Polyelectrolyte adsorption and charge inversion

J.F. Joanny[a]

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

Abstract. We discuss theoretically the adsorption of linear weakly charged polyelectrolyte solutions on an oppositely charged solid surface using the classical self-consistent mean field theory. If the solid surface has an indifferent short range interaction with the polymer (at the crossover point between attraction and repulsion), we show that its charge is always overcompensated by the adsorption of the polymer. At low ionic strength, the overcompensated charge per unit area is proportional to the inverse screening length κ and the thickness of the adsorbed layer is of the order of the thickness of a single adsorbed chain. At higher ionic strength, the electrostatic interaction is strongly screened and is equivalent to an effective excluded volume. The overcompensated charge is then proportional to the bare surface charge. These results provide a theoretical basis to explain the formation of the polyelectrolyte multilayers that have been made by successive adsorption of polyelectrolyte layers of opposite signs.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 68.10.-m Fluid surfaces and fluid-fluid interfaces – 41.20.-q Electric, magnetic, and electromagnetic fields

1 Introduction

Charged polymers or polyelectrolytes play an important role in many problems of physical chemistry or formulation in aqueous solvents. Typical examples would be waste water treatment or paper making where charged polymers are used to control the stabilisation of charged colloidal suspensions or all the physical problems related to biopolymers which are mostly polyelectrolytes. The precise description of the chain properties and the thermodynamics in polyelectrolyte solutions are formidable problems which have not been fully solved yet [1,2]. Some of the simplest questions such as the influence of the ionic strength on the local stiffness of the chains or the chain conformation in semidilute solutions where they overlap are still a matter of important controversies [3,4].

In most of the important applications (colloidal stabilisation, interaction of biopolymers with charged proteins), the polyelectrolyte molecules interact with charged objects to form charged complexes. Another widely studied example is the formation of polyelectrolyte multilayers introduced by Decher [5,6]: one starts from a charged surface and forms successive layers of positively charged and negatively charged polymer by successive adsorption. All these experiments have prompted theoretical studies of polyelectrolyte adsorption either on a flat surface [7–10,12] or on a curved surface (small spheres) [13,14].

In this paper we want to focus on one specific aspect of polyelectrolyte adsorption namely charge inversion: under which condition can the charge of a planar surface

a e-mail: joanny@ics.u-strasbg.fr

be inverted by adsorption of an oppositely charged polyelectrolyte and what are the parameters monitoring this inversion. Charge inversion at each step seems to be the driving force for polyelectrolyte multilayer formation and has been experimentally demonstrated in this case [15], it has also been shown to occur in various adsorption experiments [16]. On the theoretical side, it has recently been proven that the adsorption of a charged chain on an oppositely charged sphere can overcompensate the charge of the sphere. Charge inversion has also been shown to be at the origin of attractive interactions between planar surfaces of identical charge [11].

As in most of the existing theoretical work, we use here a mean field self-consistent approach; we try to set the limit of the approximations involved in this approach by using scaling laws. We consider two limits of adsorption at low ionic strength and high ionic strength in the two following sections and the last section presents our concluding remarks.

2 Polyelectrolyte adsorption at low ionic strength

We consider a dilute polyelectrolyte solution in a θ solvent where the polyelectrolyte chains of degree of polymerisation N have fN positively charged monomers, f is the charge fraction. The solution is in contact with a negatively charged surface perpendicular to the z direction carrying σ charges per unit area. Because of the finite ionic strength of the solution, the electrostatic interactions are screened over the Debye length κ^{-1}.

The adsorption of a single polyelectrolyte chain on a charged surface has been studied by several authors [8,17]. The chain adsorbs in a flat configuration with a thickness $\delta = (4\pi\ell_B f\sigma)^{-1/3}$ where ℓ_B is the Bjerrum length related to the dielectric constant of water ϵ_w, the elementary charge q and the temperature T by $\ell_B = \frac{q^2}{4\pi\epsilon_w k_B T}$; for simplicity, we have chosen the unit length such that the size a of a monomer satisfies $a^2/6 = 1$. This result is valid at large enough surface charge as long as δ is smaller than the Gaussian radius of gyration of the chains $R = N^{1/2}$. In this section, we study the limit of low ionic strength corresponding to $\kappa\delta \ll 1$.

In order to describe the chain statistics close to the surface, we use Edwards propagator approach in the ground state dominance approximation. We thus introduce a chain order parameter ψ related to the local concentration by $c(z) = \psi^2$. This mean field description implicitly assumes that the chains are Gaussian. As the thickness of the adsorbed layer turns out to be very small (of order δ) the stretched polyelectrolyte chains lie parallel to the surface and in order to study the concentration variation in the z direction, we need only to study the transverse fluctuations of the chains which have Gaussian statistics. We thus expect the propagator approach to be accurate for this purpose. Our mean field description does not however take into account the concentration fluctuations in the directions parallel to the plane and thus does not give a good description in these directions where the chains are stretched. The ground state dominance approximation is not sufficient to study the adsorption of neutral polymer chains as it ignores the existence of the tail sections of the chains [18]; for polyelectrolytes, it can be shown *a posteriori* that the monomers belonging to the tails play a negligible role and can be ignored. In a first step, we consider only electrostatic interactions so that the polymer chains only feel the local average electrostatic potential $V(z)$ (we use here dimensionless units, the real potential is $\frac{k_B T V}{q}$). The Edwards equation for the order parameter reads

$$0 = -\frac{\partial^2\psi}{\partial z^2} + (fV(z) + \epsilon)\psi. \tag{1}$$

The ground state binding energy ϵ is determined below. The electrostatic potential in the mean field approximation satisfies the Poisson-Boltzmann equation. We assume throughout this paper that the surface charge is not too high and that this equation can be linearised (Debye-Hückel approximation)

$$\frac{\partial^2 V}{\partial z^2} = \kappa^2 V - 4\pi\ell_B f\psi^2. \tag{2}$$

The boundary condition on the adsorbing surface is $\frac{\partial V}{\partial z} = 4\pi\ell_B\sigma$. The mean field equations for the concentration profile and the electrostatic potential are similar to those solved numerically by Varoqui [12] and Borukhov and coworkers [10] who did not linearise the Poisson-Boltzmann equation; these authors have also given scaling laws to interpret their results on the layer thickness and on

the adsorbed polymer amounts. In reference [10], a maximum in the electrostatic potential is found numerically; this is the signature of charge inversion.

In addition to the mean field assumption, the two basic equations make two further approximations: excluded volume is neglected and the electrostatic potential is considered as small so that the equation (2) can be linearised. Even in a θ solvent where the second virial coefficient vanishes, excluded volume interactions can become important close to the surface where the concentration is high (the third term in the virial expansion may become important); this is discussed below. In the limit of high ionic strength the electrostatic potential is small and the Debye-Hückel equation can always be used. In the limit of low ionic strength the Debye-Hückel approximation can be used if the single adsorbed chain thickness δ is smaller than the so-called Gouy-Chapman length $\lambda = \frac{1}{2\pi\sigma\ell_B}$.

In the asymptotic limit of low ionic strength $\kappa\delta \ll 1$, we solve these equations by matching asymptotic expansions. In the outer region, at large distances (of order κ^{-1}), the adsorbed polymer layer can be considered as infinitely thin and in a first approximation, it only renormalises the surface charge. If the adsorbance (the total number of adsorbed monomers per unit area) is Γ, the effective charge of the surface is $\Delta\sigma = f\Gamma - \sigma$ and the electrostatic potential is given by the standard Debye-Hückel formula $V(z) = \frac{4\pi\ell_B\Delta\sigma}{\kappa}\exp-\kappa z$. We are studying here the overcompensation of the surface charge by polyelectrolyte adsorption, therefore $\Delta\sigma$ and the electrostatic potential are positive.

In the inner region (the adsorbed layer), the small ions can be neglected and we ignore the term proportional to κ^2 in the Debye-Hückel equation. It is then useful to define reduced units by $y = z/\delta$, $V = 4\pi\ell_B\sigma\delta\tilde{V}$, $\psi = (\frac{\sigma}{f\delta})^{1/2}\tilde{\psi}$ and $\tilde{\epsilon} = \delta^2\epsilon$. We find the concentration in two steps. We first integrate the Poisson equation in order to express the electrostatic potential as a function of the polymer order parameter. The integration constant is found by matching the potential with the outer region. The charge overcompensation is small and we write $\Delta\sigma = \sigma\kappa\delta\alpha^2$. The matching of the potential leads to $\tilde{V}(\infty) = \alpha^2$ and if we assume as checked below that α is or order one, the matching of the electric field gives a vanishing electric field at infinity in the inner region. The electrostatic potential then reads

$$\tilde{V}(y) = \alpha^2 - \int_y^\infty dy'(y' - y)\tilde{\psi}^2(y'). \tag{3}$$

We then obtain an independent equation for the order parameter. This equation can be simplified by a further rescaling. We introduce $\beta^2 = \alpha^2 + \tilde{\epsilon}$ and define $x = \beta y$ and $\phi = \tilde{\psi}/\beta^2$ The equation for the order parameter then reads

$$0 = -\frac{\partial^2\phi}{\partial x^2} - \phi\int_x^\infty dx'(x' - x)\phi^2(x') + \phi. \tag{4}$$

We need two boundary conditions; at infinity ϕ must vanish and clearly, $\phi \propto \exp-x$; the boundary condition at the surface is fixed by the non electrostatic short range interaction between the monomers and the surface. In general,

this is taken into account by imposing the logarithmic derivative of the order parameter on the surface. We consider here only the two limiting cases of a hard surface ($\phi(0) = 0$) and an indifferent surface ($\frac{\partial \phi}{\partial x}(0) = 0$). In these cases, the equation for ϕ does not depend on any parameter and could be for example solved numerically.

At lowest order in κ, the charge over compensation is small and $\Gamma = \sigma/f$. This imposes that $1 = \int_0^\infty dy \tilde{\psi}^2$ and leads to

$$\beta^2 = \alpha^2 + \tilde{\epsilon} = [\int_0^\infty dx \phi^2]^{-2/3}. \tag{5}$$

The constant β is smaller in case of adsorption on a hard surface than in case of adsorption on an indifferent surface. The thickness of the adsorbed layer is $\frac{\delta}{2\beta}$; it is of the same order as the thickness of an isolated adsorbed chain and it is larger for a hard surface *i.e.* when the surface is more repulsive as expected. The scaling variation of the adsorbed layer thickness with the surface charge and the charge fraction is similar to that obtained in reference [10] (the thickness is there expressed in terms of the surface potential).

The reduced binding energy is obtained by balancing the chemical potential of adsorbed chains with the chemical potential of free chains in the bulk. The chemical potential of free chains is $\mu_b = k_B T \log(c_b/N) + N F_b$ where c_b is the bulk concentration and F_b the free energy per monomer of one chain in the bulk taking as a reference state a noninteracting Gaussian chain. The single chain free energy F_b cannot be obtained simply from mean field arguments. We calculate it here using scaling arguments and the electrostatic blob model appropriate to describe isolated weakly charged chains [1], the free energy is $F_b \propto \frac{k_B T}{\xi_e^2}$ where $\xi_e \propto (f^2 \ell_B)^{-1/3}$ is the so-called electrostatic blob size. The chemical potential of one chain in the adsorbed layer is calculated in a similar way as for adsorbed neutral chains

$$\mu_s/k_B T = -N\epsilon - k_B T \log Z + k_B T \log(\Gamma/N)$$

where Z is the chain partition function that can be calculated from the chain order parameter $Z = \delta \beta^2 K^2$ with $K = \int_0^\infty dx \phi(x)$. The reduced binding energy is then

$$\tilde{\epsilon} = \frac{\delta^2}{N} \log\left(\frac{\Gamma}{\delta \beta^2 K^2 c_b}\right) - \delta^2 \frac{F_b}{k_B T}. \tag{6}$$

Note that if the bulk concentration is not too low, $\tilde{\epsilon}$ is negative; this is due to the fact that the electrostatic energy of the chains decreases as they adsorb.

For very long chains, there is always overcompensation of the charge of the surface and the excess charge is $\frac{\Delta\sigma}{\sigma} \propto \kappa\delta(1 + \frac{\delta^2}{\xi_e^2})$ (all numerical prefactors have been omitted). The excess charge increases thus with ionic strength at low ionic strength. The excess charge also increases very weakly with the bulk concentration due to the logarithmic term in the binding energy.

So far, we have neglected any excluded volume interaction. The concentration in the adsorbed polyelectrolyte

layer varies with the surface charge as $\frac{\sigma}{f\delta} \simeq \sigma^{4/3}$. Even in a θ solvent as the concentration gets very high, the excluded volume interaction can become relevant. The excluded volume in a θ solvent is due to the three body interactions, each monomer feeling a mean field potential $U_{mf} = w^2 c^2$ where the third virial coefficient w^2 is of order 1. The excluded volume potential is small compared to the electrostatic potential if the thickness of the adsorbed layer δ is larger than the size of the electrostatic blobs ξ_e *i.e.* when $\sigma \ll \sigma_c \simeq f$. At high surface charge $\sigma \gg \sigma_c$, the chain entropy becomes small and the structure of the adsorbed layer results from a balance between the electrostatic attraction by the surface and the excluded volume. We were not able in this case to make a full analysis of the adsorbed layer as the one presented above. However assuming that the concentration in the adsorbed layer is constant, one finds by direct minimisation of the total free energy that the adsorbed layer thickness δ_{ev} is not equal to the single chain value, but δ_{ev} varies as $\delta_{ev} \simeq \frac{\xi_e^2}{\delta} \simeq (\frac{\sigma}{4\pi\ell_B f^3})^{1/3}$. The adsorbed layer thickness has thus a non monotonic variation with the surface charge, it is equal to δ and decays with σ at low surface charge and it increases at high surface charge. There is also charge inversion at high surface charge and the excess charge is found to scale as $\frac{\Delta\sigma}{\sigma} \simeq \kappa\delta_{ev}$.

In the limit where the surface charge is small, the structure of the adsorbed layer can be given a simple interpretation in terms of electrostatic blobs. In the dilute bulk solution, the different chains interact only weakly and they can be considered as linear chains of electrostatic blobs with a radius $R \simeq \frac{N}{\xi_e} \simeq N(f^2\ell_B)^{1/3}$. The chain conformation is very anisotropic and the transverse radius of the chains is due to Gaussian fluctuations $R_{perp} \simeq N^{1/2}$. The thickness of the adsorbed layer is very small compared to the chain size and in the adsorbed layer the chains lie almost flat parallel to the adsorbing surface. Locally the chains keep their stretched structure as a linear string of blobs and form a two dimensional semidilute solution. The distance between chains can be estimated from a scaling argument and varies as $\xi_2 \simeq \frac{f\xi_e}{\sigma}$. Sections of chain with a size ξ_2 can be considered as independent and approximately retain their bulk structure; like isolated chains, they are confined upon adsorption in a flat conformation with a thickness δ in agreement with the mean field calculation. One can check explicitly that the Gaussian radius of these sections is indeed larger than the layer thickness δ and that these chain sections are indeed confined. If the surface charge becomes too low, $\sigma \ll \sigma^* \simeq 1/(Nf^{1/3}\ell_B^{2/3})$, the two dimensional density of chains required to neutralise the charged surface is smaller than the overlap density and the adsorbed chains form a dilute solution.

The mean field calculation neglects the charge fluctuations in the plane parallel to the adsorbing surface; this can be important in the small density limit. The energy associated to these fluctuations should be taken into account in the chemical potential balance of equation (6) and must be substracted from the bulk energy F_b. The precise value of this energy is however difficult to estimate as it would require a precise knowledge of the structure of

the adsorbed solution. In particular it is not clear whether the adsorbed two-dimensional solution remains isotropic or has a two dimensional nematic order. We still believe nevertheless, that the qualitative result of the mean field approach remains correct: there is overcompensation of the surface charge and the excess charge is proportional to the inverse screening length κ.

3 Polyelectrolyte adsorption at high ionic strength

We now study the adsorption of the polyelectrolyte solution on the charged surface when the ionic strength is large *i.e.* when the Debye-Hückel screening length is smaller than the thickness of the adsorbed layer in the absence of salt (δ or δ_{ev}). As in the previous section, in a first step, we use a mean field approach and we ignore any excluded volume interaction. The local monomer concentration or the propagator (in the ground state dominance approximation) and the electrostatic potential are obtained from equations (1, 2). In the strong adsorption limit, it can be checked *a posteriori* that at any point in the adsorbed layer, $fc(z)/\kappa \ll \sigma$. Using this approximation, the Poisson equation for the electrostatic potential can be solved by assuming that the typical distance over which the concentration varies is larger than the screening length. A uniformly valid solution is

$$V(z) = -\frac{4\pi\ell_B\sigma}{\kappa}\exp-(\kappa z) + \frac{4\pi\ell_B f\psi^2}{\kappa^2}\,.\qquad(7)$$

At short distances the screening of the electrostatic field by the monomers is small and the electrostatic potential is that of the bare charged surface in the salt solution. At distances larger than the screening length the surface field is screened and the electrostatic interactions between monomers are equivalent to an effective excluded volume between monomers $v_{el} = \frac{4\pi\ell_B f^2}{\kappa^2}$. In order to solve the propagator equation, we also match asymptotic solutions. In the vicinity of the surface, the relevant length scale is the screening length κ^{-1}. In the limit of strong screening there is no adsorption if the adsorbing surface is too repulsive for the monomers (there is for example no adsorption on a hard wall as discussed by Varoqui [12]). We consider here only an almost indifferent surface and characterise the short range non-electrostatic interactions by an extrapolation length d which imposes the boundary condition for the order parameter on the solid surface $\frac{1}{\psi}\frac{\partial\psi}{\partial z}(z=0) = -\frac{1}{d}$. (This is equivalent to introducing a localised delta function potential on the wall). We assume throughout the paper that $|d| \gg \kappa^{-1}$. Note that d can be negative if the short range potential is repulsive. We choose a distance d_1 from the adsorbing surface which is larger than the screening length ($d_1 \gg \kappa^{-1}$) but smaller than any characteristic length scale for the concentration variation in the external part of the adsorbed layer (the outer region). Within a distance d_1 from the surface, the concentration and thus the order parameter are

roughly constant. Using this approximation, we integrate the propagator equation for z between 0 and d_1. At leading order, the electrostatic excluded volume term only gives a small contribution and we find

$$-\frac{1}{\psi}\frac{\partial\psi}{\partial z}(z = d_1) = \frac{1}{d_{eff}} = \frac{1}{d} + \frac{1}{d_{el}}\qquad(8)$$

where we have defined the electrostatic extrapolation length $d_{el} = \kappa^2\delta^3$. Note that the effective extrapolation length gives exactly the thickness of a single adsorbed chain on the same surface as can be obtained by solving the propagator equation for a single chain in the ground state dominance approximation. This length was also found from the scaling arguments of Borukhov and coworkers [10]; and it was interpreted as the thickness of the adsorbed layer. If the short range potential is repulsive, there is no adsorption if the surface charge is too weak (d_{eff} negative), the adsorption threshold is given by $\sigma_a = -\frac{\kappa^2}{4\pi\ell_B fd}$.

In the external part of the adsorbed layer, the surface electric field is entirely screened and within our mean field approximations, the polyelectrolyte behaves as a polymer in a good solvent with an electrostatic excluded volume $v_{el} = \frac{4\pi\ell_B f^2}{\kappa^2}$. The boundary condition for the propagator equation on the surface is obtained by matching with the inner layer and using equation (8) as the boundary condition when $z \to 0$. All the results that have been obtained for polymers in a good solvent [18] concerning the loops and tails structure of the adsorbed layer or the adsorbance can be used directly. We will suppose here that the polymer molecular weight is very large and thus that the chain radius of gyration is much larger than d_{eff}. The adsorbed monomer amount is then

$$\Gamma = \frac{2\sigma}{f} + \frac{2\kappa^2}{4\pi\ell_B f^2 d}\,.\qquad(9)$$

If d is not negative and too small, *i.e.* if the short range potential is not too repulsive, our calculation predicts charge inversion. In the limit where the adsorbing surface is indifferent, the adsorbed charge is exactly twice the charge of the adsorbing surface. This is the exact asymptotic result obtained from the mean field equations in the high salt limit ($\kappa\delta \gg 1$); for finite ionic strength, corrections to this result may become important but we were not able to calculate them.

So far, we have neglected any excluded volume interaction. In order to decide whether excluded volume is relevant, we compare the mean field potential due to the three body interactions (third virial coefficient) to the effective electrostatic excluded volume. As in the absence of salt, the excluded volume interaction is negligible as long as $\xi_e \ll \delta$ *i.e.* when the surface charge is smaller than the critical value $\sigma_c \simeq f$. If the surface charge is larger than this value the three body interactions become important in the vicinity of the adsorbing surface. We were not in this case able to solve systematically the self-consistent mean field equations. Qualitatively, the polyelectrolyte adsorbs as a neutral polymer in a θ solvent with an interaction

with the surface characterised by the extrapolation length d_{eff}. The adsorbed amount increases then with the surface charge as $\Gamma \simeq \log \frac{\sigma}{f}$. It increases thus slower than the surface charge at high charge and we do not expect charge inversion in this case.

4 Concluding remarks

The main result of our study is that in many cases polyelectrolyte adsorption leads to an overcompensation of the surface charge and thus to an inversion of the surface charge. This is always the case in the limit of weak screening where the Debye screening length is larger than the thickness of the adsorbed polymer layer. The electrostatic interaction is in this case long ranged; the chains in the solution experience an attractive force from any oppositely charged surface and adsorption continues until the effective surface charge does not have the same sign as that of the adsorbing chains. In the absence of salt, the excess surface charge must vanish since the electrostatic free energy diverges. The mean field theory predicts that the excess charge vanishes linearly with the inverse screening length. In practice, even if the bulk polymer concentration is very low the counterions contribute to the screening and must be included in the calculation of the screening length; the overcompensated charge then does not exactly vanish in the limit of no added salt; there exists however a broad range of salt concentration where the asymptotic laws found in this paper can be used. In the limit of high ionic strength the electric field of the surface is screened and charge inversion occurs only if the short range interaction between the monomers and the surface is not too strong and if the surface charge is not too high. Note also that the existence of excluded volume interactions strongly reduces the adsorbed polymer amount and eventually suppresses the charge inversion.

These results provide a good starting point for the theoretical description of the so-called polyelectrolytes multilayers. If the ionic strength is weak, the charge can be inverted at each step and a new layer of opposite sign can be added to the multilayer. The case of high ionic strength is different. Even if there is no charge inversion, the electrostatic potential at the surface of the adsorbed layer has the same sign as the polymer charge as long as the adsorbed polymer layer is thicker than the screening length. The addition of a next layer of opposite charge then occurs via the formation of complexes between polyelectrolytes of opposite charges at the interface between consecutive layers.

The main limitation of this work is the use of the self consistent mean field theory. In the low ionic strength case, the thickness of the adsorbed layer is very small and very long chains almost lay flat parallel to the interface. They have Gaussian statistics in the transverse direction as assumed in the mean field theory. There are however strong concentration fluctuations in the direction parallel to the adsorbing surface. The energy associated to these fluctuations provokes at least locally the chain stretching. It must be taken into account in the free energy balances to have a more accurate description. We do not expect that to change qualitatively the transverse structure of the layer but it would certainly affect the precise value of the excess surface charge. When the surface charge is high ($\sigma \gg \sigma_c$), the excluded volume interaction becomes relevant even at the θ point. We were not able to give a complete description and we only propose scaling laws in this limit; a more detailed study would be needed.

In the limit of high ionic strength, as for neutral polymer chains, the adsorbed layer locally has the structure of a semidilute polymer solution. The mean field approach ignores the concentration fluctuations and gives only a qualitative description. The theoretical description of semidilute polymer solutions and more precisely the problem of the chain conformation in semidilute solutions are highly controversial subjects [1,3]. Even if it is not fully justified theoretically, the scaling theory of Pfeuty and coworkers [19] gives a rather good description of the properties of semidilute solutions. The same scaling approach can be used to study adsorbed polyelectrolyte layers at strong ionic strength following the lines of de Gennes [20]. One however needs to make a scaling estimate of the extrapolation length which corresponds to the thickness of a single adsorbed chain. This however would require a detailed understanding of the short range effects (the special transition effect) that does not seem available at the present time. If we ignore the associated divergence of the concentration profile, we find a polymer adsorbed amount $\Gamma \simeq (\sigma/f)^{1/2}$. When the surface charge is small ($\sigma \ll \sigma_c \propto f$) there is still overcompensation of the charge as in the mean field theory.

We have assumed throughout the paper that the surface charge is uniformly distributed on the surface. In most practical cases the surface has discrete charges. The discreteness of the charges is not relevant if the average distance between charges $L = \sigma^{-1/2}$ is smaller than the relevant length of the problem. In the absence of salt, this criterion is satisfied at high enough surface charge $\sigma \gg (f\ell_B)^2$. If this criterion is not satisfied, a more detailed theory is needed. We only expect logarithmic corrections to the results presented here.

A final limitation of our work is that we *a priori* assume that the adsorbed polyelectrolyte layer has a thermodynamic equilibrium structure. There may however exist strong potential barriers to reach the equilibrium structure in particular in the case where the electrostatic interactions are not screened and the actual structure could be very different from the equilibrium one.

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