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Polyelectrolyte brushes are formed by charged macromolecules tethered by the end segment to a solid-liquid interface. At low ionic strength of the solution, the intermolecular electrostatic interactions lead to strong stretching of the macromolecules that may, as a result, approach the limit of their extensibility (the contour length). Here, we present an analytical theory of polyelectrolyte brushes developed within the Poisson-Boltzmann approximation which explicitly accounts for finite extensibility of the brush-forming chains. In contrast to earlier theories based on the approximation of Gaussian elasticity of the brush-forming chains, the current approach enables avoiding artificial result of stretching of the chains beyond the contour length at high degrees of ionization or/and large grafting densities. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4984101]

I. INTRODUCTION

Polyelectrolyte brushes formed by long charged macromolecules anchored at the solid-liquid interface were actively investigated both experimentally[1–10] (see also reviews[11–14] for additional references) and theoretically[15–32] over past two decades due to their outstanding performance in providing the stability of colloidal dispersions[19,33–35] and improving the boundary lubrication between sliding surfaces.[36–41] Basic theoretical understanding of structure-property relations for polyelectrolyte brushes was achieved relatively early on the basis of simple scaling-type theoretical approach[19–23] that has motivated subsequent experimental developments in the field.

It was also demonstrated that an analytical self-consistent field (SCF) theory proposed earlier for non-ionic polymer brushes[42–45] allows for the extension of the Poisson-Boltzmann framework for a charged surface in contact with the electrolyte solution to a surface at which the charges are immobilized on tethered flexible macroions.[26–28] The theories were based on the strong stretching (SS) approximation according to which the tethered macroions are noticeably extended with respect to the unperturbed size and exhibited linear (Gaussian) elasticity. The SS approximation gives rise to a parabolic shape of the molecular potential acting at monomers of the tethered chains and ensures a unified description of the neutral and charged polymer brushes. The theories based on the parabolic molecular potential provided a detailed description of the structure and properties of polyelectrolyte-modified interfaces including interaction forces acting between such surfaces and polyelectrolyte-decorated particles.[26,28–30,32] The analytical SCF approach[26,28,29] confirmed the values of exponents that followed from the scaling models for various regimes of the polyelectrolyte brush behavior and demonstrated additional features beyond the scaling predictions. In particular, the analytical theory predicted a logarithmic increase in the brush thickness upon an increase in the polyion grafting density in the osmotic regime, a feature which is not captured by a simple scaling model. The analytical theory also predicted a jump in the polymer density profile at the polyelectrolyte brush boundary.[26,28,29] The latter is smoothed by the thermal fluctuations that give rise to a non-classical tail composed of terminal segments of the polyions. In contrast to neutral polymers, the segments of polyions in the tail zone are stretched by the electric field created by escaped counterions. As a result, the width of the fluctuation-induced tail is larger and obeys a different scaling law compared to a similar tail in neutral brushes.[29,31]

An approximation of the Gaussian (linear) elasticity for the brush-forming chains is justified as long as the chain end-to-end distance remains considerably below its contour length. At elongations approaching the chain counter length, the SS-SCF model underestimates the restoring entropic force and thereby overestimates the extension of chains in the brush. Due to the long-range nature of electrostatic interactions in polyelectrolyte brushes (particularly, at low ionic strength of the solution), the highly charged brush-forming chains could get extended almost up to the contour length at moderate grafting densities. In this case, a theory based on the Gaussian elasticity approximation overestimates the thickness of the polyelectrolyte brush. Moreover, it might lead to unphysical results, i.e., "overstretching" of the brush-forming chains beyond their contour length.

The attempts to account for finite extensibility of the tethered polyions were taken in numerous theoretical studies. The numerical SCF methods to study polymer brushes (e.g., Scheutjens-Fleer lattice[17,35] and off-lattice[29,46] models) account for finite extensibility of polyions automatically.

In the analytical studies, finite extensibility of polyions was first introduced in Ref. 47 following the pioneering publications[15,16] on the planar polyelectrolyte brushes. The former was based on an empirical modification[48] of the molecular potential, which was revised in the subsequent studies.[49] Explicit analytical expressions for the molecular potential have been formulated for a number of lattice models in which the chain segments were restricted to lattice sites. However, an introduction of finite chain extensibility was often accompanied by a simplified formulation of the electrostatic contribution to the brush free energy. For example, the condition of local electroneutrality imposed in Ref. 50 leads to the polymer density profile with no peripheral double layer and the power law dependence for the width of fluctuation-induced tail similar to that for neutral brushes. While steplike polymer density turned out to be a reasonable approximation at strong brush compressions[28] and is practical in the rationalization of the experimental data,[28,51] it oversimplifies the structure of isolated or weakly compressed polyelectrolyte brushes. A cylindrical cell model introduced in Ref. 52 for strongly stretched polyions accounted for the lateral variation in counterion density but ignored its decay in the normal direction and assumed the entrapment of all counterions inside the brush.

To the best of our knowledge, up to now there is no analytical theory which uses the Poisson-Boltzmann framework to describe a planar polyelectrolyte brush with finite extensibility of the tethered polyions without *a priori* assumptions on the polymer/ion distributions. Here we present a theory which combines an explicit formulation of the molecular potential in a strongly stretched polyelectrolyte brush on a body-centered-cubic (bcc) lattice with the Poisson-Boltzmann framework used by us previously.[26,27,31] This model enables avoiding the artificial result concerning chain overstretching at high degrees of ionization or/and large grafting densities. Furthermore it allows for an analytical description of the structural rearrangements in the brush that occur upon approaching by the brush chains the limit of their extensibility.

II. GENERAL FORMALISM AND RESULTS

To study the brushes of ionic macromolecules (polyelectrolytes), we use the analytical self-consistent field (SCF) approach combined with the *non-linear* Poisson-Boltzmann framework to account for the electrostatic interactions between charged species. These interactions are described in terms of the self-consistent electrostatic potential $\Psi(x)$ originating due to the charged monomer units and thermally equilibrated mobile ions.

Consider the brush formed by long flexible chain macromolecules with quenched (positive) fractional charge α per monomer unit tethered by the end segment to the impermeable planar surface. The number of monomer units in a chain is $N \gg 1$, and the length of a monomer unit (which coincides with the statistical segment length) is a. Hence, the contour length of the chain is $L = Na$. The grafting density $\sigma = a^2/s$, where s is the surface area per chain, is large enough to ensure the predominance of the intermolecular interactions over the intramolecular ones. The brush is immersed in a solution of monovalent salt with the bulk concentrations $c_+ = c_- = c_s$ of coions and counterions, respectively.

The molecular potential $U(x)$ acting at the monomer units in the brush (and equal to their exchange chemical potential) is dominated by intermolecular ionic interactions and coincides with the electrostatic energy $\alpha e\Psi_{in}$ per monomer. That is,

$$\frac{U(x)}{k_BT} \approx \frac{\alpha e\Psi_{in}(x)}{k_BT} = \alpha\psi_{in}(x), \tag{1}$$

where $\psi_{in}(x) = e\Psi_{in}(x)/k_BT$ is the (dimensionless) electrostatic energy of elementary charge e at distance x from the surface measured in k_BT units.

The employed mean-field approximation accounts only for gradients in the electrostatic potential and local densities (of charged monomer units and mobile ions) in the direction perpendicular to the grafting surface (i.e., along the x coordinate). In the linear elasticity regime, the transverse dimensions of the polyion are fairly unaffected by their stretching along the x direction. However, the transverse dimensions are substantially reduced when the polyions approach the limit of extensibility, $H \to L$. The excluded volume interactions between monomer units can be neglected as long as the steric repulsion between monomers is compensated by the short-ranged attraction, that is, the solvent is close to the θ-solvent for the uncharged monomer units. Indeed, many synthetic polyelectrolytes are soluble in water only due to the presence of charges, whereas the uncharged backbone is only marginally or even poorly soluble in water.

When the chains in the polyelectrolyte brush are strongly extended due to the Coulomb repulsions, the intra-chain short-range interactions do not affect the conformational elasticity. Within the linear elasticity regime, the criterion is that the elastic blob is smaller than the thermal blob. When the chains approach the limit of extensibility, the intra-chain short-range interactions can be safely neglected. The short-range ternary repulsive inter-chain interactions become non-negligible and contribute to the swelling of the brush at high grafting densities,[23] when the brush is found in the so-called quasi-neutral regime. The boundary of the quasi-neutral regime (for the salt-free brush) can be evaluated by comparing the osmotic pressure $\Pi_{ion}/k_BT \cong \alpha N/sH$ of the counterions entrapped inside the brush and the contribution to the osmotic pressure from ternary repulsions $\Pi_{conc}/k_BT \cong a^6(N/sH)^3$, where H is the brush thickness. In the linear elasticity regime $H \sim \alpha^{1/2}L$, non-linear elasticity comes into play at $H \to L$. Therefore, ternary interactions can be safely neglected at grafting densities $(a^2/s) \le \alpha$. Below we assume that this condition is fulfilled.

Within the strong stretching self-consistent field approximation, the molecular potential in the brush is specified as

$$\frac{U(z)}{k_BT} = \frac{3\pi^2}{8L^2}(H^2 - x^2), \tag{2}$$

where H is the overall brush thickness. Equation (2) is valid provided that the stretched chains exhibit the Gaussian (linear) conformational elasticity at any length scale.[42] This approximation applies if the extension of any chain segment is larger

than its Gaussian (ideal) size, but much smaller than the segment contour length.

A quadratic shape of the molecular field $U(x)$ in the brush is modified at strong chain extensions (i.e., when the end-to-end distance approaches the chain contour length). According to the findings in Refs. 49 and 50, the molecular potential in the brush of linear chains with finite extensibility can be conveniently approximated as

$$\frac{U(x)}{k_BT} = 3\ln\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}. \tag{3}$$

This particular functional form of the self-consistent potential applies for a brush of flexible chains placed onto the body-centered-cubic (bcc) lattice. The discrete model allows one to obtain a simple analytical relation between local stretching and elastic tension acting in the chain with the account of finite chain extensibility and derive an explicit analytical expression [Eq. (3)] for the self-consistent potential. To the best of our knowledge, no other model accounting for finite chain extensibility provides an analytical expression for the self-consistent potential. When $x, H \ll L$, Eq. (3) reduces to the quadratic potential given by Eq. (2), whereas at strong extensions $x \simeq L$, the molecular potential in Eq. (3) ensures finite extensibility of the polyions.

The local stretching of a chain at height x with its end-point position x',

$$E(x', x) = \frac{dx}{dn},$$

is given by

$$E(x', x) = a\sqrt{1 - \frac{\cos^2(\pi x'/2L)}{\cos^2(\pi x/2L)}}. \tag{4}$$

Expansion of Eq. (4) with respect to the small parameter x'/L, $x/L \ll 1$ leads to the classical expression for the local chain stretching valid in the linear elasticity regime,[42]

$$E(x', x) = \frac{\pi a}{2L}\sqrt{x'^2 - x^2}, \tag{5}$$

whereas for highly extended chains with $x'/L \to 1$, one finds $E(L, x) \to a$.

By using Eq. (2), one specifies the dimensionless electrostatic potential in the polyelectrolyte brush in the linear elasticity regime as

$$\psi_{in}(x) = \frac{U(x)}{\alpha k_BT} = \frac{H^2 - x^2}{H_0^2}, \tag{6}$$

where

$$H_0 = \sqrt{\frac{8}{3\pi^2}}\alpha^{1/2}L$$

is the characteristic electrostatic length.

For polyions with finite extensibility, Eq. (3) specifies the dimensionless electrostatic potential as

$$\psi_{in}(x) = \frac{U(x)}{\alpha k_BT} = \frac{3}{\alpha}\ln\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}. \tag{7}$$

We remarked that the calibration of the self-consistent electrostatic potential in Eqs. (6) and (7) corresponds to its vanishing at the edge of the brush, $x = H$.

As soon as the distribution of electrostatic potential is specified, the density of net (positive) charge density $\rho(x)$ in the brush is determined from the Poisson equation

$$\frac{d^2\psi(x)}{d^2x} = -4\pi l_B\rho(x)$$

to give

$$\rho(x) = \frac{3\pi}{16a^2l_B\alpha N^2}\sec^2\left(\frac{\pi x}{2L}\right). \tag{8}$$

Remarkably, Eq. (8) predicts an increase in the local charge density in the brush as a function of the distance x from the grafting surface, whereas in the linear elasticity regime ($x, H \ll L$), the local charge density is virtually constant and equal to $\rho = 3\pi/16a^2l_B\alpha N^2$.

The total residual (uncompensated) charge per unit area of the brush is

$$\widetilde{Q} = \int_0^H \rho(x)dx = \frac{3}{8\alpha l_BL}\tan(\pi H/2L) = \frac{3\pi aH}{16l_B\alpha L^2}\frac{\tan(\pi H/2L)}{(\pi H/2L)}. \tag{9}$$

Then, the Gouy-Chapman length $\widetilde{\Lambda} = 1/(2\pi l_B\widetilde{Q})$ associated with the ion distribution outside the brush is specified by

$$\widetilde{\Lambda} = \frac{4}{3\pi}\frac{\alpha L}{\tan(\pi H/2L)} = \frac{H_0^2}{H}\frac{(\pi H/2L)}{\tan(\pi H/2L)}. \tag{10}$$

Expansion of Eq. (10) with respect to the small parameter $H/L \ll 1$ leads to the expression $\widetilde{\Lambda} = H_0^2/H$ formulated earlier[26] for the brushes of moderately stretched polyelectrolytes.

It is instructive to compare the predictions of the theory concerning the value of the residual charge in the brush obtained within the linear elasticity approximation and with the account of finite chain extensibility. As follows from Eq. (9),

$$\frac{\tilde{Q}_{linear}}{\tilde{Q}_{nonlinear}} = \frac{\pi H_{linear}}{2L}\cot\left(\frac{\pi H_{nonlinear}}{2L}\right) \approx \frac{H_{linear}}{H_{nonlinear}} > 1.$$

Hence, finite extensibility of the polyions leads to the smaller value of residual charge $\tilde{Q}$, i.e., a larger fraction of counterions localized in the brush.

A. General case: Salt-added solution

The distributions of mobile coions and counterions inside the brush [with respective concentrations $c_+(x)$ and $c_-(x)$] follow the Boltzmann law,

$$c_+(x) = c_+(H)\exp(-\psi(x)),$$

$$c_-(x) = c_-(H)\exp(\psi(x)),$$

with electrostatic potential $\psi(x)$ given by Eq. (7), and the concentrations of co- and counterions, $c_+(H)$ and $c_-(H)$, at the brush edge coinciding with the concentrations of ions of the corresponding sign at the uniformly charged planar surface with the surface charge density $\tilde{Q}$ (measured in the elementary charge units). This follows from the continuity of the

electrostatic potential at $x = H$. The concentrations $c_+(H)$ and $c_-(H)$ are given by (see, e.g., Ref. 27)

$$c_+(H) = c_s\left(\frac{\sqrt{(\kappa\tilde{\Lambda})^2+1}-1}{\kappa\tilde{\Lambda}}\right)^2,$$

$$c_-(H) = c_s\left(\frac{\sqrt{(\kappa\tilde{\Lambda})^2+1}+1}{\kappa\tilde{\Lambda}}\right)^2,$$

where

$$\kappa^2 = 8\pi l_B c_s$$

is the inverse square of the Debye screening length. Using Eqs. (8) and (10), and the condition

$$\rho(x) = \alpha c_p(x) + c_+(x) - c_-(x),$$

we find the expression for the polymer concentration profile in the brush,

$$\alpha c_p(x) = \frac{1}{2\pi l_B H_0^2}\left[\sec^2\left(\frac{\pi x}{2L}\right) + \left(\sqrt{\left(\frac{\kappa H_0}{2}\right)^2 + \left(\frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2} + \frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2\left(\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right)^{\frac{3}{\alpha}}\right.$$
$$\left. - \left(\sqrt{\left(\frac{\kappa H_0}{2}\right)^2 + \left(\frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2} - \frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2\left(\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right)^{-\frac{3}{\alpha}}\right]. \quad (11)$$

By integrating the density profile $\alpha c_p(x)$,

$$\int_0^H \alpha c_p(x)dx = \frac{\alpha N}{s}, \quad (12)$$

one arrives to a closed equation for the brush thickness H,

$$\zeta = \frac{2L}{\pi H_0}\left[\tan\frac{\pi H}{2L} + \left(\sqrt{\left(\frac{\kappa H_0}{2}\right)^2 + \left(\frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2} + \frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2\int_0^{\pi H/2L} dy\left(\frac{\cos(y)}{\cos(\pi H/2L)}\right)^{\frac{3}{\alpha}}\right.$$
$$\left. - \left(\sqrt{\left(\frac{\kappa H_0}{2}\right)^2 + \left(\frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2} - \frac{L}{\pi H_0}\tan\left(\frac{\pi H}{2L}\right)\right)^2\int_0^{\pi H/2L} dy\left(\frac{\cos(y)}{\cos(\pi H/2L)}\right)^{-\frac{3}{\alpha}}\right]. \quad (13)$$

Here, following Refs. 26 and 27, we have introduced the dimensionless parameter

$$\zeta = H_0/\Lambda,$$

which is proportional to the grafting density σ of polyions.

Obviously, at $x, H \ll L$, Eqs. (11) and (13) reduce to the corresponding equations obtained previously in Ref. 27 under the assumption of Gaussian elasticity of the brush-forming polyions.

B. Salt-free solution

Below we consider a polyelectrolyte brush immersed into a salt-free solution containing (monovalent) counterions only. In salt-free solution, the brush-forming polyelectrolyte chains are most strongly extended, and thus the finite extensibility effects are important.

The distribution of mobile counterions outside of the brush is similar to that from a uniformly charged surface with the surface number charge density $\widetilde{Q}$. That is, the concentration profile of mobile ions at distances $x \geq H$ yields

$$c_-(x) = \frac{1}{2\pi l_B(\widetilde{\Lambda} + H - x)^2}. \quad (14)$$

Because the electrostatic potential and the distribution of counterions are continuous at the brush edge ($x = H$), the concentration of ions,

$$c_-(H) = \frac{1}{2\pi l_B\widetilde{\Lambda}^2}, \quad (15)$$

specifies the distribution of counterions inside the brush (i.e., at distances $0 \leq x \leq H$) as

$$c_-(x) = c_-(H)\exp\psi(x) = \frac{1}{2\pi l_B\widetilde{\Lambda}^2}\left[\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right]^{\frac{3}{\alpha}}. \quad (16)$$

The concentration profile of (charged) monomer units in the brush can be found from the relation $\rho(x) = \alpha c_p(x) - c_-(x)$ with the account of Eqs. (8) and (16) and is given by

$$\alpha c_p(x) = \frac{3\pi}{16 l_B\alpha L^2}\sec^2\left(\frac{\pi x}{2L}\right) + \frac{1}{2\pi l_B\widetilde{\Lambda}^2}\left[\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right]^{\frac{3}{\alpha}}. \quad (17)$$

By integrating the density profile $\alpha c_p(x)$, we obtain the equation for the brush thickness H in the salt-free case,

$$\frac{\alpha L}{as} = \frac{3}{8 l_B\alpha L}\tan\left(\frac{\pi H}{2L}\right) + \frac{1}{2\pi l_B\widetilde{\Lambda}^2}\int_0^H\left[\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right]^{\frac{3}{\alpha}}dx. \quad (18)$$

At this point, we introduce the reduced brush thickness

$$h \equiv \frac{H}{H_0}$$

and the "charging" parameter

$$u = \pi H_0/2L = \sqrt{2\alpha/3}. \quad (19)$$

We remark that the condition $uh = \pi H/2L \leq \pi/2$ implies $H \leq L$.

Then, Eq. (18) for the brush thickness can be presented in two equivalent forms:

$$\zeta = u^{-1}\tan(\pi H/2L) + u^{-3}\tan^2(\pi H/2L) \times \int_0^{\pi H/2L}\left[\frac{\cos(y)}{\cos(\pi H/2L)}\right]^{\frac{2}{u^2}} dy \quad (20)$$

and

$$\zeta = h\left[\frac{\tan(uh)}{uh}\right] + h^2\left[\frac{\tan(uh)}{uh}\right]^2 \int_0^h \left[\frac{\cos(ut)}{\cos(uh)}\right]^{\frac{2}{u^2}} dt. \quad (21)$$

By introducing the renormalized grafting density parameter,

$$\tilde{\zeta} = \zeta u^{-3} = 6N^2 a l_B/s,$$

which is independent of the degree of chain ionization α, we present Eq. (20) in the form

$$\tilde{\zeta} = u^{-4}\tan(\pi H/2L) + u^{-6}\tan^2(\pi H/2L) \times \int_0^{\pi H/2L}\left[\frac{\cos(y)}{\cos(\pi H/2L)}\right]^{\frac{2}{u^2}} dy. \quad (22)$$

Equation (22) specifies the reduced brush thickness H/N as a function of the grafting density at fixed ionization parameter u, and vice versa. As follows from Eq. (22), $H \to L$ at $\tilde{\zeta} \to \infty$.

At moderate extension of polyions when $uh \ll 1$ and $\tan(uh) \approx uh$, Eq. (21) reduces to the previously obtained equation for thickness of the brush with the Gaussian elasticity,

$$\zeta = h + \frac{\sqrt{\pi}}{2}h^2 \exp h^2 \mathrm{erf}(h), \quad (23)$$

which can also be formulated as

$$\tilde{\zeta} = u^{-3}\left[(\pi H/2uL) + \frac{\sqrt{\pi}}{2}(\pi H/2uL)^2 \exp(\pi H/2uL)^2 \times \mathrm{erf}(\pi H/2uL)\right], \quad (24)$$

where

$$\mathrm{erf}(y) = \frac{2}{\sqrt{\pi}}\int_0^y \exp(-t^2)dt$$

is the error function.

In Fig. 1, we present the reduced brush thickness H/L as a function of $\tilde{\zeta}$ for various values of degree of ionization α calculated according to Eq. (22), which takes into account the finite extensibility of the polyions. For comparison, we present also the result obtained from Eq. (24) derived within the Gaussian elasticity approximation. Both equations give similar results at $H \ll aN$. However, as it follows from Fig. 1, the brush thickness obtained with the account of finite extensibility increases upon an increase in the grafting density or/and degree of ionization and asymptotically approaches the value of $H = L$. Notably, Eq. (24) based on the Gaussian elasticity approximation leads to an artificial result—overstretching of the brush-forming chains beyond the contour length. This is also illustrated by Fig. 2, where the thickness of the brush formed by the chains of $N = 100$ monomer units is plotted as a function of the degree of ionization for varied values of grafting density.

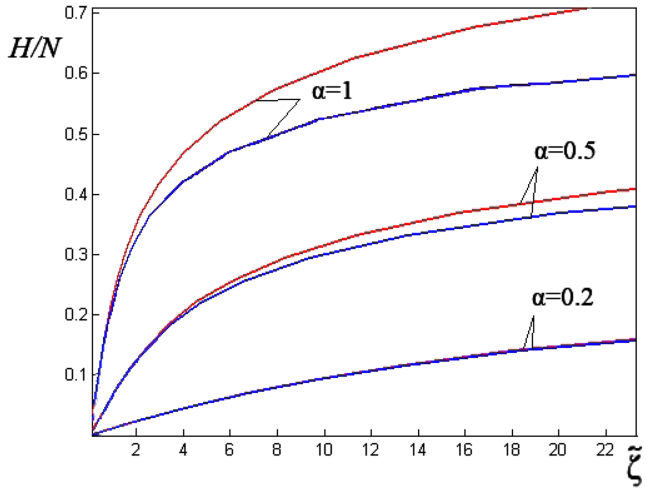

FIG. 1. Reduced thickness H/L of a polyelectrolyte brush as a function of the grafting density parameter $\tilde{\zeta}$ for different values of degree of ionization α (indicated at the curves) calculated within the Gaussian elasticity approximation (red curves) and with the account of finite extensibility (blue curves).

The polymer density profile can be presented as

$$\frac{\alpha c_p}{c_0} = \frac{sa}{(2\pi l_B)\,\alpha L H_0}\sec^2\left(\frac{\pi x}{2L}\right) + \frac{sa}{(2\pi l_B)\,\alpha L}\frac{H^2}{H_0^3} \times \left[\frac{\tan(\pi H/2L)}{\pi H/2L}\right]^2 \exp\left[\frac{2}{u^2}\ln\frac{\cos(\pi x/2L)}{\cos(\pi H/2L)}\right], \quad (25)$$

where the notation $c_0 = \alpha N/sH_0$ is used. By introducing reduced distance $t = x/H_0$, the polymer density profile can be presented as

$$\frac{\alpha c_p(t)}{c_0} = \zeta^{-1}\left[\sec^2(ut) + h^2\left(\frac{\tan(uh)}{uh}\right)^2 \times \exp\left(\frac{2}{u^2}\ln\frac{\cos(ut)}{\cos(uh)}\right)\right]. \quad (26)$$

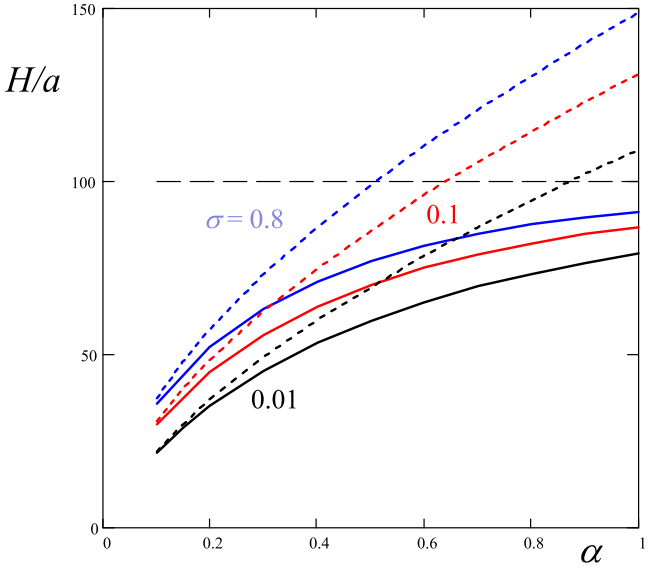

FIG. 2. The thickness H/a of a polyelectrolyte brush as a function of the degree of ionization α for different values of grafting density σ (indicated at the curves) calculated within the Gaussian elasticity approximation (dashed curves) and with the account of finite extensibility (solid lines).

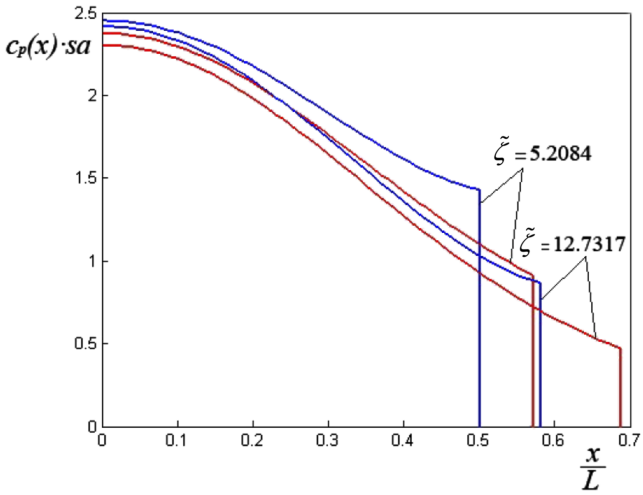

FIG. 3. The polymer density profiles calculated within the linear elasticity (red curves) and with the account of finite extensibility (blue curves) for different values of the grafting density parameter $\tilde{\zeta}$ at $\alpha = 0.5$.

At $uh \ll 1$, the latter equation is reduced to

$$\frac{\alpha c_p(t)}{c_0} = \zeta^{-1}\left[1 + h^2 \exp\left(h^2 - t^2\right)\right]. \qquad (27)$$

The polymer density profiles in the polyelectrolyte brush calculated within the Gaussian (linear) elasticity approximation and with the account of finite extensibility of the polyions are presented in Fig. 3. Although the shapes of the density profiles are similar, in the latter case, the cutoff of the density profiles (the brush thickness) is smaller while the jump in the polymer density at the brush edge $z = H$ is larger.

III. CONCLUSIONS

The account of finite extensibility of the end-tethered polyions in a polyelectrolyte brush leads to a number of features that were not captured by a simplified theory based on the assumption of the Gaussian (linear) conformational elasticity:

- For the same set of the brush parameters (chain length N, grafting density σ, and degree of ionization α), the theory based on non-linear elasticity of the polyions predicts a smaller thickness of the brush and larger magnitude of the jump in polymer density at the edge of the brush, $x = H$, as compared to the predictions of the earlier theory based on the approximation of the polyion Gaussian elasticity.
- In contrast to a constant value of net charge density $\rho_{linear} = 3\pi/(16a^2 l_B \alpha N^2)$ in brushes of polyions with linear (Gaussian) elasticity, net charge density $\rho_{nonlinear}(x) = \rho_{linear}\sec^2(\pi x/2L)$ in the brushes of polyions with nonlinear elasticity increases as a function of distance x from the surface.
- In spite of this increase, the ratio of residual charges $(\tilde{Q})_{lin}/(\tilde{Q})_{nonlinear} > 1$ indicates a larger fraction of counterions entrapped inside and a weaker electric field outside for the polyelectrolyte brush exhibiting nonlinear elasticity compared to the brush of polyions with the linear chain elasticity.
- The employed strong stretching approximation leads to discontinuity of the polymer density profile at the edge of the brush, at $x = H$. Fluctuations of the terminal segments of the chains subjected to the extensional field at $x \geq H$ lead to the formation of exponentially decaying "tail" in polymer density beyond the edge of the brush. These fluctuations can be accounted for following the lines of the approach suggested in Refs. 29 and 30. Due to a weaker electric field acting at the terminal segments of polyions outside of the brush and larger penalty for extra stretching of the part of the chain remaining inside the brush, the width of the fluctuation-induced tail $L_{tail,nonlinear}$ of the polymer density distribution decreases compared to the tail width $L_{tail,linear} \simeq a^{4/5}N^{2/5}H^{1/5}$ for polyions with linear chain elasticity.[29] The latter relation is applied as long as $aN^{1/2} \leq H << Na$. At the same time, there is no simple scaling for L_{tail} in the $H \to L$ limit.

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