Volume exclusion effects in the ground-state dominance approximation for polyelectrolyte adsorption on charged interfaces

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Abstract. We consider the problem of polyelectrolyte molecules adsorbing on oppositely charged interfaces. For sufficiently long chains, the ground-state dominance approximation can be used which results in a (semi-)analytical solution of the self-consistent field equations (aSCF). Whereas existing aSCF theory assumes a low polyelectrolyte density, here the required electrostatic corrections for a high polymer density are implemented. Adsorbed polymer excludes volume for the solvent and small ions, a volume effect that also leads to a reduced dielectric permittivity and a resulting polarization term in the exchange potential. Calculations show the influence of volume exclusion on the polymer density profile.

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1 Introduction

The adsorption of polyelectrolytes on charged and non-charged interfaces is a fundamental problem in many biological and technological systems. The adsorbed amount and polyelectrolyte density profile depend on the polymer concentration in bulk solution, polymer and surface charge, polymer rigidity (statistical Kuhn length), enthalpic (hydrophobic) interactions between polyelectrolyte molecules, and with the surface, ionic strength, etc. For ionizable materials, the charge on the surface and of the polyelectrolyte chains depends on the local pH, which in turn is related to the bulk pH and the local electrostatic potential, which is a self-consistent function of all prior parameters (polymer density profile, proximity to surface, etc.) [1–8]. The influence of these parameters on the adsorbed amount can be described by several theoretical approaches such as Monte Carlo [9] and numerical (lattice-based) self-consistent mean-field techniques (nSCF) [1,3,10].

A significant simplication of nSCF methods can be made for long polyelectrolyte chains when the ranking number dependence can be neglected [2,4,11–15]. This is the ground-state dominance approximation which results in a (semi)analytical version of the self-consistent field equations (aSCF). Existing aSCF models assume a low polymer density ϕ and therefore use the expression for Flory-Huggins mixing free energy in the low-ϕ limit

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(third and higher virial coefficients set to zero), while in the electrostatic equations the polymer is assumed to be volumeless.

Because polyelectrolyte adsorption on charged interfaces can lead to high volume fractions ϕ, it is interesting to present the required corrections to the existing aSCF theory, and investigate their influence on the predicted adsorption profile. To that end we will not linearize the Flory-Huggins (FH) expression for mixing free energy, and implement the fact that adsorbed polymer 1) excludes solvent and thus small ions from the surface, and 2) decreases the local permittivity. All three corrections lead to a decreased polyelectrolyte adsorption.

2 Theory

Of earlier aSCF work based on the ground-state dominance approximation [2,4,11–15], only Andelman and coworkers [2,4,14,15] include a Flory-Huggins mixing free-energy contribution (in the low-ϕ limit). Comparing with that work, we define the ionic strength n_∞ in a (virtual) phase without polyelectrolyte, ∞, and not in the bulk phase, b, that contains polyelectrolyte. The ionic strength, n_∞, in our work is therefore slightly higher than in references [2,4,14,15]. Because we set the electrostatic potential y_∞ equal to zero, and not y_b, an additional term $-\lambda \cdot y_b$ is added to the expression for the exchange potential u (λ is the line charge density). The advantage is

that a simplified Poisson-Boltzmann equation is obtained, because we do not have to distinguish between added salt and polyelectrolyte counterions (*i.e.*, the counterion term of Refs. [2,4,14,15] can be removed). We consider the situation of a high polyelectrolyte concentration, include solvent exclusion by the polymer, a possible difference in permittivity between polymer and solvent, and add the corresponding ion exclusion and polarization terms to the chemical potential, μ, and exchange potential, u. All thermodynamic functions are scaled with kT.

2.1 Free energy density

We consider the following contribution to the free energy density:

1) *Mixing.* For a system of solvent molecules and one type of polymer, the Helmholtz free energy density f according to the Flory-Huggins mean-field theory is given by

$$v_{\text{FH}} f = \frac{\phi}{N} \ln \phi + (1 - \phi) \ln (1 - \phi) + \chi \phi (1 - \phi). \quad (1)$$

The lattice site volume in the Flory-Huggins theory is v_{FH} and not necessarily equals the segment volume v; ϕ is the polymer volume fraction. We will assume N sufficiently large and therefore neglect the first term from this point onward. For a fixed bulk polymer concentration, ϕ_{b}, we must subtract $\mu_{\text{b}} \cdot (\phi - \phi_{\text{b}})$ to obtain the related grand potential (with μ_{b} given by Eq. (7) with ϕ_{b} replacing ϕ) [2,14].

2) The first *electrostatic* contribution to the free energy density is the field energy [5,16]:

$$\frac{\varepsilon}{2kT} (\nabla \psi)^2 = \frac{\varepsilon}{\varepsilon_0 \varepsilon^{\text{w}}} \frac{n_\infty}{\kappa^2} (\nabla y)^2 \quad (2)$$

with ε the local permittivity of the mixed polymer/solvent phase, ε_0 the permittivity of vacuum, ε^{w} the relative permittivity of water, ψ the electrostatic potential, y the dimensionless electrostatic potential, $y = e\psi/kT$; k, T and e have their usual meaning. The ionic strength n_∞ and the Debye length κ^{-1} are defined in the polymer-free phase containing small ions only, and are related by

$$\kappa^2 = \frac{2 n_\infty e^2}{\varepsilon_0 \varepsilon^{\text{w}} kT}. \quad (3)$$

The second contribution is the entropy of the small ions, given by [2,5,15]

$$-T \Delta S = (1 - \phi) \sum_{\text{i}} \left(n_{\text{i}} \ln \frac{n_{\text{i}}}{n_{\text{i},\infty}} - n_{\text{i}} + n_{\text{i},\infty} \right) =$$
$$2 n_\infty (1 - \phi) (y \sinh y + 1 - \cosh y), \quad (4)$$

assuming a fixed chemical potential for the small ions ($n_{\text{i},\infty}$ constant).

3) In case of ionizable (annealed) polyelectrolyte, a *chemical* contribution must be added [8],

$$f^{\text{C}} = \frac{\phi}{v} (-\lambda y + \lambda^* \ln (1 - \alpha)) \quad (5)$$

with λ the line charge density, λ^* the line density of ionizable groups along the polyelectrolyte chain (a positive number), $\lambda = z\alpha\lambda^*$, z the charge sign ($+1$ for a polycation and -1 for a polyanion), and α the ionization degree. When the surface is ionizable, an analoguous chemical term must be implemented as well.

4) The contribution from *chain stretching* is given by [2,14]

$$f = \frac{a^2}{6} (\nabla G)^2 \quad (6)$$

with a the Kuhn length and G (ϕ in Refs. [2,4,15]; ψ in Ref. [13]) the chain order parameter.

2.2 Chemical potential

The exchange potential at a certain location in the adsorbed layer, u, is the difference between the local chemical potential of a polymer segment, μ, and the chemical potential in bulk solution, μ_{b}. Chain stretching contributions (elasticity) are not included in u but are described by the Edwards equation. In this work, a polymer segment is a segment of unit length (*i.e.*, 1 nm) and of volume v. The chemical potential has five contributions: 1) Flory-Huggins mixing terms, 2) electrostatics, 3) a chemical contribution related to the ionization of the polyelectrolyte molecules, 4) ion exclusion, and 5) polarization.

1) *Flory-Huggins.* Differentiating the free energy f of equation (1) with respect to ϕ results for the contribution to the chemical potential μ in ($\mu = v \cdot \partial f / \partial \phi$)

$$\mu^{\text{FH}} = -\frac{v}{v_{\text{FH}}} (\ln (1 - \phi) + 2\chi\phi). \quad (7)$$

Expanding equation (7) around $\phi = 0$ results in

$$\mu^{\text{FH}} = \frac{v}{v_{\text{FH}}} (1 - 2\chi) \phi = \upsilon \phi \quad (8)$$

with υ the second virial coefficient.

2) *Electrostatics.* In a mean field the electrostatic contribution to μ is

$$\mu^{\text{el}} = \lambda y. \quad (9)$$

3) *Ionization.* For an ionizable polyelectrolyte charge, typically described by a Langmuir isotherm, the ionization degree α is related to bulk pH (in the phase without polyelectrolyte where $y_\infty = 0$), the intrinsic pK-value, and a local y according to [5,8]

$$\alpha = \frac{1}{1 + 10^{z(p\text{H} - p\text{K})} e^{zy}}. \quad (10)$$

α is related to α_{b} in bulk solution according to [1]

$$\frac{1 - \alpha}{\alpha} \frac{\alpha_{\text{b}}}{1 - \alpha_{\text{b}}} = e^{z(y - y_{\text{b}})}. \quad (11)$$

The corresponding chemical contribution to the chemical potential is given by [5,7,8]

$$\mu^{\text{chem}} = -z\lambda^* \int_0^\alpha y' \text{d}\alpha' = -\lambda y + \lambda^* \ln (1 - \alpha). \quad (12)$$

In equation (12), y' and α' are related by an adsorption isotherm such as equation (10).

4) *Volume exclusion.* The polyelectrolyte excludes volume for the small ions and solvent, which results in the additional term [5,8]

$$\mu^{\text{vol excl}} = 2vn_\infty \left(\cosh y - 1\right), \qquad (13)$$

which simply is the excess number of ions (both anions and cations) in the displaced volume; n_∞ is the ionic strength.

5) *Polarization.* According to Prigogine *et al.* [17] and Sparnaay [18], when one of the components has a permittivity different from the solvent, then, in a potential gradient ∇y, the chemical potential has a polarization contribution given by

$$\mu^{\text{pol}} = -\frac{v}{2}\frac{kT}{e^2}\frac{\partial \varepsilon}{\partial \phi}\left(\nabla y\right)^2. \qquad (14)$$

We assume that the permittivity ε is a linear function of the polymer volume fraction ϕ which results in [1,5]

$$\frac{\varepsilon}{\varepsilon_0} = \phi\varepsilon^{\text{p}} + \left(1 - \phi\right)\varepsilon^{\text{w}}, \qquad (15)$$

where ε^{p} is the relative permittivity of the polymer. Equation (15) can be rewritten to

$$\frac{\varepsilon}{\varepsilon_0\varepsilon^{\text{w}}} = 1 - \phi\vartheta, \qquad (16)$$

where we have introduced ϑ which is given by

$$\vartheta = \frac{\varepsilon^{\text{w}} - \varepsilon^{\text{p}}}{\varepsilon^{\text{w}}} \quad , \quad 0 \leqslant \vartheta < 1. \qquad (17)$$

When the polyelectrolyte has the same permittivity as the solvent, the parameter ϑ equals zero and the polarization term is zero. However, for polyelectrolyte of a very low permittivity (say, $\varepsilon^{\text{p}} = 5$), ϑ can be as high as $\vartheta = 0.94$ (but it will never reach unity). Based on equation (16), $\partial\varepsilon/\partial\phi$ is given by

$$\frac{1}{\varepsilon_0\varepsilon^{\text{w}}}\frac{\partial \varepsilon}{\partial \phi} = -\vartheta. \qquad (18)$$

With equation (18), equation (14) can be rewritten to [5,19]

$$\mu^{\text{pol}} = +\frac{vn_\infty}{\kappa^2}\vartheta\left(\nabla y\right)^2. \qquad (19)$$

Equation (19) can be shown to be correct for the simple situation of two oppositely charged walls interacting across an ion-free medium, see Appendix A. Instead of equation (15), Maxwell Garnett theory can be used which gives, at high ϑ, a modified expression for the polarization term, see Appendix B.

2.3 Exchange potential

Combining equations (8) and (9) results, for the exchange potential of a polyelectrolyte segment with a fixed line charge, λ, in [2,4,14,15]

$$u = v\left(\phi - \phi_{\text{b}}\right) + \lambda\left(y - y_{\text{b}}\right). \qquad (20)$$

For ionizable polyelectrolyte, we must add equation (12) which results in [2,4]

$$u = v\left(\phi - \phi_{\text{b}}\right) + \lambda^* \ln\frac{1 - \alpha}{1 - \alpha_{\text{b}}}. \qquad (21)$$

Equation (21) is exactly the exchange potential for ionizable polyelectrolyte given in references [2,4] (α and α_{b} in the present report are $p_{\text{a}}(r)$ and p in Refs. [2,4]).

In the present report we will not linearize Flory-Huggins entropy and add the volume exclusion and polarization terms, resulting for polyelectrolyte with a fixed line charge in

$$u = -\frac{v}{v_{\text{FH}}}\left[\ln\frac{1 - \phi}{1 - \phi_{\text{b}}} + 2\chi\left(\phi - \phi_{\text{b}}\right)\right] + \lambda\left(y - y_{\text{b}}\right)$$
$$+ 2vn_\infty\left(\cosh y - \cosh y_{\text{b}}\right) + \frac{vn_\infty}{\kappa^2}\vartheta\left(\nabla y\right)^2. \qquad (22)$$

For ionizable polyelectrolyte we must replace the term $\lambda\left(y - y_{\text{b}}\right)$ by

$$u^{\text{el+chem}} = \lambda^* \ln\frac{1 - \alpha}{1 - \alpha_{\text{b}}} = z\lambda^*\left(y - y_{\text{b}}\right)\ln\frac{\alpha_{\text{b}}}{\alpha}. \qquad (23)$$

2.4 Edwards and Poisson-Boltzmann equation

The Edwards equation in the ground-state dominance approximation is given by [2,4,11–15]

$$\frac{a^2}{6}\nabla^2 G = u \cdot a \cdot G. \qquad (24)$$

The product $u{\cdot}a$ is the exchange potential per Kuhn segment. The polymer volume fraction ϕ relates to G according to

$$\phi = a \cdot v \cdot G^2. \qquad (25)$$

The differential form of Gauss' law is given by [20]

$$\nabla\left(\varepsilon\nabla y\right) = -\frac{e}{kT}\rho \qquad (26)$$

with ρ the local (external) charge density.

Equation (26) results after implementing the polyelectrolyte charge, and Boltzmann for the small ions, in the following modified Poisson-Boltzmann (PB) equation:

$$\varepsilon\nabla^2 y + \nabla\varepsilon \cdot \nabla y = \frac{e^2}{kT}\left(2n_\infty\left(1 - \phi\right)\sinh y - \frac{\phi}{v}\lambda\right), \quad (27)$$

and, using equations (3), (16) and (18), in

$$\left(1 - \vartheta\phi\right)\nabla^2 y - \vartheta \cdot \nabla\phi \cdot \nabla y = \kappa^2\left(\left(1 - \phi\right)\sinh y - \frac{\phi\lambda}{2vn_\infty}\right). \qquad (28)$$

Without gradients in ϕ, equation (28) becomes [5,6]

$$\left(1 - \vartheta\phi\right)\nabla^2 y = \kappa^2\left(\left(1 - \phi\right)\sinh y - \frac{\phi\lambda}{2vn_\infty}\right), \qquad (29)$$

and when volume effects are neglected completely, equation (28) simplifies to [2,4,14,15]

$$\nabla^2 y = \kappa^2 \left(\sinh y - \frac{\phi\lambda}{2vn_\infty} \right). \quad (30)$$

In case of ionizable polyelectrolyte, the line charge density must be replaced by $\lambda = z\alpha\lambda^*$ with α given by equation (10). The surface charge N (in m^{-2}) relates to dy/dx according to Gauss' law,

$$N = -\frac{2n_\infty}{\kappa^2}\left(1 - \vartheta\phi\right)\frac{dy}{dx}, \quad (31)$$

correct when the coordinate x is perpendicular to the surface and points into the solution, and when dy/dx is zero within the adjacent material. An ionizable surface charge is implemented when we interpret N as the surface density of ionizable sites, multiply the left-hand side of equation (31) by $z_s\alpha_s$, and use equation (10) for α_s.

In bulk solution, y_b follows from setting the left-hand side of equation (28) equal to zero, resulting in

$$y_b = \text{arcsinh}\frac{\phi_b\lambda}{2vn_\infty\left(1 - \phi_b\right)}. \quad (32)$$

The Cahn boundary condition at the surface is $\nabla G = G/D$ with D the polymer adsorption length [2,15]. Far away from the surface, all first- and second-order derivatives of y, ϕ and G with x are zero.

3 Results and discussion

Calculations are made for adsorption of polyelectrolyte with fixed charge on a planar interface with a fixed charge of opposite sign (one-dimensional plane-parallel geometry). We solve the PB and Edwards equation numerically with the boundary conditions discussed. In the calculations we set the polymer adsorption length D to infinity, that is we assume an "indifferent surface" which results in $\nabla G = \nabla\phi = 0$ at the interface [13,15]. Equations (24) and (28), or (30), are discretized and together with equations (22), or (20), and (25) solved using the software program *Maple*. Some constants used in the calculation are as follows: the unit length is 1 nm and χ is set to zero (no hydrophobic or other enthalpic interactions between polymer and water). We assume a polymer volume per unit length of $v = 0.50$ nm^3. The data used in reference [8] for a spherical polyelectrolyte brush lead with this value of v to a Flory-Huggins lattice site volume of $v_{\text{FH}} = 0.18$ nm^3. The second virial coefficient is then $v = 3$ (when $\chi = 0$). The surface charge is $N = -1$ nm^{-2} and in Figure 1 the polyelectrolyte line charge is $\lambda = +1$ nm^{-1}. We use for the relative permittivities $\varepsilon^w = 78$ and $\varepsilon^p = 20$ ($\vartheta = 0.744$), while we use a polymer bulk concentration of $\phi_b = 0.001$, an ionic strength of 10 mM ($n_\infty = 0.006$ nm^{-3}, $\kappa^{-1} = 3.03$ nm) and a Kuhn length of $a = 1$ nm.

Figure 1 compares the polyelectrolyte density profile for four cases: I) The classical approach in which the second virial coefficient v is set to zero, and the chemical
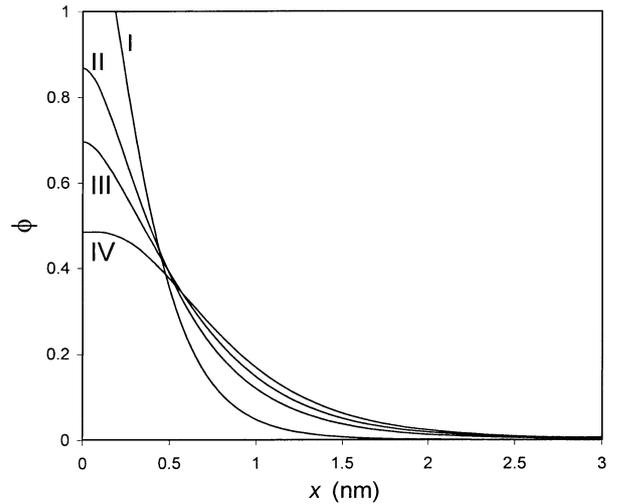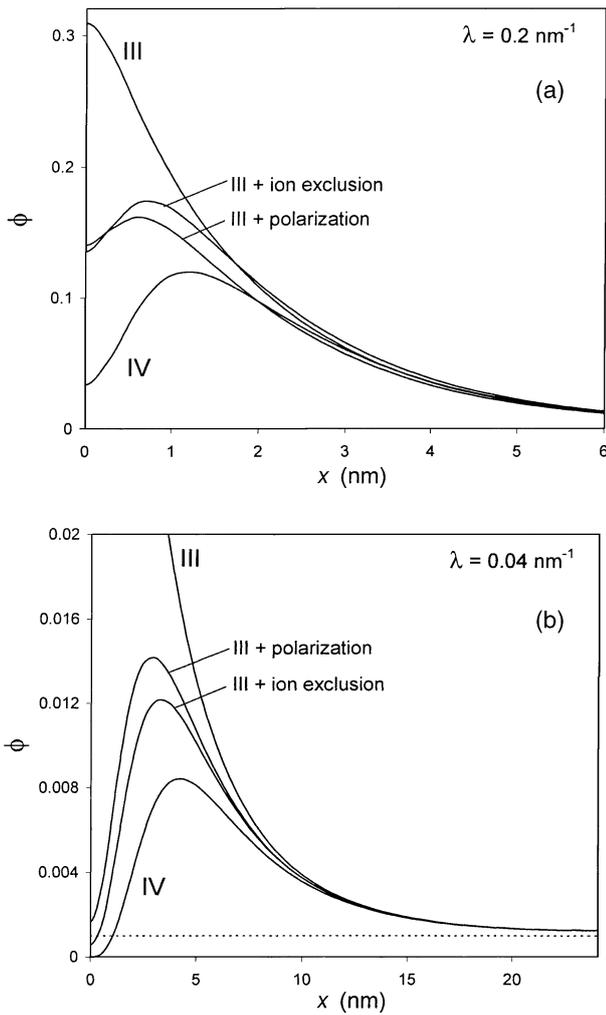

Fig. 1. Polyelectrolyte adsorption on an oppositely charged interface. ϕ is the polyelectrolyte volume fraction and x the distance from the surface. I) Classical approach with $v = 0$. II) as I) but including linearized FH theory, $v = 3$. III) as II) but without linearizing the FH theory. IV) as III) but including ion exclusion and dielectric permittivity gradients ($\sigma = -1$ nm^{-2}, $\lambda = 1$ nm^{-1}, $n_\infty = 10$ mM).

potential only consists of the electrostatic term zy, see references [11–13]; II) The model as used by Andelman and co-workers, including Flory-Huggins volume exclusion in the low-ϕ limit, based on equations (20) and (30); III) The same as II) but without linearizing the Flory-Huggins expression; IV) The same as III) but including volume effects of polymer on the electrostatic equations —based on equations (22) and (28). Clearly, not linearizing the FH expression already gives a significant effect, while the influence of the polymer volume on the electrostatic equations results in a further decrease of adsorbed amount.

In Figure 1 the effect of ion exclusion on the predicted adsorption profile is very low and the reduced adsorption is almost completely due to permittivity effects, the reason being that because of the high polyelectrolyte charge the small ions do not significantly contribute to the neutralization of the surface charge. However, the volume exclusion for small ions becomes important when the polyelectrolyte has a much lower charge/volume ratio, or the ionic strength increases. This effect was observed in calculations for lysozyme adsorption on charged silica [5], and BSA adsorption on carboxylic-acid–terminated self-assembled monolayers [6]. Below the isoelectric point, the protein is positively charged and adsorbs on the negative surface. However, when pI is approached, and at sufficiently high ionic strength, the system prefers the surface charge to be compensated by small ions instead: the protein molecules "bring in" too few positive charges to compensate for the small ions expelled from the surface and for the decrease in permittivity. A similar conclusion was reached by Vermeer *et al.* [3] based on numerical SCF calculations.

To analyze the relevance of the ion exclusion term further, we use in Figure 2 a reduced line charge λ (by 5 and 25 times). In these cases the ion exclusion term is
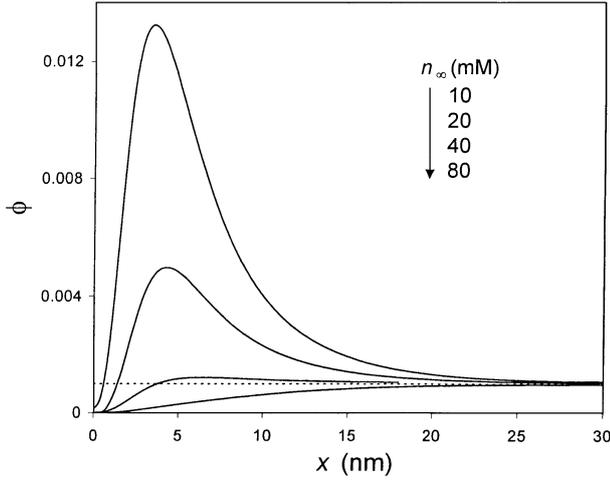
Fig. 2. Polyelectrolyte adsorption on an oppositely charged interface according to models III and IV of Figure 1, for different values of the polyelectrolyte line charge ($\sigma = -1$ nm^{-2}, $n_\infty = 10$ mM).

Fig. 3. Polyelectrolyte adsorption on an oppositely charged interface according to model IV of Figure 1, for different values of the polyelectrolyte line charge ($\sigma = -1$ nm^{-2}, $n_\infty = 10$ mM).

about equally important in reducing the ϕ-profile as the polarization term. In Figure 2b for the lowest line charge, the ion exclusion term is even more important than the polarization term. Figure 2b shows that volume effects strongly influence the adsorption behavior. First, the surface concentration, ϕ_0, without any of these corrections (model III) is ~ 0.065 (6.5 vol%), whereas in model IV ϕ_0 is about 4000 times lower. Second, without volume corrections the polymer concentration profile decreases monotonously from the surface (when using $\mathrm{d}\phi/\mathrm{d}x = 0$ at the surface), but has a pronounced maximum when either of the corrections (or both) is implemented. Clearly, the two corrections that we introduce not only reduce the polymer concentration but may also influence the concentration profile, resulting in a maximum polymer density at a location somewhat off the surface, even without assuming $\phi_0 = 0$. A small remark is that at these lower values for ϕ (< 0.30), the linearised form of the Flory-Huggins expression, see equations (8) and (20), becomes increasingly accurate.
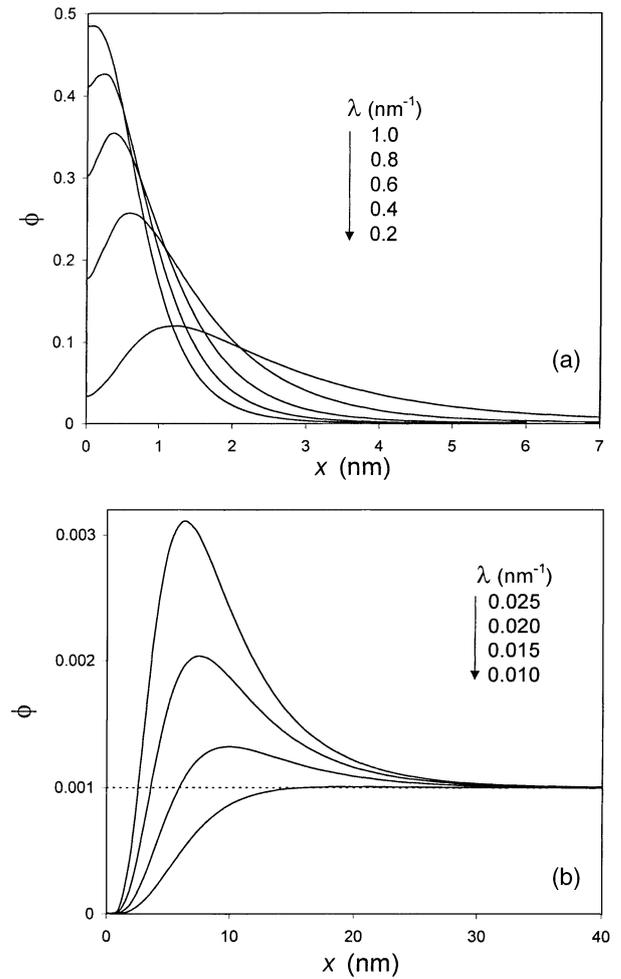
Figure 3 uses model IV in all cases, and shows the influence of reducing the line charge λ in more detail. As mentioned, reducing λ leads to a non-monotonic polyelectrolyte profile with a maximum in density at a slight distance from the surface. The position of the maximum shifts away from the surface with decreasing λ. The polymer concentration at the surface, ϕ_0, decreases steadily and becomes lower than ϕ_b for $\lambda < 0.05$ nm^{-1}. In Figure 3b we see that a net depletion of polyelectrolyte occurs below $\lambda \sim 0.015$ nm^{-1} with ϕ_0 rapidly going to zero for lower values of λ. Interestingly, similar non-monotonous adsorption profiles as in Figure 2 were calculated before (Refs. [11,12,14,21]) but based on the assumption of $\phi_0 = 0$ (corresponding to a strongly repulsive, or hard, surface, Refs. [13,15]). In the present calculation, $\mathrm{d}\phi/\mathrm{d}x$ is set to zero at the interface, and depletion is due to ion exclusion and polarization effects, not to the choice of boundary condition. Thus, for electrostatic reasons the charged interface repels the (oppositely charged!) polyelectrolyte chains from the surface, unless the polyelectrolyte is charged high enough (in our case, $\lambda \geqslant 1$ nm^{-1}). The

Fig. 4. Polyelectrolyte adsorption on an oppositely charged interface according to model IV of Figure 1, for different values of the ionic strength ($\lambda = 0.05$ nm^{-1}, $\sigma = -1$ nm^{-2}, $\phi_{\rm b} = 0.001$).

influence of ionic strength, n_∞, is discussed in Figure 4 and results in a similar behavior as in Figure 3 with the polyelectrolyte depleting from the interface at a high enough ionic strength.

4 Conclusion

For the problem of polyelectrolyte adsorbing to an oppositely charged interface, the ground-state dominance approximation of the Edwards equation is a useful simplification for sufficiently long polymers. The Poisson-Boltzmann equation is modified to include the exclusion by the polyelectrolyte of solvent and small ions, as well as the reduced permittivity and permittivity gradients. These corrections lead to two additional contributions to the exchange potential, namely for ion exclusion and for polarization, which both result in a (much) lower predicted polyelectrolyte density. Due to ion exclusion and polarization the polyelectrolyte is depleted from the surface (with a maximum density some nm's away from the surface) for a sufficiently high ionic strength or a sufficiently low polyelectrolyte charge.

Appendix A. Polarization contribution in homogeneous field

We assume two oppositely charged walls of charge $+\sigma$ and $-\sigma$, interacting across a homogeneous medium of a relative permittivity $\varepsilon^{\rm w}$ that does not contain any charges (small ions). We add a volume fraction ϕ of uncharged particles of volume v and a different permittivity, $\varepsilon^{\rm p}$, leading to a non-zero value for ϑ, see equation (17). The electric field dy/dx is independent of location, and is given by

$$\sigma = \varepsilon_0\varepsilon^{\rm w}\left(1 - \phi\vartheta\right)\left(\frac{kT}{e}\right)\left(\frac{dy}{dx}\right). \qquad (A.1)$$

For a fixed charge σ, the free energy density f only contains the contribution from the field energy, equation (2), resulting in

$$f = \left(1 - \phi\vartheta\right)\frac{\varepsilon_0\varepsilon^{\rm w}}{2}\left(\frac{kT}{e^2}\right)\left(\frac{dy}{dx}\right)^2 =$$
$$\frac{1}{2kT\left(1 - \phi\vartheta\right)}\frac{\sigma^2}{\varepsilon_0\varepsilon^{\rm w}} = \left(1 - \phi\vartheta\right)\frac{n_\infty}{\kappa^2}\left(\frac{dy}{dx}\right)^2. \quad (A.2)$$

The chemical potential of the particles is then given by differentiating the second equality in equation (A.2) with respect to ϕ, resulting in

$$\mu = v\frac{df}{d\phi} = \frac{v\vartheta}{2kT\left(1 - \phi\vartheta\right)^2}\frac{\sigma^2}{\varepsilon_0\varepsilon^{\rm w}} =$$
$$\frac{v\vartheta\varepsilon_0\varepsilon^{\rm w}kT}{2e^2}\left(\frac{dy}{dx}\right)^2 = v\vartheta\frac{n_\infty}{\kappa^2}\left(\frac{dy}{dx}\right)^2 \qquad (A.3)$$

which equals equation (19).

Appendix B. Polarization contribution, based on Maxwell Garnett

Expressed in ϑ and ϕ, the permittivity according to Maxwell Garnett is given by [22,23]

$$\frac{\varepsilon}{\varepsilon_0\varepsilon^{\rm w}} = \frac{\varepsilon^{\rm p} + 2\varepsilon^{\rm w} + 2\phi\left(\varepsilon^{\rm p} - \varepsilon^{\rm w}\right)}{\varepsilon^{\rm p} + 2\varepsilon^{\rm w} - \phi\left(\varepsilon^{\rm p} - \varepsilon^{\rm w}\right)} = \frac{3 - \left(1 + 2\phi\right)\vartheta}{3 - \left(1 - \phi\right)\vartheta}. \qquad (B.1)$$

The first derivative of ε with ϕ is given by

$$\frac{1}{\varepsilon_0\varepsilon^{\rm w}}\frac{\partial\varepsilon}{\partial\phi} = \frac{-3\cdot\vartheta\left(3 - \vartheta\right)}{\left(3 - \left(1 - \phi\right)\vartheta\right)^2}, \qquad (B.2)$$

which results for the polarization contribution to μ in

$$\mu^{\rm pol} = +\frac{vn_\infty}{\kappa^2}\frac{3\cdot\vartheta\left(3 - \vartheta\right)}{\left(3 - \left(1 - \phi\right)\vartheta\right)^2}\left(\nabla y\right)^2. \qquad (B.3)$$

For ϑ close enough to zero, equation (B.1) simplifies to equation (16), equation (B.2) becomes equation (18), and equation (B.3) simplifies to equation (19).

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