Poisson–Boltzmann theory of the charge-induced adsorption of semi-flexible polyelectrolytes

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A model is suggested for the structure of an adsorbed layer of a highly charged semi-flexible polyelectrolyte on a weakly charged surface of opposite charge sign. The adsorbed phase is thin, owing to the effective reversal of the charge sign of the surface upon adsorption, and ordered, owing to the high surface density of polyelectrolyte strands caused by the generally strong binding between polyelectrolyte and surface. The Poisson-Boltzmann equation for the electrostatic interaction between the array of adsorbed polyelectrolytes and the charged surface is solved for a cylindrical geometry, both numerically, using a finite element method, and analytically within the weak curvature limit under the assumption of excess monovalent salt. For small separations, repulsive surface polarization and counterion osmotic pressure effects dominate over the electrostatic attraction and the resulting electrostatic interaction curve shows a minimum at nonzero separations on the Angstrom scale. The equilibrium density of the adsorbed phase is obtained by minimizing the total free energy under the condition of equality of chemical potential and osmotic pressure of the polyelectrolyte in solution and in the adsorbed phase. For a wide range of ionic conditions and charge densities of the charged surface, the interstrand separation as predicted by the Poisson-Boltzmann model and the analytical theory closely agree. For low to moderate charge densities of the adsorbing surface, the interstrand spacing decreases as a function of the charge density of the charged surface. Above about 0.1 M excess monovalent salt, it is only weakly dependent on the ionic strength. At high charge densities of the adsorbing surface, the interstrand spacing increases with increasing ionic strength, in line with the experiments by Fang and Yang [J. Phys. Chem. B **101**, 441 (1997)]. © 2004 American Institute of Physics. [DOI: 10.1063/1.1647048]

INTRODUCTION

Adsorption or binding of polyelectrolytes to oppositely charged surfaces is a phenomenon which is of great significance both for biological systems and in various physicochemical applications. One can, for instance, think of the complex coacervation of anionic polysaccharides with positively charged proteins,^{1,2} charged micelles³ or emulsion interfaces,⁴ the interaction of DNA with cationic membranes,^{5,6} the formation of Langmuir–Blodgett type monolayers of stiff polyelectrolytes on charged interfaces⁷ or the adsorption of alternating layers of positively and negatively charged polyelectrolytes on a charged substrate.^{8–12} In all these cases, electrostatic interactions are at least partially responsible for the stability and structure of the complexes formed.

The theory of the adsorption of flexible polyelectrolytes has received abundant attention during the last decades, generating a large body of literature.^{13–21} However, many polyelectrolytes, including most ionic biopolymers, are semi-flexible rather than flexible. Because a persistence-length

^{a)}Address for correspondence: Nestlé Research Center, Vers-chez-les-Blanc, CH-1000 Lausanne 26, Switzerland. Electronic mail: johan.ubbink@rdls.nestle.com segment is highly anisometric, we expect the adsorption behavior of semi-flexible polyelectrolytes to differ qualitatively from that of flexible polyelectrolytes. In particular, in the case of polyelectrolytes strongly interacting with the charged surface, ordered phases of adsorbed polyelectrolytes will be formed in order to maximize the surface density of polyelectrolyte chains and thereby the attractive free energy of adsorption.

Recently, the adsorption of semi-flexible and rodlike polyelectrolytes has attracted theoretical attention.^{22–27} The problems encountered, in particular, in formulating a sufficiently rigorous theory of the charge-induced adsorption of semi-flexible polyelectrolytes are formidable.

One theoretical obstacle is the often intractable mathematics of the semi-flexible chain, another is that the often high charge density of the polyelectrolyte excludes Debye– Hückel type approximations in the treatment of the electrostatic interactions. The Debye–Hückel approximation is used in modeling the adsorption behavior of semi-flexible polyelectrolytes^{24,26} because of its straightforward mathematics, but application to highly charged polyelectrolytes like DNA is of course excluded.

In recent years, the theory of the semi-flexible chain has advanced considerably, leading, in particular, to a basic un-

5353



FIG. 1. The adsorbed phase of semi-flexible polyelectrolytes. The average spacing between the adsorbed strands is denoted by a. $\lambda = P^{1/3}a^{2/3}$ is the deflection length governing the statistics of the semi-flexible chain undulating parallel to the adsorbing surface and P is the persistence length.

derstanding of the effects of confinement on the statistics of the semi-flexible chain.²⁸⁻³⁴ This enables us to deal in an approximate way with the entropy a semi-flexible chain confined within an ordered surface phase.

It is the objective of the present article to combine the statistics of the semi-flexible chain and the electrostatics at the Poisson–Boltzmann level in a theory of the charge-induced adsorption of polyelectrolytes. Although at the small separations relevant to adsorption, other interactions, like van der Waals forces, ion-ion correlation forces, and hydration forces, could be comparable in magnitude to the screened electrostatic interaction, we restrict ourselves to the latter.

The electrostatic interactions in the adsorbed complex of polyelectrolytes are assumed to be screened by an excess of monovalent salt. We consider the case where the attractive interaction is strong enough to enforce complete adsorption of the polyelectrolyte chain. We furthermore assume that the polyelectrolyte is long, i.e., its contour length is much longer than the persistence length. Consequently, end effects may be neglected. As the polymer chain is semi-flexible, excursions away from the surface are energetically costly so that the chain remains parallel to the surface when adsorbed.

The adsorbed layer is thin, consisting of a single layer of polymer, as reversal of the effective charge sign of the surface upon adsorption will hamper the buildup of a thicker layer (for some recent theoretical work on the charge reversal on adsorption of charged polymers or colloidal bodies, see, e.g., Refs. 24-27).

Already at low charge-densities of the adsorbing surface the surface density of the adsorbed polyelectrolyte will be high, even for a highly dilute polyelectrolyte solution. The surface density is so high, in fact, that excluded volume interactions between adsorbed polyelectrolytes enforce a twodimensionally ordered phase in which the polyelectrolyte strands are aligned more or less in parallel at a well-defined spacing *a* (Fig. 1). The statistics of the semi-flexible chain confined near the adsorbing surface is then governed by a deflection length $\lambda = P^{1/3}a^{2/3}$, which replaces the persistence length P as the relevant statistical length scale.²⁹

The electrostatic interaction between the charged surface, assumed to be perfectly flat, uniformly charged and of low dielectric constant, and the polyelectrolyte strand, which we view as a uniformly charged cylinder of low dielectric constant, is taken into account using the Poisson–Boltzmann equation. The use of a cylinder model to calculate the electrostatic field around a semi-flexible polyelectrolyte is justified as long as the local radius of curvature of the polyelectrolyte, induced either by bending or by thermal fluctuations, is much larger than the Debye length. This was argued before for the analogous case of the electrostatic interaction in lyotropic polyelectrolyte liquid crystals.^{33,35,36} For the cylinder model to be applicable, we therefore require the deflection length to be much larger than the Debye screening length.

As uniformly valid analytical approximations are not obvious for the present geometry, we start by numerically solving the Poisson–Boltzmann equation for an array of adsorbed cylindrical polyelectrolytes near a charged surface using a finite element method. The integrated electrostatic free energy is subsequently used for a numerical minimization of the free energy of an adsorbed polyelectrolyte complex.

Afterwards, an approximate theory for the chargeinduced adsorption is introduced. We start by deriving a convenient approximate expression for the Poisson–Boltzmann potential between a highly charged and a weakly charged surface. The cylindrical geometry of the polyelectrolyte surface is taken into account in the weak curvature limit via a Derjaguin approximation and the free energy of interaction is calculated numerically.

The polyelectrolyte strands on the surface interact via an electrostatic excluded volume, for which we introduce a simple analytical expression. The equilibrium state is calculated by minimizing the total free energy of the system taking into account the coexistence relations. Numerical results are obtained for the adsorption of DNA on a positively charged surface of varying charge density and for a number of concentrations of excess monovalent salt.

At high charge densities of the positively charged surface or at very small separations between the surface and the cylinder the electrostatic adsorption free energy may become very high, of order 100–1000 k_BT per persistence length. In this case, the statistical-physical description of the structure and properties of the adsorbed layer could become invalid. Even in this case our approach is of value, however, as the strength of the electrostatic binding between polyelectrolyte and surface is a quantity of experimental interest.

FREE ENERGY OF ADSORPTION AND ADSORPTION EQUILIBRIUM

The adsorption of polyelectrolytes with a contour length L much longer than the persistence length P is considered. In our simplified picture, the structure of the adsorbed layer is characterized completely by the interstrand spacing a, the polyelectrolyte radius r and the separation between surface and polyelectrolyte d. (Figs. 1 and 2).

For adsorbed semi-flexible polyelectrolytes in the ordered phase depicted in Fig. 1, the free energy per unit length



FIG. 2. Cross-sectional view of the charged substrate and the adsorbed layer of polyelectrolyte cylinders.

of adsorbed strand may generally be written as

$$\mathcal{F} = \mathcal{F}_{el} + \mathcal{F}_{conf}, \tag{1}$$

where \mathcal{F}_{el} is the electrostatic free energy of the adsorbed complex and \mathcal{F}_{conf} is the free energy of entropic confinement of the semi-flexible chain in the adsorbed layer. The free energy contributions are functions of the interstrand spacing *a* and the distance to the adsorbing surface *d*.

In order to arrive at the equilibrium structure and packing density of the adsorbed layer, two conditions need to be fulfilled. First, the osmotic pressure should be equal in the adsorbed phase and in the polyelectrolyte solution:

$$\Pi_a = \Pi_s \,. \tag{2}$$

The subscripts a and s refer to the adsorbed and solution phases, respectively. Second, we require the equality of the chemical potential of the polyelectrolyte in both phases:

$$\mu_a = \mu_s \,. \tag{3}$$

The osmotic pressure of the adsorbed polyelectrolyte phase in equilibrium with an excess monovalent salt solution is defined as³⁷

$$\Pi_{p} = \left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{1}{a} \frac{\partial \mathcal{F}}{\partial d},\tag{4}$$

where F is the total free energy of the adsorbed polyelectrolyte phase, V is its volume and N is the number of persistence length segments in the adsorbed phase.

As the polyelectrolyte concentration in the solution is assumed to be low, osmotic effects of the polyelectrolyte in solution may be neglected, i.e., we set $\Pi_p = 0$. It should be noted at this point that we always consider polyelectrolyte solutions containing excess monovalent salt. Stability of the adsorbed phase with respect to the separation with the surface is therefore given by the following condition:

$$\frac{\partial \mathcal{F}}{\partial d} = 0. \tag{5}$$

It needs to be verified that the free energy is indeed a minimum:

$$\frac{\partial^2 \mathcal{F}}{\partial d^2} \ge 0. \tag{6}$$

In effect, we will find that the polyelectrolyte chains are undulating around the minimum of a steep potential energy well so that even a slight solution osmotic pressure of the polyelectrolytes will not significantly perturb the equilibrium value for d.

At constant temperature and volume, the chemical potential of the adsorbed phase takes the following form:³⁸

$$\mu_a = \left(\frac{\partial F}{\partial N}\right)_{T,V} = P \mathcal{F} - P a \frac{\partial \mathcal{F}}{\partial a}.$$
(7)

Here and in the following, we take the chemical potential per persistence length of polyelectrolyte, assuming that the concentration of excess monovalent salt is high enough to ensure that electrostatic stiffening effects are small.

The polyelectrolyte solution is a very large reservoir, so that the polyelectrolyte concentration remains virtually constant under variations in density of the adsorbed phase. Hence, the second condition for coexistence may be written

$$\frac{\partial \mathcal{F}}{\partial a} = \frac{\mathcal{F}}{a} - \frac{\mu_s}{Pa}.$$
(8)

In Eq. (8), the second term on the right hand side is virtually always negligible as the chemical potential of a semi-flexible chain is of the order of k_BT per persistence length whereas the free energy of an electrostatically adsorbed chain is often of the order of 10 to 1000 k_BT per persistence length. The equilibrium state of the system is obtained by minimizing the free energy equation (1) following Eqs. (5) and (8).

In a convenient, albeit more restricted formulation of the free energy of adsorption we may split the free energy of the adsorbed polyelectrolytes in a part containing only the free energy of a single adsorbed chain and a free energy of interaction of adsorbed chains:

$$\mathcal{F} = \mathcal{F}_{ads} + \mathcal{F}_2, \tag{9}$$

where \mathcal{F}_{ads} is the free energy of adsorption of a single chain and \mathcal{F}_2 is the free energy taking into account the excluded volume interactions between strands adsorbed on the surface. Both free energy contributions are per unit length of polyelectrolyte. The division of the free energy in these two contributions is convenient because \mathcal{F}_{ads} depends only on *d* and \mathcal{F}_2 is a function of *a* only.

The condition for phase coexistence Eq. (8) is then simply

$$\frac{\partial \mathcal{F}_2}{\partial a} = \frac{\mathcal{F}}{a}.$$
(10)

Both \mathcal{F}_{ads} and \mathcal{F}_2 contain a free energy contribution taking into account the confinement of the semi-flexible chain close to the surface and an electrostatic contribution to the free energy:

$$\mathcal{F}_{ads}(d) = \mathcal{F}_{int}(d) + \mathcal{F}_{conf}^{\perp}(d), \qquad (11)$$

$$\mathcal{F}_2(a) = \mathcal{F}_{el}(a) + \mathcal{F}_{conf}^{\parallel}(a), \qquad (12)$$

 \mathcal{F}_{int} is the free energy of electrostatic interaction between the polyelectrolyte cylinder and the charged surface, \mathcal{F}_{el} is the free energy of electrostatic interaction between the adsorbed strands and $\mathcal{F}_{conf}^{\perp}$ and $\mathcal{F}_{conf}^{\parallel}$ are the free energy contributions due to the entropic confinement of the strand close to the charged surface and within the two-dimensional array of adsorbed polyelectrolytes, respectively.

For a semi-flexible chain confined independently in two dimensions it can be shown that the confinement free energy

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FIG. 3. Electrostatic far field between adsorbed polyelectrolytes.

partitions into two independent terms, like in Eqs. (11) and (12).^{31,34} Following Refs. 30, 31, and 34, the free energy of confinement may therefore be expressed as

$$\frac{\mathcal{F}_{conf}^{\perp}}{k_B T} = \frac{c^{\perp}}{P^{1/3} d^{2/3}},$$
(13)

$$\frac{\mathcal{F}_{conf}^{\parallel}}{k_B T} = \frac{c^{\parallel}}{P^{1/3} a_0^{2/3}},\tag{14}$$

where $a_0 = a - d$. The form of Eq. (13) is presumably independent of the precise form of the mean field theory.^{28,30–34} The value of the coefficients c^{\perp} and c^{\parallel} is dependent on the form of the confining potential, in the case of confinement by a quadratic potential of a worm undulating in one dimension $c = 3/2^{8/3}$.^{32–34} Here, we will use the same value.

A discussion of \mathcal{F}_{el} is the subject of the next section.

ELECTROSTATIC FREE ENERGY

We consider the case where the electrostatic interactions both between the adsorbed polyelectrolytes and between a polyelectrolyte strand and the charged surface are screened by monovalent ions only. The ions originate from the polyelectrolytes, the surface as well as excess monovalent salt.

The surface, considered smooth, is variably charged but the primary focus is here on surfaces of a charge density lower than the surface charge density of the polyelectrolyte. The charge density of the surface is uniform. The discrete nature of the charges, though important especially at low surface charge densities and when close to the surface, is neglected here. The polyelectrolyte, which we model as a uniformly charged dielectric cylinder, is highly charged, so that its electrostatics have to be evaluated within the nonlinear Poisson-Boltzmann approximation.^{39,40} The approximation of the electrostatic field around a semi-flexible polyelectrolyte by the electrostatcs of a cylinder is justified as long as the deflection length is much larger than the Debye length. Both the surface and the polyelectrolyte cylinder are considered to be ideally polarizable and of low dielectric permittivity. Consequently, image charge effects are important.

The problem of the electrostatics is difficult as it stands. In principle, we not only have to consider the interaction of one polyelectrolyte strand with the charged surface, but also the electrostatic interaction between two polyelectrolytes adsorbed on the surface (Fig. 3). As no quantitative analytical approximation is immediately obvious, apart from linearizing the Poisson–Boltzmann equation, we initially opt for the



FIG. 4. The Derjaguin approximation.

following numerical approach. The Poisson–Boltzmann equation is numerically solved for the appropriate geometry and boundary conditions on a discrete grid spanned by the independent variables a and d. The equilibrium conditions following Eqs. (1), (5) and (8) are obtained using the numerically integrated electrostatic free energy.

The merits of the analytical approach which is introduced later in the article, and which is based on a free energy division as in Eq. (9), can then be evaluated within the relevant parameter space.

The Poisson–Boltzmann equation for a solution containing monovalent salt is given by

$$\nabla^2 \phi = \sinh(\phi). \tag{15}$$

The electrostatic potential ψ is rendered dimensionless as $\phi = q \psi/(k_B T)$. All geometric length scales are scaled by the Debye length κ^{-1} : $R = \kappa r$, $A = \kappa a$, $A_0 = \kappa a_0$ and D_0 $= \kappa d_0$. In a solution containing excess monovalent salt, the Debye length is defined by $\kappa^2 = 8 \pi Q_B n_s$. Q_B $= q^2/(4 \pi \epsilon k_B T)$ is the Bjerrum length with q the elementary charge, ϵ is the dielectric permittivity, k_B is Boltzmann's constant and T is the absolute temperature. Expressed in (nm⁻³), the number concentration of monovalent salt is related to the molar concentration $c_{1:1}$ by $n_s \approx 0.602c_{1:1}$.

The assumption of constant charge density of the surface of both polyelectrolyte and surface provides two of the boundary conditions:

$$\left. \frac{\partial \phi}{\partial \rho} \right|_{\rho=A} = -4 \, \pi \Sigma_p \,, \tag{16}$$

where ρ is the radial coordinate from the cylinder axis, and

$$\left. \frac{\partial \phi}{\partial Y} \right|_{Y=0} = -4 \,\pi \Sigma_w, \tag{17}$$

where *Y* denotes the coordinate perpendicular to the charged surface (Fig. 4). The dimensionless surface charge densities are determined by $\Sigma_p \equiv Q_B \sigma_p / (\kappa q)$ and $\Sigma_w \equiv Q_B \sigma_w / (\kappa q)$ where σ_p and σ_w are the signed surface charge densities of, respectively, polyelectrolyte and surface, measured in elementary charges per unit surface area. By the boundary conditions Eqs. (16) and (17) we assume the dielectric permit-

tivities of both surfaces, ϵ_p for the polyelectrolyte cylinder and ϵ_s for the charged substrate (Fig. 2), to be negligible to the one of the aqueous solution.

A number of additional boundary conditions complement the set of equations. First, we require that the electrostatic potential vanishes into the solution:

$$\phi(Y \to \infty) \to 0. \tag{18}$$

Second, the potential is symmetric with respect to the plane perpendicular to the surface which runs through the center of the adsorbed polyelectrolyte:

$$\left. \frac{\partial \phi}{\partial X} \right|_{X=0} = 0, \tag{19}$$

where X denotes the coordinate parallel to the charged surface (Fig. 4). Third, the potential is symmetric with respect to the plane perpendicular to the surface which divides the space between two adsorbed polyelectrolytes into two:

$$\left. \frac{\partial \phi}{\partial X} \right|_{X=A/2} = 0.$$
(20)

The set of equations (15)-(20) is solved numerically using a finite element method (see the Appendix for details). The total electrostatic free energy associated with unit length of adsorbed polyelectrolyte is then calculated via a numerical integration over the electric field and the entropy of the small ions:⁴¹

$$\frac{\mathcal{F}_{el,\text{tot}}}{k_B T} = \frac{\kappa}{8 \pi Q_B} \int_S dS \bigg[(\nabla \phi)^2 + n_+ \bigg(\ln \frac{n_+}{n_s} - 1 \bigg) + n_- \bigg(\ln \frac{n_-}{n_s} - 1 \bigg) + 2n_s \bigg], \qquad (21)$$

where the domain of integration extends from X = -A/2 to X = A/2 and from Y = 0 to $Y \rightarrow \infty$. The distributions of positive and negative small ions are given by $n_{+} = n_s \exp(-\phi)$ and $n_{-} = n_s \exp(\phi)$, where n_s is the concentration of small ions in the solution outside of the slit.

We obtain the free energy of double layer interaction by subtracting the free energies of the isolated double layers of polyelectrolyte cylinder $\mathcal{F}_{el,p}^0$ and charged surface F_{el}^0 (see the Appendix):

$$\mathcal{F}_{el} = \mathcal{F}_{el,\text{tot}} - \mathcal{F}_{el,p}^0 - aF_{el}^0.$$
⁽²²⁾

The free energy per unit surface area of an isolated double layer is given by.^{41,42}

$$\frac{F_{el}^{0}}{k_{B}T} = \frac{2\kappa\Sigma}{Q_{B}} [\ln(\sinh(|\phi_{i}(0)|/2) + (\sinh^{2}(|\phi_{i}(0)|/2) + 1)^{1/2}) + \sinh^{-1}(|\phi_{i}(0)|/2) + (1 - (\sinh^{2}(|\phi_{i}(0)|/2) + 1)^{1/2}]].$$
(23)

As a fully numerical approach towards the electrostatic free energy of highly charged polyelectrolytes in adsorbed states is rather inconvenient, in particular when further free energy contributions are to be taken into account in the minimization of the free energy, we forward here an approximate analytical method based on the Poisson–Boltzmann equation.

TABLE I. Poisson–Boltzmann parameter ξ as calculated following Ref. 37. DNA hardcore radius r=1.0 nm, DNA linear charge density $\nu = -5.9$ q/nm. ξ has been computed with the help of the analytical solution to the cylindrical Poisson–Boltzmann equation listed in Ref. 44.

c (M)	κ^{-1} (nm)	ξ
0.001	9.61	0.647
0.01	3.04	1.34
0.1	0.961	4.07
0.2	0.680	6.38
0.5	0.430	14.8
0.75	0.351	24.5
1	0.304	37.3

First, we focus on the electrostatic interaction between two polyelectrolytes adsorbed on the charged surface.

As two adsorbed strands will generally strongly repel one another, we anticipate that, in prevailing cases, the closest distance between the surfaces of the strands in the adsorbed state will remain relatively large, i.e., larger than about two times the Debye length (Fig. 3). For two isolated polyelectrolytes, the inner double layers, which are nonlinearly screened, are then left unperturbed by the interaction between the polyelectrolytes (for some additional justification, see also Ref. 25). The effective charge density of the polyelectrolytes, for which the far field of the electrostatic potential matches the Poisson-Boltzmann potential, is subsequently calculated following the procedure by Stroobants et al.³⁷ The free energy of electrostatic interaction of two strands may then simply be calculated by multiplying the electrostatic field of one of the polyelectrolytes by the effective charge of the other one:^{37,43}

$$\frac{\mathcal{F}_{el}}{k_B T} = \frac{\xi^2}{Q_B} \left(\frac{2\pi}{\kappa a}\right)^{1/2} \exp[-\kappa a].$$
(24)

 ξ is an effective charge parameter, which is most conveniently evaluated using Philip and Wooding's solution to the cylindrical Poisson–Boltzmann equation.^{37,44} In Table I, values of ξ for an idealized DNA cylinder are collected for various concentrations of monovalent salt. In Eq. (24), a factor $\frac{1}{2}$, to avoid double counting, and a factor 2, because of the presence of two nearest neighbors in the adsorbed polyelectrolyte lattice, mutually cancel.

As a first approximation, we assume that κ is not influenced by the presence of the surface. At low charge density of the charged surface and at moderate to high concentrations of excess salt, this seems plausible, but its ultimate validity is to be determined from a comparison with the numerical results. In fact, an analogous assumption was made long ago in a famous paper by Onsager and Samaras.⁴⁵

In the second place, we need to derive an expression for the electrostatic potential between a cylinder and a surface based on the Poisson–Boltzmann equation. We start with the one-dimensional Poisson–Boltzmann equation, which, in terms of the scaled variables ϕ and $Y \equiv \kappa y$, becomes

$$\frac{d^2\phi}{dY^2} = \sinh\phi. \tag{25}$$

For two interacting surfaces of dimensionless surface charge densities Σ_p and Σ_w the boundary conditions

$$\left. \frac{d\phi}{dY} \right|_{Y=D} = -4\pi\Sigma_p, \quad \left. \frac{d\phi}{dY} \right|_{Y=0} = -4\pi\Sigma_w \tag{26}$$

have to be satisfied.

Equation (25) may be integrated to give the potential ϕ , but, for two interacting surfaces, the potential can be expressed in terms of elliptic integrals only.⁴² We can substantially simplify the problem, however, by recognizing that of principal relevance here is a highly charged polyelectrolyte interacting with a fairly weakly charged surface, at small separations (Fig. 2). For the corresponding problem of two interacting surfaces the restriction to $\Sigma_p \gg \Sigma_w$ and a slit width $D \ll 1$ means that the potential is negative everywhere in the slit. Due to the strongly negative Boltzmann weighting, the slit is essentially depleted of the co-ions of the negatively charged surface, which are the counter-ions of the positively charged surface. We therefore approximate:

$$\sinh\phi \approx -\frac{1}{2}\exp(-\phi). \tag{27}$$

Using $d^2\phi/dY^2 = 1/2d/d\phi(d\phi/dY)^2$, Eq. (25) is readily integrated one time:

$$\frac{d\phi}{dY} = \pm [\exp(\phi) + C]^{1/2}, \qquad (28)$$

where the approximation Eq. (27) has been used. In our case, the minus sign holds as $d\phi/dY < 0$ everywhere. The second integration can be written as

$$Y = -\int d\phi \frac{1}{[\exp(\phi) + C]^{1/2}}.$$
 (29)

Depending on the value of the integration constant C, this may be integrated to give

$$\phi = \ln \left[\frac{1}{C} \sinh^2 \left[\frac{1}{2} C^{1/2} (B - Y) \right] \right], \quad 0 < C < 16 \pi^2 \Sigma_w^2,$$
(30)

$$\phi = -\ln \left[-C \left[\cos^2 \left[\frac{1}{2} (-C)^{1/2} [B - Y] \right] \right] \right], \quad C < 0.$$
(31)

The integration constants B and C are determined by the boundary conditions Eq. (26) and the slit width D. For a given value of D, C has to be determined from the implicit relations

$$D = \frac{2}{C^{1/2}} \left[\operatorname{arctanh} \left(-\frac{4\pi\Sigma_p}{C^{1/2}} \right) - \operatorname{arctanh} \left(-\frac{4\pi\Sigma_w}{C^{1/2}} \right) \right],$$

$$0 < C < 16\pi^2 \Sigma_w^2, \quad (32)$$

$$D = \frac{2}{(-C)^{1/2}} \left[\frac{1}{2} \ln \left(\frac{-4\pi\Sigma_p^{1/2} + C^{1/2}}{-4\pi\Sigma_p^{1/2} - C^{1/2}} \right) - \ln \left(\frac{-4\pi\Sigma_w^{1/2} + C^{1/2}}{-4\pi\Sigma_w^{1/2} - C^{1/2}} \right) \right], \quad C < 0. \quad (33)$$

B is given by

$$B = \frac{2}{C^{1/2}} \operatorname{arctanh} \left(-\frac{4\pi\Sigma_p}{C^{1/2}} \right), \quad 0 < C < 16\pi^2 \Sigma_w^2, \quad (34)$$

$$B = -\frac{2}{(-C)^{1/2}} \arctan\left(-\frac{4\pi\Sigma_p}{(-C)^{1/2}}\right), \quad C < 0.$$
(35)

Again, we obtain the total electrostatic free energy of the double layer from the energy of the electric field in the double layer and the entropy of the small ions:

$$\frac{F_{el}(D)}{k_B T} = \frac{\kappa}{8 \pi Q_B} \int_0^D dY \left[\left(\frac{d\phi}{dY} \right)^2 + n_+ \left(\ln \frac{n_+}{n_0} - 1 \right) + n_- \left(\ln \frac{n_-}{n_0} - 1 \right) + 2n_0 \right].$$
(36)

We obtain the free energy of interaction of the double layers by subtracting the free energies of the isolated double layers:

$$F_{el} = F_{el,\text{tot}} - F_{el,p}^0 - F_{el,w}^0.$$
(37)

 $F_{el,-}^0$ and $F_{el,+}^0$ are the electrostatic free energies of the isolated double layers.

We next consider the free energy of electrostatic interaction of the charged polyelectrolyte cylinder and the charged surface, typically at separations smaller than a Debye length. We take the curvature of the cylinder surface into account via a Derjaguin approximation.⁴² The potential exerted by the curved surface is viewed as a superposition of potentials exerted by infinitesimally small parallel surfaces at separations corresponding to their position along the cylinder surface. In effect, we thus neglect the effect of curvature on the distribution of small ions in the diffusive double layer. For these corrections to be small, the radius of cylinder should be larger than approximately one Debye length.

The separation between a point on the cylinder surface and the surface may be written (Fig. 4)

$$D_w(X) = D + R - [R^2 + X^2]^{1/2} \approx D + \frac{X^2}{2R},$$
(38)

where we anticipate that for X near R the contribution to the total free energy is small.

The electrostatic free energy of interaction of cylinder and surface may be written

$$\frac{\mathcal{F}_{int}(d)}{k_B T} = \frac{2}{\kappa} \int_0^R dX F_{el}(D).$$
(39)

The free energy is per unit length of polyelectrolyte cylinder. In the subsequent analysis we will use the electrostatic free energy of interaction, calculated either via the depletion and Derjaguin approximations [Eq. (39)], or via the numerical solution of the Poisson–Boltzmann equation [Eq. (15)] supplemented by the boundary conditions Eqs. (16)-(20) on the appropriate grid (Fig. 8). The various approximations made in the derivation of the analytical theory are summarized in Table II.

TABLE II. Approximations inherent in the analytical theory.

Ordered phase of parallel polyelectrolytes	$a \ll P$
Long polyelectrolytes	$L \gg P$
Cylindrical geometry for electrostatic potential of	<i>κ</i> λ≥1
semi-flexible polyelectrolytes	
Derjaguin approximation	<i>κr</i> ≥1
Depletion approximation	кd≤1
Depletion approximation	$ \sigma_p \gg \sigma_w $
Electrostatic far field between polyelectrolytes	$a \ge 2r + 2\kappa^{-}$
Electrostatic superposition	$\psi q/k_BT \leq 1$

DISCUSSION

Electrostatic interaction

We investigate the properties of the electrostatic free energy of interaction between polyelectrolyte cylinder and charged surface by numerical examples. The parameters characterizing the polyelectrolyte are chosen to mimic double-helical DNA in the B-form, i.e., we set the surface charge density of the polyelectrolyte equal to $\sigma_p = -1.0 \text{ q/m}^2$, which corresponds to the unhydrated DNA radius of about 1.0 nm and the charge density of two negative phosphate charges per base pair of 0.34 nm axial length.

The free energy of interaction is negative at large separations, due to the electrostatic attraction between the oppositely charged surfaces, but, owing to the dielectric polarization of the polyelectrolyte cylinder and the charged surface both assumed to have a dielectric permittivity of zero—and the osmotic pressure of the small ions in the slit, the free energy becomes positive at very small separations, giving rise to an effective repulsion between polyelectrolyte and surface. The electrostatic free energy curves therefore display a minimum as function of the separation between charged surface and polyelectrolyte because of image charge effects.

At the given charge density of the polyelectrolyte surface, this minimum occurs at polyelectrolyte-charged surface separations on the Angstrom scale for charge densities of the adsorbing surface which are not too high (i.e., around 0.1 q/nm^2). In the establishment of a binding equilibrium, it is therefore the minimum of the electrostatic free energy as a function of d which is of importance. An adsorbed strand is in effect undulating around the minimum of this potential energy well. A complete quenching of the adsorbed layer of polyelectrolyte is prohibited by this minimum and the relative flatness of its slopes. For charge densities of the adsorbing surface which are very high (around 1 q/nm^2), the minimum shifts to values of d which are much smaller than the typical molecular or ionic dimensions. In these cases, a cutoff length d_0 has to be set in the free energy minimization (see below).

For charge densities σ_w lower than a critical value, the free energy of interaction increases continuously with decreasing separation, the effective force thus being repulsive at all separations. For strands to remain adsorbed, the minimum in the interaction free energy should of course be lower, in order to overcome the thermal energy of the semi-flexible chains.

In Table III(a) and (b), we compare the electrostatic

TABLE III. (a) Minimum of the electrostatic free energy of interaction at infinite separation of adsorbed polyelectrolytes as function of the charge density of the positively charged surface. $\sigma_p = -1 \text{ q/m}^2$, concentration of monovalent salt $c_{1:1} = 0.1$ M, polyelectrolyte radius r = 1.0 nm, persistence length P = 50 nm, $Q_B = 0.715$ nm. (b) Minimum of the electrostatic free energy of interaction at infinite separation of adsorbed polyelectrolytes as function of the concentration of monovalent salt. $\sigma_p = -1 \text{ q/m}^2$, $\sigma_w = 0.2 \text{ q/m}^2$, polyelectrolyte radius r = 1.0 nm, persistence length P = 50 nm, $Q_B = 0.715$ nm.

(a) σ_w (q/nm ²)	$\min(\mathcal{F}_{el}(A = \infty))$ $(k_B \text{T/nm})$	$\frac{\min(\mathcal{F}_{el,anal})}{(k_B \mathrm{T/nm})}$	
0.05	-0.116	-0.108	
0.1	-0.402	-0.212	
0.2	-1.34	-0.660	
0.3	-2.58	-1.37	
0.4	-3.98	-2.28	
0.5	-5.38	-3.35	
0.75	-9.31	-6.43	
1	- 12.0	-6.24	
(b)	$\min(\mathcal{F}_{el}(A=\infty))$	$\min(\mathcal{F}_{el,anal})$	
<i>c</i> (M)	$(k_B T/nm)$	$(k_B T/nm)$	
0.001	- 14.8	-3.12	
0.01	-5.39	-1.64	
0.1	-1.34	-0.660	
0.2	-0.810	-0.502	
0.5	-0.411	-0.384	
1	-0.238	-0.330	

binding energy of an isolated polyelectrolyte adsorbed on the charged surface. In the second column of both tables, the electrostatic free energy minimum of the polyelectrolyte-charged surface as calculated using the finite element method is given at infinite separation of adsorbed polyelectrolytes. This equals the electrostatic binding free energy of an isolated polyelectrolyte and can directly be compared with the electrostatic free energy calculated via the analytical approximation, which is given in the last column of Table III(a) and (b).

From Table III(a), it is seen that the agreement between the electrostatic binding free energy calculated numerically and analytically is fairly good. As anticipated, this agreeement is good in particular at lower charge densities of the charged surface. For the whole range of charge densities of the adsorbing surface, the difference between the numerical and analytical values is smaller than a factor 2. The electrostatic binding free energy within the fully numerical analysis is higher than with the analytical analysis, which can be understood as the electric field extends beyond that part of the surface which is directly covered by the adsorbed polyelectrolyte.

The electrostatic binding free energy varies strongly as a function of the concentration of excess monovalent salt (Table IIIb). Whereas the electrostatic binding free energy is about 740 k_BT per persistence length at an ionic concentration of 0.001 M, it decreases to $12 k_BT$ per persistence length at 1 M excess monovalent salt. The analytical route leads to an underestimate of the binding free energy at lower ionic strengths, but, as expected, provides rather accurate values at higher salt concentrations. It is clear that by "salting-out,"



FIG. 5. Minimum of the free energy of electrostatic interaction between polyelectrolyte and surface as function of the distance of closest approach between adsorbed polyelectrolytes, plotted as the ratio with the minimum of the free energy at infinite separation. $\sigma_p = -1 \text{ q/mm}^2$; r = 1.0 nm, $Q_B = 0.715 \text{ nm}$. (a) Variation in charge density of the positively charged surface; curves from bottom to top: $\sigma_w = 0.05 \text{ q/nm}^2$, 0.1 q/nm^2 ; 0.2 q/nm^2 ; 0.3 q/nm^2 ; 0.4 q/nm^2 ; 0.5 q/nm^2 ; 0.75 q/nm^2 ; 1 q/nm^2 . (b) Variation in salt concentration; upper dashed curve: $c_{1:1} = 0.01 \text{ M}$; lower dashed curve: $c_{1:1} = 0.1 \text{ M}$; 0.2 M; 0.5 M, 1 M.

the adsorbed polyelectrolytes can in principle be made to desorb from the charged surface.

The electrostatic interaction of an adsorbed polyelectrolyte is influenced by the presence of nearest neighbors in the array of adsorbed polyelectrolytes. In Figs. 5(a) and 5(b), we plot the variation in the minimum of the free energy of interaction between an adsorbed polyelectrolyte and the charged surface as function of the separation between neighboring polyelectrolytes in the polyelectrolyte-charged surface complex. It is seen that the effective electrostatic interaction diminishes strongly when the adsorbed polyelectrolytes approach one another to within about 3 Debye lengths. These nonlinear effects are pronounced in particular when the ionic concentration is low and the charge density of the adsorbing surface is high and limit the applicability of the analytical theory.

In addition, in the analytical theory, it is assumed that the electrostatic interaction between adsorbed polyelectrolyte chains is not influenced by the presence of the surface. This is likely to be a good approximation at low charge densities of the charged surface, but its validity is uncertain otherwise. We do not provide graphical results on the effect of the charged surface on the electrostatic interaction between the adsorbed polyelectrolytes, but, instead, in Table IV, the fitting coefficients for the effective interaction is given. As it turns out that, for salt concentrations above about 0.01 M, the functional form of the effective interaction between adsorbed polyelectrolytes is close to the form of Eq. (24), we may represent the electrostatic interaction by two parameters: an effective linear charge density ξ_{eff} and an effective (local) Debye screening length κ^{-1} . From Table IV, we observe that, for the conditions of interest to our study, the effective Debye length is very close to the Debye length in the bulk solution, provided that the ionic concentration is about 0.1 M or higher and the dimensionless separation between surface and adsorbed polyelectrolytes larger than about 0.01. At low ionic strengths and very close to the charged surface, we find that the effective Debye length becomes somewhat shorter than the bulk one. The fitted values for the effective linear charge density ξ_{eff} are close to the values derived for an isolated polyelectrolyte (Table I), but at high salt concentrations they remain somewhat lower.

Our results confirm and extend the findings of Ospeck and Fraden,⁴⁶ who studied the effects of confinement by two surfaces on the electrostatic interaction between parallel cylinders. However, in our case, the reduction of the effective screening length at separations down to about 0.1 Debye length is much weaker than in their study. This is in part the case because the confinement by two surfaces or by a pore is much stronger than the confinement effected by a single sur-

TABLE IV. Free energy of electrostatic interaction between adsorbed polyelectrolytes from the finite-element calculations. The data are represented by an effective charge parameter ξ_{eff} and an effective screening length κ_{eff}^{-1} as fitted to Eq. (24). $\sigma_p = -1 \text{ q/m}^2$, $\sigma_w = 0.2 \text{ q/m}^2$, polyelectrolyte radius r = 1.0 nm, persistence length P = 50 nm, $Q_B = 0.715 \text{ nm}$. Data for $c_{1:1} = 0.001 \text{ M}$ are not given as the interaction curve can not well be represented using a fit to Eq. (24).

	0.01 M		0.1 M		0.2 M		0.5 M		1 M	
D	$\xi_{ m eff}$	$\kappa_{\rm eff} ({\rm nm}^{-1})$	$\xi_{\rm eff}$	$\kappa_{\rm eff} ({\rm nm}^{-1})$	$\xi_{ m eff}$	$\kappa_{\rm eff} ({\rm nm}^{-1})$	$\xi_{ m eff}$	$\kappa_{\rm eff} ({\rm nm}^{-1})$	$\xi_{\rm eff}$	$\kappa_{\rm eff} ({\rm nm}^{-1})$
0.01	2.75	0.415	3.85	1.01	5.07	1.38	9.05	2.12	20.3	1.34
0.05	2.80	0.415	4.13	1.03	5.16	1.39	9.23	2.13	20.1	1.33
0.1	2.82	0.414	4.02	1.02	5.16	1.39	9.59	2.16	19.7	1.29
0.5	2.53	0.389	3.92	1.02	5.25	1.41	9.56	2.17	20.4	1.32
1	2.07	0.362	3.54	1.00	4.67	1.38	9.33	2.17	20.5	1.30
5	1.35	0.306	2.84	0.97	4.16	1.37	9.21	2.19	21.0	1.29
10	1.28	0.298	2.79	0.96	4.16	1.37	9.11	2.18	21.1	1.29

face. In addition, from an electrostatic point of view, we focus here on a regime which is the opposite from the one studied in Ref. 46, namely a strongly charged polyelectrolyte cylinder and a weakly charged surface. Because of its high charge density, the polyelectrolyte remains the dominating factor in the electric double layer and the effective screening length is only weakly perturbed from the solution one, in particular for concentrations of excess monovalent salt above 0.01 M.

Concomitant with the decrease in screening length, the effective charge density of the polyelectrolyte increases with decreasing separation d. This effect, which is pronounced in particular at low salt concentrations, shows the influence of the approaching surface on the surface potential of the polyelectrolyte.

For separations between surface and cylindrical polyelectrolyte which are smaller than about 0.1 Debye length, we find that both the effective screening length and the effective charge density decrease slightly with decreasing d. This is caused by the dielectric discontinuity at the adsorbing surface, which is now very nearby.

Adsorption equilibrium

The equilibrium structure of the adsorbed phase is obtained by minimizing the total free energy following Eq. (5)and Eq. (8) or Eq. (10) for, respectively, the full Poisson-Boltzmann model and the analytical theory. The parameter characterizing the system which is of main experimental interest is a, the average separation between the adsorbed strands.

At this point, we emphasize again that coexistence of the adsorbed phase with the polyelectrolyte solution is essential to determine the equilibrium density of the adsorbed polyelectrolytes, even if any realistic value of the chemical potential of the polyelectrolyte in solution does only weakly influence the interstrand spacing. In effect, the pecise value of chemical potential of the polyelectrolyte in solution does not matter that much, but polyelectrolyte molecules must be able to adsorb from the solution onto the surface, or desorb from the surface into the solution in order to establish the equilibrium adsorbed state. In coexistence with the polyelectrolyte solution, it is then the (attractive) interaction between polyelectrolyte and surface, the (repulsive) interaction between two adsorbed polyelectrolytes and the free energy of confinement of the semi-flexible chains which control the interstrand spacing.

We investigate the properties of the model by way of numerical predictions for the adsorption of DNA in the B-form. The surface charge density of DNA is approximately 1 negative phosphate charge per nm² and the DNA hardcore radius is about 1.0 nm. The DNA persistence length P is taken to be 50 nm, independent of the ionic conditions. The chemical potential of the polyelectrolyte in solution is neglected, since, as argued above, the density of the adsorbed phase is only very weakly dependent on the chemical potential of the polyelectrolytes in solution and, consequently, in the dilute regime, on the bulk concentration of polyelectrolyte.

Charge induced adsorption of semi-flexible polyelectrolytes

5361

TABLE V. (a) Interstrand spacing and separation between polyelectrolyte and surface as a function of the charge density of the charged surface calculated using the Poisson-Boltzmann equation and the analytical approximation following Eqs. (24) and (39). PB: Poisson-Boltzmann theory; Anal.: Analytical theory. $\sigma_p = -1 \text{ q/m}^2$, $c_{1:1} = 0.1 \text{ M}$, polyelectrolyte hardcore diameter r = 1.0 nm, polyelectrolyte persistence length P = 50 nm, Q_B =0.715 nm. (b) Interstrand spacing and separation between polyelectrolyte and surface as a function of the excess monovalent salt concentration calculated using the Poisson-Boltzmann equation and the analytical approximation following Eqs. (24) and (39). PB: Poisson-Boltzmann theory; Anal.: Analytical theory. $\sigma_p = -1 \text{ q/m}^2$, $\sigma_w = 0.2 \text{ q/m}^2$, polyelectrolyte hardcore diameter r = 1.0 nm, polyelectrolyte persistence length P = 50 nm, Q_B = 0.715 nm. Numbers in italics refer to conditions outside the range of validity of the analytical theory.

(a)	a	(nm)	<i>d</i> (nm)		
σ_w (q/nm ²) (M)	PB	Anal.	PB	Anal.	
0.05	а	9.86	а	2.09	
0.1	6.52	7.38	1.01	1.45	
0.2	4.78	5.58	0.58	0.75	
0.3	3.92	4.67	0.34	0.47	
0.4	3.39	4.08	0.23	0.40	
0.5	2.68	3.66	0.17	0.21	
0.75	2.34	2.94	0.10	0.10	
1	2.07	2.58	0.05	0.02	
(b)	a	(nm)	<i>d</i> (nm)		
(U) c (M)	PB	Anal.	PB	Anal.	
0.001	6.90	1.31	0.58	0.87	
0.01	5.95	6.20	0.61	0.85	
0.1	4.78	5.58	0.58	0.78	
0.2	4.46	4.95	0.48	0.68	
0.5	4.47	4.27	0.43	0.53	
1	а	4.29	а	0.37	

^aNo adsorbed state.

the polyelectrolyte-surface spacing d are given for a range of values of the charge density of the positively charged surface, from both the full Poisson-Boltzmann model and the analytical theory. As expected, the average spacing between the adsorbed polyelectrolytes decreases continuously with increasing charge density of the charged surface, from about 7 nm at 0.1 q/nm^2 to about almost close packing at 1 q/nm^2 . Below a critical charge density of the charged surface, the polyelectrolytes do not adsorb. This critical value for the surface charge density is about 0.07 q/m^2 according to the full Poisson-Boltzmann model and about 0.03 q/nm² according to the analytical theory. The excellent agreement between the full Poisson-Boltzmann model and the analytical theory [Table V(a), Fig. 6] is somewhat fortuitous, as several of the basic assumptions of the analytical theory (Table II), most importantly the additivity of the electrostatic potentials for two adsorbed polyelectrolytes and the depletion of counter ions from the spacing between surface and polyelectrolyte, are clearly violated at high values of the charge density of the adsorbing surface (see, e.g., the last entry of Table IIIa). The values for d agree well between both versions of the theory.

In Table V(b), we have collected a range of values of the interstrand spacing a as a function of the concentration excess salt. Again, we observe that the predictions from the Poisson-Boltzmann theory are close to those of the analyti-

In Table V(a), values for the interstrand spacing a and



FIG. 6. Equilibrium strand spacing *a* as function of the charge density of the charged surface, $\kappa^{-1}=0.96$ nm (0.1 M 1:1 salt). $\sigma_p=-1$ q/nm², *P* = 50 nm, *r*=1.0 nm, *Q*_B=0.715 nm. Line: analytical theory; symbols: Poisson–Boltzmann theory.

cal theory for ionic concentrations above about 0.01 M. The quantitative agreement between both versions of the theory is a priori expected only at higher salt concentrations. Most likely by some coincidental cancellation of electrostatic effects, the agreement between the Poisson-Boltzmann theory and the analytical theory holds down to fairly low ionic strengths. The collapse witnessed in the interstrand spacing at very low salt concentrations (see the entry for a at 0.001) M for the analytical theory in Table Vb) is probably an artifact of the analytical theory, although some reduction of interstrand spacing with decreasing salt concentration is also observed for the full Poisson-Boltzmann model. An important and nontrivial observation from Table V(b) is that the interstrand spacing is only a very weak function of the salt concentration above about 0.1 M of excess monovalent salt. Note that from the results presented in Table V(a) and (b) it can be seen that the approximations made in deriving the theory are fulfilled (Table II).

As stated in the previous section, desorption of the adsorbed strands can be achieved by increasing the concentration of monovalent salt. Based on the Poisson–Boltzmann calculations, we expect the salt-induced desorption of DNA to occur at salt concentrations around 1 M, for charge densities of the positively charged surface which are less than about 0.2 q/nm². In Fig. 7, the phase diagram depicting the stability of the adsorbed phase of ordered polyelectrolytes is shown for the case of the idealized DNA cylinder.

An issue of final interest is the effective charge of the surface with adsorbed polyelectrolytes. A rough estimate of the onset charge reversal is straightforward:²⁷

$$\frac{2\pi r\sigma_p}{a\sigma_w} \approx 1. \tag{40}$$

As can immediately be inferred from Tables V and VI, reversal of the effective charge of the surface occurs for virtualy all values of the surface charge density in the case of adsorption of a highly charged polyelectrolyte like DNA. How the electrostatic potential of the polyelectrolyte-covered surface is probed in experiment, for instance by zeta-



FIG. 7. Phase diagram of the two-dimensionally ordered state of adsorbed semi-flexible polyelectrolytes. $\sigma_p = -1 \text{ q/nm}^2$, P = 50 nm, r = 1.0 nm. $Q_B = 0.715 \text{ nm}$.

potential or streaming-potential measurements⁴⁷ or by functionalized tips in atomic force microscopy (AFM),⁴⁸ is entirely another matter, however.

Experimental situation

During the last decade, a significant number of experimental studies were directed towards the electrostatic adsorption of polyelectrolytes (see, e.g., Refs. 8, 16 and 49). The general conclusion is that, in contrast with the adsorption of neutral polymers, polyelectrolytes form a dense, thin layer on adsorption, the effective thickness of which is often only of the order of the diameter of the polyelectrolyte chain. The reversal of the charge sign of the surface upon adsorption effectively blocks the building up of a thicker layer. Only for very weakly charged flexible polyelectrolytes one expects a more loose, spatially extended structure of the adsorbed layer.

Ordered phases of adsorbed charged species have been witnessed for DNA^{5,6} and virus particles.⁵⁰ The experiments by Fang and Yang⁵ turn out to be most useful for a first qualitative assessment of our theory. Using AFM they have visualized the structure of relatively short fragments of DNA adsorbed on supported cationic membranes. The surface charge density of the surface was estimated to be about 2.5 elementary charges per square nanometer, which is about one order of magnitude higher than the surface charge densities we are aiming at. Therefore, a quantitative comparison of our

TABLE VI. Interstrand spacing as a function of the excess monovalent salt concentration. The electrostatic interaction is calculated using the Poisson–Boltzmann equation and the total free energy is minimized using the set value of the cut-off length d_0 . $\sigma_p = -1 \text{ q/nm}^2$, $\sigma_w = 1 \text{ q/nm}^2$, polyelectrolyte hardcore diameter r = 1.0 nm, polyelectrolyte persistence length P = 50 nm, $Q_B = 0.715 \text{ nm}$.

	a (nm)				
c (M)	$d_0 = 0.3 \text{ nm}$	$d_0 = 0.5 \text{ nm}$	$d_0 = 0.7 \text{ nm}$		
0.1	2.20	2.48	2.80		
0.2	2.34	2.70	3.01		
0.5	2.54	3.08	3.33		
1	2.68	3.37	3.64		

theoretical results with the data of Fang and Yang is not feasible. A number of important qualitative conclusions can be drawn, nevertheless.

Fang and Yang have found that under conditions where the lipid surface layer exhibited two-dimensional fluidlike behavior, the DNA adsorbed in ordered domains in which the strands were oriented more-or-less in parallel. The regularity of the ordering was such, that, upon Fourier transforming the AFM image, well-defined Bragg peaks were observed. From these Bragg peaks, the average interstrand spacing of the adsorbed phase was determined as a function of the concentration excess NaCl in the bulk solution. Interestingly, the spacing was found to increase with increasing bulk salt concentration. At 20 mM NaCl, the spacing was approximately 4.2 nm, within the margins of experimental error increasing almost linearly to 5.8 nm at 1 M NaCl. Although we are principally aiming at charge densities of the adsorbing surface which are about an order of magnitude lower than those in the experiments by Fang and Yang, it still is of interest to see what occurs when the surface charge density is strongly increased. In Table VI, the lattice spacing a, calculated using the Poisson-Boltzmann equation, is given as function of the concentration of excess monovalent salt, at a charge density of the adsorbing surface of 1 q/nm². As under these conditions, no physically realistic minimum is observed in the total free energy as function of d, we minimize the free energy of the system under the condition $d = d_0$, where d_0 is a fixed separation between surface and polyelectrolyte cylinder determined by the molecular detail of surface and polyelectrolyte. In Table VI, values of the interstrand spacing are calculated by setting the minimum distance of approach d_0 to 0.3, 0.5 and 0.7 nm. Interestingly, in line with the observations of Fang and Yang, we find that a indeed increases with the ionic strength at these higher values of the charge density of the charged surface.

CONCLUDING REMARKS

In the current paper, an analytical theory based on a two-dimensional model is forwarded to describe the electrostatic adsorption of semi-flexible polyelectrolytes. The theory incorporates three principal physical effects: the entropy of the adsorbed polyelectrolytes adsorbed into the twodimensional lattice, the electrostatic interaction between charged surface and adsorbed polyelectrolyte and the electrostatic interaction between the adsorbed polyelectrolytes. We stress again the limited scope of the theory. In Table II, the principal approximations made in its derivation are listed. It is clear that, in specific cases, additional factors could become important, like those related to the state of hydration of the surface. The satisfying agreement of our predictions on the ionic strength dependence of the interstrand spacing of DNA adsorbed on supported cationic membranes with the experimental data⁵ might be fortuitous. However, we note that recent experimental work on the characterization of the interactions in DNA-cationic lipid complexes⁵¹ supports the notion that the interactions in such systems are indeed predominantly electrostatic. A Poisson-Boltzmann theory of the charge-induced adsorption is therefore of value.

The electrostatics of adsorption are addressed analytically within the Poisson–Boltzmann approximation. Various approximations made in deriving the analytical theory have been corroborated by more elaborate numerical calculations based on the full Poisson–Boltzmann equation. The analytical theory gives virtually quantitative results for charge densities of the positively charged surface of about 0.2 q/nm² and lower and salt concentrations between about 0.01 M and 1M. A main conclusion arising from this work is that the balancing of the electrostatic forces in the charged-induced formation of adsorbed complexes is of a subtle nature, but some of the effects associated with the numerical solution of the Poisson–Boltzmann equation for geometry of an array of adsorbed polyelectrolytes in fact cancel and a simple analytical model works rather well.

In the present work, we have neglected the consequences of the dimensionality of the system for the formation of ordered structures. Order in two dimensions is in general of a different nature than order in three. Long-range order may exist in specific cases but in many others the order is essentially local as the total displacements of the twodimensionally ordered particles diverge logarithmically even if the root-mean-square amplitude of the undulations remains finite.⁵² This should not significantly affect the local packing of adsorbed strands, however.

One general consequence of order in two dimensions is that the defect density is high. Indeed, one qualitative observation from the experiments on the adsorption of DNA on supported cationic membranes^{5,6} is that the defect density of the two-dimensionally structured layer is high, although the interstrand separation is well-defined. Another explanation for this could be that, although the adsorbed DNA strands may have sufficient time to find their equilibrium position locally, the system is not in equilibrium since some of the complex entanglements and defect-like structures formed in the initial phase of the adsorption process may have relaxation times much longer than the time frame of the experiment.

These remarks are not more than speculations at present; moreover, given the complex phenomena witnessed, further study into the nature of these two-dimensionally ordered systems and their electrostatics is required.

APPENDIX: NUMERICAL EVALUATION OF THE ADSORPTION EQUILIBRIUM

The Poisson–Boltzmann equation [Eq. (15)] is implemented in the finite-element software package FlexPDE version 3.01 (Ref. 53) and is numerically solved on the domain shown in Fig. 8 subject to the boundary conditions Eqs. (16)-(20). The electrostatic free energy is obtained by integrating the electrostatic potential over the domain following the discretized version of Eq. (21).

FlexPDE employs an adaptive routine to mesh the finite element grid according to the gradients in the dependent variable and the desired accuracy. An estimated error of at maximum 0.1% in the integrated free energy is ensured by setting the tolerated estimated error over any individual cell to 3×10^{-5} . A sufficiently accurate representation of the polyelectrolyte surface is obtained by setting the maximum



FIG. 8. Domain of the finite element calculations of the electrostatic free energy of an array of adsorbed polyelectrolytes. Boundary conditions are as described in the text [Eqs. (16)-(20)].

tolerated angle spanned by a cell at the cylinder surface to 6° . The integration domain extends into the solution always 10 Debye lengths beyond the polyelectrolyte [Ly = 10 (Fig. 8)]. Depending on the size of the domain and the steepness of the electric field gradients, between 1500 and 20 000 cells are employed to represent the electrostatic potential over the grid with the desired accuracy.

The accuracy of the finite element calculations is independently verified by comparing its numerical values for the potential of a charged surface with the analytical solution of the Poisson–Boltzmann equation for a range of values of the surface charge density and Debye length. In all cases tested, the error with respect to the analytical solution is of the order of 10^{-4} to 10^{-5} . In addition, the error in the numerically integrated free energy is smaller than 0.1%.

In order to obtain the free energy of electrostatic interaction, the self energies of the surface [Eq. (23)] and the cylinder at given salt concentration and surface charge density are subtracted. The electrostatic self energy of the cylinder is numerically determined by subtracting the electrostatic self energy from the integrated total electrostatic free energy for A = 20 and D = 10. For the domain in Fig. 8, the free energy of electrostatic interaction is obtained by multiplying the resulting free energy by a factor 2.

The equilibrium adsorbed state is determined by first calculating the electrostatic free energy on an approximately exponentially spaced grid spanning the two-dimensional parameter space (A,D), with A varying between 0.2 and 20 and D between 0.01 and 10. The relevant roots are bracketed using successive refinements in the spacing of the grid in the region where

$$\frac{\Delta \mathcal{F}}{\Delta D} = \frac{\mathcal{F}(D_{i+1}) - \mathcal{F}(D_{i-1})}{2(D_{i+1} - D_{i-1}) \cdot \Delta_D} \tag{A1}$$

and

$$\frac{1}{P}\mu_{a} = \frac{\mathcal{F}(X_{i+1}) - \mathcal{F}(X_{i-1})}{2(A_{i+1} - A_{i-1}) \cdot \Delta_{A}} - \frac{\mathcal{F}(A_{i})}{X_{i}}$$
(A2)

change sign. In Eqs. (A1) and (A2), it is the total free energy per unit length of polyelectrolyte [Eq. (1)] which is of interest. A_i and D_i count along the grid parallel respectively per-

pendicular to the charged surface and Δ_A and Δ_D denote the local spacing of the grid in A and D. The reported values of A and D are determined by linear interpolation between the two closest values after the final refinement of the grid spacing. The inaccuracy in the equilibrium values of A and D is estimated to be about 0.01.

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- ¹H. G. Bungenberg de Jong, Protoplasma **15**, 110 (1932).
- ² V. Tolstoguzov, Crit. Rev. Biotechnol. 22, 89 (2002).
- ³Y. Li, P. L. Dubin, H. A. Havel, S. L. Edwards, and H. Dautzenberg, Macromolecules **28**, 3098 (1995).
- ⁴J. G. Nairn, Adv. Pharm. Sci. 7, 93 (1995).
- ⁵Y. Fang and J. Yang, J. Phys. Chem. B **101**, 441 (1997).
- ⁶Y. Fang and J. Yang, J. Phys. Chem. B **101**, 3453 (1997).
- ⁷ V. Erokhin, B. Popov, B. Samori, and A. Yakovlev, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **215**, 213 (1992).
- ⁸G. Decher and J. Schmitt, Prog. Colloid Polym. Sci. 89, 160 (1992).
- ⁹Y. Lvov, G. Decher, and G. Sukhorukov, Macromolecules **26**, 5396 (1993).
- ¹⁰G. B. Sukhorukov, H. Möhwald, G. Decher, and Y. M. Lvov, Thin Solid Films **284–285**, 220 (1996).
- ¹¹K. Lowack and C. A. Helm, Macromolecules **31**, 823 (1998).
- ¹²T. Salditt, I. Koltover, J. O. R\u00e4dler, and C. R. Safinya, Phys. Rev. Lett. 79, 2582 (1998).
- ¹³M. J. Muthukumar, J. Chem. Phys. 86, 7230 (1987).
- ¹⁴ M. R. Böhmer, O. A. Evers, and J. M. H. M. Scheutjens, Macromolecules 23, 2288 (1990).
- ¹⁵ R. Israëls, J. M. H. M. Scheutjens, and G. J. Fleer, Macromolecules 26, 5405 (1993).
- ¹⁶G. J. Fleer, M. A. Cohen Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and
- B. Vincent, *Polymers at Interfaces* (Chapman and Hall, London, 1994).
- ¹⁷I. Borukhov, D. Andelman, and H. Orland, Europhys. Lett. **32**, 499 (1995).
- ¹⁸X. Châtellier and J.-F. Joanny, J. Phys. II **6**, 1669 (1996).
- ¹⁹I. Borukhov, D. Andelman, and H. Orland, Macromolecules **31**, 1665 (1998).
- ²⁰ A. V. Dobrynin, A. Deshkovski, and M. Rubinstein, Phys. Rev. Lett. 84, 3101 (2000).
- ²¹ A. V. Dobrynin, A. Deshkovski, and M. Rubinstein, Macromolecules 34, 3421 (2001).
- ²²D. V. Kuznetsov and W. Sung, Macromolecules **31**, 2679 (1998).
- ²³K. S. Schmitz, Langmuir **15**, 2854 (1999).
- ²⁴R. R. Netz and J.-F. Joanny, Macromolecules **32**, 9013 (1999).
- ²⁵T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, J. Chem. Phys. **113**, 1110 (2000).
- ²⁶K.-K. Kunze and R. R. Netz, Europhys. Lett. 58, 299 (2002).
- ²⁷ A. Yu. Grosberg, T. T. Nguyen, and B. I. Shklovskii, Rev. Mod. Phys. **74**, 329 (2002).
- ²⁸A. R. Khokhlov and A. N. Semenov, Physica A **108**, 546 (1981).
- ²⁹T. Odijk, Macromolecules 16, 1340 (1983).
- ³⁰W. Helfrich and W. Harbich, Chem. Scr. 25, 32 (1985).
- ³¹T. Odijk, Macromolecules **19**, 2313 (1986).
- ³²T. W. Burkhardt, J. Phys. A 28, L629 (1995).
- ³³S. Jain and D. R. Nelson, Macromolecules **29**, 8523 (1996).
- ³⁴J. Ubbink and T. Odijk, Biophys. J. **76**, 2502 (1999).
- ³⁵ T. Odijk, Biophys. Chem. **46**, 69 (1993).
- ³⁶J. Ubbink and T. Odijk, Biophys. J. 68, 54 (1995).
- ³⁷A. Stroobants, H. N. W. Lekkerkerker, and T. Odijk, Macromolecules 19, 2232 (1986).
- ³⁸J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961).
- ³⁹M. Fixman, J. Chem. Phys. **70**, 4995 (1979).
- ⁴⁰T. Odijk (unpublished).

- ⁴¹D. F. Evans and H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet* (VCH, New York, 1994).
- ⁴²B. V. Derjaguin, *Theory of the Stability of Colloids and Thin Films* (Consultants Bureau, New York, 1989).
- ⁴³S. L. Brenner and V. A. Parsegian, Biophys. J. 14, 327 (1974).
- ⁴⁴J. R. Philip and R. A. Wooding, J. Chem. Phys. 52, 953 (1970).
- ⁴⁵L. Onsager and N. N. T. Samaras, J. Chem. Phys. 2, 528 (1934).
- ⁴⁶M. Ospeck and S. Fraden, J. Chem. Phys. **109**, 9166 (1998).
- ⁴⁷R. J. Hunter, Zeta Potental in Colloid Science (Academic, London, 1981).
- ⁴⁸ W. A. Ducker, T. J. Senden, and R. M. Pashley, Nature (London) **353**, 239 (1991).
- ⁴⁹M. A. Cohen Stuart, J. Phys. (France) **49**, 1001 (1988).
- ⁵⁰Y. Lvov, H. Haas, G. Decher, H. Möhwald, A. Mikhailov, B. Mtchedlishvily, E. Morgunova, and B. Vainshtein, Langmuir **10**, 4232 (1994).
- ⁵¹S. Soosakoonkriang, C. M. Wiethoff, T. J. Anchordoquy, G. S. Koe, J. G. Smith, and C. R. Middaugh, J. Biol. Chem. **276**, 8037 (2001).
- ⁵²L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980).
- ⁵³PDE Solutions Inc., Antioch, CA (2002).