Charge regulation of weak polyelectrolytes at low- and high-dielectric-constant substrates

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Abstract
As is well known, the effective charge of weak polyelectrolytes (PEs) decreases
with decreasing salt concentration due to the electrostatic repulsion between
dissociated charges. Close to dielectric boundaries, image-charge effects
influence the dissociation equilibrium. At low-dielectric-constant substrates,
one finds a further charge decrease and repulsion from the interface, while at
high-dielectric-constant (e.g. metallic) substrates, the effective charge increases
and the PE is attracted to the interface.

1. Introduction

The degree of charge of most polyelectrolytes (PEs) is controlled by a chemical equilibrium
between the charged and uncharged versions of the monomers, which can be tuned by the
pH of the solution. Strong PEs are typically fully charged whereas weak PEs are only
partially charged at normal conditions (pH $\approx$ 7). Electrostatic repulsion between charges
on neighbouring monomers tends to decrease the effective charge of a PE. This effect is
stronger at low salt concentrations (i.e. for long-ranged electrostatic interactions) [1]. The
situation is more complicated at dielectric boundaries, since here the charge on each monomer
is interacting with its neighbours but also with its own image charge and the image charges of
all neighbours. As a result, the fraction of charged monomers decreases as the PE approaches
a low-dielectric-constant substrate (for example, a water–air interface), and increases upon
approach to a high-dielectric-constant substrate (e.g. a metal). In the former case, even a
strong PE is eventually turned into a weak PE as it comes closer to the substrate, and the
resulting repulsion stays finite even when the PE touches the substrate. This can explain
previously puzzling experiments where poly-styrene-sulfonate (PSS, a strong PE) has been
found to adsorb on the (supposedly) neutral water–air interface [2–5]. In contrast, on a metallic
surface, even a weak PE will become fully charged and experience a strong attractive force.

2. The model

In order to treat the effects of added salt and dielectric boundaries on a manageable level, we use screened Debye–Hückel (DH) interactions between all charges (which is valid as long as the electrostatic potential is small everywhere, i.e. if the charge density is not too high or if the salt concentration is large enough). In the absence of an interface, the interaction between two unit electric charges (which is also called the Green function) in units of thermal energy k_BT is given by $v_{DH}(r) = \ell_B e^{-\kappa r}/r$ where $\ell_B = e^2/(4\pi\varepsilon k_B T)$ is the Bjerrum length and denotes the distance at which two unit charges interact with thermal energy (in water, one has $\ell_B \approx 0.8$ nm) and κ^{-1} is the screening length which is related to the salt concentration c_s by $\kappa^2 = 8\pi\ell_B q^2 c_s$. The valency of the salt ions is denoted by q. The interactions between charges are weakened (i.e., *screened*) due to the presence of mobile ions in the surrounding space.

In the presence of a dielectric interface, the Green function can in general not be calculated in closed form [6] except:

(i) for a metallic substrate (with a substrate dielectric constant $\varepsilon' = \infty$); and
(ii) for $\varepsilon' = 0$ (which is a fairly accurate approximation for a substrate with a low dielectric constant).

For two unit charges at positions r and r' one obtains for the total electrostatic interaction including screening and dielectric boundary effects

$$v_{DH}(r, r') = \ell_B \frac{e^{-\kappa|r-r'|}}{|r - r'|} \mp \ell_B \frac{e^{-\kappa\sqrt{(r-r')^2+4zz'}}}{\sqrt{(r - r')^2 + 4zz'}} \tag{1}$$

where z and z' denote the distances of the unit charges from the interface. One sees that the second term, which is due to the dielectric interface, becomes of the same order as the first term (the ordinary bulk interaction) as one goes closer to the interface, i.e., when z and z' approach zero. Right at the interface, for $z = z' = 0$, the total interaction vanishes for a metallic substrate (minus sign in front of the second term) and becomes twice as large for $\varepsilon' = 0$ (plus sign).

The ionic self-energy, i.e. the interaction of one charge with its own image charge, is given by $v_{DH}^{self}(z) = v_{DH}(r, r' = r)/2$ and measures the free energetic cost (or gain) of:

(i) immersing a single ion in an electrolyte solution; and
(ii) moving this ion to a distance z from the surface.

One obtains

$$v_{DH}^{self}(z) = -\ell_B\kappa/2 \mp \ell_B \frac{e^{-2\kappa z}}{4z}, \tag{2}$$

where the divergent Coulomb self-energy has been subtracted off. As a result, charges are attracted to metallic substrates (minus sign in front of the second term) and repelled from low-dielectric-constant substrates (plus sign).

A PE monomer, which in all that follows is assumed to be an acid, can be either charged (dissociated) or neutral (associated), which is described by a chemical reaction $AH + H_2O \rightleftharpoons A^- + H_3O^+$ where AH denotes the associated (neutral) acidic monomer and A^- denotes the dissociated (charged) monomer. At infinite dilution, the law of mass action relates the concentrations to the equilibrium constant $K = [A^-][H_3O^+]/[AH][H_2O]$. Since the water concentration is for most purposes a constant, one defines an acid-equilibrium constant as $K_a = [A^-][H_3O^+]/[AH]$ which now has units of concentration. Defining the negative
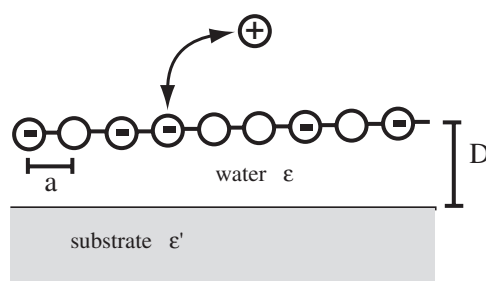
Figure 1. A straight PE chain consisting of N dissociable monomers is placed parallel, at a distance D, to a dielectric interface.

common logarithm of the H_3O^+ concentration and the acid constant as $pH = -\log_{10}[H_3O^+]$ and $pK_a = -\log_{10} K_a$, the law of mass action can be rewritten as $[A^-]/[AH] = 10^{pH-pK_a}$. The degree of dissociation α, defined as $\alpha = [A^-]/([AH] + [A^-])$, follows as

$$\alpha = \frac{1}{1 + 10^{pK_a - pH}}. \tag{3}$$

In the present simplified model, we neglect conformational degrees of freedom of the PE and assume a straight polymer consisting of N monomers with a bond length (i.e. distance between dissociable groups) a, located at a distance D from a dielectric interface, as depicted in figure 1. This model is applicable to stiff PEs and for strongly adsorbed PEs, since they are indeed flat. The exact partition function for monovalent monomers reads

$$Z = \sum_{\{s_i\}=0,1} \exp\left(-\mu \sum_i s_i - \sum_{i>j} s_i s_j v_{DH}(r_i, r_j)\right) \tag{4}$$

where s_i is a spin variable which is 1 (0) if the ith monomer is charged (uncharged) and r_i denotes its position. The chemical potential for a charge on a monomer is given by $\mu = -2.303(pH - pK_a) + v_{DH}^{self}(D) - \ell_B \kappa/2$; the first term is the chemical free energy gained by dissociation, the second term, defined in equation (2), is the electrostatic interaction between the charged monomer and the substrate, and the last term is the self-energy of the released proton. All different charge distributions are explicitly summed in equation (4), which, together with the long-ranged interaction $v_{DH}(r_i, r_j)$ between charged monomers, defined in equation (1), makes the problem difficult. From the partition function, one derives the free energy per monomer, $f/k_B T = -\ln(Z)/N$, and the fraction of charged monomers as $\alpha = -\partial Z/N \, \partial \mu$. Previously, similar problems have been solved using mean-field theory [1, 7, 8], restriction to nearest-neighbour repulsions only [9–11], and computer simulations [12, 13]. For the following results, the partition function is summed explicitly by an exact enumeration for a finite chain length $N = 20$.

3. Results

In figure 2 the fraction of charged monomers is presented infinitely far from the interface, i.e., in the bulk. For a screening length $\kappa^{-1} = 0.3$ nm, i.e. of the order of the monomer distance $a = 0.254$ nm, the electrostatic repulsion between monomers becomes irrelevant and the dissociation curve is close to law-of-mass-action equation (3) (note a small horizontal shift due to the increasingly negative self-energy of the separated charges in the salt solution). As the salt concentration decreases, the effective charge goes down, or, as it is usually put,
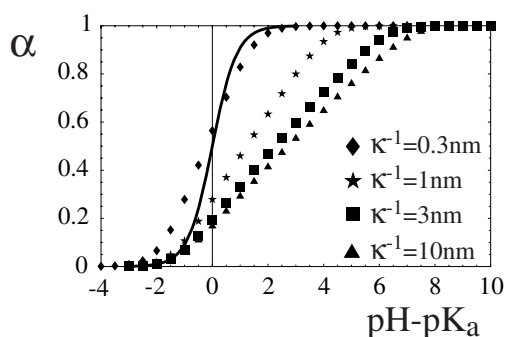
Figure 2. Fraction of dissociated monomers α in the bulk (infinitely far away from the interface) as a function of the pH and for different salt concentrations. The polymer consists of $N = 20$ monomers with a bond length $a = 0.254$ nm. The solid curve denotes the dissociation of non-interacting charges at infinite dilution.
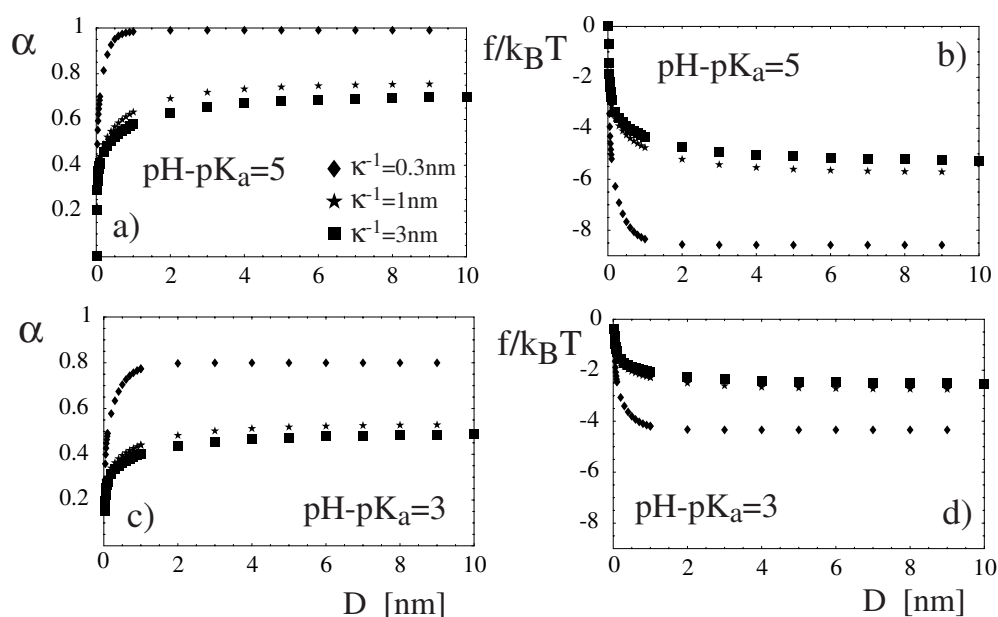

Figure 3. Dissociation of a polymer with $N = 20$ monomers as a function of the distance D from the interface to a low-dielectric-constant half-space (idealized by $\varepsilon' = 0$; see the text). Shown are the degree of dissociation α and free energy per monomer, $f/k_\mathrm{B}T$, for fixed $\mathrm{pH} - \mathrm{pK_a} = 3$ and 5 for different salt concentrations. As the polymer moves towards the interface, the degree of dissociation and the free energy approach zero, and the PE is repelled from the interface.

the apparent dissociation constant shifts. For $\kappa^{-1} = 3$ nm at $\mathrm{pH} - \mathrm{pK_a} = 3$, only half of the charges are dissociated. One notes that for screening lengths larger than the size of the polymer, $L = Na = 5.1$ nm, no dramatic changes are observed. As a main result, even rather strong PEs are only partially charged at low salt concentrations [1] (where we have not taken additional complications due to chemical binding of metal ions into account [11, 14]).

In figure 3, results for two fixed values of the pH are shown as a function of the distance from a low-dielectric-constant substrate. Due to the strong image-charge repulsion, the charge
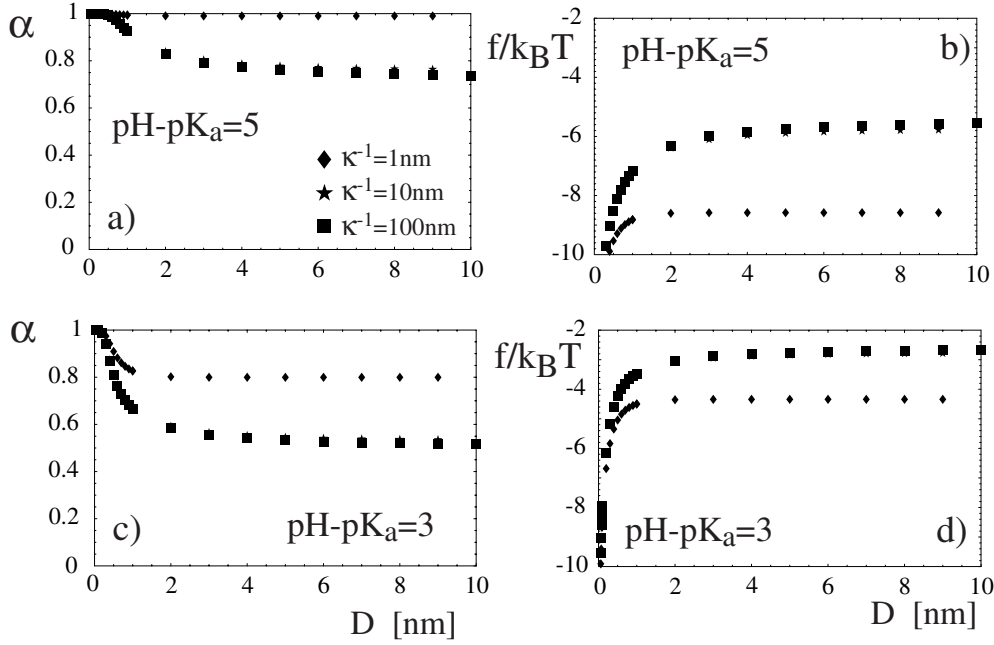
Figure 4. Dissociation of a polymer with $N = 20$ monomers as a function of the distance D from the interface to a metallic half-space (characterized by $\varepsilon' = \infty$). As the PE approaches the interface the degree of dissociation approaches unity and the free energy goes down. As a result, the PE is attracted to the metallic substrate even in the absence of a net charge on the substrate.

fraction α goes to zero as the distance from the substrate decreases. The free energy exhibits a strong repulsion from the substrate, but since the charge fraction becomes zero at the substrate, the free energy stays finite all the way and is strictly bounded by zero from above. This is true whatever the PE strength or salt concentration, i.e., even a strong PE becomes weak at a low-dielectric-constant substrate. Accordingly, the maximal free energy penalty for moving a PE from the bulk to the substrate is $f/k_B T = 2.303(\text{pH} - pK_a) + \ell_B \kappa$. Since for lower salt concentration the charge fraction in the bulk goes down and the free energy is raised, while the free energy reaches zero at the interface independently of the salt concentration, one arrives at the surprising result that the repulsion from the substrate is weaker at low salt concentrations, although the electrostatic interaction by itself is more long ranged and thus more pronounced. This is a consequence of the fact that a PE is self-adjusting or regulating its degree of charge for varying salt concentrations.

These results can help to explain the recent experimental findings that strong PEs such as PSS (with roughly $pK_a \approx 2$) spontaneously adsorb at the water–air interface [2–5] or other low-dielectric-constant substrates [15]. The driving force for the adsorption is the hydrophobicity of the benzene groups and the backbone, which tends to push these groups out of the water. The counteracting force is due to the charges on the sulfonic groups, which experience an image-charge repulsion from the low-dielectric-constant half-space. Naively, without taking into account the charge-regulation mechanism discussed here, one would predict the image-charge repulsion to become dominant at low salt concentration and to prevent any adsorption at the interface. However, as shown here, the free energy penalty for bringing a PSS monomer (for which at neutral conditions $\text{pH} - pK_a \approx 5$, as shown in figures 3(a), (b)) to a distance $D \approx 0.5$ nm from the interface is only a few $k_B T$, accompanied by a drastic decrease of the

effective charge. This penalty can with ease be overcome by the hydrophobic attraction. For weaker PEs (for example polyacrylic acid with $pH - pK_a \approx 3$, as shown in figures 3(c), (d)) this mechanism is even more likely to occur.

For the adsorption on metallic substrates the situation is reversed, as shown in figure 4: the degree of dissociation increases as the distance to the substrate goes down and reaches unity right on the interface. A strong image-charge attraction develops, which leads to free energy curves which diverge upon approach to the substrate. As a result, one predicts all PEs to strongly adsorb on metallic substrates, including weak PEs in neutral or even acidic pH conditions.

4. Conclusions

The charge regulation of short PEs with $N = 20$ monomers at a dielectric interface has been studied within the DH approximation by exact enumeration of the charge distribution. Conformational degrees of freedom have been neglected, as is appropriate for stiff PEs and for PEs adsorbed at the interface in a flat conformation. Our results might be best applied to single-stranded oligo-DNA fragments which are adsorbed in a flat configuration.

For low-dielectric-constant substrates the fraction of charged monomers goes down upon approach to the interface and the free energy increases. The repulsion is stronger at large salt concentrations. In this respect it seems interesting to note that in a recent experiment the fraction of dissociated charges of polymethacrylic acid has been measured as a function of time as it adsorbs on a low-dielectric-constant substrate (made of a supported neutral lipid bilayer) and found to decrease from the bulk value of $\alpha \approx 0.58$ to a value of about $\alpha \approx 0.2$ over a period of a few hours [16]. One interpretation of this is that the mean distance between dissociable groups on the polymer and the low-dielectric-constant substrate decreases slowly as a function of time, leading to the observed behaviour of the dissociation fraction.

For high-dielectric-constant materials (metals) the degree of charging goes up, while a strong and divergent image-charge attraction is observed. These results can be summarized by saying that low-dielectric-constant substrates make strong PEs weak, while metallic substrates make weak PEs strong.

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