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Ionic strength dependence of polyelectrolyte brush thickness

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Abstract

Intramolecular repulsion between charged monomers imposes intrinsic tension in polyion, modifies its elasticity, and changes the dependence of polyelectrolyte brush thickness on salt concentration. We demonstrate that intrinsic polyion tension gives rise to a plateau of the brush thickness in the middle of salt dominated regime and to a subsequent steeper brush contraction with increasing salt concentration.

1 Introduction

Polyelectrolyte (PE) brushes have attracted attention of polymer scientists for a number of years. Brush-like structures are found in nature[1, 2] and emerge in various applications in materials science and nanotechnology[3, 4]. Combination of short-range excluded volume interactions, long-range electrostatic repulsion and translational entropy of counterions makes PE brush behavior rather complex.

Due to electrostatic repulsion between charged monomers, a PE brush in contact with solution of monovalent salt is more stretched than its neutral counterpart[5]. Quantitative understanding of PE brushes has been reached upon the development of scaling models of individual polyions [6, 7] and PE solutions[6, 8]. In their pioneering works Pincus[9] and Borisov et al[10] identified main scaling regimes of PE brushes under salt-free conditions:

- a. mushroom regime with intermolecular distance larger than chain size,
- b. polyelectrolyte (charged) brush dominated by intermolecular electrostatic repulsion,
- c. osmotic brush (counterion dominated regime),
- d. quasi-neutral brush with interactions between monomers governed by the short-range non-electrostatic forces.

In a mushroom regime (a), the chain size is similar to that of a free (not grafted) PE. In PE regime (b), the fraction of counterions inside the charged brush is small, and the chains are stretched due to “bare” Coulomb repulsion between polyions.[9]. Counterions are localized inside the osmotic brush in regime (c) and the net polyion charge is almost fully compensated.[9, 10].

Addition of salt ions leads to screening of electrostatic interactions between charged monomers, and eventual brush contraction. Scaling models[9, 10] assumed Gaussian elasticity of polyions and predicted decreasing brush thickness H with increasing salt concentration c_s as

$$H \sim c_s^{-1/3} \text{ for } c_s > c_s^l \quad (1)$$

starting at salt concentration c_s^l on the order of counterion concentration in the brush in the osmotic regime (c). The theoretical value of exponent $-1/3$ was found to be in reasonable agreement with experiments [11, 12, 13, 14, 15, 16, 17] and computer simulations [18, 19].

In the present study we revisit the scaling model of PE brush and incorporate into it the intramolecular repulsion between charged monomers that imposes intrinsic tension in polyelectrolyte chains and thereby affects the elasticity of polyions [20, 21, 22, 23]. The result of this intrinsic tension is that, instead of a single power law dependence of brush thickness H on ionic strength in the high salt regime, we predict several different sub-regimes. For example, in the case of weakly charged polyions in a θ -solvent for the uncharged sections of the backbone, the brush thickness H initially decreases with salt concentration c_s with classical exponent $-1/3$, followed by an unexpected plateau in $H(c_s)$, and then by a steeper brush contraction with exponent $-3/7$ at higher salt concentrations.

2 Stretching of a polyelectrolyte chain by external force

To explain the modifications in the polyion elasticity due to intramolecular electrostatic repulsion [21, 23], we first consider the response of a polyion with degree of polymerization N , monomer size a , Kuhn segment length b , and fraction of charged monomers α to an external force f . The polyion exhibits Gaussian elasticity under theta solvent conditions for uncharged backbone, and acquires a stretched conformation in a salt-free solution even for zero external force $f = 0$. The average size R_e of the polyion is dictated by the balance of Gaussian chain elasticity and intramolecular Coulomb repulsions between charged monomers. The polyion free energy without external force is

$$\frac{F}{k_B T} \simeq \frac{R_e^2}{bL} + l_B \frac{(\alpha N)^2}{R_e} \quad (2)$$

where $L = aN$ is the contour chain length and $l_B = e^2/(\epsilon k_B T)$ is the Bjerrum length (e is the elementary charge, ϵ is the dielectric constant, k_B is the Boltzmann constant, and T is the absolute temperature). Minimization of this free energy F (Eq 2) with respect to chain size R_e gives the size of a polyelectrolyte chain in salt-free dilute solution

$$R_e \simeq b^{1/3} l_B^{1/3} \alpha^{2/3} N^{2/3} L^{1/3} \simeq L(u\beta^2)^{1/3} \quad (3)$$

Here, $u = l_B/b$ is the ratio of Bjerrum length and Kuhn segment length, and $\beta = \alpha b/a$ is the number of charges per Kuhn segment length b . In this regime, polyion is envisioned as an array of electrostatic blobs [6, 8] with size

$$\xi_e \simeq bL/R_e \simeq b(u\beta^2)^{-1/3} \text{ for } \beta < u^{-1/2} \quad (4)$$

and Coulomb interaction energy $\simeq k_B T$ per blob. A chain segment in electrostatic blob exhibits Gaussian statistics in a θ -solvent and comprises of

$$g_e \simeq (\xi_e/b)^2 \simeq (u\beta^2)^{-2/3} \text{ for } \beta < u^{-1/2} \quad (5)$$

Kuhn segments. Note that since Kuhn length is typically larger than Bjerrum length ($u < 1$), polyelectrolyte is close to maximal extension ($g_e \simeq 1$, $\xi_e \simeq b$, and $R_e \simeq L$) at number of charges per Kuhn segment $\beta \simeq u^{-1/2}$. This charge density is still below Manning counterion condensation threshold[24], which is reached for this almost fully stretched regime at higher number of charges per Kuhn segment $\beta \simeq u^{-1}$. Throughout most of this paper we will concentrate on the case of weakly charged chain with small number of charges per Kuhn segment $\beta < u^{-1/2}$ and many Kuhn segments in an electrostatic blob $g_e > 1$, so that chain is flexible on scales smaller than electrostatic blob ($\xi_e > b$).

Addition of salt ions screens electrostatic interactions between charges along the chain. The screening of electrostatic repulsion between sections of PE by monovalent salt ions occurs on length scale of the Debye screening length

$$r_D = (8\pi l_B c_s)^{-1/2} \quad (6)$$

The size of the chain in salt solutions depends on the electrostatic persistence length and its variations with Debye length r_D . The dependence of electrostatic persistence length l_p on Debye length r_D is still an issue of discussions in the literature. The theory of Odijk-

Skolnick-Fixman[25, 26] predicts $l_p \sim r_D^2$ while variational calculations[27] suggest $l_p \sim r_D$. The results of computer modeling are contradictory: some Monte Carlo simulations[28, 29] are consistent with $l_p \sim r_D^2$, while recent MD simulations[30] support $l_p \sim r_D$ at least in the range of experimentally relevant N . The latter dependence is also consistent with experimental observations[13, 31]. In the following we focus on the case $l_p \simeq r_D$, and only briefly discuss the modification of our results for the alternative salt dependence of electrostatic persistence length[25, 26], extended by Khokhlov and Khachaturian for intrinsically flexible polymers[7] $l_p \simeq r_D^2/\xi_e$.

A polyion retains its unperturbed size R_e at very low salt concentrations, corresponding to very large Debye screening length $r_D \gg R_e$. At higher salt concentrations with Debye length $r_D < R_e$, the chain can be subdivided into segments of size r_D . The chain retains conformation of a salt-free polyion on length scales $r < r_D$. Chain segment of size r_D contains $g_D = g_e(r_D/\xi_e) \simeq r_D \xi_e/b^2$ Kuhn segments. The chain adopts conformations of a swollen coil of Debye segments on length scales larger than Debye length, $r > r_D$, assuming that r_D is on the order of electrostatic persistence length l_p . These segments with size r_D interact with each other via second virial coefficient $\simeq r_D^3$. The average size R_s of PE chain at these salt concentrations (with $l_p \simeq r_D < R_e$) is

$$R_s \simeq r_D N_D^{3/5} = r_D^{2/5} L^{3/5} (u\beta^2)^{1/5} \quad \text{for } l_p \simeq r_D < R_e \quad (7)$$

where $N_D = N/g_D$ is the total number of r_D -segments per chain.

Application of external force f to chain ends leads to elongation of the macromolecule. Figure 1 demonstrates the scaling regimes for chain elongation in the case $l_p \simeq r_D$ [27, 30] (solid lines). At small values of force $f < k_B T/R_s$, polyion is essentially undeformed and maintains unperturbed size R_s . At larger forces $f > k_B T/R_s$, the chain exhibits Pincus elasticity[32] with sublinear dependence of the end-to-end distance R on applied force f , $R \sim f^{2/3}$. This regime lasts for forces up to $f \simeq k_B T/r_D$ at which the size of the tension blob becomes on the order of Debye length. The end-to-end distance R at this external force approaches the size R_e of a free polyion in dilute salt-free solution. Further increase of the external force f does not lead to noticeable elongation of the chain (see plateau regime in

figure 1 with $H \approx R_e$) as long as this force f is weaker than the intrinsic polyion tension $k_B T / \xi_e$ imposed by the intramolecular Coulomb repulsion. At larger forces $f > k_B T / \xi_e$, the chain is stretched on length scales smaller than the size ξ_e of electrostatic blob and exhibits Gaussian elasticity. Note that this dependence of the chain size R on the stretching force f (solid line in figure 1) is qualitatively different from that for a Gaussian chain (dashed line in figure 1) assumed by the classical brush theories[9, 10].

Conformation of a polyelectrolyte chain with electrostatic persistence length larger than Debye length ($l_p > r_D$) is a stretched array of electrostatic blobs of size ξ_e up to the length scale of persistence length l_p , an ideal chain of these persistence segments of size l_p on length scale up to “thermal” blob size l_p^2/r_D , and a swollen chain of these “thermal” blobs¹ on larger length scales[21, 23]. Therefore the size of this PE in solutions with high salt concentration and no external force ($f = 0$) is

$$R_s \approx l_p^{1/5} r_D^{1/5} R_e^{3/5} \quad \text{for } r_D < l_p < l_p^2/r_D < R_e \quad (8)$$

where R_e is the size of the chain in salt-free solution (Eq 3). One could substitute the Odijk-Skolnick-Fixman-Khokhlov-Khachaturian (OSFKK) estimate of the electrostatic persistence length[25, 26, 7] $l_p \approx r_D^2/\xi_e \gg r_D$ into Eq 8. The size of this PE chain stretched by external force f is shown in figure 1 by dotted lines. The elongation of this polymer starts earlier (because its size R_s is larger than in the case of persistence length $l_p \approx r_D$), and Pincus elasticity is followed by Gaussian chain elasticity before the end-to-end distance R reaches the plateau value R_e . The crossover between Pincus and Gaussian elasticity occurs at the extension force $f \approx k_B T r_D / l_p^2$ with tension blob on the order of “thermal” blob size $l_p^2/r_D \approx r_D^3/\xi_e^2$. An increase in the external force above the intrinsic tension $f > k_B T / \xi_e$ leads to linear dependence $R(f)$ similar to that for a flexible Gaussian chain with Kuhn length b (dashed line in figure 1).

3 Polyelectrolyte brush

To illustrate the effect of intrinsic polyion tension on the salt-induced contraction of polyelectrolyte brush, we consider a brush of flexible PEs with intrinsic Kuhn length b , number of charges per Kuhn segment $\beta < u^{-1/2}$, chain contour length $L = aN$ and grafting density σ . We assume θ -solvent condition for the uncharged backbone of PE. At low grafting density σ in the mushroom regime, the intramolecular repulsion between polyions is weak, and each PE chain retains its unperturbed size R_e . The crossover between this mushroom regime of individual polyions and PE brush with thickness $H > R_e$ occurs at grafting density $\sigma \approx R_e^{-2}$ where R_e is given by Eq 3. Coulomb interaction between polyions at this grafting density ($\sigma \approx R_e^{-2}$) is comparable to intramolecular repulsion. With increasing grafting density one passes a narrow polyelectrolyte brush regime[9] for

$R_e^{-2} < \sigma < R_e^{-2} (u\beta^2)^{-1/3}$ and enters the osmotic brush regime at $\sigma > R_e^{-2} (u\beta^2)^{-1/3}$ with polyion charge almost fully compensated by mobile counterions.[9, 10]

Addition of monovalent salt leads to the screening of the Coulomb repulsion between charged monomers. To determine the scaling dependences of the brush thickness H , we

¹The term “thermal” is used following the nomenclature adopted for neutral polymers. There, the second virial coefficient v is determined by the relative temperature deviation from the θ -temperature, $\tau = (T - \theta)/\theta$. Chain segment with size $\xi_T \approx a\tau^{-1}$ (thermal blob) remains Gaussian whereas at length scales $r > \xi_T$, the chain is swollen by the repulsive binary contacts between monomers. In contrast, the binary repulsions between monomers in our system are determined by the screened Coulomb interaction.

adopt the model wherein the free chain ends are localized at the brush edge and the gradients in polymer and ions distributions are neglected. PE brush with the average monomer concentration (number density) $c = N\sigma/H$ is stretched by the differential osmotic ion pressure $\Delta\Pi$ between brush interior and buffer solution

$$\frac{\Delta\Pi}{k_B T} = c_+ + c_- - 2c_s \quad (9)$$

where c_+ and c_- are the average concentrations of monovalent mobile cations and anions inside the brush. To specify the values of c_+ and c_- we take advantage of (i) PE brush electroneutrality, $c_+ \approx \alpha c + c_-$, and (ii) the Boltzmann distribution of mobile ions, $c_{\pm} = c_s \exp(\mp e\Delta\psi/k_B T)$, which is equivalent to the Donnan equilibrium condition $c_+ c_- = c_s^2$. Here, $\Delta\psi$ is the electrostatic potential difference between inside and outside of the brush associated with the narrow boundary between PE brush and salt solution.

The differential osmotic pressure[33] is

$$\frac{\Delta\Pi}{k_B T} = 2c_s \left[\sqrt{\left(\frac{\alpha c}{2c_s}\right)^2 + 1} - 1 \right] \simeq \begin{cases} \alpha c & c_s \ll \alpha c \quad (a) \\ (\alpha c)^2 / c_s & \alpha c \ll c_s \quad (b) \end{cases} \quad (10)$$

The osmotic pressure is dominated by counterions at low salt concentration $c_s \ll \alpha c$ (Eq 10a). The difference in concentrations of mobile ions inside and outside PE brush decreases with increasing ionic strength leading to the corresponding decrease in osmotic pressure $\Delta\Pi$ (Eq 10b for high salt concentrations $c_s \gg \alpha c$).

A tethered chain in the osmotic brush experiences stretching force due to differential osmotic pressure of ions, $f = \Delta\Pi/\sigma$, Eq 10. The average extension H of polyions in the brush depends both on this force and on chain elasticity depicted in figure 1. Below we consider different regimes of PE brush behavior upon increasing concentration c_s of salt ions.

Regime I

In the low salt regime, the size of the chain in the osmotic brush is determined by the balance of Gaussian elastic force

$$f_{elastic} \simeq k_B T \frac{H}{bL} \quad (11)$$

and osmotic force per chain due to counterions, Eq 10a, resulting in the brush thickness

$$H = H_0 \simeq \beta^{1/2} L \quad \text{regime I: } 0 < c_s < c_s^I \quad (12)$$

where the salt concentration

$$c_s^I = \alpha N\sigma / H_0 \simeq b^{-3} \beta^{1/2} (\sigma b^2) \quad (13)$$

is equal to the average concentration of counterions in the brush. The brush thickness $H_0 > R_e$ in the low salt regime $c_s \ll c_s^I$ is almost unaffected by the presence of salt ions (the first

plateau in the salt concentration dependence of the brush thickness $H(c_s)$ presented in figure 2). A typical value of H_0 is marked by the filled circle in figure 1.

Regime II

The differential osmotic pressure $\Delta\Pi$ of ions and the resulting osmotic force per chain decreases with increasing salt concentration $c_s > c_s^I$ (Eq 10b). By balancing this osmotic force per chain $\Delta\Pi/\sigma$ with Gaussian elastic force, Eq 11, one finds that the brush thickness H decreases with increasing ionic strength as

$$H \simeq H_0(c_s^I/c_s)^{1/3} \simeq L(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{1/3} \quad \text{regime II: } c_s^I < c_s < c_s^{II} \quad (14)$$

where c_s^{II} is specified in Eq 15 below.

This power law decrease of brush thickness H with increasing salt concentration c_s (Eq 14) continues as long as H is larger than R_e , the size of an isolated polyion in a salt-free solution given by Eq 3. The crossover between *regimes II* and *III* occurs at ionic strength corresponding to Debye length $r_D \simeq (l_B c_s)^{-1/2}$ on the order of the distance between neighboring chains $\sigma^{-1/2}$ or, equivalently, at salt concentration

$$c_s^{II} \simeq \sigma/l_B = (\sigma b^2) u^{-1} b^{-3} \quad (15)$$

Regime III

Further increase in salt concentration $c_s > c_s^{II}$ leads to the decrease in stretching force $\Delta\Pi/\sigma$ below the intrinsic polyion tension. Here, polyions are envisioned as linear arrays of electrostatic blobs with size $\xi_e < r_D$. The chains experience “intrinsic” tension $k_B T/\xi_e$ created by intramolecular repulsions between charged monomers. Average thickness $H \simeq R_e$ and polymer concentration $c_e \simeq N\sigma/R_e$ do not change upon additions of salt until osmotic force $\Delta\Pi/\sigma$ (Eq 10b) becomes smaller than $k_B T$ per persistence length l_p (assumed to be $\sim r_D$). This crossover $\Delta\Pi/\sigma \simeq k_B T/r_D$ occurs at salt concentration

$$c_s^{III} \simeq \beta^{4/9}(\sigma b^2)^{2/3} u^{-7/9} b^{-3} \quad (16)$$

Therefore in the whole range of salt concentrations $c_s^{II} < c_s < c_s^{III}$, the brush thickness is almost independent of salt concentration,

$$H \simeq R_e \simeq (u\beta^2)^{1/3} L \quad \text{regime III: } c_s^{II} < c_s < c_s^{III} \quad (17)$$

(the second plateau in salt dependence of brush thickness H - solid line in figure 2).

Regime IV

PE brush contracts again at salt concentrations $c_s > c_s^{III}$. Here, polyion exhibits the statistics of a single chain composed of r_D -segments interacting via the second virial coefficient $\simeq r_D^3$. The tension [32]

$$k_B T / \xi_t \simeq k_B T H^{3/2} / (r_D^{5/2} N_D^{3/2}) \quad (18)$$

in a stretched swollen chain of N_D Debye segments of size $r_D \simeq l_p$ is balanced by the osmotic force (Eq 10b), resulting in the brush thickness

$$H \simeq R_e (c_s^{III} / c_s)^{3/7} \simeq L(\sigma b^2)^{2/7} (\beta^2 / b^3 c_s)^{3/7} \quad \text{regime IV: } c_s^{III} < c_s < c_s^{IV} \quad (19)$$

where salt concentration c_s^{IV} is defined in Eq 21 below. The modified elasticity of tethered PE leads to stronger salt dependence (Eq 19) of brush thickness $H \sim c_s^{-3/7}$ than the classical dependence $H \sim c_s^{-1/3}$ (Eq 1) predicted earlier[9, 10] (compare solid and dashed lines in figure 2).

Debye length r_D approaches the size of electrostatic blob ξ_e in the middle of regime IV of brush contraction at the crossover salt concentration

$$c_s^* \simeq \beta^{4/3} u^{-1/3} b^{-3} \quad (20)$$

At higher salt concentrations $c_s > c_s^*$, the Debye length is very small, $r_D < \xi_e$ and the concept of electrostatic blob is no longer applicable. The repulsion between charged monomers is described in this regime by the electrostatic second virial coefficient of interactions between Kuhn segments, $v \simeq l_B \beta^2 r_D^2$. The latter determines the size of “thermal” blob $\xi_T \simeq b^4 / v$. The electrostatic repulsion is weak (Coulomb energy is less than $k_B T$) on length scales smaller than thermal blob with g_T monomers, and PE chain exhibits Gaussian statistics with thermal blob size $\xi_T \simeq b \sqrt{g_T}$. Thermal blobs repeal each other, and the chain adopts conformation of a stretched swollen coil on length scales $r > \xi_T$ larger than thermal blob size. The tension kT/ξ_t in this regime can be written similar to Eq 18 as $kTH^{3/2} / (\xi_T^{5/2} N_T^{3/2})$, where $N_T = N/g_T$ is the number of thermal blobs per polyion. The balance of this tension kT/ξ_t with osmotic force $\Delta\Pi/\sigma$ (Eq 10b), results in the same dependence of brush thickness H as given by Eq 19.

Regime IV'

At very high salt concentration

$$c_s^{IV} = \beta^2 (\sigma b^2)^{-1/2} b^{-3} \quad (21)$$

the sizes of both tension (ξ_D) and thermal (ξ_T) blobs become on the order of the distance $\sigma^{-1/2}$ between grafting points. At higher salt concentrations $c_s > c_s^{IV}$, tethered polyions exhibit Gaussian statistics, Eq 11. Balancing $f_{elastic}$ (Eq 11) with $\Delta\Pi/\sigma$ (Eq 10b) leads to classical salt dependence (Eq 1) of the brush thickness

$$H \simeq L(\sigma b^2)^{1/3} (\beta^2 / b^3 c_s)^{1/3} \sim c^{1/3} \quad \text{regime IV': } c_s^{IV} < c_s < c_s^{IV'} \quad (22)$$

Regime V

At even higher salt concentrations $c_s > c_s^{IV'} \approx p^{9/4} \beta^2 (\sigma b^2)^{-1/2} b^{-3}$, where $p = b/a$ is Kuhn segment asymmetry, the non-electrostatic ternary interaction between monomers dominates over binary electrostatic repulsion. The stretching force $\Delta\Pi/\sigma$ per chain in this quasi-neutral regime is governed by the ternary contacts between monomers interacting via the third virial coefficient $w \approx a^6$. [34] The brush thickness, determined by the balance between this osmotic stretching force $\Delta\Pi/\sigma \approx k_B T w c^3/\sigma$ and Gaussian elasticity (Eq 11)

$$H_n \approx L p^{-3/4} (\sigma b^2)^{1/2} \quad \text{regime V: } c_s > c_s^{IV'} \quad (23)$$

becomes independent of salt concentration c_s (the third plateau in figure 2).

The scaling dependences of the brush thickness $H(c_s)$ in regimes $i = I - V$ and the crossover concentrations between these regimes are summarized in Table 1. A typical values of Kuhn length for flexible PE is $b \approx 1.4 \text{ nm}$ and using $l_B = 0.7 \text{ nm}$ we estimate $u = l_B/b \approx 0.5$. For weakly charged PE chains with $\beta = u^{-1/2} \approx 1.4$ charges per Kuhn segment and grafting chain density of a brush $\sigma = 10^{15} \text{ chains}/\text{m}^2$, the crossover concentration of NaCl salt at the end of the first plateau (Eq 13) $c_s^I \approx \beta^{1/2} \sigma/b \approx 1.5 \times 10^{-3} \text{ M}$ is an order of magnitude lower than the crossover concentration at the end of the second plateau (Eq 16)

$$c_s^{III} \approx \beta^{4/9} \sigma^{2/3} u^{-7/9} b^{-5/3} \approx 2 \times 10^{-2} \text{ M (see figure 2).}$$

4 Discussion

In this **paper** we revise the scaling model of polyelectrolyte brushes by incorporating the effect of intramolecular Coulomb repulsion on polyion elasticity [20, 21, 22] and brush thickness H . Revision of polyion elasticity in curved PE brushes (spherical [22] and cylindrical) leads to a qualitatively similar behavior of brush thickness H with the second plateau in the middle of salt dominated regime.

Classical scaling models of PE brushes [9, 10] established a clear distinction between low and high salt conditions (also referred in the literature as the osmotic and salt dominated PE brush regimes). PE brush is stretched by the osmotic pressure of counterions at low salt concentrations, whereas at high salt concentrations (in the salt dominated regime), osmotic pressure is governed by the salt ions, see Eq 10. The assumption of Gaussian chain elasticity in the whole range of salt concentrations, made by classical theories [9, 10], leads to two different regimes for the average brush thickness $H(c_s)$: the plateau H_0 (Eq 12) for osmotic brush at low salt concentrations $0 < c_s < c_s^I$ and brush contraction with $H \sim c^{-1/3}$ (Eq 1) for higher salt concentrations $c_s^I < c_s < c_s^{IV}$ (shown by dashed line in figure 2).

4.1 Weakly Charged Polyions

4.1.1 Electrostatic persistence length $l_p \sim r_D$ —We have demonstrated that *intramolecular* repulsion between charged monomers modifies the elasticity of polyions by inducing intrinsic tension in the chains (compare solid and dashed lines in figure 1). In agreement with the previous studies, PE brush with degree of ionization $\beta < u^{-1/2}$ is predicted to be in the counterion-dominated regime at low salt (*regime I* with $0 < c_s < c_s^I$ in figure 2) with its thickness H_0 almost independent of salt concentration c_s (Eq 12). However, in contrast to the single exponent $-1/3$ in the salt dependence of brush thickness $H(c_s)$ in the salt dominated regime (Eq 1) predicted by the classical theories (dashed line in figure 2), we find three regimes (see Table 1): regime *II* identical to the classical regime within much narrower salt concentration range (Eq 14) and two novel regimes *III* and *IV*

with exponents 0 and $-3/7$ (under theta solvent conditions and assumption $l_p \sim r_D$). The two new dependences of brush thickness are sketched in figure 2 by two solid lines replacing single dashed line for $c_s^{II} < c_s < c_s^{IV}$.

The tension in tethered PEs in *regime II* with $c_s^I < c_s < c_s^{II}$ is larger than in an isolated polyion, and chains exhibit Gaussian elasticity. As a result, Eq 14 holds and the classical value of exponent $-1/3$ is not modified.

In *regime III* with $c_s^{II} < c_s < c_s^{III}$, the brush thickness $H \approx R_e$ is almost independent of the salt concentration c_s . Here, the osmotic force is smaller than the intrinsic tension imposed by intramolecular repulsion between charged monomers.

In *regime IV* with $c_s^{III} < c_s < c_s^{IV}$, the brush thickness $H(c_s)$ decreases with exponent $-3/7$ (Eq 19). Here, the chain is still a stretched array of electrostatic blobs with intrinsic tension at length scales $\xi_e < r < r_D$, while intrachain repulsion is screened on length scales larger than Debye length r_D . A polyion with electrostatic persistence length $l_p \approx r_D$ is swollen by Coulomb excluded volume repulsion and exhibits Pincus elasticity in *regime IV*. Due to the modified chain elasticity, the dependence of brush thickness H on salt concentration c_s , degree of ionization β , and grafting density σ differs from classical prediction (compare Eqs. 19 and 1). [9, 10]

Regime IV' is characterized by the Gaussian chain elasticity and the binary electrostatic excluded volume interactions between monomers. The classical salt dependence of brush thickness is recovered in this regime (Eq 22). The electrostatic binary interactions between monomers become weaker than non-electrostatic ternary interactions in the quasi-neutral *regime V* with salt-independent brush thickness (Eq 23).

4.1.2 Electrostatic persistence length $l_p \sim r_D^2$ —The alternative OSFCK expression for the electrostatic persistence length [25, 26, 7], $l_p \approx r_D^2/\xi_e$, leads to the modification of chain elasticity (dotted line in figure 1) and therefore revised salt dependence of the brush thickness $H(c_s)$, presented in Table 2. The regimes *I* and *II* with Gaussian polyion elasticity and brush thickness $H \approx R_e$ are not affected by electrostatic persistence length. A softer PE chain leaves the second plateau at higher crossover salt concentration c_s^{III} determined by the lower osmotic force per chain $\Delta\Pi/\sigma \approx k_B T/l_p$ and exhibits two subregimes of contraction (*IV*₁ and *IV*₂) at $c_s^{III} < c_s < c_s^*$. These subregimes are specified by different polyion elasticity governed by the strength of the excluded volume electrostatic repulsion between polyion segments of size r_D . The osmotic force (Eq 10b) in *regime IV*₁ is balanced by the Gaussian elastic force $k_B T H / (r_D l_p N_D)$ corresponding to ideal chain statistics with persistence length l_p , resulting in the salt dependence of brush thickness $H \sim c_s^{-2/3}$ at $c_s^{III} < c_s < c_s^{IV_1}$ (see Table 2). At higher salt concentrations (in *regime IV*₂) the same osmotic force (Eq 10b) is balanced by the Pincus elastic force $k_B T H^{3/2} / (r_D^2 l_p^{1/2} N_D^{3/2})$ with swollen tension blobs ξ_t , leading to brush thickness $H \sim c_s^{-1/2}$ at $c_s^{IV_1} < c_s < c_s^*$ (see Table 2). At salt concentration $c_s = c_s^*$ both electrostatic blob size ξ_e and electrostatic persistence length l_p become on the order of Debye radius r_D . At higher salt concentrations there is no additional electrostatic tension and brush thickness $H(c_s)$ follows the dependence of Eq 19 at $c_s > c_s^*$ which is different from classical (Eq 14) due to electrostatically induced excluded volume interactions.

4.2 Strongly Charged Polyions

4.2.1 Electrostatic persistence length $l_p \sim r_D$ —The increase in chain ionization up to one charge per Kuhn segment $\beta \approx 1$ leads to almost full stretching of polyions, $H_0 \approx L$, in

the counterion dominated *regime I*. At even higher degree of ionization $\beta \approx u^{-1/2}$, the size R_e of isolated polyions in dilute solution approaches contour length L , and *regime II* separating the two plateaus disappears (see solid and dotted lines in figure 3). At $\beta \approx u^{-1}$ (corresponding to the threshold of counterion condensation) tethered polyion is envisioned as an almost fully stretched chain with one charge per Bjerrum length l_B . With further increases in the number of charges per Kuhn segment $\beta > u^{-1}$, the effective polyion ionization $\approx u^{-1}$ does not change due to the counterion condensation. If one assumes that electrostatic persistence length is proportional to Debye length, $l_p \approx r_D$, the salt-induced brush contraction starts at the crossover concentration c_s^{III} corresponding to the force per chain $\Delta\Pi/\sigma \approx k_B T/r_D$. For strongly stretched polyions with $H \approx L$ and effective degree of ionization u^{-1} , this crossover concentration is given by $c_s^{III} \approx (\sigma b^2)^{2/3} u^{-5/3} b^{-3}$. At higher salt concentrations $c_s > c_s^{III}$ (*regime IV*), the brush thickness decreases as $H \approx L(c_s/c_s^{III})^{-3/7}$ (see solid line in figure 3). Most experimentally studied brushes contain strongly charged polyions that are stretched to the limit of linear elasticity at low salt concentrations. In such systems, counterion dominated *regime I* and salt controlled *regime III* become indistinguishable on scaling level, while *regime II* disappears and *regime IV* with $c_s > c_s^{III} \approx u^{-5/3} (\sigma b^2)^{2/3} b^{-3}$ extends to salt concentrations $c_s \approx u^{-1} b^{-3}$ at which Debye radius r_D becomes comparable to Kuhn segment length b . For intrinsically flexible polyions, this occurs at very high salt concentration. As a result, a single exponent $-3/7$ is expected in a wide range of salt-induced PE brush contraction (for $c_s > c_s^{III}$, solid line in figure 3).

4.2.2 Electrostatic persistence length $l_p \sim r_D^2$ —The salt dependence of the brush thickness $H(c_s)$ for the case of Odijk-Skolnick-Fixman electrostatic persistence length $l_p \sim r_D^2/l_b$ for strongly charged polyions above the counterion condensation threshold ($\beta \approx u^{-1}$, $\xi_e \approx l_B$) is shown by dotted lines in figure 3. The crossover salt concentration $c_s^{III} \approx (\sigma b^2)^{1/2} u^{-2} b^{-3}$ is higher in this case because the polyion is softer than in the case of $l_p \approx r_D$. At $c_s > c_s^{III}$, the brush thickness decreases sharply with salt concentration as $H \approx L(c_s/c_s^{III})^{-2/3}$ (*regime IV₁* in figure 3) until the sizes of tension blob ($\xi_t \approx l_p L/H$) and thermal blob ($\xi_r \approx l_p^2/r_D$) become comparable at the crossover concentration $c_s^{IV_1} \approx (\sigma b^2)^{2/7} u^{-16/7} b^{-3}$. At higher salt concentrations $c_s > c_s^{IV_1}$, the brush thickness follows a somewhat weaker c_s scaling dependence $H \approx H(c_s^{IV_1})(c_s/c_s^{IV_1})^{-1/2} \sim c_s^{-1/2}$ (*regime IV₂* in figure 3).

4.3 Effects of Solvent Quality for Uncharged Backbone Segments

Variations in the solvent quality for polyion backbone modify the exponents of the salt dependence of brush thickness $H(c_s)$. To illustrate this effect, we focus on flexible polyions with Kuhn length $b \approx a$, $u = l_B/b \gtrsim 1$, and assume that electrostatic persistence length $l_p \approx r_D$. Below we briefly discuss the cases of athermal and moderately poor solvents.

4.3.1 Athermal solvent—The electrostatic blob in an athermal solvent for the uncharged backbone is swollen by non-electrostatic excluded volume interactions and therefore polyion exhibits Pincus elasticity[32] on length scales smaller than electrostatic blob size ξ_e . As a result of this non-linear elasticity, brush thickness H_0 in the counterion dominated *regime I* (first plateau in $H(c_s)$ dependence) is given by $H_0 \approx L\beta^{2/5}$ with $\beta < 1$, while the second plateau in the salt dependence of brush thickness $H(c_s)$ is given by $H \approx R_e \approx L(u\beta^2)^{2/7}$ in *regime III*. Due to this intrinsic (Pincus) elasticity of the backbone, the value of the exponent of the salt dependence of brush thickness $H(c_s)$ in *regime II* with $c_s^I < c_s < c_s^{II}$ and in the part of

regime IV with $c_s^* < c_s < c_s^{IV}$ changes from $-3/7$ to $-2/7$. [35] However, in the part of *regime IV* with $c_s^{III} < c_s < c_s^*$ (where polyion elasticity is dictated by the electrostatic interactions between chain segments of Debye length r_D , see Eq 18) the value of the exponent $-3/7$ is not modified.

4.3.2 Poor solvent—The stretching of tethered polyions at low salt conditions in poor solvent with relative deviation from θ -temperature for the uncharged backbone $\tau = (\tau - T)/T < \beta^{1/2}$, is similar to that in a θ -solvent (*regimes I* and *II* in figure 4 and in Table 3). The size of the tension blob $\xi_t \approx bL/H$ in these regimes is smaller than size of the thermal blob $\xi_T \approx b/\tau$. At salt concentrations c_s larger than crossover concentration c_s^{II} (see Table 3 for the expressions of crossover concentrations), thermal blobs associate into beads with size ξ_e . The chain statistics is Gaussian on length scales smaller than the bead size ξ_e , and each bead is densely packed with thermal blobs of size ξ_T . The beads are connected by spacers (strings of thermal blobs) under constant tension $k_B T \tau / b$ [36] (*regime II'* in figure 4 and in Table 3).

At crossover concentration $c_s^{II'}$, the chain conformation is necklace-like (linear array of beads and strings) similar to that of free PE in dilute solution with size $R_e \approx L(u\beta^2)^{1/2} \tau^{-1/2}$ [37], and polyion retains this size R_e in *regime III* at $c_s > c_s^{II'}$. The electrostatic repulsion between Debye-size segments in *regime IV* modifies the polyion elasticity as formulated in Eq 18, and exponent $-3/7$ in the salt dependence of brush thickness $H(c_s)$ is recovered. The number of monomers in a Debye segment in this regime is $g_D \approx r_D \tau (\xi_e/b)^3 / h$, where

$$h \approx b\tau^{1/2}(u\beta^2)^{-1/2} \quad (24)$$

is the length of a spacer between beads (see figure 4). The Debye radius becomes shorter than spacer, $r_D < h$, at higher salt concentrations (in *regime IV'*) and there is only one bead per Debye r_D -segment, so that the number of monomers $g_D \approx \tau (\xi_e/b)^3$ within segment of size r_D does not depend on salt concentration c_s in this regime. Finally, the Debye radius r_D becomes on the order of bead size ξ_e at the crossover concentration $c_s^{IV'} = c_s^*$. The electrostatic repulsion at $c_s > c_s^{IV'}$ is insufficient to overcome the non-electrostatic attraction between monomers, and tethered polyions collapse, forming a uniform brush with polymer volume fraction $\approx \tau$ as sketched in figure 4 (*regime V*). The scaling prediction for the salt dependences of the brush thickness H in *regimes i = I – V* and the crossover concentrations c_s^i are presented in Table 3.

The increase in the degree of chain ionization β leads to strong stretching of polyions up to $H \approx L$ in *regimes I* and *III* and to the disappearance of *regimes II* and *II'*. *Regime IV* of brush contraction at $c_s > c_s^{III}$ expands up to very high salt concentrations c_s similar to the case of highly charged polyions in a θ -solvent. Therefore, a single exponent $-3/7$ in $H(c_s)$ dependence is expected for strongly charged polyions with electrostatic persistence length $l_p \approx r_D$, at $c_s > c_s^{III}$ under all solvent conditions for the uncharged sections of polymer backbone.

4.4 How to Test the Model

Incorporation of intrinsic polyion tension in the scaling model of PE brush and the corresponding revision of polyion elasticity suggests a different combination of variables for “universal plot” of experimental data from the one suggested by classical theories and used in reference [17]. In view of our findings, the “universal” combination of variables is $H/N \sim (\sigma^{2/3}/c_s)^{3/7}$ according to Eq 19. The crossover salt concentration c_s^{III} (end of plateau) *does not* correspond to the boundary between counterion and salt dominated regimes of osmotic

pressure (see Eq 10). Unfortunately, the accuracy of the available data[13, 12, 14, 15, 16, 17] does not allow one to discriminate between exponents $-1/3$ and $-3/7$ of the salt dependence of brush thickness $H(c_s)$.

The Odijk-Skolnick-Fixman prediction of the electrostatic persistence length $l_p \simeq r_D^2$ leads to even stronger difference between new predictions $(-2/3, -1/2)$ and the classical value $(-1/3)$ of scaling exponent for $H(c_s)$. Although the predicted values of exponents are asymptotic (expected for very long chains $N \rightarrow \infty$), the assumption $l_p \simeq r_D$ and the corresponding value of exponent $-3/7$ seem to be more consistent with existing experimental data[13, 12, 14, 15, 16, 17] on PE brushes.

We suggest two possible strategies to test our predictions using both weakly and strongly charged PEs.

- i. Weakly charged polyelectrolytes: According to our theory, the counterion dominated *regime I* with salt-independent brush thickness H_0 and *regime II* of salt-induced brush contraction are unchanged upon the revision of polyion elasticity and are identical to the classical predictions for weakly charged PE.[9, 10] However, the height and the extend of the second plateau can be manipulated by varying degree of ionization β and grafting density σ . For example, for weakly charged PE chains with $\beta = 0.5$ charges per Kuhn segment and the ratio of Bjerrum and Kuhn length $u = l_B/b \simeq 0.5$, the ratio of heights of the two plateaus is $H_0/R_e \simeq (u^2\beta)^{-1/6} \approx 1.4$ and could be increased even further by decreasing these two parameters β and u .
- ii. Strongly charged polyelectrolytes: The two plateaus in $H(c_s)$ dependence are hardly distinguishable for strongly charged polyelectrolytes (figure 3). For such polyions, we predict a weaker grafting density (σ) dependence of the crossover salt concentration c_s^{III} at the end of the plateau (see figure 3) than expected by classical theories. The crossover salt concentration c_s^{III} is predicted by our theory to increase with grafting density σ as $c_s^{III} \sim \sigma^{2/3}$ (in contrast to the classical boundary of the plateau $c_s^I \sim \sigma$ - see Eq 13). The counterion dominated brush regime for PE chains is found in salt-free solutions in a range of grafting densities, $L^{-2}(u\beta^2)^{-1} < \sigma < b^2 p^{3/2} \beta$, where the upper boundary is fixed by the structural parameters of PE (b , p and β) whereas the lower boundary $\sim L^{-2} \sim N^{-2}$ can be manipulated (shifted to lower grafting densities σ) by increasing the degree of polymerization N of polyions. By systematically varying grafting density σ over this range, one could determine the σ -dependence of the crossover salt concentration, separating plateau at low salt concentrations from the decreasing part in the salt dependence of the brush thickness $H(c_s)$ at high salt concentrations, and thus distinguish between classical and new PE brush models.

We are looking forward to new experiments and computer simulations testing the predictions of our model.

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Figure 1.

Scaling regimes for the average end-to-end distance R of a polyion with electrostatic persistence length $l_p \simeq r_D$ (solid lines) and $l_p \simeq r_D^2/\xi_e$ (dotted lines), stretched by the external force f . Elastic response of a Gaussian chain with unperturbed size $R_o \sim b^{1/2}L^{1/2}$ is shown by dashed lines. Both axis have logarithmic scales. Inset depicts important length scales - electrostatic blob size ξ_e and Debye length r_D .

Figure 2.

Brush thickness H dependence on salt concentration c_s . Solid lines represent predictions of the new model with electrostatic persistence length $l_p \approx r_D$. Dashed line corresponds to the classical prediction[9, 10]. Both axis have logarithmic scales and slopes are indicated next to the lines. Insets illustrate the brush structure in the corresponding regimes: Gaussian tension blobs in the osmotic regime *I*, r_D -segments with sequences of electrostatic blobs with size ξ_e (indicated by thick solid lines) in regime *III*, and (outmost) Pincus tension blobs comprising of r_D -segments in regime *IV*.

Figure 3. Brush thickness H as a function of salt concentration c_s for strongly charged polyions with effective degree of ionization $\beta = u^{-1}$ (corresponding to uncondensed ions). Solid and dotted lines correspond to predictions of the new model for two different assumptions of salt (Debye length r_D) dependence of the electrostatic persistence length $l_p \simeq r_D$ and $l_p \simeq r_D^2/\xi_e$, respectively. Dashed line indicates the prediction of the classical scaling model. Both axes have logarithmic scales and slopes are indicated next to the lines.

Figure 4.

Brush thickness H as a function of salt concentration c_s in a poor solvent. Values of parameters: $b = a$, $a < 1$, $u = l_B/b > 1$, $(ua^2)^{1/3} < \tau = (\theta - T)/T < a^{1/2}$, electrostatic persistence length $l_p \simeq r_D$. Insets illustrate the brush structure in the corresponding regimes: Gaussian tension blobs in the osmotic regime *I*, necklace-like chain conformation with beads of size ξ_e and spacers of length h (sequences of the thermal blobs of size ξ_T) in regime *III*, and densely packed thermal blobs of size ξ_T in laterally uniform collapsed brush in regime *V*.

Table 1

Ratio of polyelectrolyte brush thickness H in a θ -solvent for uncharged sections of backbone and polyion contour length $L = aN$, and crossover salt concentrations $b^3 c_s^i$ separating i and $i + 1$ regimes of salt-induced contraction ($i = I, II \dots V$). Electrostatic persistence length is assumed to be $l_p \approx r_D$. Dimensionless parameters: the ratio of Bjerrum and Kuhn lengths $u = l_B/b < 1$, the number of charges per Kuhn segment $\beta = ab/a < 1$, and the number of monomers in a Kuhn segment $p = b/a > 1$.

Regime	H/L	$b^3 c_s^i$
<i>I</i>	$\beta^{1/2}$	$\beta^{1/2}(\sigma b^2)$
<i>II</i>	$(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{1/3}$	$u^{-1}(\sigma b^2)$
<i>III</i>	$(\beta^2 u)^{1/3}$	$\beta^{4/9} u^{-7/9}(\sigma b^2)^{2/3}$
<i>IV</i>	$(\sigma b^2)^{2/7}(\beta^2/b^3 c_s)^{3/7}$	$\beta^2(\sigma b^2)^{-1/2}$
<i>IV'</i>	$(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{1/3}$	$p^{9/4} \beta^2(\sigma b^2)^{-1/2}$
<i>V</i>	$p^{-3/4}(\sigma b^2)^{1/2}$	—

Table 2

Ratio of polyelectrolyte brush thickness H in a θ -solvent for uncharged sections of backbone and polyion contour length $L = aN$, and crossover salt concentrations $b^3 c_s^i$ separating i and $i+1$ regimes of salt-induced contraction ($i = I, II \dots V$). Electrostatic persistence length is assumed to be $l_p \simeq r_D^2 / \xi_e$. Dimensionless parameters: the ratio of Bjerrum and Kuhn lengths $u = l_B / b < 1$, the number of charges per Kuhn segment $\beta = ab/a < 1$, and the number of monomers in a Kuhn segment $p = b/a > 1$.

Regime	H/L	$b^3 c_s^i$
<i>I</i>	$\beta^{1/2}$	$\beta^{1/2}(\sigma b^2)$
<i>II</i>	$(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{1/3}$	$u^{-1}(\sigma b^2)$
<i>III</i>	$(\beta^2 u)^{1/3}$	$\beta^{2/3}(\sigma b^2)^{1/2} u^{-2/3}$
<i>IV₁</i>	$(\beta^2/b^3 c_s)^{2/3}(\sigma b^2)^{1/3}(u\beta^2)^{-1/9}$	$\beta^{20/21}(\sigma b^2)^{2/7} u^{-11/21}$
<i>IV₂</i>	$(\beta^2/b^3 c_s)^{1/2}(\sigma b^2)^{2/7}(u\beta^2)^{-1/42}$	$\beta^{4/3} u^{-1/3}$
<i>IV</i>	$(\beta^2/b^3 c_s)^{3/7}(\sigma b^2)^{2/7}$	$\beta^2(\sigma b^2)^{-1/2}$
<i>IV'</i>	$(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{-1/3}$	$p^{9/4} \beta^2(\sigma b^2)^{-1/2}$
<i>V</i>	$p^{-3/4}(\sigma b^2)^{1/2}$	–

Table 3

Ratio of polyelectrolyte brush thickness H in a poor solvent with $(u\alpha^2)^{1/3} < \tau = (\theta - T)/T < \alpha^{1/2}$, and polyion contour length $L = aN$, and crossover salt concentrations $b^3 c_s^i$ separating i and $i + 1$ regimes of salt-induced contraction ($i = I, II \dots V$). Electrostatic persistence length is assumed to be $l_p \simeq r_D$. Dimensionless parameters: the ratio of Bjerrum and Kuhn lengths $u = l_B/b > 1$, the number of monomers in a Kuhn segment $p = b/a = 1$, and the number of charges per Kuhn length $\beta < u^{-2}$.

Regime	H/L	$b^3 c_s^i$
<i>I</i>	$\beta^{1/2}$	$\beta^{1/2}(\sigma b^2)$
<i>II</i>	$(\sigma b^2)^{1/3}(\beta^2/b^3 c_s)^{1/3}$	$\beta^2(\sigma b^2) \tau^{-3}$
<i>II'</i>	$(\sigma b^2)^{1/2}(\beta^2/b^3 c_s)^{1/2} \tau^{-1/2}$	$(\sigma b^2) u^{-1}$
<i>III</i>	$(u\beta^2)^{1/2} \tau^{-1/2}$	$\tau^{2/3}(\sigma b^2)^{2/3} u^{-1}$
<i>IV</i>	$(u\beta^2)^{1/14}(\sigma b^2)^{2/7}(\beta^2/b^3 c_s)^{3/7} \tau^{-3/14}$	$\beta^2 \tau^{-1}$
<i>IV'</i>	$(u\beta^2)^{1/14}(\sigma b^2)^{2/7}(\beta^2/b^3 c_s)^{9/14} \tau^{-3/7}$	$\beta^{4/3} u^{-1/3}$
<i>V</i>	$(\sigma b^2) \tau^{-1}$	–