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# Structure of Weakly Charged Polyelectrolyte Brushes: Monomer Density Profiles

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**Abstract.** — The internal structure (the monomer density profiles) of weakly charged polyelectrolyte brushes of different morphologies has been analyzed on the basis of the self-consistent-field approach. In contrast to previous studies based on the local electroneutrality approximation valid for sufficiently strongly charged or densely grafted (“osmotic”) brushes we consider the opposite limit of sparse brushes which are unable to retain the counterions inside the brush. We have shown that an exact analytical solution of the SCF-equations is available in the case of a planar brush. In contrast to Gaussian monomer density profile known for “osmotic” polyelectrolyte brushes we have found that weakly charged brushes are characterized by constant monomer density. At the same time free ends of grafted polyions are distributed throughout the brush. Thus, the structural cross-over between polyelectrolyte “mushrooms” and dense brush regimes is established.

## 1. Introduction

Equilibrium structure and properties of polyelectrolyte brushes, *i.e.* of the monolayers formed by long polyelectrolyte chains tethered onto interfaces of different geometry and immersed in solution, have been studied extensively during last 5 years [1–7]. Interest to these systems has been initiated primarily by the aims of colloid stabilization in polar solvents [8], design of drug-delivery systems [9], *etc.*

Existing scaling theories [1–7] give us a valuable insight to the large-scale behavior of chains in the polyelectrolyte brushes and to the dependence of such average characteristics as the brush thickness, chains gyration radius *etc.* on the main molecular parameters (chain length, density of grafting, degree of ionization of monomers). On the other hand, SCF approach made it possible to consider internal structure of polyelectrolyte brushes and to calculate numerically the distributions of monomers and the free chain ends in a planar brush [10–12]. Further progress in the field manifested itself in the analytical SCF description of polyelectrolyte brushes. An analytical SCF theory [5] was developed in the frames of the local electroneutrality approximation (LEA). This approximation assumes local compensation of net charge throughout the

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system. Whereas at high ionic strengths of solution LEA provides adequate description of polyelectrolyte brushes in a wide range of grafting densities and degrees of ionization (the so-called “salted” brushes), at low ionic strengths, LEA is applicable only to relatively dense and strongly charged brushes, providing high surface density of the immobilized charge [6, 12].

As has been discussed in [1, 6, 13], the equilibrium distribution of mobile counterions and, consequently, the electrostatic field and the shape of the monomer density profile in the brush depend strongly on the density of the immobilized charge.

If the immobilized charge density is sufficiently large (that is the case for comparatively dense brushes formed by sufficiently strongly charged chains), then most of counterions are retained inside the brush due to strong Coulomb attraction to the grafted polyions. In this case the brush is almost electroneutral as a whole. Moreover, the Debye screening length in the brush appears to be much smaller than the total brush thickness providing the basis of the LEA. Stretching electrostatic force applied to the grafted polyions is proportional to osmotic pressure of the counterions inside the brush. As a result, in the scaling approximation the brush thickness is independent of the grafting density and of the brush geometry and is equal to  $H \cong N\alpha\alpha^{1/2}$  where  $N$  is the degree of polymerization of grafted chains and  $\alpha$  is the fraction of charged monomers. Simple scaling arguments result in the monomer density profile  $c_{\text{osm}}(r) \sim r^{d-1}$ . More sophisticated SCF-analysis [5] shows that due to strong fluctuations of stretching of every particular chain in the planar brush and due to the inhomogeneity of this stretching, the monomer density profile in osmotic planar brush has a Gaussian shape. Recent experiments [14] confirm this prediction.

In the opposite limit of sparse grafting (which is attainable for planar and cylindrical brushes) the distance between grafted polyions is so large that the effect of intramolecular interaction is negligibly weak. We can refer to this regime as to “charged mushrooms” regime. In this regime each polyion is partially stretched,  $H \sim N$ , due to intramolecular Coulomb repulsion of charged monomers while counterions are spread in all the available volume of the solution (in the case of the cylindrical brush) or localized in an extended region above the surface (in the case of a planar brush) within a characteristic Gouy-Chapman length. This length is inversely proportional to the density of immobilized charge per unit area and exceeds by far the dimension of grafted polyions. The orientation of polyions is random if they are grafted far apart from each other. However as the distance between grafted points decreases the intermolecular interactions come into play causing orientation of grafted polyions in the direction perpendicular to the grafting surface (see [6] for details).

As has been shown in [6, 13], in pronounced contrast to neutral polymer brushes there is no cross-over between “charged mushroom” and dense “osmotic brush” regime. Instead of this, an additional intermediate regime appears where the stretching of polyions is determined primarily by intramolecular Coulomb interactions while the surface density of immobilized charge is still too small to retain counterions inside the brush. Thus, the brush is nearly barely charged here. The corresponding range of grafting densities increases with a decrease in the degree of ionization of grafted chains. Moreover, this range increases in the row planar brush — cylindrical brush — spherical brush. In the case of a spherical brush, the ranges of the “charged” brush and the “osmotic” brush regimes become comparable [13]. Thus, for spherical polyelectrolyte brushes which mimic, in particular, polymer stars and star-like micelles in aqueous solutions, the investigation of the “charged” brush regime becomes of particular importance.

In our recent paper [13] we examined the equilibrium structure of non-planar (spherical and cylindrical) polyelectrolyte brushes focusing at the effect of brush curvature and the effect of charge annealing. This investigation was, however, carried out in the frames of the LEA and, thus, covered the range of relatively dense grafting and highly charged chains. On the

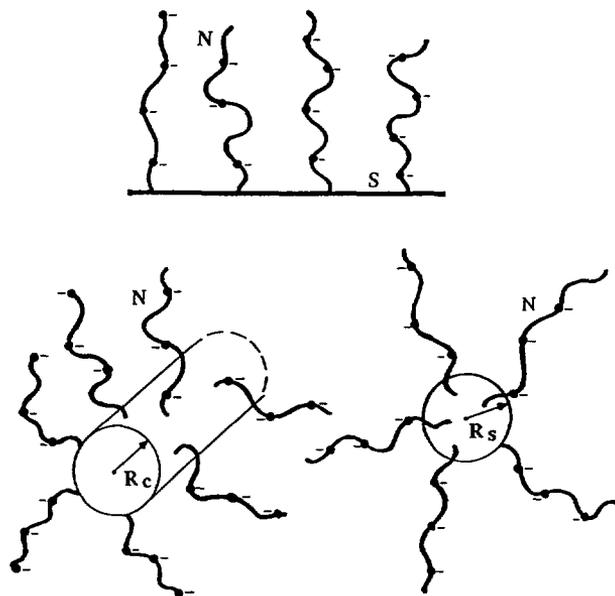


Fig. 1. — Polyelectrolyte brushes: planar (high), cylindrical (bottom left), spherical (bottom right).

other hand, in many realistic systems the grafting density is not too high and the chains are charged rather weakly. Typical example is a very dilute solution of polyelectrolyte stars with few relatively short branches. In this case, the star cannot retain its counterions and LEA is not applicable anymore.

The aim of the present paper is to examine the equilibrium structure of weakly charged (non-osmotic) polyelectrolyte brushes of different morphologies. In order to do this we have to go beyond LEA and to treat explicitly the Coulomb interactions inside the brush.

## 2. Model

We consider polyelectrolyte brushes formed by long weakly charged polyelectrolyte chains grafted at one end onto an impermeable planar or cylindrical or spherical surface and immersed in a salt-free solution, Figure 1. The curvature radius  $r_s$  of the sphere or of the cylinder is supposed to be small compared to the brush thickness  $H$ .

Let  $N$  be the degree of polymerization of grafted chains and  $\alpha$  be the fraction of elementary charged monomer. We assume  $\alpha$  to be small (we specify this condition below) and fixed,  $\alpha = \text{const}$  (quenched polyelectrolyte). The total charge of one polyion is  $Q = eN\alpha$ .

It is convenient to introduce the “effective dimensionality”  $d$  of the grafted chains in the brush;  $d$  is equal to 1, 2 and 3 for planar, cylindrical and spherical brushes, respectively. The density of grafting  $\sigma_d$  is characterized by the number of grafted chains per surface area  $\sigma_1 = 1/s$ , per unit length  $\sigma_2 = 1/2\pi h$  or per unit angle  $\sigma_3 = f/4\pi$ . The corresponding immobilized charge density is  $q_d = Q\sigma_d$ .

We assume that the Bjerrum length  $l_B = e^2/kT\epsilon$  is of the order of a monomer unit length  $a$  ( $\epsilon$  is a dielectric constant of the solvent). The solution contains mobile counterions compensating the brush charge and ensuring total electroneutrality of the system.

As has been shown in [1, 4, 13], the Coulomb attraction cannot retain counterions inside the brush when the density of grafting  $\sigma_d$  or the degree of ionization of grafted chains  $\alpha$  or both of them are small.

In the planar brush this is the case at  $s \gg N^2 \alpha^{3/2} a l_B$ . The latter condition implies that the Guoy-Chapman length  $\lambda \cong es/ql_B$  which can be interpreted as the thickness of the counterions cloud above the surface exceeds by far the thickness of the brush. On the other hand, the density of grafting must be sufficiently large to ensure predominance of intermolecular Coulomb interaction over intramolecular ones that is the case at  $s \ll N^2 \alpha^{4/3} a^2 (l_B/a)^{2/3}$  [6].

In the cylindrical case the "counterion condensation" threshold can be estimated from the condition  $Q/h \cong e/l_B$  so that weakly charged brush regime is determined by the condition  $\alpha N l_B \ll h \ll N a \alpha^{2/3} (l_B/a)^{1/3}$  [13].

For spherical polyelectrolyte brush of small curvature radius,  $r_s \ll H$ , the intermolecular Coulomb repulsion predominates over intramolecular one at any  $f \geq 1$  while the counterions remain essentially free if  $fQ \ll eH/l_B$ , *i.e.* at  $f \ll \alpha^{-1/2} a l_B^{-1}$  [13, 15, 16].

Hence, the width of the weakly charged brush regime increases as the fraction of charged monomers decreases and as the morphology is changed from planar to cylindrical and then to spherical brush.

We remark that in spite of comparative weakness of Coulomb interaction in the range of grafting densities specified above, their effect on the brush structure is stronger than the effect of excluded volume interactions between uncharged monomers [13] provided the solvent is not too poor for uncharged monomers. Hereby we neglect the contribution of the excluded volume interactions to the free energy of the brush.

As most of counterions leave the brush, we can use a simplified "capacitor" model [6] according to which the charges of one sign (immobilized charges) are localized in the range of  $r_s < r < H$ . where  $r_s$  is the radial co-ordinate of the grafting surface ( $r_s = 0$  in the planar case while  $r_s$  is equal to the curvature radius in other cases) while the opposite charges (counterions) spread infinitely far above the edge of the brush, *i.e.* in the range  $r > H$ .

In the framework of this capacitor model the conformational-dependent part of the free energy of the system "brush + counterions" can be presented as a functional of normalized density,  $g(r)$ , of the free chain ends and of the local chain stretching  $E(r, r') = dr/dn$ . This functional includes two principal terms: the elastic free energy of the chain stretching

$$\frac{F_{\text{elastic}}\{g(r), E(r, r')\}}{kT} = \frac{3}{2a^2} \int_{r_s}^H g(r') dr' \int_{r_s}^{r'} E(r, r') dr \quad (1)$$

and the free energy of Coulomb interaction

$$\frac{F_{\text{Coulomb}}}{kT} = \frac{\epsilon}{8\pi kT} \int_V (\nabla\psi)^2 dv.$$

Using the Poisson equation  $\Delta\psi = -4\pi e\alpha\phi(r)/\epsilon$  for the electrostatic potential  $\psi$  inside the brush we can present this interaction term as a functional of the monomer density  $\phi(r)$ :

$$\frac{F_{\text{Coulomb}}\{\phi(r)\}}{kT} = \frac{3}{2a^2} \kappa \sigma_d^{-1} \int_{r_s}^H r^{1-d} dr \left( \int_{r_s}^r r'^{d-1} \phi(r') dr' \right)^2 + \frac{3}{2a^2} \sigma_d \kappa \mathcal{F}_d(H) \quad (2)$$

where  $\kappa = (4/3)\pi l_B \alpha^2 a^2$  and function  $\mathcal{F}_d(H)$  is defined as  $\mathcal{F}_1(H) = -N^2 H$ ,  $\mathcal{F}_2(H) = N^2 \ln(1/H)$  and  $\mathcal{F}_3(H) = N^2/H$  for planar, cylindrical and spherical brushes, respectively. The monomer density profile  $\phi(r)$  is related to the normalized density of the free ends,  $g(r)$ , and

local chain stretching,  $E(r, r')$ , via conventional equation

$$\phi(r) = \sigma_d r^{1-d} \int_r^H \frac{g(r') dr'}{E(r, r')}. \tag{3}$$

In the case of a planar brush,  $d = 1$ , equation (2) presents the zero-order term of the expansion of the Coulomb free energy in powers of the small parameter  $H/\lambda$ . The subsequent terms describe the contribution of mobile counterions partially penetrating the brush. These terms can be obtained from the self-consistent solution of the Poisson-Boltzmann equation inside and outside the brush [17]. Hereby we restrict our consideration to the limit of  $H/\lambda \ll 1$  when only a negligibly small fraction of counterions is retained inside the brush so that we can neglect their effect on the brush structure.

### 3. Equal Stretching Approximation

As the problem of minimization of the free energy functional defined by equations (1–3) can not be solved in general case analytically, we need some reasonable approximation. As has been shown in [18], the internal structure of curved noncharged polymer brushes can be well-described on the basis of the “equal stretching” approximation (ESA). According to this approximation, all the chains in the brush are assumed to be stretched similarly (although inhomogeneously in nonplanar geometries), *i.e.* all the free ends of the chains are assumed to be localized at the outer edge of the brush,  $g(r) = \delta(r - H)$ . For a planar brush this approximation is also known as the Alexander-de Gennes model [19,20]. Though “equal stretching” approximation underestimates the fluctuations of the free ends of the grafted chains, it provides correct scaling asymptotics for average brush characteristics and even gives reasonable description for the polymeric profiles within the internal parts of the neutral brushes [18]. For charged brushes which are stretched more than neutral ones, the fluctuations of the free ends are expected to become even less important than for neutral systems. Thus, one can use ESA as a reasonable approach to consider the charged brushes at least at initial stage.

In the frame of ESA the elastic contribution to the free energy can be expressed as a functional of local monomer density

$$\frac{F_{\text{elastic}}\{\phi(r)\}}{kT} = \frac{3}{2a^2} \sigma_d \int_{r_s}^H \frac{r^{1-d} dr}{\phi(r)} \tag{4}$$

Let us introduce the “trajectory”  $r(n)$ , specifying the position  $r$  of the  $n$ -th monomer above the surface as

$$n(r) = \sigma_d^{-1} \int_{r_s}^r \phi(r') r'^{d-1} dr' \tag{5}$$

where  $n(r_s) = 0$  (the ends are grafted onto the surface) and  $n(H) = N$  (the free ends are fixed at the outer edge of the brush). In terms of “trajectory”  $r(n)$ , the free energy functional for the brush with fixed free ends transforms into

$$\frac{F}{kT} = \frac{3}{2a^2} \int_0^N \left[ \left( \frac{dr}{dn} \right)^2 + \kappa \sigma_d r^{1-d}(n) \left( \frac{dr}{dn} \right) n^2 \right] dn + \frac{3}{2a^2} \kappa \sigma_d \mathcal{F}_d(H). \tag{6}$$

Introducing the rescaled variables

$$x = \frac{n}{N}; \quad y = \frac{r}{(\kappa \sigma_d N^3)^{1/d}}; \quad \Phi_d = \frac{2a^2 N}{3(\kappa \sigma_d N^3)^{2/d}} \frac{F}{kT} \tag{7}$$

we represent equation (6) in the following form

$$\Phi_d = \text{const} + \int_0^1 \left[ \left( \frac{dy}{dx} \right)^2 + \frac{x^2}{y^{d-1}} \left( \frac{dy}{dx} \right) \right] dx + \mathcal{G}_d \quad (8)$$

where  $\mathcal{G}_1 = -y(1)$ ,  $\mathcal{G}_2 = -\log y(1)$ ,  $\mathcal{G}_3 = 1/y(1)$  and  $y(1) = H/(\kappa\sigma_d N^3)^{1/d}$ . Variation of  $\Phi_d$  provides the rescaled trajectory  $y(x)$  described by the differential equation

$$y^{d-1} \frac{d^2 y}{dx^2} + x = 0 \quad (9)$$

with the two boundary conditions,  $y(0) = r_s/(\kappa\sigma_d N^3)^{1/d}$  and  $y(1) = H/(\kappa\sigma_d N^3)^{1/d}$

As follows from the structure of  $\Phi_d$  and equation (9), the minimum of the functional  $\Phi_d$  is attained at some certain value of  $y(1)$ . Thus, the equilibrium thickness  $H_0$  of a free, undeformed brush should scale as

$$H_0 \simeq (\kappa\sigma_d N^3)^{1/d} \quad (10)$$

This result is consistent with earlier scaling predictions [1, 6, 13]. The numerical coefficient in the dependence (10) depends on the model and geometry of the brush. For brushes with fixed free ends, analytical solution of equation (9) is available only in the planar case,  $d = 1$ . Here we have  $r_s = 0$  and

$$y(x) = -\frac{x^3}{6} + x \left[ \frac{1}{6} + y(1) \right]. \quad (11)$$

Returning to the  $r, n$  variables, one has

$$r(n) = -\frac{\kappa n^3}{6s} + n \left( \frac{H}{N} + \frac{\kappa N^2}{6s} \right) \quad (12)$$

and the corresponding profile of monomer units,

$$\phi(n(r)) = \left( \frac{sH}{N} + \frac{\kappa N^2}{6} \right) - \frac{\kappa n(r)^2}{2} \quad (13)$$

Applying the condition  $(dr/dn)|_{H_0} = 0$  we obtain the equilibrium brush thickness

$$H_0 = \frac{\kappa N^3}{3s} = \frac{4\pi}{9} N^3 \alpha^2 l_B a^2 s^{-1}, \quad d = 1 \quad (14)$$

and the corresponding chain trajectory

$$r(n) = -\frac{\kappa}{6s} n^3 + \frac{\kappa N^2}{2s} n \quad (15)$$

resulting in the equilibrium monomer density profile

$$\phi(r) = 2\kappa^{-1} (N^2 - n^2(r))^{-1} \quad (16)$$

As follows from equations (13) and (16), the monomer density is an increasing function of the distance  $r$  from the grafting surface. If the brush is free to acquire the equilibrium thickness  $H_0$ , then the density diverges at the edge of the brush, *i.e.* at  $r = H_0$ , that is related to the zero tension at the free chain ends and their imposed localization at the edge of the brush. In the case  $H > H_0$  corresponding to the situation when the chains in the brush are stretched

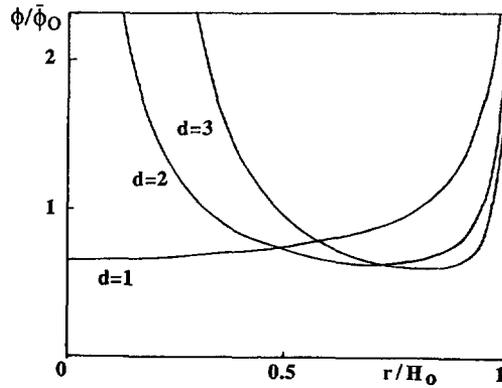


Fig. 2. — Profiles of polymer units  $\phi/\bar{\phi}_0$  in the undeformed brushes as function of the reduced distance  $t = r/H_0$  from the grafting surface.

additionally by applied external force the density remains finite at  $r = H$  because now the tension does not vanish at the ends of the chains.

For cylindrical and spherical brushes,  $d = 2$  and  $3$ , only numerical solutions of equation (9) are available. Numerical minimization of the free energy functional  $\Phi_d$  gives  $H_0/a(\kappa\sigma_2)^{1/2}N^{3/2} \approx 0.628$  for a cylindrical brush ( $d = 2$ ) and  $H_0/a(\kappa\sigma_3)^{1/3}N \approx 0.779$  for a spherical brush ( $d = 3$ ).

Figure 2 demonstrates the profiles of polymer units  $\phi/\bar{\phi}_0$  as functions of the reduced distance  $t = r/H_0$  calculated according to equations (5), (7) and (9). Here  $\bar{\phi}_0 = (d\sigma_d N a^3)/H_0^d$  is the average concentration of polymer units and the profiles are normalized as

$$d \int_0^1 \frac{\phi(t)}{\bar{\phi}_0} t^{d-1} dt = 1. \quad (17)$$

As seen from Figure 2, in the internal region of the brush the monomer concentration decreases with  $r$  in the cases of cylindrical and spherical brushes or weakly increases in the case of a planar brush. Figure 3 shows the density profiles for cylindrical and spherical brushes in log-log co-ordinates. We find that the decay rate of the profiles corresponds approximately to  $1/r$  and  $1/r^2$  laws, respectively.

All the equilibrium density profiles in undeformed brushes presented at Figures 2 and 3 demonstrate the divergence near the upper boundary of the brush, *i.e.* at  $r = H_0$ . As we discuss below, this is related to the imposed fixation of all chain ends at the edge of the brush.

If the brush is stretched with respect to its equilibrium height, *i.e.* if  $H > H_0$ , the monomer density remains finite at  $r = H$  and decreases with increase in  $H$ . This situation takes place if any additional stretching force is applied to the free ends of grafted chains.

#### 4. Fluctuating Free Ends: Exact Solution

We now take off the ESA, *i.e.* we assume that free ends of the chains are distributed throughout the layer so that the elastic and the Coulomb contributions to the free energy are described by equations (1) and (2), respectively.

Since the interaction energy described by equation (2), is presented as a functional of the monomer density only, we can apply the same procedure of minimization of the full free energy functional as we used before (see for example [21, 22]) for neutral polymer brushes.

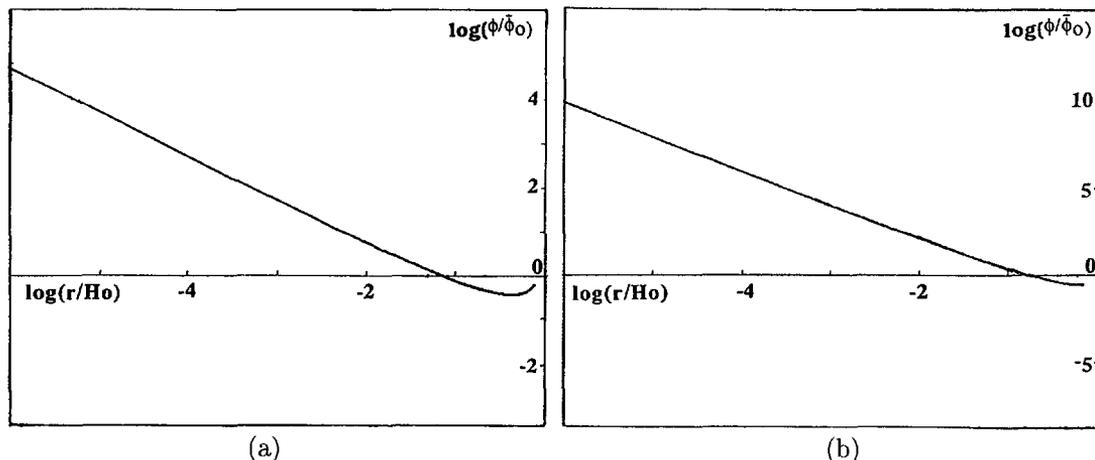


Fig. 3. — Profiles of polymer units for cylindrical (a) and spherical (b) brushes from Figure 2 plotted in log-log coordinates.

The variation of the total free energy with respect to the average local chain stretching  $E(r, r')$  with the account of the condition of vanishing stretching at the free end,  $E(r', r') = 0$ , results in the universal dependence

$$E(r, r') = (\pi/2N)(r'^2 - r^2)^{1/2}$$

and in the following implicit equation for the monomer density profile:

$$\frac{\delta}{\delta\phi(r)} F_{\text{Coulomb}}\{\phi(r)\} = \Lambda - \frac{3kT\pi^2 s}{8N^2 a^2} r^2 \quad (18)$$

where the Lagrange multiplier  $\Lambda$  is to be determined using conservation condition. Substituting equation (2) into equation (18), we obtain

$$\int_r^H r'^{1-d} dr' \int_0^{r'} \phi(r'') r''^{d-1} dr'' = \Lambda' - \frac{\pi^2}{8N^2 \kappa} r^2. \quad (19)$$

Since parabolic potential is known to provide the dead zones (regions without the free ends) in non-planar geometries [23], we restrict ourselves here only to the planar case  $d = 1$ .

As follows from equation (19) at  $d = 1$ , a weakly charged polyelectrolyte brush is characterized by the step-wise density profile

$$\phi = \frac{3\pi}{16} (N^2 \alpha^2 l_B a^2)^{-1}, \quad r \leq H. \quad (20)$$

This result is in pronounced contrast to previously obtained Gaussian density profile in strongly charged, “osmotic” polyelectrolyte brushes. Since the “osmotic” and the “charged” brushes correspond to two opposite limits of the counterions screening (the system is electroneutral in the “osmotic brush” limit and is barely charged in the “charged brush” limit), one expects that in the intermediate case of partial screening, the polymeric profile will incorporate the features of both, step-wise and Gaussian profiles. We shall focus at this case in our forthcoming publication [17].

It should be noted that constant density inside the charged brush does not mean that all the chain ends reach the edge of the brush. Inverting equation (3) as integral equation for  $g(r)$ , we obtain the normalized density of the free ends

$$g(r) = \frac{r}{H_0^2} \left( 1 - \frac{r^2}{H_0^2} \right)^{-1/2} \quad (21)$$

which increases monotonically with  $r$  increasing.

The equilibrium height of the brush is equal  $H_0 = (16/3\pi)N^3s^{-1}\alpha^2l_Ba^2$  that coincides with the accuracy of the numerical prefactor with the value obtained above in the frames of ESA.

Comparing numerical prefactors in the expressions for the equilibrium brush thickness  $H_0$  obtained under the constraint of ESA and in the case when the ends are really free to fluctuate, we find that the brush thickness is larger in the latter case. The similar relationship has been found for the thickness of neutral brushes in Alexander-de Gennes [19, 20] and SCF-models [21, 22], respectively.

## 5. Discussion

The main common feature of all the density profiles obtained under the constraint of equal chain stretching and presented at Figures 2 and 3, is an increase (divergence) of density at the edge of a free (non-stretched) brush,  $H = H_0$ . This divergence is, of course, a straightforward consequence of the approximation  $g(r) = \delta(H - r)$ . Really, the force applied to the ends of the chains in the free brush is zero and, consequently, the local stretching  $E(H, H)$  at the ends is equal to zero as well. However, if all the ends reach the edge of the layer, the monomer concentration at  $r = H$  must diverge as  $\sim 1/E(H, H)$ . Physically, this means that real equilibrium corresponds to a non-delta-functional distribution of the free chain ends: due to the fluctuations in the stretching of particular chains in the brush only a negligibly small fraction of chain ends reach the edge of the brush ensuring monotonous behavior of the concentration profile.

It follows from equation (21) that if the ends of the chains are not localized at the brush edge (at  $r = H$ ), but are free to fluctuate, they are found to be distributed all over the brush thickness,  $0 < r < H$ , although the maximum of the distribution (divergence in  $g(r)$ ) is still near the edge of the brush. However, as the fraction of the free ends localized at  $r = H$  is zero, the density profile remains finite and does not demonstrate any growth near the edge of the brush.

As follows from equation (16), in frames of ESA the profile of polymer units near the grafting surface is given by a constant value,  $\phi(r) \simeq 1/\kappa N^2$ . This is in accordance with the exact result given by equation (20). Thus, in the planar case one finds the consistency between the approximate consideration based on the ESA and the exact solution: the profile of polymer units  $\phi(r)$  scales as  $r^0$  in the internal part of a planar charged brush. One can expect the similar tendency in the curved brushes: a decay in  $\phi(r)$  in the internal parts of cylindrical and spherical brushes as shown in Figure 3.

Let us also mention, that constant monomer density in a planar weakly charged polyelectrolyte brush corresponds to a parabolic profile of the electrostatic potential  $\psi(r)$  which coincides (in the absence of excluded volume interactions and with the accuracy of the factor  $\alpha$ ) with a chemical potential of a monomer. This makes the result  $\phi(r) = \text{const}$  obtained in the frame of SCF approach more transparent.

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