

Effect of solvent quality on polyelectrolyte adsorption at an oppositely charged surface

Andrey V. Dobrynin

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

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The effects of the solvent quality on the adsorption of weakly charged polyelectrolytes at an oppositely charged surface are investigated using the self-consistent mean field theory. The analytical solutions of the self-consistent field equations are obtained in the case of θ , good and poor solvents for the polymer backbone. Using these analytical solutions the thickness of the adsorbed layer is calculated as a function of the surface charge density, salt concentration, and solvent quality. It is shown that for polyelectrolyte adsorption from θ and good solvents the surface charge is always overcompensated by adsorbed chains. For low ionic strengths the surface overcharging is inversely proportional to the Debye screening length. However, in the case of adsorption from a poor solvent the adsorbed polyelectrolytes undercompensate the surface charge. © 2001 American Institute of Physics. [DOI: 10.1063/1.1350818]

I. INTRODUCTION

Adsorption of polyelectrolytes^{1,2} presents considerable practical interest.^{3–5} This phenomena have found its application in different areas of science and technology such as colloids, medical science, pharmacy, food processing, water purification, etc. Over the last 30 years much experimental and theoretical efforts have been made to uncover the factors governing adsorption of polyelectrolytes at charged surfaces.^{3–5}

The majority of theoretical works dealing with polyelectrolyte adsorption on a charged surface has been carried out within the framework of the self-consistent field (SCF) method.⁴ In these theories the polymer density distribution is coupled to the local electrostatic potential through the combination of the Poisson–Boltzmann equation and the Edwards equation describing the polymer conformations in the effective external potential (see for review Refs. 4 and 5). This approach was first applied by Van der Schee and Lyklema⁶ and Evers *et al.*⁷ They have shown that in salt free-solutions strong repulsion between charged monomers leads to very thin adsorbed layers. If this interaction is screened, by adding salt, the adsorbed amount increases and the adsorbed layer becomes thicker.⁸ The extension of the Van der Schee and Lyklema theory to the case of weak polyelectrolytes was done by Bohmer *et al.*⁹

Polyelectrolyte adsorption has also been studied using the ground-state dominance approximation of the SCF method.^{10–13} The linearized solutions of the Poisson–Boltzmann and diffusive equations were obtained by Varoqui *et al.*¹⁰ They have considered the conformation of weakly charged polyelectrolytes at the liquid–solid interface and calculated the adsorption isotherm and the concentration profile of the polymers near the charged interface. The numerical solution of the nonlinear Poisson–Boltzmann equation was presented by Borukhov *et al.*¹² These authors have calculated the concentration profile of the weakly charged polyelectrolytes between two charged surfaces.

Despite the significant success of the SCF method in uncovering the major factors governing polyelectrolyte adsorption,⁴ this method relies on the numerical solution of a system of self-consistent equations which makes it extremely difficult to separate effects of different factors on polyelectrolyte adsorption and to provide simple physical interpretation of the obtained results. I will show in the present paper that it is possible to obtain the analytical solution of the self-consistent field equations in the case when the equilibrium polyelectrolyte concentration near a charged surface is determined by the balance between the electrostatic attraction of the charged monomers to the charged surface and the excluded volume interactions. For example, in the case of a θ -solvent for the polymer backbone this balance results in parabolic density profile of polyelectrolytes in the adsorbed layer. The paper is organized as follows. Section II is devoted to the solution of the nonlinear Poisson–Boltzmann equation for the polyelectrolyte adsorption in a θ -solvent. In Secs. III and IV, I generalize my results to the case of poor and good solvents.

II. STRUCTURE OF THE ADSORBED LAYER NEAR THE CHARGED SURFACE IN THE θ -SOLVENT

A. Model

Consider the adsorption of polyelectrolyte chains with the degree of polymerization N and having fraction f of the negative charges randomly distributed along the chains on a positively charged surface with the surface charge density $e\sigma$. The surface is located parallel to the xy -plane at point $z=0$. The chains adsorb from a dilute solution with the dielectric constant ϵ and the average polymer concentration and salt concentration are given by ρ_{bulk} and ρ_{salt} , respectively. The dissociated counterions of the polymer chains are distributed in the solutions with average density $f\rho_{\text{bulk}}$. Far from the charged surface the conformations of the polymer chains are not perturbed by electrostatic interactions with the oppositely charged surface and conformation of a polyelec-

trolyte chain is controlled by Coulomb repulsion between the charged monomers. This electrostatic repulsion leads to chain stretching on length scales larger than electrostatic blob^{17,18} of size D_e . The conformation of a chain inside the electrostatic blob is almost unperturbed by electrostatic interactions with the number of monomers in it being $g_e \approx (D_e/a)^2$ for a θ -solvent for polymer backbone. The size of the electrostatic blob D_e containing g_e monomers can be found by comparing the electrostatic energy of a blob $e^2 g_e^2 f^2 / \epsilon D_e$ with the thermal energy kT . This leads to the electrostatic blob size $D_e \approx au^{-1/3} f^{-2/3}$ and the number of monomers in it $g_e \approx u^{-2/3} f^{-4/3}$ (where $u = l_B/a$ is the ratio of the Bjerrum length $l_B = e^2 / \epsilon kT$ to the bond size a). In a dilute solution the polyelectrolyte configuration is that of an extended chain of N/g_e electrostatic blobs of length,

$$L \approx \frac{N}{g_e} D_e \approx au^{1/3} f^{2/3} N. \quad (1)$$

The electrostatic self-energy of the polyelectrolyte chain W_{pe} is proportional to the thermal energy kT times the number of electrostatic blobs N/g_e in the polyelectrolyte chain,

$$W_{pe} \approx kT u^{2/3} f^{4/3} N \approx kT \frac{N}{g_e}. \quad (2)$$

Combining this energy with the contribution due to translational degrees of freedom of the chains one can obtain the chemical potential of a polyelectrolyte chain far from the charged surface,

$$\mu_{ch} \approx kT \ln \left(\frac{\rho_{bulk} a^3}{N} \right) + kT \frac{N}{g_e}. \quad (3)$$

Near the charged surface the polyelectrolyte chains form a concentrated polymer solution. In this region the distribution of the polymer density can be described in the framework of the mean-field approximation, assuming that the electrostatic interactions of polyelectrolyte with the effective field created by other chains dominate over its electrostatic self-energy. In this approximation the polymer density $\rho(z)$ and the small ion density $\rho_\alpha(z)$ depends only on the distance z from the charged surface. This approximation is correct as long as the local polymer density $\rho(z)$ is higher than that inside the electrostatic blob $\rho_e \approx g_e / D_e^3 \approx a^{-3} u^{1/3} f^{2/3}$.

Within the mean-field approximation the free energy of the system has three terms,^{10–15} which include the electrostatic interactions between counterions, polyelectrolyte chains, and the surface charges, V_{elect} , the translational entropy of counterions F_{count} , and the free energy of polymer chains F_{pol} ,

$$\Delta F = V_{elect} + F_{pol} + F_{count}. \quad (4)$$

The part of the free energy describing the electrostatic interactions of the surface charges with the solution density fluctuations, V_{elect} , is

$$\begin{aligned} \frac{V_{elect}}{kT} &= 2\pi l_B \sigma S \int_0^\infty z q(z) dz - \pi l_B S \\ &\times \int_0^\infty \int_0^\infty |z - z'| q(z) q(z') dz dz'. \end{aligned} \quad (5)$$

The first term in the r.h.s. describes the effects of electrostatic interactions between charged surface and charge distribution $q(z)$ in the system

$$q(z) = -f\rho(z) + \sum_\alpha q_\alpha \rho_\alpha(z), \quad (6)$$

where q_α and $\rho_\alpha(z)$ are the valency and the local density of small ions in the system, $\rho(z)$ is the local polymer concentration. The second term in the r.h.s. of Eq. (5) describes the electrostatic interactions between the charged layers located at distances z and z' from the charged surface. The polymeric contribution F_{pol} to the free energy includes three terms, the conformational entropy of the polymer chains, the third virial term describing the monomer–monomer interactions in a θ -solvent, and the ideal gas contribution due to chains translational entropy in the adsorbed layer,

$$\begin{aligned} \frac{1}{S} \frac{F_{pol}}{kT} &= \frac{a^2}{6} \int_0^D \left(\frac{d}{dz} \sqrt{\rho(z)} \right)^2 dz \\ &+ \frac{a^6}{3} \int_0^D \rho(z)^3 dz + \frac{\Gamma}{N} \ln \left(\frac{\Gamma a^3}{DN e} \right), \end{aligned} \quad (7)$$

where Γ is the polymer surface coverage,

$$\Gamma = \int_0^D \rho(z) dz. \quad (8)$$

The polyelectrolyte chains are localized within the layer of thickness D and are in thermal equilibrium with the bulk. At equilibrium the chemical potential of the polyelectrolyte chains in the adsorbed layer,

$$\mu_{ads} = kT \ln \left(\frac{\Gamma a^3}{DN} \right) + N\mu, \quad (9)$$

where μ is the Lagrange multiplier for the constraint Eq. (8), is equal to that in the bulk.

The nonelectrostatic contribution of the small ions to the free energy (4) is taken into account at the level of their ideal gas entropy,

$$\frac{1}{S} \frac{F_{count}}{kT} = \sum_\alpha \int_0^\infty \rho_\alpha(z) \ln \left(\frac{\rho_\alpha(z)}{e} \right) dz. \quad (10)$$

To find the equilibrium polymer and counterion density distributions near the charged surface one has to take the variational derivative of the free energy with respect to polymer $\rho(z)$ and small ions $\rho_\alpha(z)$ densities subject to additional constraints that fix the total number of molecules in the system. The extremal equation for the polymer density distribution is

$$\frac{\mu}{kT} = a^6 \rho(z)^2 - f\varphi(z) - \frac{a^2}{6} \frac{1}{\sqrt{\rho(z)}} \frac{d^2 \sqrt{\rho(z)}}{dz^2}. \quad (11)$$

This parameter μ can be found from the condition that at equilibrium the chemical potentials of polyelectrolyte chains in the bulk μ_{ch} Eq. (3) and in the adsorbed layer μ_{ads} Eq. (9) are equal. For long polyelectrolyte chains ($N \gg 1$) the parameter μ is equal to $kT g_e^{-1}$ and can be considered as a chemical potential of the monomer in the bulk.

In Eq. (11), I have introduced the reduced electrostatic potential $\varphi(z)$,

$$\varphi(z) = -2\pi l_B \sigma z - 2\pi l_B \int_0^\infty |z - z'| q(z') dz' \quad (12)$$

that satisfies the Poisson equation

$$\frac{d^2 \varphi(z)}{dz^2} = 4\pi l_B \left(f\rho(z) - \sum_\alpha q_\alpha \rho_\alpha(z) \right), \quad (13)$$

with the boundary condition at the charged surface

$$\left. \frac{d\varphi(z)}{dz} \right|_{z=0} = -4\pi l_B \sigma. \quad (14)$$

I will assume that there is no specific interactions between polymers and surface except electrostatic ones and the surface is impenetrable to monomers. This gives the following boundary condition for polymer concentration at the charged surface:

$$\rho(0) = 0. \quad (15)$$

The distribution of small ions in the adsorbed polymer layer is given by the Boltzmann distribution,

$$\rho_\alpha(z) = \rho_\alpha \exp(-q_\alpha \varphi(z)), \quad (16)$$

where ρ_α is the bulk concentration of the small ions. Thus the system of Eqs. (11)–(13) together with the boundary conditions (14) and (15) describes the polyelectrolyte adsorption from a dilute polymer solution.

B. Self-similar adsorbed layer

The system of differential Eqs. (11)–(13) can be solved analytically when the screening of the charge surface is dominated by adsorbed polyelectrolyte chains and salt ions. In the case of the weak electrostatic potential $\varphi(z) \ll 1$ this system can be reduced to

$$\frac{\mu}{kT} = a^6 \rho(z)^2 - f\varphi(z) - \frac{a^2}{6} \frac{1}{\sqrt{\rho(z)}} \frac{d^2 \sqrt{\rho(z)}}{dz^2}, \quad (17)$$

$$\frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = 4\pi l_B f \rho(z), \quad (18)$$

where r_D is the Debye radius due to the salt ions ($r_D^{-2} = 8\pi l_B \rho_{\text{salt}}$). In my analysis of these equations I will first ignore the last term in the r.h.s. of Eq. (17), that is due to conformational entropy of the polyelectrolyte chains, and disregard the boundary condition for polymer concentration at the charged surface Eq. (15). The limitations of this approximation will be discussed below. For long polyelectrolyte chains ($N \gg 1$) the Lagrange multiplier μ is of the order of $kT g_e^{-1}$ and can be neglected if the local monomer concentration $\rho(z)$ is larger than $a^{-3} u^{1/3} f^{2/3}$. Taking this into account one can solve Eq. (17) for polymer density,^{16–19}

$$a^6 \rho(z)^2 \approx f\varphi(z), \quad (19)$$

and rewrite Eq. (18) as follows:

$$\frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = \frac{4\pi l_B f^{3/2}}{a^3} \sqrt{\varphi(z)}. \quad (20)$$

This equation is solved by the polymer density profile,

$$\rho(z) = \frac{16\pi}{3} \frac{u f^2 r_D^2}{a^5} \sinh^2 \left(\frac{D-z}{4r_D} \right), \quad (21)$$

where the thickness of the adsorbed layer D can be found from the boundary condition Eq. (14),

$$\frac{64\pi}{9} \frac{u f^3 r_D^3}{a^3} \sinh^3 \left(\frac{D}{4r_D} \right) \cosh \left(\frac{D}{4r_D} \right) = \sigma a^2. \quad (22)$$

For low salt concentrations ($r_D \gg D$) the polymer density profile has parabolic form,^{20,21}

$$\rho(z) = \frac{\pi}{3} \frac{u f^2 (D-z)^2}{a^5}, \theta\text{-solvent}, \quad (23)$$

and the layer thickness D is given by the following expression:

$$D = \left(\frac{9}{\pi} \right)^{1/3} a^{5/3} u^{-1/3} f^{-1} \sigma^{1/3}, \theta\text{-solvent}. \quad (24)$$

The adsorbed layer can be considered as built of the blobs with gradually increasing size $\xi(z)$ (see Fig. 1).^{20,21} The number of monomers $g(z)$ in a blob is determined from the fact that these blobs are space-filling $g(z) \approx \rho(z) \xi^3(z)$ and the statistics of a chain inside a blob is Gaussian $\xi^2(z) \approx a^2 g(z)$. This gives the dependence of the blob size,

$$\xi(z) \approx \frac{a^3}{u f^2 (D-z)^2}, \theta\text{-solvent} \quad (25)$$

and the number of monomers in them,

$$g(z) \approx \frac{a^4}{u^2 f^4 (D-z)^4}, \theta\text{-solvent} \quad (26)$$

at a distance z from a surface. These blobs are multivalent sections of polyions with the valency $q(z) = f g(z)$.

The density profile given by Eq. (23) is incorrect near the charge surface ($z \approx 0$) and at the edge of the adsorbing layer ($z \approx D$)—the regions with large gradients of polymer density. Close to the charged surface typical density fluctuations occur at length scales of the order of the correlation length $\xi(z) \approx (\rho(z) a^2)^{-1}$. Thus, the thickness of polymer depletion layer near charged surface is of the order of $\xi(0) \approx a^{1/3} u^{-1/3} \sigma^{-2/3}$. The contribution from this layer is negligible as long as the correlation length $\xi(0)$ is smaller than the thickness of the adsorbed layer D or for surface charge densities, σ , larger than

$$\sigma_e \approx f/a^2, \theta\text{-solvent}. \quad (27)$$

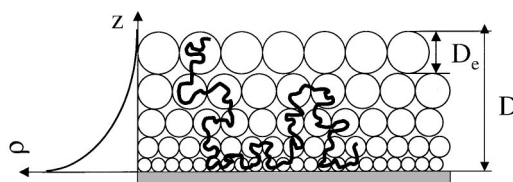


FIG. 1. Polymer density profile and layer structure in the self-similar adsorbed layer for polyelectrolyte adsorption from the θ -solvent ($\sigma_e < \sigma < \sigma_{\text{ion}}$).

At the edge of the adsorbing layer the three-body interactions $a^6\rho(z)^3$ becomes of the order of the chain conformational entropy,

$$\frac{u^3 f^6 (D-z)^6}{a^9} \approx a^6 \rho(z)^3 \approx \frac{a^2}{6} \left(\frac{d\sqrt{\rho(z)}}{dz} \right)^2 \approx \frac{u f^2}{a^3} \quad (28)$$

at a distance z from a charged surface of the order of

$$z \approx D - a(u f^2)^{-1/3} \approx D - D_e. \quad (29)$$

At these length scales the gradient term in Eq. (17) has to be taken into account. However, the contribution from this layer can also be neglected if the thickness of the adsorbed layer D is larger than the size of the electrostatic blob D_e or $\sigma > \sigma_e$.

Integration of the polymer density profile $\rho(z)$ between 0 and D gives the polymer surface excess,

$$\begin{aligned} \Gamma &= \int_0^D \rho(z) dz = \frac{3}{8} \frac{\sigma}{f} \left(\frac{2 \sinh(y/2) - y}{\sinh^3(y/4) \cosh(y/4)} \right) \\ &\approx \frac{\sigma}{f} \left(1 - \frac{D^2}{20 r_D^2} \right), \end{aligned} \quad (30)$$

where y is the ratio of the layer thickness D to the Debye screening length r_D ($y = D/r_D$). Thus at zero salt concentration the adsorbed polyelectrolytes compensate the surface charge σ .

The addition of salt decreases the polymer adsorbed amount, because the salt ions also taking part in screening of the surface charge. The power law dependence of the polymer surface excess on the salt concentration can be understood by following simple arguments. The typical excess charge density $\delta\rho_{\text{salt}}$ of the salt ions in the adsorbing layer is

$$\delta\rho_{\text{salt}}(z) \approx \rho_{\text{salt}}^-(z) - \rho_{\text{salt}}^+(z) \approx \rho_{\text{salt}}\varphi(z), \quad (31)$$

where $\varphi(z)$ is the value of the electrostatic potential at distance z from the charged surface. A typical value of the electrostatic potential $\varphi(z)$ in the adsorbed layer can be estimated as $l_B \sigma D$. Multiplying the excess charge density $\delta\rho_{\text{salt}}$ by the layer thickness D one obtains the counterion surface excess,

$$\Gamma_{\text{salt}} \approx \delta\rho_{\text{salt}} D \approx l_B \rho_{\text{salt}} \sigma D^2 \approx \sigma \frac{D^2}{r_D^2}. \quad (32)$$

Thus the part $\sigma D^2/r_D^2$ of the surface charge is screened by the salt ions that leaves for polyelectrolyte chains to screen only $\sigma - \sigma D^2/r_D^2$ part of the surface charge.

C. Surface overcharging

As I have already pointed out the mean-field description of the polyelectrolyte adsorbed layer presented above is incorrect at distances z from the surface larger than $D - D_e$. At these length scales the fluctuations of the polymer density $a^{-3}(u f^2)^{1/3}$ become larger than the average polymer density given by Eq. (23). In order to obtain the surface overcharging by adsorbed polyelectrolytes, due to fluctuations of polymer density at the edge of the adsorbed layer, the solution is divided into two regions. Region I of the thickness D is where the screening of surface charge is due to polyelectro-

lyte chains and salt ions. Region II ($z > D$) is where the polymer concentration is equal to zero and the screening of the surface charge is controlled by the salt ions.

In region II the electrostatic potential satisfies the following differential equation:

$$\frac{d^2 \varphi_{\text{II}}(z)}{dz^2} = \frac{\varphi_{\text{II}}(z)}{r_D^2}, \quad (33)$$

with the boundary condition

$$\left. \frac{d\varphi_{\text{II}}(z)}{dz} \right|_{z=D} = -4\pi l_B \delta\sigma, \quad (34)$$

where $\delta\sigma = \sigma - f\Gamma - \Gamma_{\text{salt}}$ is the effective surface charge density whose value has to be found self-consistently to match the electrostatic potential and its derivative within region I at $z \approx D$. A positive value of $\delta\sigma$ corresponds to undercharging of a charged surface. The electrostatic potential in region II is

$$\varphi_{\text{II}}(z) = 4\pi l_B r_D \delta\sigma \exp\left(-\frac{z-D}{r_D}\right). \quad (35)$$

In region I the local electrostatic potential and polymer concentration are related through the system of equations,

$$g_e^{-1} = a^6 \rho(z)^2 - f \varphi_{\text{I}}(z) - \frac{a^2}{6} \frac{1}{\sqrt{\rho(z)}} \frac{d^2 \sqrt{\rho(z)}}{dz^2}, \quad (36)$$

$$\frac{d^2 \varphi_{\text{I}}(z)}{dz^2} - \frac{\varphi_{\text{I}}(z)}{r_D^2} = 4\pi l_B f \rho(z). \quad (37)$$

The order of magnitude estimate for the effective surface charge density, $\delta\sigma$, can be obtained by estimating the terms in the last equation at $z = D$ as follows:

$$g_e^{-1} \approx -4\pi f l_B \delta\sigma r_D - \frac{a^2}{6} \frac{1}{\sqrt{\rho(z)}} \frac{d^2 \sqrt{\rho(z)}}{dz^2} \Big|_{z=D}. \quad (38)$$

The second term in the r.h.s. of Eq. (38) can be estimated by taking the square root from both sides of Eq. (37) and by taking the second derivative with respect to z . Once again using the continuity condition of the electrostatic potential, one can obtain the necessary derivatives of the electrostatic potential $\varphi_{\text{I}}(z)$ at $z = D$ from that of the potential $\varphi_{\text{II}}(z)$ in region II. After some algebra Eq. (38) can be rewritten as follows:

$$g_e^{-1} \approx -4\pi f l_B \delta\sigma r_D - \frac{a^2}{24 r_D^2}. \quad (39)$$

Solving this equation for $\delta\sigma$ one finds

$$\delta\sigma \approx -\frac{f^{1/3}}{u^{1/3} a r_D} - \frac{a}{f u r_D^3} \approx -\sigma_e \frac{D_e}{r_D} \left(1 + \frac{D_e^2}{r_D^2} \right), \quad \theta\text{-solvent} \quad (40)$$

for the surface overcharging by adsorbed polyelectrolyte chains in region I. The overcompensation of the surface charge by the adsorbed polyelectrolytes is due to positive chemical potential of monomers in the bulk g_e^{-1} . It is important to point out that the surface overcharging $\delta\sigma$ is universal and is independent on the bare surface charge density σ .

A different result obtained by a similar approach for the surface overcharging $\delta\sigma$ was recently derived by Joanny,¹⁵ who showed that the surface overcharging $\delta\sigma$ is proportional to the thickness of the adsorbed layer D and inversely proportional to the Debye radius r_D ($\delta\sigma \approx \sigma D/r_D$). I believe that the discrepancy with the result presented above is due to the constant polymer density profile in the adsorbed layer assumed in Ref. 15.

D. Screening of the adsorbing surface by small ions

The screening of the charged surface is dominated by polyelectrolytes as long as the thickness of the adsorbed layer D is smaller than the Gouy–Chapman length $\lambda = (2\pi l_B \sigma)^{-1}$ or the surface charge density σ is smaller than σ_{ion} , where

$$\sigma_{\text{ion}} \approx \frac{f^{3/4}}{a^{2u/1/2}}, \theta\text{-solvent.} \quad (41)$$

There will be on average one charged monomer per surface blob $fg(0)$ at the surface charge density $\sigma \approx \sigma_{\text{ion}}$. At this surface charge density the monomer concentration at the surface is equal to $a^{-3}f^{1/2}$. The further increase of polymer density is unfavorable due to the high cost of the short-range monomer–monomer repulsive interactions. For higher surface charge densities, $\sigma > \sigma_{\text{ion}}$, counterions start to dominate the screening of the surface potential inside a layer of thickness h . A counterion pays of the order kT in translational entropy when it is localized at surface inside the layer of thickness h , while it will cost more than kT in repulsive energy between monomers to produce similar screening effects by increasing polymer concentration above $a^{-3}f^{1/2}$.

In order to obtain analytical expressions for polymer and counterion density distributions the adsorbed layer is divided into two regions. Inside region I with the thickness h (see Fig. 2) the screening of the surface electric field is dominated by counterions. The Poisson–Boltzmann equation for this region is

$$\frac{d^2 \delta \varphi(z)}{dz^2} = 4 \pi l_B \rho_S(h) \exp(\delta \varphi(z)), \quad (42)$$

where $\rho_S(h)$ is the counterion density at $z=h$ and $\delta\varphi(z)$ is the electrostatic potential measured with respect to its value $\varphi(h)$ at $z=h$ ($\delta\varphi(z) = \varphi(z) - \varphi(h)$). The electrostatic potential inside region I has a logarithmic form,

$$\delta\varphi(z) = -2 \ln\left(1 + \frac{z-h}{\lambda_2}\right), \quad (43)$$

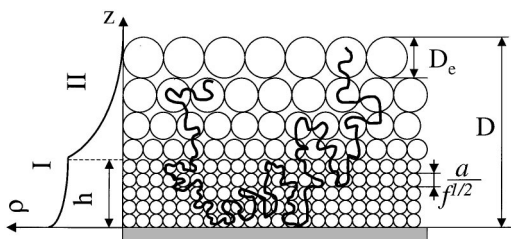


FIG. 2. Polymer density profile and layer structure for polyelectrolyte adsorption from the θ -solvent ($\sigma > \sigma_{\text{ion}}$).

where the parameter λ_2 is equal to $1/\sqrt{2\pi l_B \rho_S(h)}$. At the charged surface the derivative of the electrostatic potential $d\varphi(z)/dz$ has to be equal to $-4\pi l_B \sigma$. This requirement gives the following relation between λ , λ_2 , and h :

$$\lambda_2 = \lambda + h. \quad (44)$$

The counterion distribution in this region is

$$\rho_S(z) = \frac{1}{2\pi l_R} (\lambda_2 + z - h)^{-2}. \quad (45)$$

The polymer density profile inside region I has a weak logarithmic dependence on the distance z from the charged surface,

$$\rho(z) \approx a^{-3} f^{1/2} \sqrt{\varphi(h) - 2 \ln \left(1 + \frac{z-h}{\lambda_2} \right)}. \quad (46)$$

The localized counterions (inside region I) reduces the surface charge density σ up to the value σ_2 that determines the boundary condition for the nonlinear Eq. (20) in region II,

$$\left. \frac{d\varphi(z)}{dz} \right|_{z=h} = -4\pi l_B \sigma_2. \quad (47)$$

In region II the screening of the charged surface is controlled by adsorbed polyelectrolytes. The solution of Eq. (20) at low salt concentrations still gives the parabolic polymer density profile,

$$\rho(z) \approx \frac{\pi}{3} \frac{uf^2(D_{\sigma_2} + h - z)^2}{a^5}, \quad (48)$$

with the thickness D_{σ_2} of region II being given by Eq. (24), where the surface charge density σ has to be substituted by the effective surface charge density σ_2 at the region boundary ($z=h$). The boundary between the two regions is defined as a plane where the local concentration of counterions $\rho_s(h)$ is equal to the concentration of the charged monomers $f\rho(h)$,

$$\frac{1}{2\pi l_B \lambda_\gamma^2} = \frac{\pi}{3} \frac{uf^3 D_{\sigma_2}^2}{a^5}. \quad (49)$$

Solving together Eqs. (44) and (49) one can find the effective surface charge density σ_γ ,

$$\sigma_2 = \frac{6^{1/4}}{2\sqrt{\pi}} \frac{f^{3/4}}{u^{1/2}a^2} \approx \sigma_{\text{ion}}. \quad (50)$$

The total thickness D of the polymer adsorbed layer is the sum of the thickness h of region I and the thickness D_{σ_2} of region II,

$$D=h+D_{\sigma_2}=\frac{4}{6^{1/4}\sqrt{\pi}}\frac{a}{u^{1/2}f^{3/4}}-\lambda. \quad (51)$$

This layer thickness saturates at $(4/6^{1/4}\sqrt{\pi})(a/u^{1/2}f^{3/4})$ for high surface charge densities, $\sigma \gg \sigma_{\text{ion}}$.

III. POLYELECTROLYTE ADSORPTION IN A POOR SOLVENT

The polyelectrolyte chains in a poor solvent form a necklacelike globule^{22–30} of beads connected by narrow strings. The monomer density ρ inside this globule is defined by the balance between the two body attraction $-\tau a^3 \rho N$ and three body repulsion $a^6 \rho^2 N$. The resulting density inside the globule is

$$\rho \approx \tau/a^3, \quad (52)$$

where the reduced temperature is given by

$$\tau = (\Theta - T)/\Theta, \quad (53)$$

and Θ is the theta temperature of the polymer.

The shape of the globule is determined by competition between electrostatic repulsion between charged monomers and surface energy of the globule.^{22,23} The size of the beads,

$$D_b \approx a(uf^2)^{-1/3} \quad (54)$$

is determined by the Rayleigh's stability condition,

$$l_B f^2 m_b^2 / D_b \approx D_b^2 \xi_T^{-2}, \quad (55a)$$

where

$$m_b \approx \tau / uf^2 \quad (56)$$

is the number of monomers in a bead ($m_b \approx \rho D_b^3$). The diameter of the strings is of the order of thermal blob size $\xi_T \approx a/\tau$. The length l_{str} of the string connecting two neighboring beads can be estimated by balancing the electrostatic repulsion between two closest beads $kT l_B f^2 m_b^2 / l_{\text{str}}$ and the surface energy of the string $kT l_{\text{str}} / \xi_T$. The equilibrium distance between beads is

$$l_{\text{str}} \approx a \left(\frac{\tau}{uf^2} \right)^{1/2} \approx a m_b^{1/2}. \quad (57)$$

The mass of the string between neighboring beads $m_{\text{str}} \approx \rho l_{\text{str}} \xi_T^2$ is much smaller than the mass of the bead m_b ,

$$\frac{m_{\text{str}}}{m_b} \approx \left(\frac{uf^2}{\tau^3} \right)^{1/2} \ll 1. \quad (58)$$

In this case the number of beads N_{bead} on a chain is approximately equal to $N/m_b \approx uf^2 N / \tau$. Since most of the necklace length is due to the strings ($l_{\text{str}} \gg D_b$), the length of the necklace can be estimated as the number of beads N_{bead} on the chain times the length of a string l_{str} between neighboring beads,

$$L_{\text{nec}} \approx N_{\text{bead}} l_{\text{str}} \approx a \left(\frac{uf^2}{\tau} \right)^{1/2} N \approx a \frac{N}{m_b^{1/2}}. \quad (59)$$

In this approximation the total free energy of the polyelectrolyte chain in a poor solvent is

$$\frac{W_{\text{nec}}}{kT} \approx N \frac{l_B f^2 m_b}{D_b} + \frac{l_B f^2 N^2}{L_{\text{nec}}} - N \frac{3\tau^2}{16}, \quad (60)$$

where the first term is the electrostatic and surface energies of the beads, the second one is the electrostatic repulsion between beads which is of the order of the surface energy of the strings, and the last one is the free energy of the polymer

backbone in a poor solvent. The electrostatic repulsion between beads [the second term in the r.h.s. of Eq. (60)] is smaller than the electrostatic energy of the beads (the first term) as long as the length of the string l_{str} between two neighboring beads is larger than the bead size D_b and can be neglected,

$$\frac{W_{\text{nec}}}{kT} \approx N(uf^2)^{1/3} \tau - N \frac{3\tau^2}{16}. \quad (61)$$

Combining this energy with the contribution due to translational degrees of freedom of the chains one can obtain the chemical potential of a polyelectrolyte chain far from the charged surface,

$$\mu_{\text{ch}} \approx kT \ln \left(\frac{\rho_{\text{bulk}} a^3}{N} \right) + kTN \left((uf^2)^{1/3} \tau - \frac{3}{16} \tau^2 \right). \quad (62)$$

The polymeric contribution F_{pol} to the free energy of the adsorbed layer in a poor solvent for the polymer backbone has the following form:

$$\begin{aligned} \frac{1}{S} \frac{F_{\text{pol}}}{kT} = & \frac{\Gamma}{N} \ln \left(\frac{\Gamma a^3}{DNe} \right) + \frac{a^2}{6} \int_0^D \left(\frac{d}{dz} \sqrt{\rho(z)} \right)^2 dz \\ & + \int_0^D \left(\frac{a^6}{3} \rho(z)^3 - \frac{a^3 \tau}{2} \rho(z)^2 \right) dz. \end{aligned} \quad (63)$$

With this modification of the polymeric contribution to the free energy of adsorbed layer the system of differential Eqs. (11)–(13) is

$$(uf^2)^{1/3} \tau - \frac{3}{16} \tau^2 \approx -\tau a^3 \rho(z) + a^6 \rho(z)^2 - f\varphi(z), \quad (64)$$

$$\frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = 4\pi l_B f \rho(z). \quad (65)$$

Solving the first equation for polymer density $\rho(z)$ in the adsorbed layer as a function of the local electrostatic potential $\varphi(z)$,

$$a^3 \rho(z) \approx \begin{cases} \frac{3}{4} \tau + \frac{2f\varphi(z)}{\tau}, & \text{for } f\varphi(z) < \tau^2/16, \\ \sqrt{f\varphi(z)}, & \text{for } f\varphi(z) > \tau^2/16, \end{cases} \quad (66)$$

one can rewrite the Poisson–Boltzmann equation in terms of the electrostatic potential $\varphi(z)$ only,

$$\begin{aligned} \frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = & \frac{4\pi l_B f}{a^3} \begin{cases} \frac{3}{4} \tau + \frac{2f\varphi(z)}{\tau}, & \text{for } f\varphi(z) < \tau^2/16, \\ \sqrt{f\varphi(z)}, & \text{for } f\varphi(z) > \tau^2/16. \end{cases} \end{aligned} \quad (67)$$

Thus depending on the solvent quality for the polymer backbone there are two different cases. In the case when $f\varphi(0) \ll \tau^2$ the solution of the Poisson–Boltzmann equation is

$$\varphi(z) \approx \frac{6\pi l_B f \tau r_{\text{eff}}^2}{a^3} \sinh^2 \left(\frac{D-z}{2r_{\text{eff}}} \right), \quad (68)$$

where the effective screening length r_{eff}^{-2} is

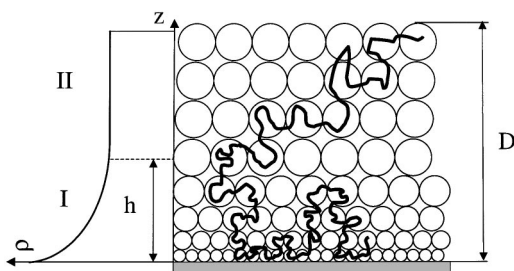


FIG. 3. Polymer density profile and layer structure for polyelectrolyte adsorption from the poor solvent ($\sigma_\theta < \sigma < \sigma_{\text{ion}}$).

$$r_{\text{eff}}^{-2} = r_D^{-2} + \frac{8\pi l_B f^2}{a^3 \tau}. \quad (69)$$

The layer thickness D can be found from the boundary condition for the electrostatic potential,

$$\frac{3f\tau r_{\text{eff}}}{2a^3} \sinh\left(\frac{D}{2r_{\text{eff}}}\right) \cosh\left(\frac{D}{2r_{\text{eff}}}\right) = \sigma. \quad (70)$$

In the limit of a thin adsorbed layer, $D/r_{\text{eff}} \ll 1$, this equation has a simple solution,

$$D \approx \frac{4a^3 \sigma}{3f\tau}, \quad \text{poor solvent.} \quad (71)$$

Thus the layer thickness in this region scales linearly with the surface charge density σ . This region starts when the thickness of the adsorbed layer D becomes larger than the bead size D_b in the range of the surface charge densities,

$$\sigma > \sigma_e \approx \frac{\tau}{a^2} \left(\frac{f}{u}\right)^{1/3}, \quad \text{poor solvent.} \quad (72)$$

The polymer density $\rho(z)$ in the adsorbed layer is almost constant and is equal to that inside beads $3\tau/4a^3$. The layer is built by the blobs of almost constant size $\xi_T \approx a\tau^{-1}$ which indicates that electrostatic attraction of charged monomers to a charged surface is weaker than two-body attractions between them.

The electrostatic attraction of charged monomers to a charged surface start to compress the adsorbed polymer layer near the charged surface at surface charge densities σ of the order of

$$\sigma_\theta \approx \frac{1}{8} \sqrt{\frac{3}{2\pi}} \frac{\tau^{3/2}}{a^{3/2} l_B^{1/2}} \approx \frac{\tau^{3/2}}{a^2 u^{1/2}}. \quad (73)$$

For higher surface charge densities ($\sigma > \sigma_\theta$) the value of the electrostatic potential at the charged surface $\varphi(0)$ is larger than $f^{-1}\tau^2$. There are two different regions in the adsorbed layer. Close to the charged surface the structure of the adsorbed layer is similar to the one for adsorption from θ -solvent where polymer density profile is determined by the balance between electrostatic attraction of charged monomers to charged surface and three-body monomer–monomer repulsion. While the polymer density in the outer layer stays almost constant and is determined by the balance between two-body attraction and three-body repulsion. The schematic representation of the adsorbed layer is given in Fig. 3. The electrostatic potential in the adsorbed layer is

$$\varphi(z) \approx \begin{cases} \left(\frac{\tau^{1/2}}{2f^{1/4}} + \sqrt{\frac{\pi}{3}} \frac{u^{1/2} f^{3/4}}{a} (D_1 - z) \right)^4, & \text{for } z \leq D_1, \\ \frac{3\pi u f \tau}{2a^2} (z - D_1)^2 - \sqrt{\frac{\pi}{12}} \frac{u^{1/2} \tau^{3/2}}{a} (z - D_1) + \frac{\tau^2}{16f}, & \text{for } z \geq D_1, \end{cases} \quad (74)$$

where D_1 is the thickness of the layer where electrostatic attraction is stabilized by the three-body repulsion,

$$D_1 \approx \left(\frac{9}{\pi} \right)^{1/3} a^{5/3} u^{-1/3} f^{-1} \sigma^{1/3} - \sqrt{\frac{3}{4\pi}} a \tau^{1/2} u^{-1/2} f^{-1}. \quad (75)$$

The total thickness of the adsorbed layer D can be estimated from the electroneutrality condition of the charged surface/adsorbed layer system,

$$D \approx \left(\frac{9}{\pi} \right)^{1/3} a^{5/3} u^{-1/3} f^{-1} \sigma^{1/3} - \frac{5}{6\sqrt{3}\pi} a \tau^{1/2} u^{-1/2} f^{-1}, \quad \text{for } \sigma_\theta < \sigma < \sigma_{\text{ion}}. \quad (76)$$

In this region the thickness of the adsorbed layer is growing as $\sigma^{1/3}$.

As in the case of θ -solvent counterions begin to screen the surface charge at surface charge densities σ larger than σ_{ion} . In this range of surface charge densities there are three different regions in the adsorbed layer. Close to the charge surface at the length scales $z < a/u^{1/2} f^{3/4}$ the polymer density is constant up to logarithmic corrections and is of the order of $a^{-3} f^{1/2}$. In the intermediate length scales ($z \approx a/u^{1/2} f^{3/4}$) the polymer density $\rho(z)$ has a parabolic profile. It is constant again near the edge of the adsorbed layer. The thickness of the adsorbed layer D in this region saturates at $au^{-1/2} f^{-3/4}$.

At the end of this section let us comment on the surface overcharging by adsorbed polyelectrolytes. In the case of the poor solvent Eq. (39) has the following form:

$$(uf^2)^{1/3} \tau - \frac{3}{16} \tau^2 \approx -4\pi f l_B \delta \sigma r_D - \frac{a^2}{24r_D^2}. \quad (77)$$

For effective temperatures $\tau > (uf^2)^{1/3}$ when the thermal blob size $\xi_T \approx a\tau^{-1}$ is smaller than the electrostatic blob size $D_e \approx a(uf^2)^{-1/3}$, the solution of this equation is

$$\delta \sigma \approx \frac{3}{64\pi} \frac{\tau^2}{f l_B r_D} - \frac{1}{96\pi} \frac{a^2}{f l_B r_D^3} \approx \frac{3}{64\pi} \frac{\tau^2}{f l_B r_D}. \quad (78)$$

$\delta \sigma$ is positive and the surface is undercharged by adsorbed polyelectrolytes at finite salt concentrations.

IV. POLYELECTROLYTE ADSORPTION IN A GOOD SOLVENT

The calculation of the polyelectrolyte adsorption in a good solvent for the polyelectrolyte backbone can be done analogously to the calculations for a θ -solvent (see Sec. II) with two modifications:

- (i) The gradient term in a good solvent differs from that in a θ -solvent;
- (ii) The density in the adsorbed layer is stabilized by the two-body monomer–monomer repulsion.

If the chains are compressed to concentration ρ , 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 $\xi(\rho) \approx a(\rho a^3)^{-3/4}$.¹⁷ The excluded volume interactions in this solution are of the order of the thermal energy kT per correlation blob. Thus, the polymeric term in good solvent is¹⁷

$$\frac{1}{S} \frac{F_{\text{pol}}}{kT} \approx \frac{C_1}{2} \int_0^D \frac{1}{\xi(\rho)^3} \left(\frac{\xi(\rho)}{\rho(z)} \frac{d\rho(z)}{dz} \right)^2 dz + \frac{4C_2}{9} \int_0^D \rho(z) [\rho(z) a^3]^{5/4} dz + \frac{\Gamma}{N} \ln \left(\frac{\Gamma a^3}{DNe} \right), \quad (79)$$

where C_1 and C_2 are numerical constants of the order of unity (in calculations below I will set $C_1 = C_2 = 1$). In this case the system of extremal equations for polymer density $\rho(z)$ and electrostatic potential $\varphi(z)$ in the adsorbed polymeric layer can be reduced to

$$(g_e^{\text{good}})^{-1} \approx (\rho(z) a^3)^{5/4} - f\varphi(z) + \frac{8}{3} a^{5/4} \frac{1}{\rho(z)^{5/8}} \frac{d^2 \rho(z)^{3/8}}{dz^2}, \quad (80)$$

$$\frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = 4\pi l_B f \rho(z), \quad (81)$$

where $g_e^{\text{good}} \approx (uf^2)^{-5/7}$ is the number of monomers in the electrostatic blob in a good solvent.^{17,18} For two-body stabilization the relation between local polymer density and electrostatic potential is

$$(\rho(z) a^3)^{5/4} \approx f\varphi(z). \quad (82)$$

Taking this into account one can rewrite the Poisson–Boltzmann equation for polymers in a good solvent as follows:

$$\frac{d^2 \varphi(z)}{dz^2} - \frac{\varphi(z)}{r_D^2} = \frac{4\pi l_B f^{9/5}}{a^3} \varphi(z)^{4/5}. \quad (83)$$

The solution of this differential equation is

$$\varphi(z) = \left(\frac{40\pi}{9} \right)^5 \frac{u^5 f^9 r_D^{10}}{a^{10}} \sinh^{10} \left(\frac{D-z}{10r_D} \right), \quad (84)$$

where the thickness of the adsorbed layer D can be found from the boundary condition Eq. (14),

$$\left(\frac{40\pi}{9} \right)^5 \frac{u^4 f^9 r_D^9}{a^9} \sinh^9 \left(\frac{D}{10r_D} \right) \cosh \left(\frac{D}{10r_D} \right) = 4\pi \sigma a^2. \quad (85)$$

For low salt concentrations ($r_D \gg D$) the polymer density profile has the following form:

$$\rho(z) = \left(\frac{4\pi}{90} \right)^4 \frac{u^4 f^8 (D-z)^8}{a^{11}}, \quad (86)$$

and the layer thickness D is

$$D = 9^{1/9} \left(\frac{90}{4\pi} \right)^{4/9} a^{11/9} u^{-4/9} f^{-1} \sigma^{1/9}. \quad (87)$$

The thickness of the adsorbed layer in a good solvent has much weaker dependence on the surface charge density σ than that in a θ -solvent. The thickness of the adsorbed layer D becomes of the order of the size of the electrostatic blob size D_e^{good} at surface charge density σ of the order of

$$\sigma_e \approx a^{-2} u^{1/7} f^{9/7}, \quad \text{good solvent.} \quad (88)$$

The adsorbed layer is build of the space-filling $g(z) \approx \rho(z) \xi^3(z)$ blobs with gradually increasing size $\xi(z)$. The statistics of the chain inside each blob is a self-avoiding walk $\xi(z) \approx a g^{3/5}(z)$. This gives the dependence of the blob size as

$$\xi(z) \approx \frac{a^7}{u^3 f^6 (D-z)^6}, \quad \text{good solvent,} \quad (89)$$

and the number of monomers in them,

$$g(z) \approx \frac{a^{10}}{u^5 f^{10} (D-z)^{10}}, \quad \text{good solvent} \quad (90)$$

at a distance z from surface.

The counterions start to dominate the screening of the charged surface when the thickness of the adsorbed layer D becomes larger than the Gouy–Chapman length $\lambda = (2\pi l_B \sigma)^{-1}$ or when the surface charge density σ becomes larger than

$$\sigma_{\text{ion}} \approx \frac{f^{9/10}}{a^2 u^{1/2}}, \quad \text{good solvent.} \quad (91)$$

For higher surface charge densities $\sigma > \sigma_{\text{ion}}$ the thickness of the adsorbed layer saturates at

$$D \approx a u^{-1/2} f^{-9/10}, \quad \text{good solvent.} \quad (92)$$

The surface overcharging by adsorbed polyelectrolyte chains in a good solvent is

$$\delta\sigma \approx -\sigma_e \frac{D_e^{\text{good}}}{r_D} \approx -\frac{f^{3/7}}{u^{2/7} a r_D}, \quad \text{good solvent.} \quad (93)$$

V. DISCUSSION

I have considered the effects of solvent quality on the adsorption of charged polymers on an oppositely charged surface. For adsorption from θ and good solvents for the polymer backbone, the equilibrium density profile in the adsorbed layer is determined by balancing the electrostatic attraction of charged monomers to the surface and short-range monomer–monomer repulsion ($\sigma_e < \sigma < \sigma_{\text{ion}}$). On the length scales $z < D - D_e$ the polyelectrolytes form a self-similar carpet with polymer density decaying as $(D-z)^2$ in a θ -solvent for the polymer backbone and as $(D-z)^8$ in a good solvent. The thickness of the adsorbed layer D increases with surface charge density as $\sigma^{1/3}$ in a θ -solvent and as $\sigma^{1/9}$ in a good solvent.

For very high surface charge densities ($\sigma > \sigma_{\text{ion}}$) near the wall the surface counterions dominate the screening of

the surface potential inside a layer of thickness h and reduce the effective surface charge density at $z \approx h$ to the crossover value σ_{ion} . The polymer density within this layer of thickness h is almost constant with one elementary charge per correlation blob. On intermediate length scales, adsorbed polyelectrolytes form a self-similar structure as described above. In this region the thickness of the adsorbed layer saturates at $au^{-1/2}f^{-3/4}$ in a θ -solvent for the polymer backbone and at $au^{-1/2}f^{-9/10}$ in a good solvent.

For adsorption of polyelectrolytes from a poor solvent for the polymer backbone in the interval of the surface charge densities $\sigma_e < \sigma < \sigma_\theta$ the thickness of the adsorbed layer grows linear with the surface charge density σ . The polymer density in the adsorbed layer is constant and equal to τa^{-3} .

If the surface charge density increases further ($\sigma_\theta < \sigma < \sigma_{\text{ion}}$), the equilibrium density profile in the adsorbed layer is determined by the balance between electrostatic attraction of charged monomers to the surface and short-range monomer–monomer repulsion in the layers close to the surface and by the balance of the two-body attraction and three-body repulsion further away from it. On length scales $z < h$ the polyelectrolytes form a self-similar carpet with polymer density decaying as $(D-z)^2$. At intermediate length scales ($h < z < D$) the polymer density in the adsorbed layer is constant and is equal to that inside the polymeric globule $a^{-3}\tau$. The layer thickness increases with surface charge density as $\sigma^{1/3}$.

As in the case of θ and good solvents for very high surface charge densities ($\sigma > \sigma_{\text{ion}}$) the surface counterions dominate the screening of the surface potential near the wall. There are three different regions in the adsorbed layer. Close to the charged surface, counterions dominate the surface screening and the polymer density is almost constant $\rho \approx a^{-3}f^{1/2}$ with one elementary charge per correlation blob. Further away from the charged surface adsorbed polyelectrolytes form a self-similar structure with a parabolic density profile. At the edge of the adsorbed layer the polymer density is constant again and is equal to $a^{-3}\tau$. The thickness of the adsorbed layer saturates at $au^{-1/2}f^{-3/4}$.

Adsorbed polyelectrolytes always overcompensate the surface charge for adsorption from θ and good solvents for the polymer backbone. At low ionic strengths the surface overcharging increases with increasing the salt concentration. Polyelectrolyte chains in a poor solvent demonstrate qualitatively different behavior. In this solvent, the adsorbed chains undercompensate the surface charge and polymer surface coverage always decreases with increasing salt concentration.

Of course the theory presented here does not cover all aspects of polyelectrolyte adsorption. I leave aside the ques-

tion of adsorption of weak polyelectrolytes where the actual charge fraction f is controlled by the pH of the solution and by the local environment. Another problem that has not been discussed in the present paper is the effect of specific interactions between the charged surface and polymer backbone. I will address these problems in future publications.

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- ¹ *Polyelectrolytes*, edited by M. Hara (Marcel Dekker, New York, 1993).
- ² K. S. Schmitz, *Macroions in Solution and Colloidal Suspension* (VCH, New York, 1993).
- ³ M. Kawaguchi and A. Takahashi, *Adv. Colloid Interface Sci.* **37**, 219 (1992).
- ⁴ G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Gasev, and B. Vincent, *Polymer at Interfaces* (Chapman and Hall, London, 1993).
- ⁵ A. K. Bajpai, *Prog. Polym. Sci.* **22**, 523 (1997).
- ⁶ H. A. Van der Schee and J. Lyklema, *J. Phys. Chem.* **88**, 6661 (1984).
- ⁷ O. A. Evers, G. J. Fleer, J. M. H. M. Scheutjens, and J. Lyklema, *J. Colloid Interface Sci.* **111**, 446 (1986).
- ⁸ J. Blaakmeer, M. R. Bohmer, M. A. Cohen Stuart, and G. J. Fleer, *Macromolecules* **23**, 2301 (1990).
- ⁹ M. R. Bohmer, O. A. Evers, and J. M. H. M. Scheutjens, *Macromolecules* **23**, 2288 (1990).
- ¹⁰ R. Varoqui, A. Johner, and A. Elaissari, *J. Chem. Phys.* **94**, 6873 (1991).
- ¹¹ R. Varoqui, *J. Phys. II* **3**, 1097 (1993).
- ¹² I. Borukhov, D. Andelman, and H. Orland, *Europhys. Lett.* **32**, 499 (1995).
- ¹³ X. Chatellier and J.-F. Joanny, *J. Phys. II* **6**, 1669 (1996).
- ¹⁴ I. Borukhov, D. Andelman, and H. Orland, *Macromolecules* **31**, 1665 (1998).
- ¹⁵ J.-F. Joanny, *Eur. Phys. J. B* **9**, 117 (1999).
- ¹⁶ P.-G. de Gennes, P. Pincus, R. M. Velasco, and F. Brochard, *J. Phys. (Paris)* **37**, 1461 (1976).
- ¹⁷ P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- ¹⁸ A. V. Dobrynin, R. H. Colby, and M. Rubinstein, *Macromolecules* **28**, 1859 (1995).
- ¹⁹ J. N. Israelachvili, *Intermolecular and Surface Forces* (Cornell University Press, Ithaca, 1985).
- ²⁰ A. V. Dobrynin, A. Deshkovskii, and M. Rubinstein, *Phys. Rev. Lett.* **84**, 3101 (2000).
- ²¹ A. V. Dobrynin, A. Deshkovskii, and M. Rubinstein, *Macromolecules* (submitted).
- ²² A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, *Macromolecules* **29**, 2974 (1996).
- ²³ A. V. Dobrynin and M. Rubinstein, *Macromolecules* **32**, 915 (1999).
- ²⁴ M. Castelnovo, P. Sens, and J.-F. Joanny, *Eur. Phys. J. E* **1**, 115 (2000).
- ²⁵ A. C. Balazs, C. Singh, E. Zhulina, G. Pickett, S. S. Chern, and Y. Lyatskaya, *Prog. Surf. Sci.* **55**, 181 (1997).
- ²⁶ F. J. Solis and M. Olvera de la Cruz, *Macromolecules* **31**, 5502 (1998).
- ²⁷ U. Micka, C. Holm, and K. Kremer, *Langmuir* **15**, 4033 (1999).
- ²⁸ A. V. Lyulin, B. Dunweg, O. V. Borisov, and A. A. Darinskii, *Macromolecules* **32**, 3264 (1999).
- ²⁹ P. Chodanowski and S. Stoll, *J. Chem. Phys.* **111**, 6069 (1999).
- ³⁰ U. Micka and K. Kremer, *Europhys. Lett.* **49**, 189 (2000).