4332 *Macromolecules* **1997,** *30,* 4332−4341

Adsorption of a Polyampholyte Chain on a Charged Surface

Andrey V. Dobrynin and Michael Rubinstein*

*Department of Chemistry, The University of North Carolina,
Chapel Hill, North Carolina, 27599-3290*

Jean-François Joanny

Institut Charles Sadron, 6 rue Boussingault, 67083 Strasbourg Cedex, France

Received March 6, 1997; Revised Manuscript Received May 7, 1997⊗

ABSTRACT: We discuss the adsorption of a single polyampholyte chain with degree of polymerization N carrying Nf charges, (Nf_+ positive and Nf_- negative charges) on a charged surface with σ charges per unit area. The adsorption is due to the electrostatic polarization of the polyampholyte chain, which acquires a dipole moment in the surface electric field. Symmetric Gaussian polyampholytes with equal numbers of positive and negative charges adsorb if the surface charge density σ is larger than $(1/al_BN)\cdot(1/f^{1/2})$ (l_B is the Bjerrum length and a is the bond size). Polyampholyte chains carrying a charge of the same sign as the surface can also adsorb if the surface charge is large enough. For a typical asymmetry $|f_- - f_+| \approx (f/N)^{1/2}$, the adsorption threshold is $\sigma > (1/al_BN^{3/4})(1/f^{1/4})$. The effect of the added salt on the adsorption is considered. Finally, we determine the adsorption threshold of a collapsed polyampholyte globule.

1. Introduction

Macromolecules carrying electric charges[1,2] constitute one of the most interesting and least understood areas of polymer physics. Charged polymers are widely used in industry and present in nature. For example, DNA is a polyelectrolyte chain containing negatively charged groups, while proteins are polyampholyte polymers carrying both positive and negative charges. The long-range Coulomb interactions are responsible both for the rich behavior of these polymeric systems and for the difficulties in developing theories to describe them. The main question concerns the role of the electrical charges in determining the physical properties of these systems. The present paper addresses part of this question. It focuses on the interaction between a polyampholyte chain and a charged surface.

The overall size and shape of polyampholytes is determined by the balance of three factors.[3−10]

(i) Chain entropy tends to keep the polymer configuration as close to the Gaussian statistics as possible.

(ii) Fluctuation-induced attractions between charges (similar to those observed in electrolyte solutions) tend to collapse the chain into a globule.

(iii) If the chain has a nonzero total charge (either positive or negative), the overall Coulomb repulsion between excess charges tends to stretch the polymer.

The relative importance of these three contributions to the free energy depends on the fraction of positive f_+ and negative f_- charges on the chain and on the degree of polymerization N. The fluctuation-induced attraction increases with the density of charged monomers (assumed monovalent) $(f_+ + f_-)N/R^3$ inside the volume occupied by the polymer R^3. The Debye radius due to the charges on the chain is

$$r_D \approx \left(\frac{R^3}{l_BN(f_+ + f_-)}\right)^{1/2} \tag{1}$$

Note that we drop numerical coefficients throughout the paper and keep the discussion at a scaling level. The Bjerrum length

$$l_B = e^2/\epsilon kT \tag{2}$$

is the length scale on which the Coulomb interaction between two elementary charges e immersed in a medium of dielectric constant ϵ is equal to the thermal energy kT, where k is the Boltzmann constant and T the absolute temperature. In water at room temperature the Bjerrum length is equal to 7 Å. The fluctuation-induced attraction between charges is of the order of the thermal energy kT per Debye volume r_D^3. If there are many Debye volumes per chain ($r_D \ll R$), this attraction energy is large and a polyampholyte with equal numbers of Nf_+ positively charged and Nf_- of negatively charged monomers forms a compact globule[4,6−8] and precipitates from solution. But if the Debye radius is larger than the chain size ($r_D > R$), the attraction energy is weak and the chain remains almost unperturbed. The condition $r_D > R_0$ for a Gaussian chain of radius $R_0 \approx aN^{1/2}$ is written in terms of the fraction of charged groups $f = f_+ + f_-$

$$N < u^{-2} f^{-2} \tag{3}$$

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 3) for which polyampholyte chain shows Gaussian statistics.

For polyampholytes with an excess charge $\Delta fN = N|f_+ - f_-|$ larger than the critical value $(Nf)^{1/2}$, there are three regimes of chain configuration (see Figure 1).[8]

(i) *Unperturbed.* For a small number of the charged groups both fluctuation-induced attraction and Coulomb repulsion are weak, and the thermal fluctuations keep the chain in the Gaussian configuration.

(ii) *Polyelectrolyte.* For the asymmetrically charged polyampholyte chain the Coulomb repulsion between excess charges is larger than the thermal energy and stretches the chain into a polyelectrolyte-like cylinder.

(iii) *Necklace.* For a strongly charged polyampholyte chain the balance of fluctuation-induced attraction and Coulomb repulsion between excess charges leads to the unusual necklace-like shape of polyampholytes.[6,7]

Another parameter that affects the behavior of polyampholytes is the charge distribution along the chain.

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

S0024-9297(97)00305-7 CCC: $14.00

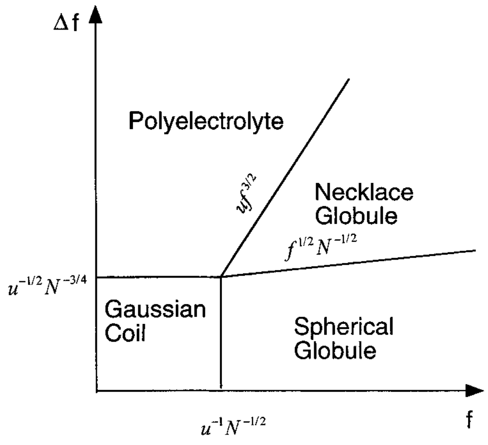

Figure 1. Diagram of states of a polyampholyte chain as function of the charge asymmetry Δf and fraction of charged monomers f. Logarithmic scales.

Polyampholytes with an alternating distribution of charges behave like polymers with short range interactions and can be characterized by an effective second virial coefficient.[11,12] These alternating polyampholytes are more soluble in water than polyampholytes with randomly distributed charged groups.

While there are many publications dealing with the statistics of a single polyampholyte chain in solution,[3−12] there are very few theoretical papers[13] that consider the adsorption of polyampholytes on a charged surface. However, the adsorption properties of polyampholytes are fundamental to the understanding their technological utilizations. Many experimental studies have been made on the adsorption of gelatin,[14−19] especially onto the silver halide crystal surface, reflecting the practical interest in its photographic use. It was 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.[19] A related problem is the interaction of polyampholyte solutions with latex particles.[20,21] The purpose of this paper is to describe the adsorption of a single random polyampholyte chain on a flat surface. We discuss the dependence of the adsorption of a polyampholyte chain on the surface charge density and on the number of charged groups on the chain.

The next section is devoted to the effect of an external electric field on the polyampholyte conformation and discusses in particular the critical value of the electric field that provokes the stretching of the chain. Section 3 discusses the adsorption of polyampholyte chains with zero net charge, and in Section 4 we present the results for the desorption threshold of a polyampholyte chain with a net charge of the same sign as the surface charge. Section 5 discusses the effect of added salt. Finally, in Section 6 we consider the adsorption of a polyampholyte globule. In the last section we summarize our results.

2. Polyampholyte Chain in an Electric Field

We consider a weakly charged polyampholyte chain in the Gaussian state ($N < u^{-2}f^{-2}$, see Figure 1) with randomly distributed charges. This chain is placed in a uniform external electric field E. The electric field polarizes the chain forcing it into an elongated configuration. We show below that the deformation of the chain on the largest length scale controls its behavior at all intermediate scales.[22]

A subchain of n monomers contains on average fn charges and $(fn)^{1/2}$ unbalanced charges (if the positions of the charges along the chain are uncorrelated). One may try to estimate the size of this subsection by balancing the electrostatic energy of a dipole of two opposite sets of charges $\pm e(fn)^{1/2}$ separated by the distance R_n in an external electric field E with the elastic stretching energy $kT(R_n^2/a_n^2) \propto Ee(fn)^{1/2}R_n$. This leads to a size of the subchain $R_n \propto Eef^{1/2}n^{3/2}a^2/kT$. Since the dependence of the size R_n on the number of monomers n is stronger than linear ($R_n \propto n^{3/2}$), the deformation of the chain is controlled by the largest length scales and the mean square end-to-end distance of the whole chain is

$$R^2 \propto \epsilon \frac{fE^2a^4l_B}{kT} N^3 \tag{4}$$

The electric field induces an elongation of the chain in the direction of the field, 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

$$E > E_1 \approx \frac{1}{N}\sqrt{\frac{kT}{\epsilon f a^2 l_B}} \tag{5}$$

In water at room temperature this onset of electric field for chain elongation is $E_1 \approx 10^8/(Nf^{1/2})$ V/m. The energy of the chain stretched by the electric field is

$$W \approx -kT\frac{R^2}{a^2N} \approx -kT\left(\frac{E}{E_1}\right)^2 \tag{6}$$

At higher electric fields ($E > E_1$) the mean square end-to-end distance grows as the cube of the degree of polymerization ($R^2 \propto N^3$). However the chain cannot be more than fully stretched $R \le aN$. This gives an upper boundary for the strength of the electric field

$$E \le E_{\max} \approx \frac{1}{N^{1/2}}\sqrt{\frac{kT}{\epsilon f a^2 l_B}} = E_1\sqrt{N} \tag{7}$$

For water at room temperature this field is $E_{\max} \approx 10^8/(Nf)^{1/2}$ V/m. The energy of the chain in the field $E_{\max}$ is of the order of NkT.

The chain deformation on smaller length scales is due to the chain stretching at the largest scales and the size of a subchain of n monomers is

$$R_n \approx \frac{Eea^2f^{1/2}}{kT} nN^{1/2} \tag{8}$$

One should note that the problem of a randomly charged polyampholyte chain in a uniform electric field E has an exact solution, given in the Appendix. This exact solution gives the same asymptotic behaviors for the mean square end-to-end distance R^2 along the field

$$\langle R_z^2\rangle = \frac{1}{3}Na^2\left(1 + \epsilon\frac{(f_+ + f_-)l_Ba^2E^2N^2}{36kT}\right) \tag{9}$$

and for the size of a subchain R_n^2 of n monomers between monomer l and l'

$$\langle [R_z(l) - R_z(l')]^2\rangle \approx \frac{|n|a^2}{3} + \epsilon\frac{fa^4l_BE^2N}{27kT}n^2 \tag{10}$$

as those derived above from simple scaling arguments.

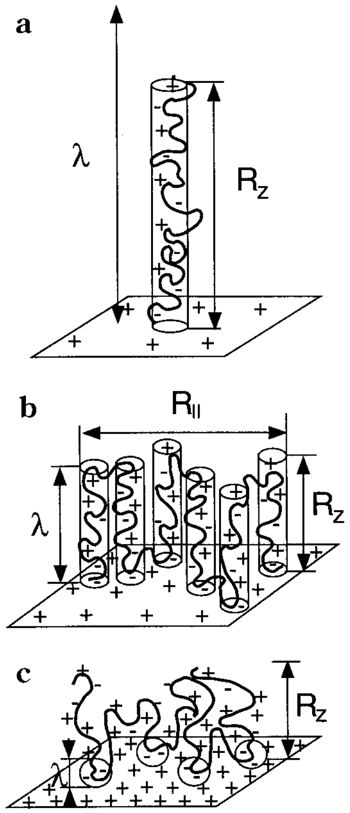

Figure 2. Schematic sketch of the configurations of a polyampholyte chain near a charged surface: (a) the pole regime; (b) the fence regime; (c) the pancake regime.

The correlations of the positions of charges along the chain are also discussed in the Appendix A.

3. Adsorption of a Symmetric Polyampholyte Chain

We now discuss the adsorption of a weakly charged polyampholyte chain ($N < u^{-2}f^{-2}$) with equal numbers of positively and negatively charged groups ($f_+ = f_-$) from a dilute solution onto an infinite plane with σ charges per unit area, immersed in a solvent of dielectric constant ϵ. In the absence of added salt, the concentration of counterions in the solution decays with the distance z from the surface and most counterions are localized within the Gouy−Chapman length[24] λ from the surface.

$$\lambda = \frac{1}{2\pi\sigma l_{\mathrm{B}}} \tag{11}$$

The electric field created by this plane decays in the vicinity of the surface as

$$E = \frac{e\sigma}{\epsilon(1 + z/\lambda)} \approx \frac{e\sigma}{\epsilon}(1 - z/\lambda) \tag{12}$$

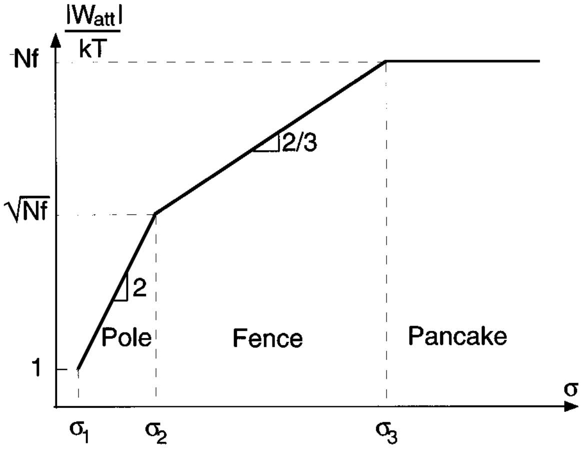

Figure 3. Dependence of the absolute value of the adsorption energy W_{ads} on the surface charge density σ. Logarithmic scales.

A. The Pole Regime. The Gouy−Chapman length λ can be much larger than the unperturbed coil size $\lambda \gg aN^{1/2}$ if the surface charge density is low. The polyampholyte chain drifts toward the surface due to the electric field gradient.[13] The electric field is higher near the surface, and the energy can be gained by redistributing the charges inside the polymer coil. This redistribution corresponds to the polarization of the chain by the surface electric field in such a way that the repelled charges are away from the surface and the attracted charges are closer to the surface. The deformation of the chain from its Gaussian shape begins at E_1 eq 5. The corresponding surface charge density is

$$\sigma_1 \approx \frac{1}{a l_{\mathrm{B}} f^{1/2} N} = \frac{1}{l_{\mathrm{B}} R_0 \sqrt{fN}} \tag{13}$$

At lower surface charge densities $\sigma < \sigma_1$ there is no adsorption because the small polarization energy gain (smaller than thermal energy kT) does not justify the entropy loss. An increase of the surface charge density results in two effects: the Gouy−Chapman length decreases and the polyampholyte chain extends in the direction of the field perpendicular to the surface (see Figure 2a). The crossover to this elongated chain regime occurs at $\sigma \approx \sigma_1$. In the crossover regime the Gouy−Chapman length λ_1 is proportional to $R_0(fN)^{1/2}$.

The attraction energy between a polyampholyte chain and the charged plane for the surface charge density $\sigma \geq \sigma_1$ of the polarized chain in the surface electric field E was calculated in section 2. This attraction energy is

$$\frac{W_{\mathrm{att}}}{kT} \approx -\frac{f l_{\mathrm{B}} \epsilon a^2 E^2 N^2}{kT} \approx -\left(\frac{\sigma}{\sigma_1}\right)^2 \tag{14}$$

The dependence of this attraction energy on the surface charge density is sketched in Figure 3. The surface charge density σ_1 corresponds to the adsorption threshold for a polyampholyte chain with zero net charge ($N_+ = N_-$). Beyond this threshold the chain size in the direction normal to the surface R_z grows linearly with charge density σ (see section 2)

$$R_z \approx R_0 \frac{\sigma}{\sigma_1} \tag{15}$$

as sketched in Figure 4.

B. The Fence Regime. The Gouy−Chapman length λ becomes comparable with the size of the chain R_z in the direction normal to the surface at the charge density

$$\sigma_2 \approx \frac{1}{a l_{\mathrm{B}} f^{1/4} N^{3/4}} = \frac{1}{l_{\mathrm{B}} R_0 (fN)^{1/4}} \tag{16}$$

If the charge on the plane were increased further (for $\sigma > \sigma_2$) the size of a fully stretched chain would be larger than the Gouy−Chapman length. The part of the chain outside the layer of thickness λ would be in a region of very weak field and would not gain electro-

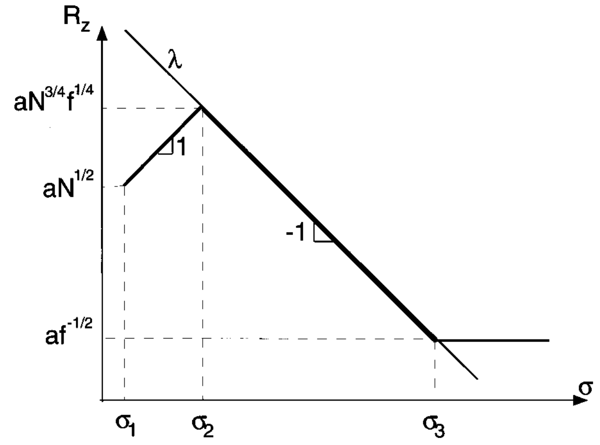

Figure 4. Dependence of the size of an adsorbed polyampholyte chain in the direction perpendicular to the adsorbing surface R_z on the surface charge density σ. Logarithmic scales.

static energy. In order to optimize the electrostatic energy, the chain remains confined within the Gouy–Chapman length λ (see Figure 4). It is divided into subsections of size λ and each is localized in the vicinity of the surface (Figure 2b). As we have shown above, the deformation of the polyampholyte chain at the largest length scales controls the chain conformation at the intermediate length scales. Therefore, we can find the number of monomers g in each subchain that stretches to the size λ by considering this subsection as an independent chain (see eq 4).

$$\lambda^2 \approx \epsilon \frac{f l_B a^4 E^2 g^3}{kT} \approx f l_B{}^2 a^4 \sigma^2 g^3 \tag{17}$$

Using the relation between the Gouy–Chapman length λ and the surface charge density σ (eq 11), this gives the number of monomers in the subchain

$$g \propto f^{-1/3} (l_B a \sigma)^{-4/3} \tag{18}$$

This chain section of g monomers has an induced dipole moment $d(g) \propto e\lambda f^{1/2} g^{1/2}$. The attraction energy between the polyampholyte chain and the surface is

$$\frac{W_{att}}{kT} \approx -\frac{N}{g}\frac{Ed(g)}{kT} \approx -(fN)^{1/2}\left(\frac{\sigma}{\sigma_2}\right)^{2/3} \tag{19}$$

In this strong adsorption (fence) regime the whole chain is localized inside the layer of size λ and the statistics of the chain on larger length scales is that of a two-dimensional random walk with excluded volume interactions dominated by the dipole–dipole repulsion between subsections of size λ.[25]

The polyampholyte chain is strongly bound to the surface if the interaction energy between each subsections of size λ and the surface is larger than the thermal energy $Ed(g) > kT$. This condition is satisfied when the charge density is smaller than σ_3

$$\sigma_3 \approx f^{1/2}/a l_B \tag{20}$$

as sketched in Figure 3.

C. The Pancake Regime. In the regime where the surface charge density is very high ($\sigma > \sigma_3$), the Gouy–Chapman length λ is smaller than the mean-square distance between charged monomers $af^{-1/2}$. The monomers with the sign of the charge opposite to that of the surface are in contact with surface while the monomers with the same sign of the charge as the surface are in the loops dangling in solution at distances $z > \lambda$. To estimate the average size of the loops, one can compare the repulsive force between the charges located at the distance z from the surface and the surface $F_{rep} \approx e^2\sigma\lambda/\epsilon z \approx kT/z$ and the elastic force due to stretching the parts of the chain with f^{-1} monomers $F_{elast} \approx kTzf/a^2$. At equilibrium these two forces are equal. This leads to the condition of an almost unperturbed strand between neighboring charges as well as the thickness of the adsorbed layer

$$z \approx R_z \approx af^{-1/2} \tag{21}$$

It is interesting to note that the thickness of the adsorbed layer in this regime does not depend on the surface charge and is universal (see Figure 4). The gain of the attraction energy due to the reorganization of monomers in the adsorbed layer is of the order of thermal energy kT per loop.

$$\frac{W_{att}}{kT} \approx -fN \tag{22}$$

To conclude this part we want emphasize our main general result: a polyampholyte chain with zero net charge adsorbs on a charged surface at surface charge densities higher than the threshold

$$\sigma \geq \sigma_1 \tag{23}$$

For example for $N = 10^3$, $f = 0.2$, $l_B = 7$ Å, and the bond length $a = 3$ Å, the adsorption threshold is at $\sigma_1 \approx 10^{-4}$ Å^{-2}, crossovers to the fence and pancake regimes occur at $\sigma_2 \approx 4 \times 10^{-4}$ Å^{-2} and $\sigma_3 \approx 10^{-2}$ Å^{-2}, respectively.

4. Adsorption of a Charged Polyampholyte Chain on a Similarly Charged Surface

The adsorption of a charged polyampholyte depends on the Coulomb interaction between the net charge on the chain $\Delta fNe = N(f_+ - f_-)e > 0$ 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 repulsive potential that the chain feels while it approaches the surface is logarithmic; thus there is a logarithmic barrier for adsorption in addition to the phenomena discussed in this section (see Appendix B). The energy of the polyampholyte chain W near the surface consists of the attractive part W_{att} due to the polarization of the chain by the electric field and the repulsive energy W_{rep} between the net charge on the chain and the field E

$$W_{rep} \approx e\Delta fNE\lambda \approx \Delta fNkT \tag{24}$$

This expression assumes that all charges are within the Gouy–Chapman length λ of the surface. Another source of repulsion is due to the image charge W_{imag}. The dielectric constant of the solvent ϵ is not equal to that of the surface ϵ_1 in most experimental situations (such as adsorption of polyampholyte chains from water onto silica or polymer latex surfaces which are nonpolar dielectric media with $\epsilon_1 \ll \epsilon$). The presence of the polyampholyte chain near the surface with dielectric constant ϵ_1 causes the polarization of both media. The result is the appearance of an image polyampholyte chain with charges q' located at the symmetric positions with respect to the adsorbing surface[28] with a local charge

$$q' = q\frac{\epsilon - \epsilon_1}{\epsilon + \epsilon_1} \approx q \tag{25}$$

The interaction of the polyampholyte chain with its image chain results in an additional repulsive force.

The polyampholyte chain with net charge of the same sign as the surface would adsorb on it if the net interaction energy W is negative (attractive) and stronger than the thermal energy kT

$$W = W_{\text{att}} + W_{\text{rep}} + W_{\text{imag}} < -kT \tag{26}$$

A. Nearly Symmetric Polyampholytes. Nearly symmetric polyampholytes with

$$\Delta f \le \sqrt{f/N} \tag{27}$$

stay almost spherical in solution. Their configuration is Gaussian for $f < (uN^{1/2})^{-1}$. In this case the repulsion energy between the chain and its image is small ($<kT$) and can be neglected. The only relevant repulsion is the Coulomb repulsion between the chain and the surface charge W_{rep} (eq 24).

If the chain, stretched by the electric field, is still smaller that the Gouy–Chapman length (pole regime, for surface charge densities $\sigma < \sigma_2$), the polarization energy is given by eq 14

$$W_{\text{att}} \approx -kT\left(\frac{\sigma}{\sigma_1}\right)^2 \tag{28}$$

The repulsion energy is $W_{\text{rep}} \approx \Delta f N kT$ (see eq 24). At the onset of adsorption the attraction become stronger than repulsion. The onset of adsorption is shifted from σ_1 (for zero net charge) to

$$\sigma \approx \sqrt{\Delta f N}\sigma_1, \quad \text{for} \quad \Delta f < \sqrt{\frac{f}{N}} \tag{29}$$

as sketched in Figure 5. Note that for randomly charged polyampholytes with a net charge $\Delta f \approx (f/N)^{1/2}$ this corresponds to $\sigma_{\text{ads}} \approx \sigma_2$ and there is no pole regime (section 3.1).

In the fence regime all monomers are inside the Gouy–Chapman length λ and the repulsion energy is still kT per uncompensated charge. In order for the chain to adsorb on the surface, the polarization attraction in this regime has to be stronger than the repulsion

$$\left|\frac{W_{\text{att}}}{kT}\right| \approx (fN)^{1/2}\left(\frac{\sigma}{\sigma_2}\right)^{2/3} > \Delta f N \tag{30}$$

The adsorption starts at a surface charge density (see Figure 5)

$$\sigma \approx \sigma_2\left(\frac{\Delta f^2 N}{f}\right)^{3/4} \approx \frac{\Delta f^{\,3/2}}{l_{\text{B}} a f}$$

$$\text{for} \qquad \Delta f > \sqrt{\frac{f}{N}} \tag{31}$$

In the pancake regime all the positive charges are close to the surface while the all the negative charges are located at a distance of order $af^{-1/2}$ from the surface. The repulsion energy can be still estimated with a logarithmic accuracy by eq 24, while the attraction energy in this regime is given by eq 22. Thus in the pancake regime ($\sigma > \sigma_3$) a nearly symmetric polyampholyte chain is always adsorbed on the surface because $\Delta f < f$ and $|W_{\text{att}}| > W_{\text{rep}}$.

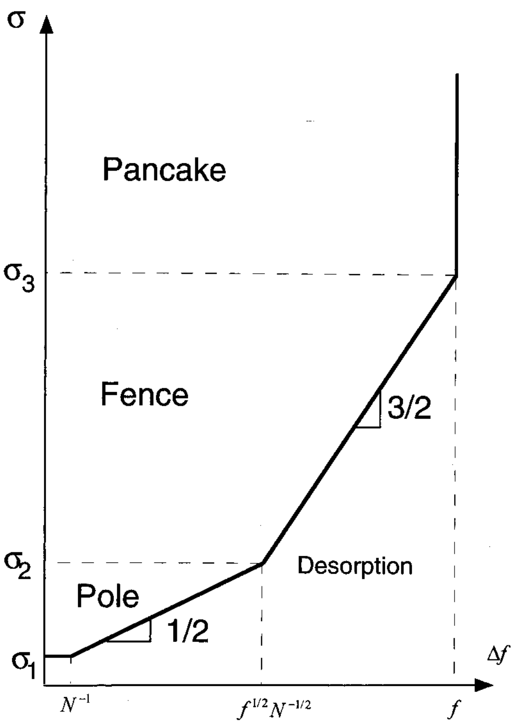

Figure 5. Adsorption diagram of a polyampholyte chain as function of the surface charge density σ and the chain charge asymmetry Δf. Logarithmic scales.

B. Asymmetric Polyampholytes. As we discussed in the introduction, polyampholytes with a large net charge $\Delta f > (f/N)^{1/2}$ can be found in one of three states (see Figure 1):[8]

(i) Gaussian conformation for

$$\Delta f N < \left(\frac{N}{u^2}\right)^{1/4} \tag{32}$$

(ii) stretched into a cylindrical shape for

$$\left(\frac{N}{u^2}\right)^{1/4} < \Delta f N, \qquad \Delta f > uf^{3/2} \tag{33}$$

(iii) collapsed into a necklace-like globule for

$$\sqrt{f/N} < \Delta f < uf^{3/2} \tag{34}$$

A Gaussian polyampholyte with the net charge $\Delta f > (f/N)^{1/2}$ can only adsorb in the pancake or in the fence regimes, as discussed in section 4.1. Below we consider adsorption of a polyampholyte stretched by the repulsion between the excess charges (in a cylindrical polyelectrolyte conformation (regime ii).

In the cylindrical regime (ii) the polyampholyte chain is a linear array of electrostatic blobs[26] of size $D_{\text{e}} \approx au^{-1/3}(\Delta f)^{-2/3}$ each containing $g_{\text{e}} \approx u^{-2/3}(\Delta f)^{-4/3}$ monomers. The energy of this self-repulsion that causes the chain stretching is of the order of the thermal energy kT per electrostatic blob

$$W_{\text{str}} \approx kTN\Delta f\,(\Delta f u^2)^{1/3} \tag{35}$$

This energy W_{str} is of the order of the repulsive energy W_{imag} between the chain and its image. Note that in the fence regime it is usually weaker than the energy of repulsion of the excess charge from the surface $W_{\mathrm{rep}} \approx kTN\Delta f$ as long as $\Delta f < u^{-2}$.

$$W_{\mathrm{str}}/W_{\mathrm{rep}} \approx (\Delta f u^2)^{1/3} \ll 1 \tag{36}$$

In order for the chain to adsorb, the attraction energy has to be larger than the repulsion energy. Therefore the stretching energy of the adsorbed chain is the weakest of the three energies

$$W_{\mathrm{str}} < W_{\mathrm{rep}} < |W_{\mathrm{att}}|$$

This implies that the self-repulsion of the excess charges in the fence regime cannot alter the chain conformation in the direction normal to the surface in any significant way ($R_z \approx \lambda$). The Coulomb repulsion between two subchains of size λ is

$$\frac{U_{\mathrm{rep}}(r)}{kT} \approx \frac{l_{\mathrm{B}}\Delta f^2 g^2}{\lambda} \ln\left(\frac{\lambda}{r} + \sqrt{1 + \left(\frac{\lambda}{r}\right)^2}\right) \tag{37}$$

where g is the number of monomers in subchains of size λ (see eq 18). This interaction decreases logarithmically at length scales smaller than the Gouy–Chapman length λ and has a $1/r$ decay at larger length scales. The electrostatic repulsion at the largest length scales controls the stretching of the chain on the intermediate length scales. The size of the chain in the directions parallel to the surface is $R \approx (N/g_{\mathrm{e}})D_{\mathrm{e}} \approx u^{1/3}\Delta f^{2/3}N$. The deformation in this direction does not affect adsorption. Therefore the adsorption–desorption threshold is given by the same equation (31) as in the case of nearly symmetric polyampholytes.[27] The crossover to the pancake regime occurs at $\sigma_3 \approx f^{1/2}/al_{\mathrm{B}}$. In the pancake regime the chain size in the direction normal to the surface $R_z \approx af^{-1/2}$ is larger than the Gouy–Chapman length λ (see eq 21).

5. Effect of Added Salt

In the previous section we have discussed the various regimes of adsorption of a polyampholyte chain in salt-free solutions. The addition of salt to a solution leads to the screening of electrostatic interactions at the Debye screening length $\kappa^{-1} = (8\pi l_{\mathrm{B}}\rho_{\mathrm{s}})^{-1/2}$.

In Figure 6 we sketch the adsorption diagram of a symmetric polyampholyte chain. At very low salt concentrations (very small κa) the screening due to added salt is unimportant and the adsorption behavior of a polyampholyte chain is almost identical to that in the absence of salt (section 3). At the lowest surface charged densities ($\sigma < \sigma_1$) the electric field created by the surface is too weak to polarize the polyampholyte chain and it does not adsorb.

Pole Regime. In the range of low surface charge densities ($\sigma_1 < \sigma < \sigma_2$) the electric field created by the surface results in the redistribution of the charges inside the polymer coil. This redistribution corresponds to polarization of the coil and the polyampholyte chain extends in the direction of the field perpendicular to the surface (the pole regime, section 3.1). With increasing the salt concentration the Debye screening length decreases. The upper boundary for the pole *regime* is determined by the salt concentration at which the Debye screening length is equal to the chain size in the direction perpendicular to the surface ($R_z \approx \kappa^{-1}$). This leads to

$$\kappa_2 a \approx f^{-1/2}(\sigma l_{\mathrm{B}} a)^{-1}\ N^{-3/2} \tag{38}$$

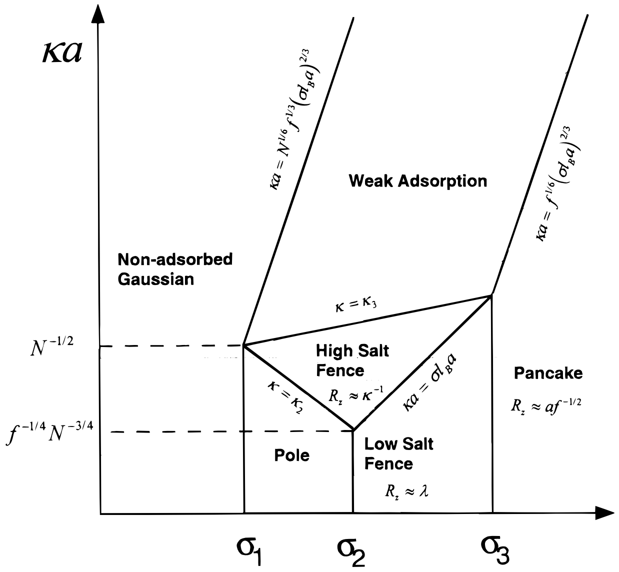

Figure 6. Adsorption diagram of a polyampholyte chain in a salt solution as function of surface charge density σ and inverse Debye screening length κ. Logarithmic scales.

At higher salt concentrations, the size of the chain perpendicular to the surface is limited by the Debye screening length $R_z \approx \kappa^{-1}$ and we enter the *fence* regime controlled by the salt.

There are two *fence* regimes on the adsorption diagram.

Low-Salt Fence Regime. In the intermediate range of surface charge densities ($\sigma_2 < \sigma < \sigma_3$) and low salt concentrations for which $\lambda < \kappa^{-1}$ the behavior of a polyampholyte chain is similar to that in the salt-free case (section 3.2). In this regime the chain folds inside the layer of thickness λ.

High-Salt Fence Regime. At higher salt concentrations the screening of the surface field is due to the salt ions and the chain is localized inside the layer of thickness κ^{-1}. With increasing salt concentration the screening length as well as the thickness of the adsorbed chain decreases. At a salt concentration for which

$$\kappa_3 a \approx f^{1/4}(\sigma l_{\mathrm{B}} a)^{1/2} \tag{39}$$

the electric field created by the charged surface is not strong enough to deform the part of the chain inside the thickness of size κ^{-1} and we crossover to the *weak adsorption regime.*

Weak Adsorption Regime. The standard Flory method[29] can be used to describe the weak adsorption of a polyampholyte chain. Since the attraction energy between the plane and a section of the chain of size κ^{-1} is now less than the thermal energy, these sections are not deformed. The size of the section κ^{-1} is related to the number of monomers in it by the Gaussian statistics, $g \approx (\kappa a)^{-2}$. The attraction energy between the surface and the section of size κ^{-1} is calculated from the polarization energy of a section with polarizability $d^2/(3kT)$ where the dipole moment is $d = (fg)^{1/2}e\kappa^{-1}$. The attraction energy per section of g monomers is $-kTfg(\sigma l_{\mathrm{B}}\kappa^{-1})^2$. The entropic loss due to the chain confinement in a thickness R_z is Na^2/R_z^2 and the energy gain due to the attraction between the surface and the chain is obtained by considering that a fraction κ^{-1}/R_z of the chain is interacting with the surface

$$\frac{W_{\rm att}}{kT} \approx -fg(\sigma l_{\rm B}\kappa^{-1})^2 \frac{N}{\kappa R_z g} \approx -f(\sigma l_{\rm B}\kappa^{-1})^2 \frac{N}{\kappa R_z} \quad (40)$$

Balancing the entropic and energetic parts of the free energy, we get the thickness of the adsorbed layer

$$R_z \approx af^{-1}(\sigma l_{\rm B} a)^{-2}(\kappa a)^3 \quad (41)$$

The chain adsorbs on the surface only if the thickness R_z is smaller than the Gaussian chain size $aN^{1/2}$. This gives the desorption threshold

$$\kappa_4 a \approx N^{1/6} f^{1/3}(\sigma a l_{\rm B})^{2/3} \quad (42)$$

In the *pancake* regime the Gouy–Chapman length λ is smaller than the mean-square distance between charged monomers $af^{-1/2}$. So, energy can be gained by redistribution of the charged monomers in such a way that the charges opposite to ones on the surface are in contact with the surface, while the monomers with the same charge as the surface are in the loops of the size $af^{-1/2}$. This redistribution of the charged monomers is due to logarithmic dependence of the potential at distances larger than the Gouy–Chapman length λ. The gain of the attraction energy due to the reorganization of monomers in the adsorbed layer is of the order of kT per loop (see eq 22). The presence of the salt results in an exponential screening of the surface potential over the distances larger than the Debye screening length κ^{-1}. Therefore, when the screening length becomes smaller than the size of the loop, the adsorbed pancake starts to swell. In fact, the crossover to the weak adsorption regime occurs at the salt concentration at which the attractive energy is of the order of the confinement energy of a pancake $kTR_0^2\kappa^2$. The boundary between the two regimes is at

$$\kappa a \approx f^{1/6}(\sigma l_{\rm B} a)^{2/3} \quad (43)$$

This line separates the *weak adsorption* and *pancake* regimes on the adsorption diagram (Figure 6).

For example of a polyampholyte chain discussed above with $N = 10^3$, $f = 0.2$, $l_{\rm B} = 7$Å, and the bond length $a = 3$ Å, the presence of the salt becomes important at concentrations of 1:1 electrolyte higher than 10^{-4} M ($\kappa^{-1} \approx af^{1/4}N^{3/4} \approx 300$ Å). The weak adsorption regime can be observed if the salt concentration is higher than 1 mM ($\kappa^{-1} \approx aN^{1/2} \approx 90$ Å).

6. Adsorption of a Polyampholyte Globule

The approach used above is only correct for a polyampholyte when the chain conformation is practically unperturbed by the attractive interactions between charged groups, i.e., when $f < u/N^{1/2}$. In the opposite limit, the polyampholyte chain is in a globular state (see Figure 1). The equilibrium density ρ inside the globule is determined by the balance between the third virial term in the free energy expansion as a function of density $N\rho^2a^6$ (in a θ-solvent when the backbone is uncharged) and the fluctuation induced attraction energy $-V(\rho l_{\rm B} f)^{3/2}$, where V is the volume of the globule. This gives a density[4,8] $\rho \approx l_{\rm B} f a^{-4}$. The polyampholyte chain in the collapsed regime can be viewed as a close-packed assembly of Gaussian blobs each of which contains $g_c = u^{-2}f^{-2}$ monomers. The globule elongates when it is placed in an external electric field.

In order to estimate the longitudinal size L of the globule in an external electric field E, one must balance the electrostatic energy of an electrical dipole corresponding to two opposite charges $e(fN)^{1/2}$ at a distance L by the surface energy term[8] $F_{\rm sur}/kT \approx RL/r_{\rm D}^2$ (where $r_{\rm D} \approx (\rho l_{\rm B} f)^{-1/2}$ is the Debye radius inside the globule and R is the transverse size of the cylinder) while keeping the globule volume constant $V \approx LR^2 \approx N/\rho$. This is done by optimizing the corresponding Flory-like free energy

$$\frac{F_{\rm def}}{kT} \approx N^{1/2}(fu)^{3/2}\sqrt{\frac{L}{a}} - \frac{Ee}{kT}\sqrt{fN}L \quad (44)$$

where the first term is the surface energy and the second one the polarization energy due to the electric field. The deformation free energy equation (44) first grows as $L^{1/2}$ and then decreases linearly with increasing the length L. The extremal value L of this dependence of the free energy (44) on the elongation L corresponds to the maximum of the free energy. The surface energy cannot stabilize the stretching of the globule at large L. The stabilization comes from the elastic stretching energy $kT(L^2/a^2N)$ that has to be taken into account when the transverse size R of the globule becomes smaller than the Debye radius[8] $r_{\rm D}$. In other words, the chain could either be in a globular or in a stretched state and there is a transition between these two states at a critical value of the external electric field $E_{\rm tr}$. This critical field can be estimated by comparing the chemical potentials of the monomers in the globular configuration

$$\frac{\mu_{\rm glob}}{kT} = \frac{1}{kT}\frac{\partial F_{\rm glob}}{\partial N} \approx -u^2f^2 \quad (45)$$

and in the stretched configuration

$$\frac{\mu_{\rm str}}{kT} = \frac{1}{kT}\frac{\partial F_{\rm str}}{\partial N} \approx -\frac{\epsilon ufa^3E^2N}{kT} \quad (46)$$

Equations 45 and 46 lead to the critical field

$$E_{\rm tr} \approx \sqrt{\frac{kTuf}{\epsilon a^3 N}} \quad (47)$$

This critical field can also be obtained by analyzing the stability of the stretched state. The configuration of the chain, characterized by eqs 4 and 8, is very similar to that of a Gaussian polymer chain under an effective tension $\tau = eEN^{1/2}f^{1/2}$. It can be viewed as a linear array of Pincus blobs each containing $g_{\rm P} = kT/(a\tau)^2$ monomers. The stretched state is stable as long as the Pincus blobs containing $g_{\rm P}$ monomers are smaller than the collapsed blobs containing $g_{\rm c}$ monomers. These considerations are meaningful only if the field $E_{\rm tr}$ is smaller than the field at which the chain is a fully stretched chain $E_{\rm str}$.[7] This is always the case for weakly charged polyampholytes where $uf < 1$. To conclude this section we want to stress that a strong enough external electric field $E > E_{\rm tr}$ dissolves the polyampholyte globule. This effect has also been studied recently by Schiessel and Blumen.[23] The estimates of the critical field give, however, very large values that seem difficult to reach experimentally in the bulk but are possible near the charged surfaces.

In order to apply the results of the previous part to the adsorption problem, one has to compare the longitudinal size of the chain $L_{\rm tr}$ at the transition point with the Gouy–Chapman length λ (to be sure that the whole chain is inside the layer of thickness λ and that our estimate of the free energy in the stretched state is correct). It turns out that for the values of the electric field $E \approx E_{\mathrm{tr}}$, the Gouy–Chapman length is always much smaller than the longitudinal size of the chain. Therefore we have to recalculate the free energy of the chain in the stretched regime. As we have shown above for the fence case ($\sigma \approx \sigma_{\mathrm{tr}} \approx a^{-2}(f/N)^{1/2} > \sigma_2$) a polyampholyte chain near a charged surface is an assembly chain section of size λ with a total energy of the order of

$$\frac{F}{kT} \approx -(\sigma a l_{\mathrm{B}} f)^{2/3}\, N \tag{48}$$

Comparing the chemical potential of the chain in the compact globular state and in the fence state in an adsorbed layer of thickness λ, we find the dissolution threshold

$$\sigma_{\mathrm{tr}} \approx u^2 f^2/a^2 \tag{49}$$

For higher surface charge densities ($\sigma > \sigma_{\mathrm{tr}}$) the compact globular state is thermodynamically unstable and we can apply the results of the previous sections.

7. Discussion

We have presented a scaling theory of the adsorption of a randomly charged polyampholyte chain on a charged plane. In the absence of salt, we have shown that there are four different adsorption regimes. At very low surface charge densities, the electric field created by the plane is too weak to bind the chain to the surface $\sigma \leq \sigma_1 \approx (f^{1/2} N a l_{\mathrm{B}})^{-1}$. If the surface charge density exceeds the critical value σ_1, the electric field, created by the plane, is strong enough to deform the polyampholyte chain; the charges are redistributed in order to decrease the electrostatic energy. This deformation was overlooked in ref 13. In this regime the attraction energy between the charged surface and the polyampholyte chain is larger than the thermal energy kT. It is thus large enough to bind the chain to the surface. The highest possible value of the attraction energy corresponds to the surface charge density $\sigma_3 \propto f^{1/2}/l_{\mathrm{B}} a$ at which the Gouy–Chapman length is of the order of the distance between charged monomers.

The most interesting predictions of this paper are the criteria for the desorption of a polyampholyte chain carrying the excess charge of the same sign as the charged surface. We find that a random polyampholyte chain with a typical charge fluctuation $\Delta f \approx (f/N)^{1/2}$ always adsorbs onto the surface for surface charge densities σ larger than σ_2 (eq 16). In the pancake regime ($\sigma_3 \leq \sigma$) the attraction interaction between a polyampholyte and a charged surface (due to the polarization of the chain) always exceeds the repulsion and any weakly charged polyampholyte adsorbs onto the surface (see Figure 5). This prediction qualitatively agrees with the experimental findings on the adsorption of polyampholyte chains onto the surfaces with the same charge.[14–19] Unfortunately, the quantitative comparison with these experiments is difficult because they were performed at solution concentrations where the interaction between adsorbed chains becomes important. We hope that this paper would encourage experiments at higher surface to volume ratio at lower polymer concentrations so that adsorbed chains do not interact. This would provide a direct test of the predictions of our model. It would also be interesting to test the ideas presented above by computer simulations.

Acknowledgment. The authors are grateful to Dr. T. Whitesides for pointing out an error in an earlier version of the paper. This work was supported in part by the Eastman Kodak Company and by the University of North Carolina.

Appendix A. Polyampholyte Chain in External Electric Field

Let us consider the conformation of a symmetric polyampholyte chain in an external electric field. Monomer s at position $\mathbf{R}(s)$ has charge $eq(s)$ with the condition of overall chain neutrality $\int_0^N q(s)\, \mathrm{d}s = 0$. The partition function of a Gaussian polyampholyte chain in a uniform electric field $\mathbf{E}$ is given by the Edwards functional integral $Z = \int D\mathbf{R}(s) \exp(-H[\mathbf{R}(s)])$ with a Hamiltonian

$$H[\mathbf{R}(s)] = \frac{3}{2a^2}\int \mathrm{d}s\left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 - \frac{e}{kT}\int \mathrm{d}s q(s)\mathbf{E}\mathbf{R}(s) \tag{A1}$$

where a is the bond size. Using the fact that $\mathbf{R}(s) - \mathbf{R}(0) = \int_0^s \mathrm{d}s'\, (\partial\mathbf{R}/\partial s')$, and inverting the order of the integrations, we rewrite the Hamiltonian as

$$H[\mathbf{R}(s)] = \frac{3}{2a^2}\int \mathrm{d}s \left(\frac{\partial \mathbf{R}}{\partial s}\right)^2 - \frac{1}{kT}\int_0^N \mathrm{d}s\mathbf{A}(s)\left(\frac{\partial \mathbf{R}}{\mathrm{d}s}\right) \tag{A2}$$

where $\mathbf{A}(s) = \mathbf{E} \int_s^N eq(s')\, \mathrm{d}s'$. The thermodynamic average value of the local chain tension is then

$$\left\langle\left(\frac{\partial \mathbf{R}}{\partial s}\right)\right\rangle = \frac{a^2 e}{3kT}\,\mathbf{A}(s) \tag{A3}$$

The average value (over the charge distribution) of the end-to-end distance of the chain in the direction of the field is thus given by

$$\langle R_z^{\,2}\rangle = \frac{Na^2}{3} + \frac{a^4 e^2 E^2}{9(kT)^2}\int_0^N \mathrm{d}s \int_s^N \mathrm{d}s_1 \int_0^N \mathrm{d}s' \int_{s'}^N \mathrm{d}s_2 \langle q(s_1)q(s_2)\rangle \tag{A4}$$

We first consider the case where the charges are randomly distributed. The average value of the charge is $q(s) = 0$ and the charge correlation is $\langle q(s)q(s')\rangle = f[\delta_{ss'} - (1/N)]$ where the second term is due to the fact that we consider an exactly neutral chain. The chain radius in the direction of the field is then obtained by inverting the orders of summation in eq A4

$$\langle R_z^{\,2}\rangle = \frac{Na^2}{3} + \frac{N^3 f a^4 e^2 E^2}{108(kT)^2} \tag{A5}$$

This result is identical to that of Schiessel and Blumen[30] and is in agreement with the more qualitative Flory approach proposed in the text. It is also interesting to calculate the end-to-end distance of a chain section containing $n = l - l'$ monomers inside the chain using the same method. We find

$$\langle [R_z(l) - R_z(l')]^2\rangle = \frac{(l-l')a^2}{3} + \frac{fa^4e^2E^2}{9(kT)^2}(l-l')^2\left[\frac{l-l'}{3} + \frac{l'(N-l)}{N} - \frac{(l-l')^2}{4N}\right] \tag{A6}$$

If the chain section is located close to the end point of the chain, (l, $l' \ll N$), the end to end distance of a subchain containing $n = l - l'$ monomers is $\langle [R_z(l) -$

$R_z(l')]^2\rangle \propto n^3 l$. On the other hand, for a chain section at the center of the chain ($l' = (N - n)/2$, $l = (N + n)/2$ the end to end distance is $\langle[R_z(l) - R_z(l')]^2\rangle = (fa^4e^2E^2/9(kT)^2)n^2[(N/4) - (n/6)]$. As explained in the text the polarization is dominated by the larger length scales $n \propto N$ and the size $r(n)$ of a central subchain grows linearly with n, $r(n) \propto nN^{1/2}$.

We now consider the correlated charge distribution. For simplicity, we consider the case where all the monomers are charged $f = 1$. In many cases, the polymerization is a Markovian process and the charge correlations only depend on one parameter h, such that $-1 < h < 1$. This parameter is the nontrivial eigenvalue of the probability matrix that a charge α $(+1,-1)$ follows a charge β along the chain. The random polymer corresponds to $h = 0$, the alternating polymer to $h = -1$ and the diblock copolymer to $h = 1$. For such a Markovian copolymer, $\langle q(s)\rangle = 0$ and $\langle q(s)q(s')\rangle = h^{|s-s'|}$. However for a Markovian process, the total charge fluctuates and can have a finite value for a given conformation of the chain. A charged chain in an electric field does not have an equilibrium position and drifts along the field. In order to consider only neutral chains, we consider here a quasi-Markovian process with a charge correlation $\langle q(s)q(s')\rangle = h^{|s-s'|} - (1 + h)/(1 - h)N$. If the charge correlation parameter h is not too close to $h = 1$ or $h = -1$, the constant term ensures the electroneutrality of the chain (in the limit where N is very large). The calculations of the mean square chain end-to-end distance are performed in a way similar to that for random chains using now discrete summations.

$$\langle R_z^{\,2}\rangle = \frac{Na^2}{3} + \frac{N^3a^4e^2E^2}{108(kT)^2}\frac{1+h}{1-h} \tag{A7}$$

This result is obviously not valid for $h = 1$, where it diverges, and for $h = -1$, where it vanishes. An alternating polyampholyte is made of consecutive dipoles between opposite charges that align along the field. Its size is thus proportional to the number of monomers. A direct calculation from eq A4 leads to

$$\langle R_z^{\,2}\rangle = \frac{Na^2}{3} + \frac{N^2a^4e^2E^2}{36(kT)^2} \tag{A8}$$

For a diblock copolymer, a Flory estimate similar to the one of section 2 gives at high fields a size proportional to N^2. It is important to note however that these results are obtained by ignoring the attraction between positive and negative charges on the chain which become extremely important when blocks of charges form (i.e., when h approaches 1).

Appendix B. Comments on the Adsorption of Charged Objects

In this appendix we point out the difference between the classical adsorption problem of the polymer chains at the attractive wall and at the charged surface. In the classical problem attraction between a polymer and a surface is caused by the short range interactions. At low surface coverage, when the adsorbed chains do not overlap, the increase of the polymer concentration at the surface is determined by the balance between the energy gain due to adsorption and entropy loss due to localization of the chains at the surface. The situation is different for the charged surface. In salt-free solutions the electrostatic potential decays logarithmically from the surface

$$\varphi(z) = -\frac{2kT}{e}\ln\left(1 + \frac{z}{\lambda}\right) \tag{B1}$$

Any time we try to bring a charged polymer with the same sign of charge as the one on the surface, we have to do work against the field created by the surface charge. However, at any finite concentrations of polymer chains this field is exponentially screened by the dissociated counterions and by the charged polyampholytes at distances larger than the Debye screening length r_D. This result can be understood using the following qualitative arguments. At distance z from the charged surface the test charge feels the effective surface charge density $\sigma(z) \approx \sigma\lambda/z$. If the Gouy–Chapman length $\lambda(z) \approx 1/l_B\sigma(z)$ due to the rest of the surface counterions is smaller than the Debye screening length r_D, the surface counterions dominate screening of the surface field. In the opposite case $\lambda(z) > r_D$ the dissociated counterions from the polyampholytes give the main contribution to the screening. The crossover from one regime to another occurs at distances of the order of the Debye screening length $z \approx r_D$. Hence, the surface charge $\sigma\lambda/r_D$ can be screened by the rearrangement of polyampholyte chains and counterions over the distances of the order of the Debye screening length r_D.

The state near the surface has the lower energy if the sum of the polarization induced attraction and electrostatic repulsion $W_{\text{att}} + W_{\text{rep}}$ is lower than the energy difference of the chain at distance r_D from the surface and the surface

$$W_{\text{att}} + W_{\text{rep}} < 2\Delta fN\ln(\lambda/r_D) \tag{B2}$$

The last inequality results in the logarithmic corrections of the expressions in section 4 as we mentioned in the text. In fact, even if the energy of the chain near the surface is lower than that in the bulk, it will be very hard to reach this local minimum due to high energy barrier separating this minimum at the surface from the bulk solution.

The modification of the last equation in the salt case is straightforward. One has only to include the contribution of the salt ions in the Debye screening length.

References and Notes

(1) *Polyelectrolytes*; Hara, M., Ed.; Marcel Dekker: New York, 1993.
(2) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961.
(3) Edwards, S. F.; King, P. R.; Pincus, P. *Ferroelectrics* **1980**, *30*, 3.
(4) Higgs, P. G.; Joanny, J. F. *J. Chem. Phys.* **1991**, *94*, 1543.
(5) Kantor, Y.; Kardar, M. *Europhys. Lett.* **1991**, *14*, 421.
(6) Kantor, Y.; Kardar, M.; Li, H. *Phys. Rev. Lett.* **1992**, *69*, 61; *Phys. Rev. E* **1994**, *49*, 1383.
(7) Kantor, Y.; Kardar, M. *Europhys. Lett.* **1994**, *27*, 643; *Phys. Rev. E* **1995**, *51*, 1299; **1995**, *52*, 835.
(8) Dobrynin, A. V.; Rubinstein, M. *J. Phys. II* **1995**, *5*, 677.
(9) Gutin, A.; Shakhnovich, E. *Phys. Rev. E* **1994**, *50*, R3322.
(10) Quan, C.; Kholodenko, A. *J. Chem. Phys.* **1988**, *89*, 5273.
(11) Wittmer, J.; Johner, A.; Joanny, J.-F. *Europhys. Lett.* **1993**, *24*, 263.
(12) Victor, J. M.; Imbert, J. B. *Europhys. Lett.* **1993**, *24*, 189.
(13) Joanny, J.-F. *J. Phys. II* **1994**, *4*, 1281.
(14) Curme, H. G.; Natale, C. C. *J. Phys. Chem.* **1964**, *68*, 3009.
(15) Berendsen, R.; Borginon, H. *J. Photogr. Sci.* **1968**, *16*, 194.
(16) Maternaghan, T.; Banghan, O. B.; Ottewill, R. H. *J. Photogr. Sci.* **1980**, *28*, 1.
(17) Kudish, A. T.; Eirich, F. R. *Proteins at Interfaces*; American Chemical Society: Washington, DC, 1987; p 261.
(18) Kawanishi, N.; Christenson, H.; Ninham, B. *J. Phys. Chem.* **1990**, *94*, 4611.

(19) Kamiyama, Y.; Israelachvili, J. *Macromolecules* **1992**, *25*, 5081.
(20) Ouali, L.; Neyret, S.; Candau, F.; Pefferkorn, E. *J. Colloid Interface Sci.* **1995**, *17*, 86.
(21) Blaackmeer, J. Thesis, University of Wageningen 1990.
(22) Panuykov, S. P.; Rubinstein, M. *Macromolecules* **1996**, *29*, 8220.
(23) Schiessel, H.; Blumen, A. *J. Chem. Phys.* **1996**, *104*, 6036.
(24) Israelchvilli, J. N. *Intermolecular and Surface Forses*; Cornell University Press: Ithaca, NY, 1985.
(25) The interaction between two dipoles, carrying a dipole moment $d(g)$, is $U(r) = d^2(g)/\epsilon r^3$, but this approximation for the interaction between two induced dipoles is correct only if the distance r between them is larger than the Gaussian size of the subchains in the direction parallel to the surface a^2g. The two-dimensional second virial coefficient for this type of interaction is

$$B = -\int \mathrm{d}^2r[\exp(-U(r)/kT) - 1] \approx \pi {a_{\mathrm{cut}}}^2 + \int_{a_{\mathrm{cut}}}^{\infty} \frac{U(r)}{kT}\, \mathrm{d}^2r$$

where a_{cut} is the length scale where the interaction becomes of the order of the thermal energy kT. This occurs at $a_{\mathrm{cut}} \approx (l_{\mathrm{B}}\lambda^2 fg)^{1/3}$. The size of the chain $R_{||}$ in the direction perpendicular to the external field (parallel to the adsorbing plane) can be found from Flory argument,[26] by balancing the entropic ${R_{||}}^2/a^2N$ and energetic ${a_{\mathrm{cut}}}^2N^2/g^2{R_{||}}^2$ contributions to the free energy for $a_{\mathrm{cut}} \gg ag^{1/2}$. This gives the size

$$R_{||} \approx (l_{\mathrm{B}}a^5)^{1/6} f^{5/18} (\sigma l_{\mathrm{B}}a)^{1/9} N^{3/4}$$

This result is consistent only if the radius is larger than the Gaussian radius $R_0 = N^{1/2}a$, i.e., if $N(\sigma a l_{\mathrm{B}})^{4/9} f^{10/9} (l_{\mathrm{B}}/a)^{2/3} \gg 1$ otherwise the chain remains Gaussian. Note however that the Flory approach is not very accurate in two dimensions and ignores the existence of the nontrivial θ point.
(26) de Gennes P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(27) The concept of the λ subchains is correct only if the electrostatic repulsion between excess charges $kT(l_{\mathrm{B}}\Delta f^2g^2/\lambda)$ is smaller than the polarization energy $kT(\lambda^2/a^2g)$. The λ-subchains is well-defined for the surface charge densities σ larger than $\mathrm{u}\Delta f^2/al_{\mathrm{B}}f$.
(28) Jackson, J. D. *Classical Electrodynamics*; Wiley & Sons: New York, 1975.
(29) de Gennes, P. G. *J. Phys. (France)* **1976**, *37*, 1445.
(30) Schiessel, H.; Oshanin, G.; Blumen, A. *Macromol. Theor. Simul.* **1996**, *5*, 45; *J. Chem. Phys.* **1995**, *103*, 5070.
(31) Odian, G. *Principle of Polymerization*; Wiley Interscience: New York, 1981.

MA9703057