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Long-Range Multichain Adsorption of Polyampholytes on a Charged Surface

Andrey V. Dobrynin,[†] Sergei P. Obukhov,[‡] and Michael Rubinstein*,[†]

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, and Department of Physics, University of Florida, Gainesville, Florida 32611

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ABSTRACT: We develop a theory of the adsorption of many polyampholyte chains on a charged surface. The adsorption is due to the polarization of polyampholyte chains in the external electric field created by the charged surface. The equilibrium polymer density profile is determined by balancing the long-range polarization-induced attraction of polyampholytes to the charged surface and the three-body repulsion between monomers in a θ-solvent for the polymer backbone (or the two-body repulsion in a good solvent). We demonstrate that the long-range nature of polyampholyte adsorption can lead to an adsorbed layer much thicker than the size of individual chains. Adsorbed polyampholytes that do not touch the surface form a multibrush of stretched chains. The chains that touch the surface form a self-similar stretched pseudobrush. Polyampholyte chains carrying the net charge of the same sign as that of the surface can also adsorb. In this case, the adsorption stops at that distance from the surface where the electrostatic repulsion between polyampholytes and a similarly charged surface becomes stronger than the polarization-induced attraction. The thickness of the adsorbed layer and the surface coverage decrease with increasing net charge on polyampholytes. The effect of added salt on polyampholyte adsorption is also discussed.

1. Introduction

Considerable theoretical and experimental work during the last two decades has been devoted to charged polymers,[1−4] macromolecules with ionizable groups. Under appropriate conditions, such as in aqueous solutions, these groups dissociate, leaving ions on chains and counterions in solutions. If the charges on polymers are all positive or all negative, these polymers are called polyelectrolytes. If after dissociation of the charged groups the polymers carry both positive and negative charges, they are called polyampholytes. Examples of polyampholytes include proteins and synthetic copolymers made of monomers with acidic and basic groups. If these groups are weak acids or bases, the net charge of polyampholytes can be changed by varying the pH of aqueous solutions.

Adsorption of charged polymers on a charged surface is one of the classical problems of polymer physics. Although polyelectrolyte adsorption has been analyzed in great detail both experimentally[5−7] and theoretically,[5,8−20] the theory of polyampholyte adsorption has not yet been developed. However, this theory is needed because understanding of the adsorption properties of polyampholytes is essential for advances in their technological utilizations. Many experimental studies have been made of the adsorption of gelatin,[21−26] especially onto silver halide crystal surfaces, reflecting practical interest in its photographic use. It has been shown experimentally that the adsorption of gelatin on a charged surface occurs even when both the polymer and the surface have the same net (negative) charge.[25,27,28] A related problem is the interaction of polyampholyte solutions with latex particles.[29,30] Theoretical studies of polyampholyte adsorption are limited to the case of a single chain adsorption.[31−33] These studies have shown that the adsorption of polyampholytes is due to the polarization of chains in the external electric field created by the charged surface. These theoretical models[31−33] have given a qualitative explanation of the experimental fact that polyampholytes can adsorb due to electrostatic interactions even if their overall charge has the same sign as that of the charged surface.[25,27,28]

In the present paper, we describe a scaling theory of the multichain adsorption of polyampholytes on a charged surface. In section 2, we briefly review the qualitative picture of single chain adsorption. In section 3, we generalize this model to the multichain case and present the results for the polymer density profile, the surface coverage, and the thickness of the adsorbed layer as a function of the surface charge density, the distribution of charges along the polymer backbone, and the polymer size. In sections 4 and 5, we discuss the effect of charge asymmetry and polymer concentration on polyampholyte adsorption. In section 6, we analyze the effects of added salt on the adsorption/desorption transition. In section 7, we generalize our model to a good solvent for the polymer backbone. Finally, in the last section, we summarize our results.

2. Three Regimes of Single Chain Adsorption[32]

Consider a polyampholyte chain containing N monomers, connected by bonds of length a, with the fraction f of charged monomers immersed in a θ-solvent of dielectric constant ϵ. For the polyampholyte chain to be soluble, the fluctuation-induced attractive interaction between charged monomers should be less than the thermal energy kT where T is the absolute temperature and k is the Boltzmann constant. This attraction is on the order of the thermal energy kT per Debye volume r_D^3, where $r_D \approx (l_B N f/R^3)^{-1/2}$ and $l_B = e^2/\epsilon kT$ is the Bjerrum length. If there are many Debye volumes per chain ($r_D \ll R$), this attraction is strong, and a polyampholyte with equal numbers of Nf_+ positively charged and of Nf_- negatively charged monomers forms a compact globule[34−37] and precipitates from solution.

[†] University of North Carolina.

[‡] University of Florida.

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However, if the Debye radius is larger than the chain size ($r_D > R$), the attraction is weak, and the chain remains almost unperturbed. The condition $r_D > R_0$ for a Gaussian chain of radius

$$R_0 \approx aN^{1/2} \tag{2.1}$$

can be written in terms of the fraction of charged groups $f = f_+ + f_-$

$$N < u^{-2} f^{-2} \tag{2.2}$$

where the coupling constant $u = l_B/a$ is the ratio of the Bjerrum length l_B to the bond size a. Thus, for a small fraction of charged groups f, there is a range of not very high degrees of polymerization (see eq 2.2) for which polyampholyte chains obey Gaussian statistics.

Consider the adsorption of a single polyampholyte chain onto an infinite plane with σ charges per unit area. In the absence of an added salt, the concentration of counterions in the solution decays with distance z from the surface, and the significant fraction of counterions is localized within the Gouy−Chapman length[38]

$$\lambda = (2\pi\, l_B\sigma)^{-1} \tag{2.3}$$

The electric field created by this plane decays with distance z from the surface[38] as

$$E(z) = \frac{4\pi e\sigma}{\epsilon}\frac{1}{(1 + z/\lambda)} \tag{2.4}$$

If the positions of the charges along the chain are uncorrelated, this chain has, on average, fN charges and $(fN)^{1/2}$ excess of positive and negative charges on the two halves of the chain. The size $R(z)$ of this chain at distance z from the charged surface can be estimated by balancing the electrostatic energy of the dipole of two opposite charges $(fN)^{1/2}$ of the two halves of the chain separated by the distance $R(z)$ in the external electric field $E(z)$ with the elastic stretching energy

$$kT\frac{R(z)^2}{a^2N} \approx E(z)e\sqrt{fN}R(z) \tag{2.5}$$

This balance leads to the size of the chain perpendicular to the surface

$$R(z) \approx \frac{E(z)ef^{1/2}N^{3/2}a^2}{kT} \approx \frac{{R_0}^2\sqrt{fN}}{(\lambda + z)} \tag{2.6}$$

At distances z from the surface shorter than the Gouy−Chapman length λ, the size of the chain perpendicular to the surface grows linearly with the surface charge density σ

$$R \approx R_0^2\sqrt{fN}/\lambda \approx l_B R^2_0\sqrt{fN}\sigma \quad \text{for } z < \lambda \tag{2.7}$$

We call this regime the "pole" regime. The electric field of the charged surface induces the elongation of the chain in the direction of the field (see Figure 1a), while in the perpendicular direction the chain keeps its Gaussian conformation. The chain is significantly elongated ($R > aN^{1/2}$) when the electric field exceeds the value

$$E_1 \approx \frac{1}{N}\sqrt{\frac{kT}{\epsilon f a^2 l_B}} \tag{2.8}$$

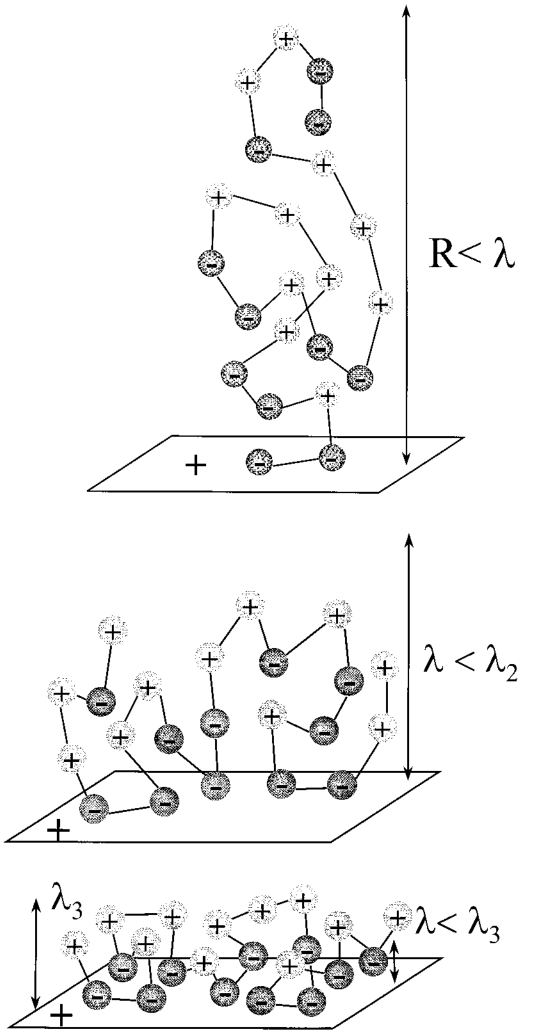

Figure 1. Schematic sketch of the configurations of a single polyampholyte chain near a charged surface. (a) Pole regime. (b) Fence regime. (c) Pancake regime.

The electric field E is higher than E_1 at distances z closer to the surface than the marginal Gouy−Chapman length

$$\lambda_1 \approx af^{1/2}N \approx R_0\sqrt{fN} \tag{2.9}$$

if the corresponding surface charge density σ is higher than the threshold value

$$\sigma_1 \approx \frac{1}{al_B f^{1/2}N} = \frac{1}{l_B R_0\sqrt{fN}} \tag{2.10}$$

For example, for a chain with $N = 500$ monomers, with the fraction of charges $f = 0.02$, and with the bond length $a = 3$ Å in the solution with the Bjerrum length $l_B = 7$ Å, the adsorption threshold is at $\sigma_1 \approx 7 \times 10^{-4}$ Å^{-2} and the marginal Gouy−Chapman length $\lambda_1 \approx 200$ Å.

The polarization energy of a polyampholyte chain in the external electric field is

$$\frac{W^{\mathrm{ch}}_{\mathrm{pol}}(z)}{kT} \approx -\left(\frac{\lambda_1}{z + \lambda}\right)^2 \tag{2.11}$$

At larger distances from the surface $z > \lambda_1$, the small polarization energy gain $-kT(\lambda_1/z)^2$ does not justify the conformational entropy loss due to stretching of the chain, and the polymer keeps its Gaussian conformation. At these distances, the attraction energy between the chains and the surface is less than the thermal energy kT, and the chains move freely through the solution.

The size of the chains near the wall $R_0\lambda_1/\lambda$ becomes on the same order of magnitude as the Gouy−Chapman length λ, when the surface charge density σ reaches the value σ_2

$$\sigma_2 \approx \frac{1}{al_B f^{1/4} N^{3/4}} = \frac{1}{l_B R_0 (fN)^{1/4}} \tag{2.12}$$

and the Gouy−Chapman length λ is equal to λ_2

$$\lambda_2 \approx R_0 (fN)^{1/4} = \sqrt{\lambda_1 R_0} \tag{2.13}$$

For our example with $N = 500$, $f = 0.02$, $l_B = 7$ Å, and $a = 3$ Å, the surface charge density $\sigma_2 \approx 10^{-3}$ Å^{-2} and the corresponding Gouy−Chapman length $\lambda_2 \approx 120$ Å. At higher surface charge densities $\sigma > \sigma_2$, the system crosses over to the “fence” regime. The chain in this regime remains confined within the Gouy−Chapman length and is divided into subsections of size λ (see Figure 1b). These subsections are strongly stretched, and the polymer is strongly attracted to the surface.

As the surface charge density increases further, the Gouy−Chapman length λ decreases, and the system crosses over to the “pancake” regime at the surface charge density

$$\sigma_3 \approx \frac{f^{1/2}}{al_B} \tag{2.14}$$

In this regime ($\sigma > \sigma_3$), the monomers with the sign of the charge opposite to that of the surface are within distance λ of the surface while monomers with the charge of the same sign as the one of the surface are in the loops dangling in solution at distances larger than λ (see Figure 1c). The average size of the loops can be estimated by comparing the repulsive force between the charges located at the distance z from the surface and the surface

$$F_{\text{rep}} \approx \frac{e^2 \sigma \lambda}{\epsilon z} \approx kT/z \tag{2.15}$$

with the elastic force due to the stretching of the parts of the chain with f^{-1} monomers

$$F_{\text{elast}} \approx kTzf/a^2 \tag{2.16}$$

At equilibrium, these two forces are equal. This leads to the condition of almost unperturbed strands of size

$$z \approx af^{-1/2} \approx \lambda_3 \tag{2.17}$$

For the above example, $\sigma_3 \approx 10^{-2}$ Å^{-2} and $\lambda_3 \approx 20$ Å. The thickness of a chain in the pancake regime is on the same order of magnitude as the root-mean-square distance between charged monomers and is almost independent of the surface charge density. The polarization energy of the chain section with f^{-1} monomers is on the order of the thermal energy kT. The gain of attraction energy due to reorganization of monomers in the adsorbed layer is kT per loop. In the following sections we will extend this model to the case of multichain adsorption.

3. Multichain Adsorption

3.1. Dilute Layers of Isolated Stretched Chains ($\sigma_1 < \sigma < \sigma_2$). If adsorbed chains near the surface do not overlap, the equilibrium monomeric density profile $c(z)$ is determined by the balance of the chemical potential of chains far from the surface (with monomer concentration c_B)

$$\mu_B = kT \ln c_B \tag{3.1}$$

with the chemical potential of the chains near the surface

$$\mu(z) = kT \ln c(z) - kT\left(\frac{\lambda_1}{z + \lambda}\right)^2 \tag{3.2}$$

At equilibrium, the monomer concentration profile is given by

$$c(z) = c_B \exp\left(\frac{\lambda_1}{z + \lambda}\right)^2 \tag{3.3}$$

The concentration $c(z)$ reaches its bulk value c_B at the distances z on the order of the marginal Gouy−Chapman length λ_1 (eq 2.9). Note that the thickness λ_1 of the layer where chains are localized near the surface is much larger than the chain size. It is on the order of the chain size R_0 times the number of unbalanced charges on half of the chain [$\sim(fN)^{1/2}$ for random charge sequence]. Chains start to overlap in the adsorbed layer when the monomer concentration near the surface

$$c(0) \approx c_B \exp(\lambda_1/\lambda)^2 \tag{3.4}$$

exceeds the overlap concentration

$$c_0^* \approx a^{-3} N^{-1/2} \tag{3.5}$$

of the Gaussian chains. (The thickness of an unsaturated adsorbed layer as a function of polymer concentration in solution is discussed in section 5.)

3.2. Multilayers of Stretched Chains ($\sigma_1 < \sigma < \sigma_2$). Above the overlap concentration in the adsorbed layer the long-range attractive interaction between polymer chains and the charged wall (eq 2.11) is stabilized by the repulsive interaction between monomers. In a θ-solvent for the polymer backbone, this repulsive interaction is due to three-body contacts and can be approximated by

$$W_{\text{rep}}(z)/kT = Na^6 c^2(z) \tag{3.6}$$

The balance between the polarization-induced attraction $W_{\text{pol}}^{\text{ch}}(z)$ (eq 2.11) and the three-body repulsion $W_{\text{rep}}(z)$ (eq 3.6) results in the equilibrium density profile

$$c(z) \approx c_0^* \frac{\lambda_1}{z + \lambda} \tag{3.7}$$

At distances larger than the Gouy−Chapman length λ we expect the hyperbolic density profile $c(z) \approx c_0^*\lambda_1/z$. The crossover from the semidilute to dilute regime of the adsorbed chains occurs at the distance $z \approx \lambda_1$ (see Figure 2). At this distance, $z \approx \lambda_1$ the attractive

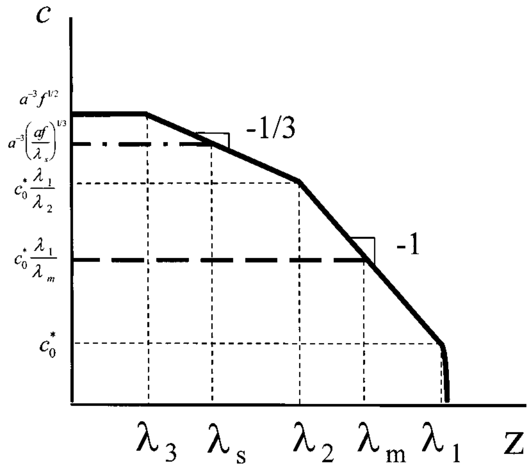

Figure 2. Polymer density profile in the adsorbed layers in a θ-solvent for three different regimes: multilayer of stretched chains for the Gouy–Chapman length $\lambda = \lambda_m$ (dashed line), self-similar stretched pseudobrush for the Gouy–Chapman length $\lambda = \lambda_s$ (dashed-dotted line), and the saturated self-similar stretched pseudobrush (solid line). Logarithmic scales.

interaction between polyampholytes and charged surface becomes comparable with the thermal energy kT. Therefore, one can consider λ_1 as the thickness of the adsorbed layer. The excess adsorbed amount Γ per unit surface area is

$$\Gamma \approx \int_0^{\lambda_1} c(z)\,dz = (\sqrt{fN}/a^2)\ln(\lambda_1/\lambda) \tag{3.8}$$

The polymer excess can be significantly higher than that for the adsorption at an uncharged surfaces[5] $\Gamma \approx a^{-2}$ and grows logarithmically with the surface charge density

$$\Gamma \approx (\sqrt{fN}/a^2)\ln(\sigma/\sigma_1) \tag{3.9}$$

A schematic sketch of the configuration of polyampholyte chains in the adsorbed layer is given in Figure 3a.

3.3. Self-Similar Stretched Pseudobrush ($\sigma_2 < \sigma < \sigma_3$). At higher surface charge densities ($\sigma > \sigma_2$), the size of the chains in the first adsorbed layer saturates at $R \approx \lambda_2$, but the subsections of the chains near the wall are more strongly stretched. The stretching of a subsection containing $g(z)$ monomers with the center of mass located at distance z from the wall can be estimated by balancing the elastic energy of this subsection $kTz^2/a^2g(z)$ by its polarization energy $e[fg(z)]^{1/2}zE(z)$. For $z < \lambda$ the external electric field $E(z) \approx e\sigma/\epsilon$ is almost constant. The chains are uniformly stretched up to length scales on the order of the Gouy–Chapman length[32] λ. The number of monomers in a subsection of size λ is

$$g \propto f^{-1/3}(\lambda/a)^{4/3} \tag{3.10}$$

At the length scales $z > \lambda$ the electric field $E(z) \approx e/\epsilon l_B z$ is inversely proportional to the distance z from the surface. The relation between the strand size z and the number of monomers $g(z)$ in it is

$$z \approx a\sqrt{g(z)}\,[fg(z)]^{1/4} \tag{3.11}$$

which is the $\lambda_2(g)$ for a chain of g monomers. In the length scale range $\lambda < z < \lambda_2$, we predict a self-similar pseudobrush of stretched strands of chains (see Figure 3b). The polarization energy per strand is proportional to $-kT[fg(z)]^{1/2}$. The density of polarization energy $U_{\text{pol}}(z)$ of the polyampholytes at distance z from the surface is equal to the concentration of the strands $c(z)/g(z)$ containing $g(z)$ monomers times the polarization energy per strand

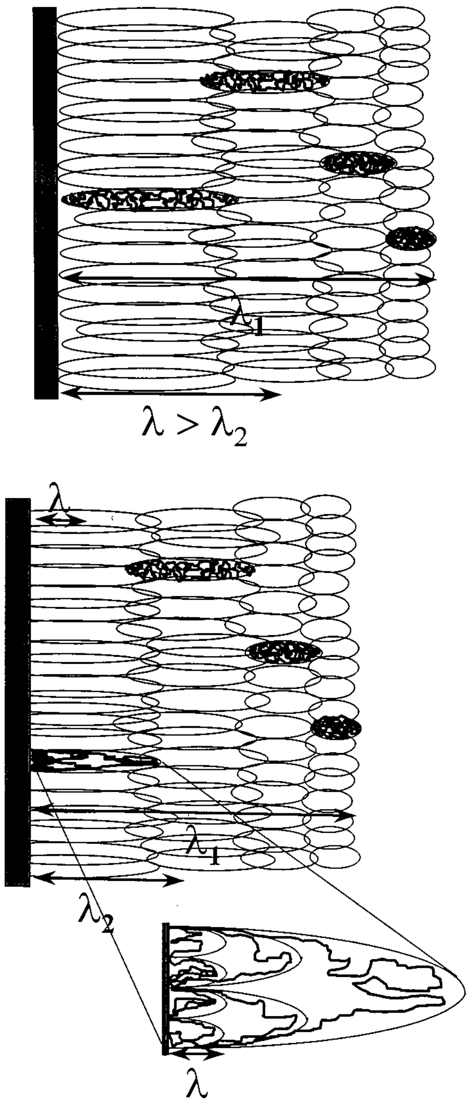

Figure 3. Schematic sketch of the configurations of polyampholyte chains in the adsorbed layers. (a) Multilayer of stretched chains. (b) Self-similar stretched pseudobrush at distances from the surface $z < \lambda_2$ and multilayer of stretched chains at $\lambda_2 < z < \lambda_1$.

$$U_{\text{pol}}(z)/kT \approx -c(z)\,(af/z)^{2/3} \tag{3.12}$$

The balance of this polarization energy density and the three-body repulsion leads to the equilibrium density profile (see Figure 2)

$$c(z) \approx a^{-3}(af/z)^{1/3} \tag{3.13}$$

Closer to the wall (for $z < \lambda$), the density $c(z)$ is almost uniform and saturates at $a^{-3}(af/\lambda)^{1/3}$. The density profile $c(z)$ in the whole interval $z < \lambda_2$ can be written as

$$c(z) \approx a^{-3}\left(\frac{af}{\lambda + z}\right)^{1/3} \tag{3.14}$$

At length scales larger than λ_2, the density has the same hyperbolic profile as that described in the previous section for multilayers of stretched chains (eq 3.7). The density profile in the adsorbed layer is sketched in Figure 2. The polymer excess in this regime is

$$\Gamma \approx a^{-2}\sqrt{fN}\,\ln\,(fN) \tag{3.15}$$

For example, for $N = 500$, $f = 0.02$, $l_B = 7$ Å, and the bond length $a = 3$ Å, the self-similar stretched pseudobrush has a thickness on the order of $\lambda_2 \approx 120$ Å, which is still larger than the chain size $R_0 \approx 70$ Å, and the surface excess $\Gamma{\approx}7a^{-2}$.

3.4. Saturated Self-Similar Stretched Pseudobrush ($\sigma > \sigma_3$). In the case of a very high surface charge density ($\sigma > \sigma_3 \approx f^{1/2}/al_B$), the Gouy–Chapman length λ is smaller than the root-mean-square distance between charged monomers $af^{-1/2}$. The size of a chain in the first adsorbed layer is still λ_2, but these chains are self-similarly stretched on all length scales between the distance between charges $af^{-1/2}$ and λ_2. In a layer of thickness $af^{-1/2}$ near the wall, the monomer density is constant and is proportional to $c \approx a^{-3}f^{1/2}$. At a distance scale between λ_2 and λ_1, we still expect a multibrush of stretched chains. The concentration profile is plotted in Figure 2.

In our analysis above, we have ignored electrostatic interactions between adsorbed polyampholytes. The range of parameters for which this approximation is valid is discussed in Appendix A.

4. Adsorption of Charged Polyampholytes on a Similarly Charged Surface

The adsorption of a charged polyampholyte ($\Delta f > 0$) depends on the Coulomb interaction between the net charge on the chain

$$\Delta fNe = N(f_+ - f_-)e \tag{4.1.}$$

and the charged surface. If this excess charge on the chain has the same sign as the charges of the surface, the Coulomb repulsion may inhibit adsorption. The chain feels logarithmic repulsive potential when it approaches the surface.[38] Ignoring the logarithmic dependence of the repulsive energy $W^{\rm el}_{\rm rep}$ between the net charge on the chain and the charged surface, one can approximate the repulsive energy per chain by

$$\frac{W^{\rm el}_{\rm rep}(z)}{kT} \approx N\Delta f \tag{4.2}$$

Due to this repulsive interaction between polymers and the surface, the adsorption will stop at distances where this repulsion is stronger than the polarization-induced attraction.

4.1. Multilayer of Stretched Chains ($\sigma_1 < \sigma < \sigma_2$). For a multilayer of stretched chains the repulsion (eq 4.2) is stronger than the polarization-induced attraction (eq 2.11) at distances larger than (see Figure 4)

$$z_{\rm cut} \approx \lambda_1/\sqrt{\Delta fN} \tag{4.3}$$

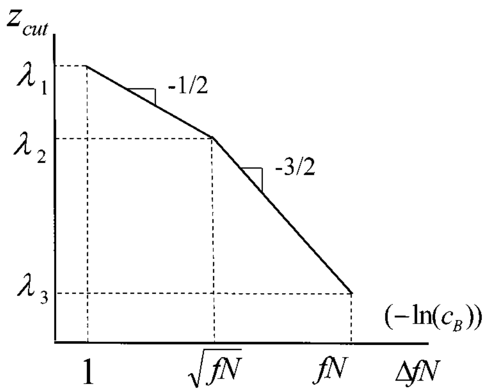

Figure 4. Dependence of the thickness $z_{\rm cut}$ of the adsorbed layer on the chain charge asymmetry ΔfN (or of the logarithm of bulk polymer concentration $-\ln c_B$). Logarithmic scales.

The thickness of the adsorbed layer is $(\Delta fN)^{1/2}$ times smaller than the thickness λ_1 for symmetric polyampholytes. Chains do not adsorb at all if this thickness $z_{\rm cut}$ becomes smaller than the Gouy–Chapman length λ. For charged polyampholytes, the onset of adsorption is shifted from σ_1 (for zero net charge) to a higher value

$$\sigma_{\rm ads} \approx \sqrt{\Delta fN}\sigma_1 \tag{4.4}$$

as sketched in Figure 5. The surface coverage Γ decreases logarithmically with increasing charge asymmetry

$$\Gamma \approx (\sqrt{fN}/a^2)\ln\left(\frac{\lambda_1}{\lambda\sqrt{\Delta fN}}\right) \tag{4.5}$$

(see Appendix B for details).

4.2. Self-Similar Stretched Pseudobrush ($\sigma > \sigma_2$). In a self-similar stretched pseudobrush regime ($\sigma_2 < \sigma < \sigma_3$), the electrostatic repulsion between polyampholytes and the surface first affects adsorption at distances $z > \lambda_2$. The cutoff distance $z_{\rm cut}$ in this case is given by eq 4.3 because at these distances adsorbed polyampholytes form multilayers of stretched chains. The cutoff distance $z_{\rm cut}$ becomes on the order of λ_2 at charge asymmetries Δf on the order of $(f/N)^{1/2}$. For larger charge asymmetries ($\Delta f > (f/N)^{1/2}$), the self-similar carpet is perturbed. The chains fold into a layer of thickness $z_{\rm cut}$. The attractive polarization energy density (eq 3.12) inside the carpet ($z < \lambda_2$) becomes on the same order of magnitude as the repulsive energy density $kTc(z)\Delta f$ at the distance (see Figure 4)

$$z_{\rm cut} \approx af/\Delta f^{\,3/2} \tag{4.6}$$

As we increase the charge on the chain (of the same sign as the surface) in $z_{\rm cut} < \lambda_2$ regime, the chain adsorbs flatter to the surface. In this regime, the layer completely desorbs as soon as the cutoff distance $z_{\rm cut}$ becomes smaller than the Gouy–Chapman length λ. This leads to the adsorption/desorption threshold at surface charge densities (see Figure 5)

$$\sigma_{\rm ads} \approx \frac{\Delta f^{\,3/2}}{l_B af} \tag{4.7}$$

In this regime, the surface coverage is inversely proportional to the charge asymmetry Δf (see Appendix B for more details)

$$\Gamma \approx a^{-2}f/\Delta f \tag{4.8}$$

Analysis similar to that presented above can be done for a surface charge density σ higher than σ_3 with chains forming a saturated self-similar stretched pseudobrush starting from the distance between charges $z \approx a/f^{1/2}$. In this regime, the chains desorb when the charge asymmetry Δf reaches the value f (see Figure 5).

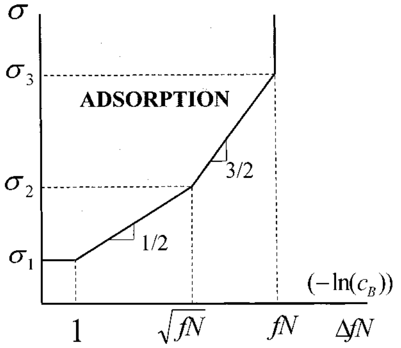

Figure 5. Adsorption diagram of polyampholyte chains as a function of the surface charge density σ and the chain charge asymmetry ΔfN (or of the logarithm of bulk polymer concentration $-\ln c_B$). Adsorption region is shaded. Logarithmic scales.

Detailed calculations of the equilibrium density profile and the surface coverage for different regimes discussed in this section are given in Appendix B.

5. Unsaturated Adsorption

The effect of bulk concentration of polyampholyte solution on adsorption/desorption behavior resembles the effect of charge asymmetry. In fact, the variation in bulk concentration corresponds to the change in the chain chemical potential $\mu_B = kT \ln c_B$ that effectively acts as a constant repulsive potential (mathematically, it corresponds to replacing $N\Delta f$ by $-\ln c_B$ in all equations of the previous section). Therefore, we expect the same unsaturated adsorption regimes to be observed by changing the bulk concentration of polyampholytes. Figures 4 and 5 can be replotted in terms of bulk polymer concentration.

6. Effects of Added Salt

In the previous sections, we have discussed various regimes of multichain polyampholyte adsorption from salt-free solutions. The addition of univalent salt at concentration c^s to a solution leads to the screening of electrostatic interactions at the Debye screening length

$$r_D = (8\pi l_B c^s)^{-1/2} \tag{6.1}$$

In Figure 6, we sketch the adsorption diagram of symmetric polyampholytes with an equal fraction of positively and negatively charged monomers $f_+ = f_- = f/2$.

Low Salt Concentrations. In the absence of added salt, the onset of adsorption occurs at surface charge densities on the order of σ_1. At surface charge densities higher than the onset value (for $\sigma > \sigma_1$), the thickness of the adsorbed layer is λ_1 (eq 2.9). As long as the Debye screening length r_D is larger than λ_1, there is very little effect of added salt on the polyampholyte adsorption. The Debye screening length decreases with increasing salt concentration. The adsorbed layer starts to "feel" the presence of the salt when the Debye screening length r_D becomes on the order of λ_1. This occurs at a salt concentration $c^s_{\lambda_1}$

$$c^s_{\lambda_1} \approx \frac{1}{l_B \lambda_1^2} \approx \frac{1}{l_B a^2 f N^2} \tag{6.2}$$

At higher salt concentrations ($c^s > c^s_{\lambda_1}$), the thickness of the adsorbed layer is limited by the Debye screening length because the electric field created by the surface is screened by the salt ions and is too weak to polarize polyampholyte chains on larger length scales. On smaller length scales ($z < r_D$), the adsorbed layer is almost unperturbed by the presence of salt. The "multilayer of stretched chains regime" (for $\sigma_1 < \sigma < \sigma_2$) stops at the salt concentration at which the Debye screening length r_D is equal to the chain size in the first adsorbed layer $R_z(0) \approx R_0\lambda_1/\lambda$ (see eq 2.7), and the system crosses over to the intermediate salt concentration regime with a single adsorbed layer of chains. The corresponding crossover salt concentration

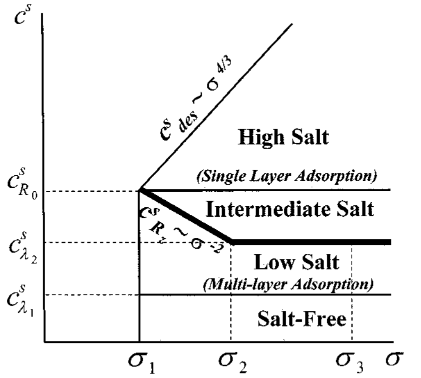

Figure 6. Adsorption diagram of polyampholyte chains in a salt solution as a function of surface charge density σ and salt concentration c^s. Adsorption region is shaded. The thick solid line separates multilayer and single layer adsorption regions. Logarithmic scales.

$$c^s_{R_z} \approx \frac{1}{l_B R_0^2}\left(\frac{\lambda}{\lambda_1}\right)^2 \approx \frac{1}{l_B a^2 N}\left(\frac{\sigma_1}{\sigma}\right)^2 \quad \text{for } \sigma_1 < \sigma < \sigma_2 \tag{6.3}$$

is shown in Figure 6. In the "self-similar stretched pseudobrush" regimes ($\sigma > \sigma_2$), the size of the chain in the first monolayer near the surface is $R_z(0) \approx \lambda_2$. The Debye screening length r_D is equal to λ_2 at the salt concentration at which the multibrush of stretched chains disappears and adsorbed chains are confined to a single layer is

$$c^s_{\lambda_2} \approx \frac{1}{l_B R_0 \lambda_1} \approx \frac{1}{l_B a^2 N \sqrt{fN}} \tag{6.4}$$

Intermediate Salt Concentrations. At intermediate salt concentrations ($c^s_{R_z} < c^s < c^s_{R_0}$ for $\sigma_1 < \sigma < \sigma_2$ or $c^s_{\lambda_2} < c^s < c^s_{R_0}$ for $\sigma > \sigma_2$, where salt concentration $c^s_{R_0}$ is defined in eq 6.10 below), there is only one remaining layer of adsorbed chains. The salt compresses the remaining monolayer of the adsorbed chains. In this intermediate range of salt concentrations, the thickness of this monolayer is on the order the Debye screening length r_D.

In the case of $\lambda < r_D$ (for higher surface charge densities), the sections of the chains are uniformly stretched on the length scales on the order of the Gouy–Chapman length λ and form a self-similar stretched pseudobrush on the length scale $\lambda < z < r_D$ (see section 3). Integrating this density profile, one obtains the adsorbed amount

$$\Gamma \approx a^{-2}(fr_D{}^2/a^2)^{1/3} \tag{6.5}$$

At lower surface charge densities or higher salt concentrations (for $\lambda > r_D$), the adsorbed chains are uniformly stretched inside the monolayer of thickness r_D. The number of monomers g in each subchain that stretches to the size r_D can be estimated by considering this subsection as an independent chain. The balance between the stretching energy of this subchain kTr_D^2/a^2g and its polarization energy $kT(fg)^{1/2}\sigma l_B r_D$ gives the number of monomers in the subchain

$$g \propto (f^{-1/2}r_D\lambda/a^2)^{2/3} \tag{6.6}$$

These chain sections of g monomers have induced dipole moments $d(g) \propto er_D(fg)^{1/2}$. The polarization-induced attractive interaction between a section of polyampholyte chain with g monomers and the surface is

$$\frac{W_g}{kT} \approx -\frac{Ed(g)}{kT} \approx -\left(\frac{f^{1/2}r_D^2}{a\lambda}\right)^{2/3} \tag{6.7}$$

At equilibrium, the polarization energy of a section of a chain in the adsorbed layer W_g is balanced by the three-body repulsion $kTg(ca^3)^2$ which gives the average monomer density in the adsorbed layer

$$c \approx a^{-3}(fr_D a/\lambda^2)^{1/3} \tag{6.8}$$

and the surface coverage

$$\Gamma \approx a^{-2}\left(\frac{f^{1/2}r_D^2}{a\lambda}\right)^{2/3} \tag{6.9}$$

The intermediate salt regime continues until the Debye screening length r_D is larger than the Gaussian size of the chain R_0 (for salt concentrations $c^s < c^s_{R_0}$).

High Salt Concentrations. At all concentrations c^s higher than

$$c^s_{R_0} \approx \frac{1}{l_B R_0^2} \approx \frac{1}{l_B a^2 N} \tag{6.10}$$

the Debye screening length r_D is smaller than the Gaussian size of the chain R_0. In this high salt concentration regime, adsorption of the polyampholyte chains is of the short-range type (similar to that for uncharged polymers). Only the sections of chains inside the Debye screening length r_D interact with the surface. The equilibrium density profile in this layer ($z < r_D$) is determined by the balance between the polarization-induced attraction and the three-body repulsion (see section 3). At distances z from the charged surface larger than the Debye screening length r_D, the chains form a de Gennes self-similar carpet with the polymer density hyperbolically decaying from the surface [$c(z) \approx z^{-1}$ in θ-solvent] up to the Gaussian chain size R_0. The thickness of the adsorbed layer is on the order of the Gaussian size R_0 of the polyampholyte chain.

The desorption of polyampholytes occurs at salt concentrations at which the attractive energy between the plane and the chain is less than the thermal energy kT. At the adsorption/desorption threshold, the chain is almost undeformed. To estimate the effective attraction of a chain to the charged surface, one can view a polyampholyte chain as a chain of blobs of size r_D. The size of the section r_D is related to the number of monomers in it by the Gaussian statistics, $g \approx (r_D/a)^2$. The attraction energy between the surface and the section of size r_D is calculated from the polarization energy of the section with polarizability d^2/kT, where the dipole moment is $d \approx (fg)^{1/2}er_D$. The attractive energy per section of g monomers is $-kT\,fg(\sigma l_B r_D)^2$. The attractive energy per chain

$$W_{\mathrm{att}}^{\mathrm{ch}} \approx -kTf(\sigma l_B r_D)^2 fNr_D/R_0 \tag{6.11}$$

is proportional to the number of contacts of N/g blobs with the adsorbing surface $(N/g)^{1/2}$ times the energy per contact $-kT\,fg(\sigma l_B r_D)^2$. This attractive energy per chain is on the order of the thermal energy kT, and chains desorb at salt concentration

$$c^s_{\mathrm{des}} \approx \frac{(fN)^{2/3}}{l_B\lambda^{4/3}R_0^{2/3}} \tag{6.12}$$

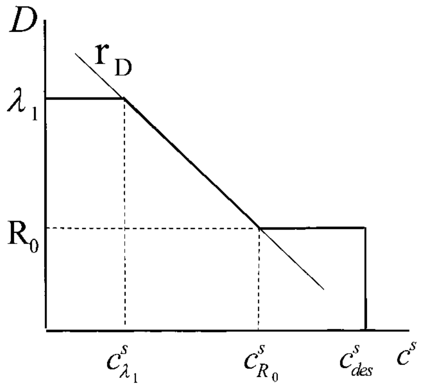

Figure 7. Dependence of the thickness of the adsorbed layer D on the salt concentration c^s. Logarithmic scales.

However, the above estimate of the attractive interaction as a polarization of the section of a chain containing g monomers is correct as long as there is more than one charge per Debye volume ($g > f^{-1}$). If the opposite inequality holds $g < f^{-1}$, close to the charged surface ($z < a/f^{1/2}$), we can neglect the effect of connectivity of the charged monomers into a chain and view them as an electrolyte solution with average charge density $c_i \approx fN/R_0^3$. The density profile of the charged monomers on these length scales is well-described by the Boltzmann distribution in the external electrostatic potential $\psi(z)$ with the local charge concentration

$$c_{+/-}(z) \approx c_i \exp[\pm e\psi(z)/kT] \tag{6.13}$$

The attractive interaction between the polyampholyte chain and the charged surface can be estimated as

$$\frac{|W_{\mathrm{att}}|}{kT} \approx R_0^2\int_0^{r_D} [c_+(z) - c_-(z)]\frac{e\psi(z)}{kT}\,dz \approx \frac{fNr_D}{R_0}\left(\frac{r_D}{\lambda}\right)^2 \tag{6.14}$$

The chain desorbs when this attractive interaction becomes on the order of the thermal energy kT. Rewriting this condition in terms of the salt concentration, one recovers eq 6.12.

In Figure 7 we present the thickness of the adsorbed layer as a function of the salt concentration c^s. The thickness of the adsorbed layer does not change as long as the Debye screening length is larger than the marginal Gouy−Chapman length λ_1. For higher salt concentrations ($c^s > c_{\lambda_1}$), the thickness of the adsorbed layer is on the order of the Debye screening length and decreases with increasing salt concentration. This is due to the screening of the long-range polarization-induced attractive interaction between polyampholytes and the charged surface by salt ions beyond the Debye screening length. The thickness of the adsorbed layer saturates when the Debye screening length becomes smaller than the Gaussian chain size R_0. The chains desorb at salt concentrations for which the adsorption energy per chain becomes smaller than the thermal energy kT. For example, for an aqueous solution of polyampholytes with degree of polymerization $N = 500$, the fraction of the charged monomers $f = 0.02$, and the bond length $a = 3$ Å, the crossover salt concentrations between different regimes are $c^{\mathrm{s}}_{\lambda_1} \approx 2 \times 10^{-4}$ M, $c^{\mathrm{s}}_{\lambda_2} \approx 6 \times 10^{-4}$ M, $c^{\mathrm{s}}_{R_0} \approx 2 \times 10^{-3}$ M; $c^{\mathrm{s}}_{\mathrm{des}} \approx 10^{-1}$ M for the number density of surface charges $\sigma \approx 10^{-2}$ Å^{-2}.

7. Polyampholyte Adsorption in a Good Solvent

7.1. Adsorption of a Single Chain. A polyampholyte chain in a good solvent for its uncharged backbone is swollen due to the two-body repulsion. (We are still restricting our consideration to the case of fluctuation-induced self-attraction of chain weaker than the thermal energy kT). In the absence of an external electric field, the chain size is

$$R_{\mathrm{F}} \approx aN^{3/5} \tag{7.1}$$

If this chain is stretched by an external field into a string of Pincus blobs of size D_{P} with the number of monomers g_{P} in each ($D_{\mathrm{P}} = ag_{\mathrm{P}}^{3/5}$), the elastic energy of this deformation is the thermal energy kT times the number of blobs R_z/D_{P}. The elastic energy of a stretched polyampholyte chain is obtained from the relation between the blob size and the number of monomers in it

$$W_{\mathrm{elas}}/kT \approx (R_z/R_{\mathrm{F}})^{5/2} \tag{7.2}$$

In the external electric field created by a charged surface, this elastic energy must be equilibrated by the polarization energy of the chain

$$W^{\mathrm{ch}}_{\mathrm{pol}}(z)/kT \approx -\sqrt{fN}R_z/(z + \lambda) \tag{7.3}$$

which yields

$$R_z \approx aN^{3/5}\left(\frac{aN^{3/5}\sqrt{fN}}{z + \lambda}\right)^{2/3} \approx R_{\mathrm{F}}\left(\frac{\lambda_1}{z + \lambda}\right)^{2/3} \quad \text{for } z + \lambda < \lambda_1 \tag{7.4}$$

where

$$\lambda_1 \approx R_{\mathrm{F}}\sqrt{fN} = 1/l_{\mathrm{B}}\sigma_1 \tag{7.5}$$

is the deformation threshold. For lower surface charge densities ($\sigma < \sigma_1$), the chain conformation is not perturbed by the external electric field. For higher surface charge densities ($\sigma_2 > \sigma > \sigma_1$), the size of the chain close to the surface ($z < \lambda$) grows as $^2/_3$ power of the surface charged density. Recall that in a θ-solvent the chain size grows linearly with the surface charge density (eq 2.7). The Gouy–Chapman length λ becomes comparable with the size of the chain R_z in direction normal to the surface at charge density

$$\sigma_2 \approx \frac{1}{al_{\mathrm{B}}f^{1/5}N^{4/5}} = \frac{1}{l_{\mathrm{B}}R_{\mathrm{F}}(fN)^{1/5}} \tag{7.6}$$

Table 1. Boundaries between Different Regimes of Chain Adsorption in Two Different Solvents for the Uncharged Backbone (θ and good)

	θ-solvent	good solvent
σ_1	$\dfrac{1}{l_{\mathrm{B}}R_0\sqrt{fN}}$	$\dfrac{1}{l_{\mathrm{B}}R_{\mathrm{F}}\sqrt{fN}}$
σ_2	$\dfrac{1}{l_{\mathrm{B}}R_0(fN)^{1/4}}$	$\dfrac{1}{l_{\mathrm{B}}R_{\mathrm{F}}(fN)^{1/5}}$
σ_3	$\dfrac{f^{1/2}}{al_{\mathrm{B}}}$	$\dfrac{f^{3/5}}{al_{\mathrm{B}}}$
λ_1	$R_0\sqrt{fN}$	$R_{\mathrm{F}}\sqrt{fN}$
λ_2	$R_0\,(fN)^{1/4}$	$R_{\mathrm{F}}\,(fN)^{1/5}$
λ_3	$af^{-1/2}$	$af^{-3/5}$

For higher surface charge densities ($\sigma > \sigma_2$), the chain is divided into stretched subsections of size λ, and each is localized in the vicinity of the surface (see Figure 1b). The number of monomers g in each subsection that stretches to the size λ can be found by considering this subsection as an independent chain.

$$kT\,\frac{\lambda^{5/2}}{g^{3/2}a^{5/2}} \approx kT\sqrt{fg}\sigma\lambda l_{\mathrm{B}} \tag{7.7}$$

Using the relation between the Gouy–Chapman length λ and the surface charge density $\sigma \approx 1/l_{\mathrm{B}}\lambda$, one can write the number of monomers in the subchain as

$$g \propto f^{-1/4}(\lambda/a)^{5/4} \tag{7.8}$$

In this regime, the whole chain is localized inside the layer of size λ. The confinement of the chain saturates when the surface charge density σ becomes on the order of

$$\sigma_3 \approx \frac{f^{3/5}}{al_{\mathrm{B}}} \tag{7.9}$$

and the Gouy–Chapman length λ_3 is on the order of the distance between charged monomers

$$\lambda_3 \approx af^{-3/5} \tag{7.10}$$

7.2. Multichain Adsorption. The calculation of the properties of multichain adsorption in a good solvent for the polyampholyte backbone can be done analogously to the similar calculations for a θ-solvent (see section 3) with two modifications (see Table 1).

(i) The elastic energy of the polyampholyte chains in a good solvent (see eq 7.2) differs from that in a θ-solvent.

(ii) The density in the adsorbed layer is stabilized by two-body (rather than three-body) monomer-monomer repulsion. Polymers in a good solvent are strongly fluctuating objects and the mean-field theory used in section 3 has to be modified to take these fluctuations into account. If the chains are compressed to concentration c, the compression is felt only on large length scales, and the semidilute solution can be represented as a solution of space-filling correlation blobs of size $\xi \approx a(ca^3)^{-3/4}$.[39] The excluded-volume interactions in this solution are on the order of the thermal energy kT per correlation blob. Thus, the stabilizing energy density term in a good solvent is[39]

$$U_{\mathrm{rep}}(z)/kT \approx c(z)[c(z)a^3]^{5/4} \tag{7.11}$$

The calculations are briefly discussed below and the results are summarized in Table 2.

Table 2. Regimes of Adsorption: Multilayer of Stretched Chains ($\sigma_1 < \sigma < \sigma_2$), Self-Similar Stretched Pseudobrush I ($\sigma_2 < \sigma < \sigma_3$), and Saturated Self-Similar Stretched Pseudobrush ($\sigma_3 < \sigma$) in Two Different Solvents (θ and good) for the Unchanged Backbone[a]

σ		θ-solvent	good solvent
$\sigma_1 < \sigma < \sigma_2$	$\phi(z)$	$N^{-1/2}\left(\frac{\lambda_1}{\lambda + z}\right)$	$N^{-4/5}\left(\frac{\lambda_1}{\lambda + z}\right)^{4/3}$
	γ	$\sqrt{fN}\ \ln(\sigma/\sigma_1)$	$a^{-1}\ N^{-4/5}\lambda_1^{4/3}\lambda^{-1/3}$
	z_{cut}	$\lambda_1/\sqrt{\Delta fN}$	$\lambda_1/(\Delta fN)^{3/5}$
$\sigma_2 < \sigma < \sigma_3$	$\phi(z)$	$\begin{cases}\left(\frac{fa}{\lambda + z}\right)^{1/3}, z < \lambda_2 \\ \frac{\lambda_1}{N^{1/2}z}, \lambda_2 < z < \lambda_1\end{cases}$	$\begin{cases}\sqrt{\frac{fa}{\lambda + z}}, z < \lambda_2 \\ N^{-4/5}(\lambda_1/z)^{4/3}, \lambda_2 < z < \lambda_1\end{cases}$
	γ	$\sqrt{fN}\ \ln(fN)$	$N^{-1/5}(fN)^{3/5}$
	z_{cut}	$\begin{cases}\lambda_1/\sqrt{\Delta fN}, \Delta f < \sqrt{f/N} \\ af/\Delta f^{\,3/2}, \sqrt{f/N} < \Delta f < (af/\lambda)^{2/3}\end{cases}$	$\begin{cases}\lambda_1/(\Delta fN)^{3/5}, \Delta f < \sqrt{f/N} \\ af/\Delta f^{\,8/5}, \sqrt{f/N} < \Delta f < (af/\lambda)^{5/8}\end{cases}$
$\sigma_3 < \sigma$	$\phi(z)$	$\begin{cases}\left(\frac{fa}{\lambda_3 + z}\right)^{1/3}, z < \lambda_2 \\ \frac{\lambda_1}{N^{1/2}z}, \lambda_2 < z < \lambda_1\end{cases}$	$\begin{cases}\sqrt{\frac{fa}{\lambda_3 + z}}, z < \lambda_2 \\ N^{-4/5}\ (\lambda_1/z)^{4/3}, \lambda_2 < z < \lambda_1\end{cases}$
	γ	$\sqrt{fN}\ \ln(fN)$	$N^{-1/5}(fN)^{3/5}$
	z_{cut}	$\begin{cases}\lambda_1/\sqrt{\Delta fN}, \Delta f < \sqrt{f/N} \\ af/\Delta f^{\,3/2}, \sqrt{f/N} < \Delta f < f\end{cases}$	$\begin{cases}\lambda_1/(\Delta fN)^{3/5}, \Delta f < \sqrt{f/N} \\ af/\Delta f^{\,8/5}, \sqrt{f/N} < \Delta f < f\end{cases}$

[a] Polymer density profile $\phi(z) = c(z)a^3$, the dimensionless surface coverage $\gamma = \Gamma a^2$, z_{cut} thickness of the adsorbed layer for asymmetric polyampholytes ($\Delta f = f_+ - f_-$).

Multilayer of stretched chains regime ($\sigma_1 < \sigma < \sigma_2$). The balance between the polarization-induced attraction

$$\frac{W_{\mathrm{pol}}^{\mathrm{ch}}(z)}{kT} \approx -\left(\frac{\lambda_1}{z + \lambda}\right)^{5/3} \tag{7.12}$$

and the two-body repulsion

$$W_{\mathrm{rep}}(z)/kT \approx N[c(z)a^3]^{5/4} \tag{7.13}$$

results in the equilibrium density profile

$$c(z) \approx c^*_{\mathrm{good}}\left(\frac{\lambda_1}{z + \lambda}\right)^{4/3} \tag{7.14}$$

where

$$c^*_{\mathrm{good}} \approx a^{-3}N^{-4/5} \tag{7.15}$$

is the overlap concentration in the good solvent. At distances larger than the Gouy–Chapman length λ, we expect the density profile $c(z) \approx (\lambda_1/z)^{4/3}$. Close to the surface (for $z < \lambda$), the density saturates at $c^*_{\mathrm{good}}\lambda_1/\lambda$ (see dashed line in Figure 8). The crossover from a semidilute to a dilute regime of the adsorbed chains occurs at the distance $z \approx \lambda_1$. Integrating this density profile between 0 and λ_1, one can get the excess adsorbed amount Γ per unit surface area

$$\Gamma \approx (N/R_{\mathrm{F}}^{\;2})\sqrt{fN}(\lambda_1/\lambda)^{1/3} \tag{7.16}$$

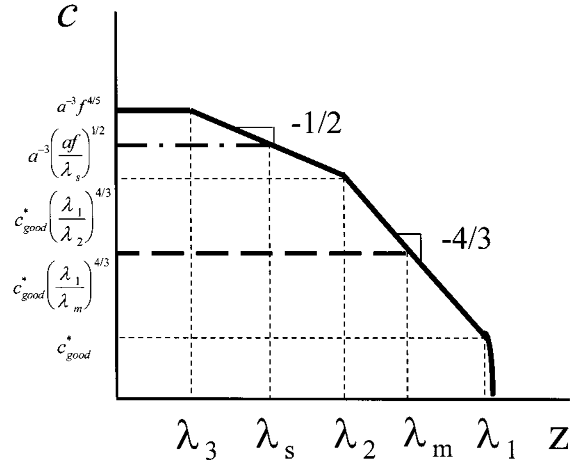

Figure 8. Polymer density profile in the adsorbed layers in a good solvent for three different regimes: the multilayer of stretched chains for the Gouy–Chapman length $\lambda = \lambda_{\mathrm{m}}$ (dashed line), the self-similar stretched pseudobrush for the Gouy–Chapman length $\lambda = \lambda_{\mathrm{s}}$ (dashed-dotted line), the saturated self-similar stretched pseudobrush (solid line). Logarithmic scales.

Self-Similar Stretched Pseudobrush Regime ($\sigma_2 < \sigma < \sigma_3$). For $z < \lambda$, the external electric field $E(z) \approx e\sigma/\epsilon$ is almost constant. The chains are uniformly stretched up to length scales on the order of the Gouy–Chapman length λ. The number of monomers in a layer of thickness λ is given by eq 7.8. At the length scales $z > \lambda$, the electric field $E(z) \approx e/\epsilon l_{\mathrm{B}}z$ is inversely proportional to the distance z from the surface. The relation between the strand length and the number of monomers $g(z)$ in it is

$$z \approx af^{\,1/5}g(z)^{4/5} \tag{7.17}$$

In the length scale range $\lambda < z < \lambda_2$, there exists a self-similar pseudobrush of stretched strands of chains. The polarization energy density $U_{\mathrm{pol}}(z)$ of the polyampholytes at distance z from the surface is equal to the concentration of the strands $c(z)/g(z)$ containing $g(z)$ monomers times the polarization energy per strand $[fg(z)]^{1/2}$

$$\frac{U_{\rm pol}(z)}{kT} \approx -c(z)\left(\frac{af}{\lambda + z}\right)^{5/8} \tag{7.18}$$

The balance of this polarization energy density with two-body repulsion leads to the equilibrium density profile

$$c(z) \approx a^{-3}\left(\frac{af}{\lambda + z}\right)^{1/2} \tag{7.19}$$

Closer to the wall (for $z < \lambda$), the density $c(z)$ is almost uniform and saturates at $a^{-3}(af/\lambda)^{1/2}$. At length scales larger than λ_2, the density has the same profile as described in the previous section for multilayers of stretched chains [$c(z) \sim (\lambda_1/z)^{4/3}$; see dashed−dotted line in Figure 8]. The surface coverage in this regime is

$$\Gamma \approx (N/R_{\rm F}^2)(fN)^{3/5} \approx a^{-2}f^{\,3/5}N^{2/5} \tag{7.20}$$

Saturated Self-Similar Stretched Pseudobrush Regime ($\sigma_3 < \sigma$). In the case of very high surface charge density ($\sigma > \sigma_3 \approx f^{3/5}/al_{\rm B}$), the Gouy−Chapman length λ is smaller than the root mean-square distance between the charged monomers $\lambda_3 \approx af^{-3/5}$. The structure of the adsorbed layer is similar to that in the self-similar stretched pseudobrush regime on all length scales between λ_3 and λ_2. In a layer of thickness λ_3 near the wall, the monomer density is constant and is proportional to $c \approx a^{-3}f^{4/5}$ (see solid line in Figure 8).

8. Discussion

We have presented a scaling analysis of multichain polyampholyte adsorption on charged surfaces. The polymer equilibrium density profile in the adsorbed layer is determined by the balance of the polarization-induced attraction of the chains to the charged surface and the monomeric repulsion. For the symmetric polyampholyte chain with an equal number of positively and negatively charged monomers, we identify three different regimes in chain adsorption.

8.1. Multilayer of Stretched Chains ($\sigma_1 < \sigma < \sigma_2$). In this regime, polyampholyte chains are polarized and stretched by the external electric field. At distances $\lambda < z < \lambda_1$ the polymer density decays as $c \approx z^{-1}$ in a θ-solvent and as $c \approx z^{-4/3}$ in a good solvent. The adsorption stops at length scales on the order of λ_1 at which the external electric field created by the surface becomes too weak to polarize the chains. The polymer excess grows logarithmically with the surface charge density σ in a θ -solvent and as $\sigma^{1/3}$ in a good solvent.

8.2. Self-Similar Stretched Pseudobrush ($\sigma_2 < \sigma < \sigma_3$). Close to the surface at distances $z < \lambda$, the electric field created by the charged surface is almost constant. The sections of the chains are uniformly stretched up to length scales on the order of the Gouy−Chapman length λ. On length scales $\lambda < z < \lambda_2$, the polyampholytes are stretched into a self-similar pseudobrush with polymer density decaying as $z^{-1/3}$ in a θ-solvent and as $z^{-1/2}$ in a good solvent. The size of the polymer chains in the first adsorbed layer is on the order of λ_2. At length scales larger than λ_2, the polymer density has the same profile as in the multilayer of stretched chains.

8.3. Saturated Self-Similar Stretched Pseudobrush ($\sigma > \sigma_3$). For these very high surface charge densities, the Gouy−Chapman length λ is smaller than the mean-square distance between charged monomers. Near the wall, inside a layer of thickness λ_3, the strands of a chain are almost unperturbed by the external electric field and the monomer density is uniform. On length scales between λ_3 and λ_2, adsorbed polyampholytes form a self-similar pseudobrush as defined above. In this regime, the surface coverage reaches its maximum value $\Gamma \approx a^{-2}(fN)^{1/2}\ln(fN)$ in a θ-solvent, and $\Gamma \approx a^{-2}f^{3/5}N^{2/5}$ in a good solvent and becomes independent of the surface charge density.

We have shown that the asymmetric polyampholytes for which the net charge has the same sign as the charge on the surface can still adsorb. For these polyampholytes, the adsorption stops at those distances from the surface at which the Coulomb repulsion between excess charges and the surface becomes stronger than the polarization-induced attraction. The thickness of the adsorbed layer and the surface coverage decreases with increasing charge asymmetry Δf.

The presence of the salt results in the screening of the surface potential at distances larger than the Debye screening length $r_{\rm D}$. The thickness of the adsorbed layer does not change as long as the Debye screening length is larger than the marginal Gouy−Chapman length λ_1. At higher salt concentrations ($c_{\rm s} > c_{\lambda_1}$), the thickness of the adsorbed layer is on the order of the Debye screening length and decreases with increasing salt concentration. This is due to the screening of the long-range polarization-induced attractive interactions between polyampholytes and the charged surface beyond the Debye screening length. The thickness of the adsorbed layer saturates when the Debye screening length becomes smaller than the Gaussian chain size R_0. The chains desorb at salt concentrations for which the adsorption energy per chain becomes lower than the thermal energy kT.

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Appendix

A. Electrostatic Interactions between Chains. In the present paper, we ignore the effects of charged monomers on the electric field. Thus, we ignore the electrostatic interactions between chains. These interactions become important when the polarization energy density of the chains in the adsorbed layer approaches the self-energy density of the electric field created by the surface

$$U_{\rm s-e}(z) \approx kT\,\sigma\lambda/(z + \lambda)^2 \tag{8.1}$$

For a θ-solvent, the polarization energy density in the multilayer of stretched chains regime (see section 3) is

$$|U_{\rm pol}(z)| \approx kT\,\frac{1}{R_0^3}\left(\frac{\lambda_1}{z + \lambda}\right)^3 \tag{8.2}$$

This polarization energy is smaller than the self-energy of the electric field as long as

$$\sigma < \sigma_{\rm b} \approx 1/l_{\rm B}^2(fN)^{3/2} \tag{8.3}$$

To ignore the interactions between polyampholyte chains in all regimes, $\sigma_{\rm b}$ has to be larger than σ_2. This implies that the fraction of the charged monomers f on the chain has to be smaller than $u^{-4/5}N^{-3/5}$, where $u = l_B/a$ is the ratio of the Bjerrum length to the bond size. The polarization energy density in the self-similar pseudobrush regime is

$$|U_{\mathrm{pol}}(z)| \approx kT\, f/a^2\lambda \quad \text{for } z < \lambda \tag{8.4}$$

and in the saturated self-similar pseudobrush regime is

$$|U_{\mathrm{pol}}(z)| \approx kT\, f^{3/2}/a^3 \quad \text{for } z < af^{-1/2} \tag{8.5}$$

The comparison of the polarization energy density (eqs 8.4 and 8.5) with the self-energy of the electric field (eq 8.1) gives the following relation between the surface charge density σ and the fraction f of the charged monomers

$$\sigma > f/a^2 \tag{8.6}$$

It easy to show that if

$$f < u^{-4/5}N^{-3/5} \tag{8.7}$$

the effect of the chains polarization on the electric field created by the surface can be ignored in all regimes. For our example of the polyampholyte chain considered in the text ($N = 500$, $f = 0.02$, $l_B = 7$ Å, and the bond length $a = 3$ Å), the fraction of the charged monomers f is close to this boundary $f_b \approx u^{-4/5}N^{-3/5} \approx 0.012$. If the opposite inequality holds $f > u^{-4/5}N^{-3/5}$, the electrostatic interactions between adsorbed chains have to be taken into account. This will result in the renormalization of the local electric field by the adsorbed chains, and one has to optimize simultaneously local electric field, polarization of the polyampholyte chains, and monomer and counterion densities to find the thickness of the adsorbed layer and the equilibrium polymer density profile. The solution of this problem will be presented in a future publication.

B. Adsorption on a Similarly Charged Surface. *Multilayer of Stretched Chains ($\sigma_1 < \sigma < \sigma_2$).* In this range of surface charge densities, the equilibrium density profile in a θ-solvent is determined by the balance between the electrostatic attraction $-(\lambda_1/z+\lambda)^2 + \Delta fN$ and the repulsive interaction due to three-body contacts $Na^6c(z)^2$

$$c(z) \approx c_0^*\sqrt{\left(\frac{\lambda_1}{z+\lambda}\right)^2 - \Delta fN} \tag{8.8}$$

The polymer concentration tends to zero at distances z from the charged surface on the order of $z_{\mathrm{cut}} \approx \lambda_1/(\Delta fN)^{1/2} - \lambda$ [in the case of $\lambda_1/(\Delta fN)^{1/2} > \lambda$, it reduces to $z_{\mathrm{cut}} \approx \lambda_1/(\Delta fN)^{1/2}$ (eq 4.3)]. At this distance, the polarization-induced attraction is on the order of the repulsion. Integrating this density profile between 0 and z_{cut}, one can find the polymer surface excess

$$\Gamma_1(\epsilon) \approx (\sqrt{fN}/a^2)[-\ln(\epsilon) + \ln(1 + \sqrt{1-\epsilon^2}) - \sqrt{1-\epsilon^2}] \tag{8.9}$$

where we have introduced $\epsilon = (\Delta fN)^{1/2}/\lambda_1$. The polymer excess in the case of charged chains decreases logarithmically for $\epsilon < 1$ (eq 4.5]) and as $(1 - \epsilon)^{3/2}$ for $\epsilon \approx 1$ with increasing charge asymmetry ΔfN. The adsorbed layer disappears when the charge asymmetry ΔfN is larger than $(\lambda_1/\lambda)^2$.

Self-Similar Stretched Pseudobrush Regime ($\sigma_2 < \sigma < \sigma_3$). The equilibrium density profile in the perturbed self-similar stretched pseudobrush regime is

$$c(z) \approx \begin{cases} \sqrt{\left(\dfrac{af}{z+\lambda}\right)^{2/3} - \Delta f} & \text{for } 0 < z < \lambda_2 \\ c_0^*\sqrt{(\lambda_1/z)^2 - \Delta fN} & \text{for } \lambda_2 < z < \lambda_1/\sqrt{\Delta fN} \end{cases} \tag{8.10}$$

The polymer surface excess decreases with increasing charge asymmetry as

$$\Gamma \approx (f/a^2\Delta f)\left\{[1 - \Delta f(\lambda/af)^{2/3}]^{3/2} - \left[1 - \Delta f\left(\frac{\lambda_2}{af}\right)^{2/3}\right]^{3/2}\right\} + \Gamma_1(\lambda_2\sqrt{\Delta fN}/\lambda_1) \tag{8.11}$$

for charge asymmetries $\Delta f < (f/N)^{1/2}$ and as

$$\Gamma \approx (f/a^2\Delta f)[1 - \Delta f(\lambda/af)^{2/3}]^{3/2} \tag{8.12}$$

for the interval $(f/N)^{1/2} < \Delta f < (af/\lambda)^{2/3}$. The polyampholytes do not adsorb at all if charge asymmetry is larger than $\Delta f \approx (af/\lambda)^{2/3}$.

Saturated Self-similar Stretched Pseudobrush ($\sigma > \sigma_3$). Analysis similar to that presented above can be carried out for a surface charge density σ higher than σ_3. The final expressions will have a form similar to the one presented in the previous section with the substitution of $\lambda_3 \approx a/(f)^{1/2}$ for λ.

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