as a function of two properly normalized correlation lengths: the Gouy−Chapman length and the Debye length. This enables to obtain proper asymptotics corresponding to physically different limiting regimes which were predicted earlier on the basis of scaling arguments and to calculate the exact numerical prefactors for the scaling dependences.

Our theory is based on the original analytical solution of the Poisson−Boltzmann equation for the system of flexible charged polymers grafted to the planar surface and immersed in the solution of a monovalent electrolyte. Together with the results presented in ref 26, this solution completes a new and unique class of exact solutions of the Poisson−Boltzmann equation for systems comprising flexible polyelectrolytes.

The intrinsic structure of the brush obeys universal properties if all the lengths are normalized to the characteristic scale H_0 which we have specified. Then all the structural properties of the brush are determined by two dimensionless scaling parameters which are given by two important screening lengths, the Gouy−Chapman length and the bulk Debye length, appropriately normalized. The former screening length describes self-screening in the brush due to counterions at low salt concentration while the latter one determines the extent of screening by added salt. The interplay between these parameters determines the conformations of grafted polyelectrolytes in the whole range of variation of the grafting density and the ionic strength of the solution.

An increase in the bulk salt concentration always result in the contraction of the brush due to screening of the interchain repulsion. However, the relative magnitude of the effect depends nonmonotonically on the grafting density: the salt-induced contraction is most pronounced at moderate grafting densities, while the same amount of added salt weaker affects densely or, in contrast, sparsely grafted brushes. An interesting theoretical prediction concerns bimodal distribution of the chain ends in sufficiently strongly charged brushes at low salt concentration. With increasing concentration of salt the brush contracts and becomes intrinsically more homogeneous. This results in a merging of two maxima in the distribution of the free ends corresponding to two different populations of chains within the brush.

Finally, we conclude that with the account of the abovementioned limitations our theory provides quantitative analytical description of the static structural properties of a polyelectrolyte brush. With the exception

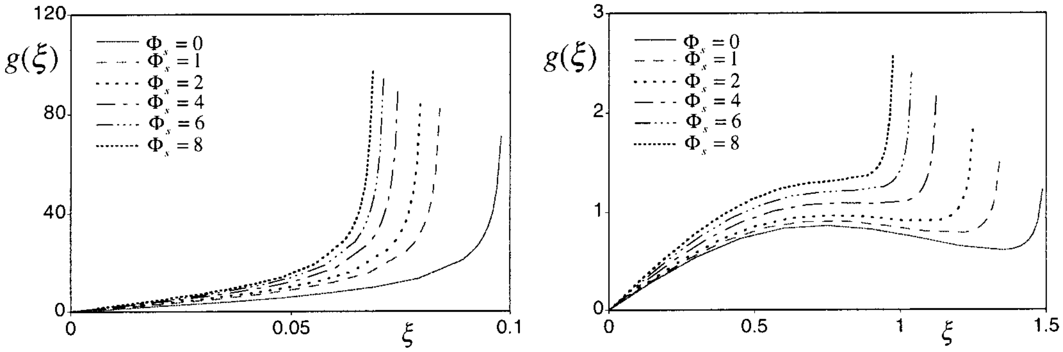

Figure 9. Normalized per one chain distribution of the end segments for $\zeta = 0.5$ (a) and $\zeta = 20$ (b) and different values of Φ_s (shown at the curves).

of the segment length, a, our equations contain no adjusting parameters and, therefore, can be directly used for fitting of the experimental data and for further quantitative predictions.

Acknowledgment. This work was partially supported by the Dutch Scientific Organization (NWO) Dutch-Russian collaboration program "Polyelectrolytes in Complex Fluids" and RFBR Grant 99-03-33319.

Appendix: Distribution of Mobile Ions near Charged Surface

The distribution of electrostatic field, $\Psi(z) \equiv e\psi(z)/l_B$, and concentrations of mobile ions, $c\_(z)$ and $c_+(z)$, near a uniformly (positively) charged infinite plane can be obtained on the basis of the solution of the Poisson–Boltzmann equation[4]

$$\frac{d^2\psi}{dz^2} = -4\pi l_B[c_+(z) - c\_(z)] \qquad (A1)$$

$$c_+(z) = c_+(0)\exp(-\psi(z)) \qquad (A2)$$

$$c\_(z) = c\_(0)\exp(\psi(z)) \qquad (A3)$$

(the electrostatic potential is assumed to vanish at $z = 0$, i.e. $\psi(z = 0) = 0$) with the boundary conditions

$$\left(\frac{d\psi}{dz}\right)_{z=0} = -\frac{2}{\tilde{\Lambda}} \qquad (A4)$$

where $\tilde{\Lambda}$ is related to the surface charge density $\tilde{Q}/s$ via eq 1 and

$$\left(\frac{d\psi}{dz}\right)_{z=\infty} = 0 \qquad (A5)$$

The first integral of eq A1 can be obtained taking into account eq A4 and reads

$$\frac{d\psi(z)}{dz} = -\sqrt{8\pi l_B[c\_(0)(\exp(\psi(z)) - 1) + c_+(0)(\exp(-\psi(z)) - 1)] + \frac{4}{\tilde{\Lambda}^2}} \qquad (A6)$$

Applying condition A5 to eq A6 and taking into account that in the bulk of the solution $c\_(z = \infty) = c_+(z = \infty) = c_s$, we obtain the system of equations for the density of co-ions and counterions near the grafting surface

$$2\pi l_B[c\_(0) + c_+(0) - 2c_s] = \tilde{\Lambda}^{-2} \qquad (A7)$$

$$c\_(0)c_+(0) = c_s^{\,2} \qquad (A8)$$

with the solution

$$c_{\mp}(0) = c_s + \frac{1}{4\pi l_B\tilde{\Lambda}^2} \pm \sqrt{\frac{c_s}{2\pi l_B\tilde{\Lambda}^2} + \left(\frac{1}{4\pi l_B\tilde{\Lambda}^2}\right)^2} \qquad (A9)$$

Then the second integral of eq A1 can be presented as

$$\psi(z) = 2\ln\left[\left(\frac{\sqrt{\kappa^2\tilde{\Lambda}^2 + 1} - 1}{\kappa\tilde{\Lambda}}\right)\frac{\kappa\tilde{\Lambda} + \sqrt{\kappa^2\tilde{\Lambda}^2 + 1} - 1 + (\kappa\tilde{\Lambda} - \sqrt{\kappa^2\tilde{\Lambda}^2 + 1} + 1)\exp(-\kappa z)}{\kappa\tilde{\Lambda} + \sqrt{\kappa^2\tilde{\Lambda}^2 + 1} - 1 - (\kappa\tilde{\Lambda} - \sqrt{\kappa^2\tilde{\Lambda}^2 + 1} + 1)\exp(-\kappa z)}\right]$$

where $\kappa^2 = 8\pi l_B c_s$ is the usual Debye screening parameter. As required, the potential $\psi(z)$ vanishes at $z = 0$. Hence, in reduced coordinates ($z/\tilde{\Lambda}$ or z/κ^{-1}) the Coulomb potential depends only on one parameter, that is the ratio between two screening lengths, $\tilde{\Lambda}$ and κ^{-1}, involved.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1990**, *100*, 31.
(2) Grest, G. S.; Murat, M. In *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*; Binder, K., Ed.; Oxford University Press: New York, 1995; p 476.
(3) Napper, D. H. *Polymeric Stabilization of Colloidal Dispersions*; Academic Press: London, 1985
(4) Israelachvili, J. N. *Intermolecular and Surface Forces*; Academic Press: London, 1985.
(5) *Stealth Liposomes*; Lasic, D., Martin, F., Eds.; CRC Press: Boca Raton, FL, London, and Tokyo, 1995.
(6) Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. *Polymers at Interfaces*; Chapman & Hall, London, 1993.
(7) Alexander, S. *J. Phys., Fr.* **1977**, *38*, 983.
(8) De Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(9) Pincus, P. A. *Macromolecules* **1991**, *24*, 2912; Ross, R.; Pincus, P. A. *Ibid.* **1992**, *25*, 1503.
(10) Borisov, O. V.; Birshtein, T. M.; Zhulina, E. B. *J. Phys. II* **1991**, *1*, 521.
(11) Wittmer, J.; Joanny, J. F. *Macromolecules* **1993**, *26*, 2691.
(12) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1994**, *27*, 4795.
(13) Guenoun, P.; Schlachli, A.; Sentenac, D.; Mays, J. W.; Benattar, J. J. *Phys. Rev. Lett.* **1995**, *74*, 3628
(14) Mir, Y.; Auroy, P.; Auvray, L. *Phys. Rev. Lett.* **1995**, *75*, 2863.
(15) Watanabe, H.; Patel, S. S.; Argillier, J. F.; Parsonage, E. E.; Mays, J.; Dan-Brandon, N.; Tirrell, M. *Mater. Res. Soc. Symp. Proc.* **1992**, *249*, 255.

(16) Tran, Y. Interfaces of grafted polyelectrolytes. Ph.D. Thesis, Université Paris 6, 1998.
(17) Ahrens, H.; Förster, S.; Helm, C. A. *Phys. Rev. Lett.* **1999**, 4798.
(18) Zhulina, E. B.; Borisov, O. V.; Birshtein T. M. *J. Phys. II* **1992**, *2*, 63.
(19) Zhulina, E. B.; Borisov, O. V.; Birshtein T. M. *J. Phys.: Condens. Matter* **1994**, *6*, 1.
(20) Misra, S.; Tirrell, M.; Mattice, W. *Macromolecules* **1996**, *29*, 6056.
(21) Lyatskaya, Yu. V,; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562
(22) Miklavic, S. J.; Marcelja, S. *J. Phys. Chem.* **1988**, *92*, 6718.
(23) Misra, S.; Varanasi, S.; Varanasi, P. P. *Macromolecules* **1989**, *22*, 4173.
(24) Israels, R.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. *Macromolecules* **1994**, *27*, 3249.
(25) Israels, R,; Leermakers, F. A. M.; Fleer, G. J. *Macromolecules* **1994**, *27*, 3087.
(26) Zhulina, E. B.; Borisov O. V. *J. Chem. Phys.* **1997**, *107*, 5952.
(27) Zhulina, E. B.; Borisov O. V. *Macromolecules* **1998**, *31*, 7413.
(28) Williams, C. E.; Wafa, E. *J. Phys. II*, **1995**, *5*, 1269. Wafa, E. Structure des Polyelectrolytes Fortement Charges. Ph.D. Thesis, Université Paris IV, 1996.
(29) Pincus, P. *Macromolecules* **1977**, *10*, 210.
(30) Semenov, A. N. *Sov. Phys. JETP* **1985**, *61*, 733.
(31) Skvortsov, A. M.; Pavlushkov, I. V.; Gorbunov, A. A.; Zhulina, E. B.; Borisov, O. V.; Pryamitsyn, V. A. *Polym. Sci. USSR* **1988**, *30*, 1706
(32) Milner, S. T.; Witten, T. A.; Cates, M. *Macromolecules* **1998**, *21*, 2610.
(33) Zhulina, E. B.; Borisov, O. V.; Pryamitsyn; V. A.; Birshtein, T. M. *Macromolecules* **1991**, *24*, 140
(34) Zhulina, E. B.; Semenov, A. N. *Polym. Sci. USSR* **1989**, *31*, 196.
(35) Zhulina, E. B.; Borisov, O. V.; Priamitsyn, V. A. *J. Colloid Interface Sci.* **1991**, *137*, 495.

MA990187I