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Pull-off of a polyelectrolyte chain from an oppositely charged surface

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The conformation at equilibrium of a single polyelectrolyte molecule adsorbed electrostatically at an ideal planar charged surface with one of its ends constrained at a distance z from the surface is investigated using different theoretical methods, and in particular a scaling theory. The force $F(z)$ applied at the fixed end of the chain is calculated. Exact results are obtained for a Gaussian chain when all screening effects are negligible, and at high salt concentration, using a self-consistent field theory. When the salt concentration is large enough, the force profile $F(z)$ reaches a plateau where the force is independent of chain length. When the electric field is screened by the counterions, a pseudoplateau is obtained, where the force increases logarithmically with z. The chain leaves the surface before it is fully extended, although the distance of detachment from the surface is proportional to the number of monomers N. The electrostatic interactions between the charged monomers of the polyelectrolyte chain can be taken into account using scaling arguments. [S1063-651X(98)12106-2]

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I. INTRODUCTION

The physics of adsorbed charged macromolecules is of central interest to such diverse fields as colloidal stabilization [1], biophysics, and lubrication. In particular, such molecules usually achieve a better solubility in water, due to the repulsion between the charged groups, and are attractive candidates for a wide range of industrial applications (water-soluble paints, etc.). The existence of long-ranged electrostatic interactions, and of additional control parameters, such as the salt concentration or the fraction of charged monomers, leads to a rich variety of behaviors, for which there is no detailed understanding. A first problem, which has already been studied in detail theoretically, is the adsorption of a single chain on a surface [2]. In this paper we focus on the reverse problem, the desorption process of a single chain when one of its ends is pulled away from the surface. We impose the constraint that one end of the chain is fixed at a distance z from the surface and consider the equilibrium configuration of the chain in response to this constraint. The stretching of a chain adsorbed at a surface has been investigated experimentally using atomic force microscopy (AFM) [3,4]. This technique measures the force required to stretch the chain. It is therefore interesting to make predictions for the force profile $F(z)$, which gives the force applied at one end of the chain to keep it at a distance z from the surface.

All over this paper, we consider a single polyelectrolyte molecule in a θ solvent (no excluded volume interactions), with a degree of polymerization N and a quenched fraction f of charged monomers. Without any loss of generality, we assume that the chain is negatively charged, and denote by $q=-ef$ the average charge per monomer. We suppose that the chain is flexible so that the Kuhn length a is equal to the monomer size. The adsorbing surface is perfectly flat and chemically homogeneous and carries a uniformly spread charge that creates a field $\vec{E}_0$ in the half-space $d>0$ (the d axis is the axis perpendicular to the surface, with $d=0$ at the surface). We characterize the strength of the field by a dimensionless parameter $x\equiv eE_0a/k_BT$. The screening of the electrostatic field by the free ions of the solution is characterized by two length scales: the Gouy-Chapman length $\lambda=2a/x$ that describes the screening due to the counterions of the surface charge and the Debye-Hückel length κ^{-1}, related to the salt concentration.

Hence, six independent parameters come into play in our description: N, a, f, x, κ^{-1}, and k_BT. As it will appear, a very rich variety of situations can be obtained, simply from these few parameters. For clarity, and as mentioned above, we decided not to include in this work other effects, for instance, excluded volume.

The many different expressions for the force $F(z)$, corresponding to the various structures adopted by the chain in response to the constraint of having one of its ends at a distance z from the surface are described in this paper. A key point is that the structure of the chain depends on the length scale at which it is considered, and can be described in a rough approximation either as rigid, i.e., rodlike, or as Gaussian, i.e., similar to that of a random walk. A few simple general results can be given without entering into the details: at very large values of z, the chain is detached from the surface and the electrostatic field is screened; obviously $F(z\rightarrow\infty)\rightarrow 0$. On the other hand, due to the impenetrability of the surface, $F(z<0)=-\infty$ (as a convention, repulsive forces are counted negatively): the conformations of the chains with monomers in the negative half-space for z are forbidden. More generally, the entropic repulsion of the chain by the surface tends to be predominant at small (positive) values of z, leading to negative values of the force $F(z)$: the end point of the chain has to be pushed toward the surface to be maintained at a short distance z from it. On the other hand, as the end point of the chain is pulled further away from the surface, the force $F(z)$ increases and reaches a maximal positive value before the chain escapes from the electrostatic attraction of the surface and $F(z)\rightarrow 0$. It will be shown that, in most cases, the attractive force is equal to the Coulombic force acting on the monomers detached from the surface. Hence, in order to estimate the force $F(z)$, we need to determine the distance H_c at which the attraction of the surface becomes larger than the entropic repulsion and the number of monomers $N_0(z)$ detached from the surface but still close enough to experience the electrostatic field E_0. For $z \gg H_c$, the force is given by $F(z) \approx N_0(z) q E_0$.

The paper is organized as follows. In Sec. II, the main length scales and the methods used throughout the paper are introduced. In Sec. III, we consider the academic case of an unscreened surface (very large values of λ and κ^{-1}). Section IV is devoted to the effect of salt. In Sec. V, we discuss the situation of a salt-free solution.

II. LENGTH SCALES AND METHODS

In this section, the basic length scales associated with a polymer chain and a polyelectrolyte chain in solution are first introduced. Then those corresponding to the charged surface and to the chain interacting with the surface are defined. The section ends with a summary of the methods used.

The independent length scales characterizing a linear homopolymer chain are the persistence length, supposed here to be equal to the size of a monomer a, and the contour length of the chain Na, where $N \gg 1$. Typically, a is of the order of 1 Å, while the contour length can reach a few micrometers for industrial polymers and centimeters in the case of human DNA. Note, however, that DNA is not a flexible polymer: its persistence length is much larger than its monomer size. A neutral polymer in a θ solvent is Gaussian. It is isotropic and its size is of the order of $R_g \equiv N^{1/2} a/6$.

Neglecting the effects related to the inhomogeneities in the distribution of the charges along the chain, a polyelectrolyte chain in a salt-free solution is characterized by two additional length scales: the average distance a/f between the charges along the chain and the Bjerrum length $l_B = e^2/(4\pi\epsilon k_B T)$, specific to the solution, ϵ being the dielectric constant of water. Since $l_B \simeq 0.7$ nm, in pure water at room temperature, l_B/a is of order unity. In the following, for the simplicity of the notations, we do not indicate the dependence of the results on l_B/a and the only independent parameters characterizing a polyelectrolyte chain are a, N, and f.

The electrostatic interactions between the charged monomers become relevant when $(Nq)^2/(\epsilon R_g) \gg k_B T$, i.e., when $f \gg N^{-3/4}$, stretching the chain up to a size $H_0 \approx N a f^{2/3} \gg R_g$ [5]. In this situation, it can be represented as a linear string of so-called electrostatic blobs, of size $\xi \simeq a f^{-2/3} \ll R_g$, with a length H_0 and a lateral size R_g. Within each blob, the chain retains its Gaussian structure of a random walk [6]. Note that when f is of order unity, ξ is of the order of a and the chain is fully stretched.

In a salt solution, electrostatic interactions are screened by the ions present in the solution at distances larger than the Debye-Hückel length $\kappa^{-1} \equiv (8\pi l_B n)^{-1/2}$, n being the concentration of salt molecules. Hence, in a salt solution, a polyelectrolyte chain is Gaussian when $\kappa^{-1} \ll \xi$. When $\kappa^{-1} \gg \xi$, the chain is Gaussian at distances smaller than ξ, stretched at distances larger than ξ but smaller than κ^{-1} and its behaves as a self-avoiding walk at distances larger than κ^{-1}. The exact large-scale structure of a flexible polyelectrolyte chain is still a matter of current research [7], but the blob representation is believed to be justified, at least at distances smaller than the screening length κ^{-1} [8].

These introductory remarks on polyelectrolytes show that even for a single chain in solution, several different structures can be found. Additional substructures would have to be considered for a chain that would not be in a θ solvent.

The adsorbing surface in our model is described by the electrostatic field E_0 that it creates. E_0 is directly related to the surface charge density, whose value is simply ϵE_0. In the following, the parameter $x \equiv e E_0 a / k_B T$ will be used in many instances as the parameter characterizing the intensity of the electrostatic field E_0. The associated length scale, the Gouy-Chapman length $\lambda = 2a/x = 2 k_B T/(e E_0)$, defines the distance at which the counter-ions of the surface start to screen the electrostatic field created by the surface.

When x is large enough, a polyelectrolyte chain adsorbs at the surface. Several lengths are usefully defined, where the attraction of the surface is found to balance another effect:

(i) The chain tends to get confined within a distance H_c from the surface. The value of H_c results from a balance between the electrostatic attraction and the entropic repulsion of the surface. We expect that adsorption can take place only when the screening of the electrostatic field occurs at distances larger than H_c.

(ii) When an adsorbed chain is pulled away from the surface, the electrostatic attraction of the surface becomes too weak to compensate the entropic stretching energy of the chain when $z = H_s$. H_s represents the maximal extension of the chain. When $z > H_s$, there are no monomers left on the surface.

(iii) When the chain has a Gaussian structure at small length scales (i.e., when $a \ll \xi$, or $f \ll 1$), the electrostatic field might be strong enough to impose a rodlike fully stretched structure when the chain is pulled away. This occurs if $F(z) > k_B T/a$, as will be shown in Sec. III B. In that case, H_g is defined as the distance from the surface at which the local Gaussian structure is lost to the benefit of a rodlike structure: $F(H_g) = k_B T/a$.

(iv) The internal stretching of the chain due to the repulsions between the charged monomers becomes smaller than the stretching due to the electrostatic field of the surface at a length H_i.

As it will appear later, the lengths H_c, H_s, H_g, and H_i determine different regimes for the force $F(z)$, together with the screening lengths κ^{-1} and λ.

In Sec. III A, the case of a Gaussian chain in an unscreened field corresponds to the limit where $H_i = 0$, and H_g, λ, $\kappa^{-1} = +\infty$. When the electrostatic field is strong enough, $H_c \ll H_s$, and three asymptotic regimes are obtained: $z \ll H_c$, $H_c \ll z \ll H_s$, and $z \gg H_s$. Section III B considers the possibility of a non-Gaussian elasticity $H_g < H_s$, while Sec. III C takes into account the intramolecular electrostatic repulsions, $H_i > H_c$. Section IV and V investigate the effect of screening due to the ions. In Sec. IV, the added ions are the screening factor ($\kappa^{-1} \ll \lambda$), while in Sec. V counterions of the surface are predominant ($\lambda \ll \kappa^{-1}$). The charged monomers are not expected to play a major role in the screening of the electrostatic field unless the density Σ^{-1} of chains on the surface becomes finite. But since a thorough study of this problem would necessitate the introduction a new parameter, the area per chain Σ, we leave it for future work.

Throughout the paper, the scaling structure of the results can be understood with simple arguments where the different entropic or energetic effects mentioned in this section are compared. Neglecting the intramolecular electrostatic repulsions between the charged monomers, exact results for the partition function are possible in the limit of an infinitely long chain ($N\rightarrow\infty$) in two cases: a Gaussian chain in an unscreened electrostatic field (Sec. III A), and a Gaussian chain in a salt solution (Sec. IV). The limit $N\rightarrow\infty$ is similar to a ground state dominance approximation in quantum mechanics. The opposite case of a fully stretched chain ($\xi \approx a$) can be modeled exactly by a rigid rod as long as the electrostatic field is not strong enough to bend it (see Appendix D and Sec. III C). In addition to scaling arguments and ''exact'' calculations, we consider a freely jointed chain model in Sec. III B, allowing one to obtain the crossover behavior of the chain between the regime of Gaussian elasticity and the regime of a fully stretched chain. Finally the position of the various monomers of the chain when it remains locally Gaussian can be obtained in a mean field theory by neglecting the fluctuations of the position of a given monomer by writing a force equilibrium on a group of consecutive monomers (Secs. III B and IV and Appendix C).

III. POLYELECTROLYTE CHAIN AT A CHARGED UNSCREENED SURFACE

A. An exact calculation of the partition function

The conformation of a polyelectrolyte chain adsorbed at a charged surface with one end fixed at a distance z from the surface is described by the partition function, denoted $Z(z,N)$, where all internal degrees of freedom except for the position of the chain end point have been integrated out. For a Gaussian chain (ignoring the electrostatic interactions between the monomers),

$$Z(z,N)=\int_{z(s=0)=z}[d\vec{r}(s)]\exp\left\{-\int_{s=0}^{N}ds\left[\frac{3}{2a^2}\left(\frac{d\vec{r}}{ds}\right)^2(s)+\frac{U(z(s))}{k_BT}\right]\right\}. \tag{1}$$

The monomers are labeled by a continuous parameter s; $\vec{r}(s)$ and $z(s)$ are respectively the position and the distance from the surface of monomer s. $\int_{z(s=0)=z}[d\vec{r}(s)]$ denotes an integration over all possible conformations of the chain such that monomer $s=0$ is at a distance z from the surface, $z(s=0)=z$, and $U(z(s))$ is the external potential experienced by monomer s. As a convention, we define the zero of energy at the surface, $U(z(s)=0)\equiv 0$. For a free Gaussian chain, $U(z(s))=0$, and we denote as $Z_{\mathrm{FG}}(N)$ the partition function. In that case, the system is translationally invariant and $Z_{\mathrm{FG}}(N)$ depends only on N. In our problem, modeling the surface as a hard wall, $U(z(s))=qE_0z(s)$ for $z(s)\geqslant 0$ and $U(z(s))=\infty$ for $z(s)<0$. A quantity related to $Z(z,N)$ is the Green function $G(z,N)$, defined by the relation $G(z,N)\equiv Z(z,N)/Z_{\mathrm{FG}}(N)$. For a free Gaussian chain, the Green function is equal to $G_{\mathrm{FG}}(z,N)=1$. Note that $G(z,N=0)=G_{\mathrm{FG}}(z,N=0)=1$. The instructive case of a polyelectrolyte Gaussian chain in infinite space with a constant field $\vec{E}_0$ is presented in Appendix A. The Green function contains the same information as the partition function and it is shown to obey a diffusionlike equation:

$$-\frac{\partial G}{\partial N}(z,N)=-\frac{a^2}{6}\frac{\partial^2 G}{\partial z^2}(z,N)+\frac{U(z)}{k_BT}G(z,N). \tag{2}$$

Equation (2) has the same structure as a Schrödinger equation. Hence, this problem is related to the behavior of an electron close to a charged surface [9]. We introduce the length $\delta\equiv a/(6fx)^{1/3}\propto E_0^{-1/3}$ and define the reduced variables $\tilde{z}\equiv z/\delta$ and $\tilde{N}\equiv \tilde{R}_g{}^2\equiv Na^2/(6\delta^2)$. Equation (2) can be rewritten in terms of the dimensionless variables $\tilde{z}$ and $\tilde{N}$. For $\tilde{z}>0$

$$-\frac{\partial G}{\partial \tilde{N}}(\tilde{z},\tilde{N})=-\frac{\partial^2 G}{\partial \tilde{z}^2}(\tilde{z},\tilde{N})+\tilde{z}G(\tilde{z},\tilde{N}). \tag{3}$$

The set of the eigenvectors of Eq. (3) forms a complete basis onto which $G(z,N)$ can be expanded. The eigenvectors $u_j(z)$ are bounded and obey the hard wall condition $u_j(z=0)=0$. We find

$$u_j(z)=\frac{1}{\delta^{1/2}\mathrm{Ai}'(-\lambda_j)}\mathrm{Ai}(\tilde{z}-\lambda_j) \tag{4}$$

where $\mathrm{Ai}(y)$ is the Airy function defined by

$$\mathrm{Ai}(y)=\pi^{-1}\int_0^\infty dt\ \cos(t^3/3+yt) \tag{5}$$

and $-\lambda_j$ is the jth negative zero of $\mathrm{Ai}(y)$ [10]. $\mathrm{Ai}'(y)$ is the derivative of $\mathrm{Ai}(y)$. The normalization constant in Eq. (4) ensures that $\int_0^\infty dz\ u_j^2(z)=1$ [11]. $G(z,N)$ is expanded as

$$G(z,N)=\sum_{j=1}^{\infty}\left(\frac{\int_{-\lambda_j}^{\infty}dy\ \mathrm{Ai}(y)}{\mathrm{Ai}'^2(-\lambda_j)}\right)\mathrm{Ai}(\tilde{z}-\lambda_j)\exp(-\tilde{N}\lambda_j). \tag{6}$$

A simpler form of the partition function is obtained by taking the Laplace transform of $G(\tilde{z},\tilde{N})$ with respect to $\tilde{N}$; it is presented in Appendix B. For $z=0$, $G(z,N)=0$, as required by the hard wall condition. Close to the surface, when $\tilde{z}\rightarrow 0$ at fixed $\tilde{N}$, $G(z,N)\propto z$. At large distances, when $\tilde{z}\rightarrow\infty$ at fixed $\tilde{N}$, the presence of the surface is no longer felt by the polyelectrolyte chain and $G(z,N)\simeq G^0(z,N)$ (see Appendix A), with

$$G^0(z,N)=\exp(\tilde{N}^3/3)\exp(-\tilde{N}\tilde{z}). \tag{7}$$

For $\tilde{N}=0$, in the absence of electrostatic interactions, $G(z,N)=G_{\mathrm{FG}}(z,N)=1$. On the other hand, when, for a given value of $\tilde{z}$, $\tilde{N}\rightarrow\infty$, the ground state dominance approximation can be used and the ground state eigenvector dominates the sum in Eq. (6)

$$G(z,N)\simeq G_{\mathrm{GSD}}(z,N)$$
$$\equiv\left(\frac{\int_{-\lambda_1}^{\infty}dx\ \mathrm{Ai}(x)}{\mathrm{Ai}'^2(-\lambda_1)}\right)\mathrm{Ai}(\tilde{z}-\lambda_1)\exp(-\tilde{N}\lambda_1). \tag{8}$$

When $\tilde{N}\gg 1$, we expect that the ground state dominance approximation is justified at small $\tilde{z}$, while $G(z,N)\simeq G^0(z,N)$ at large $\tilde{z}$. The crossover occurs when $G_{\mathrm{GSD}}(z,N)\simeq G^0(z,N)$, namely, for $\tilde{z}\approx\tilde{N}^2$, since $\mathrm{Ai}(y)\propto\exp(-2y^{3/2}/3)$ when $y\rightarrow\infty$. In this limit, the chain properties do not depend on the hard wall and $z_0\equiv\tilde{N}^2\delta=N^2fxa/6$ gives an estimation of the distance at which the adsorbed chain leaves the surface when it is pulled away.

The Green function can be used to compute the force required to maintain the chain end point at a distance z from the surface

$$F(z)=-\frac{k_BT}{G(z,N)}\frac{\partial G}{\partial z}(z,N). \tag{9}$$

Different limits can be simply considered:

(i) Close to the surface, when $\tilde{z}\rightarrow 0$ at fixed $\tilde{N}$, we obtain $F(z\rightarrow 0)\simeq -k_BT/z$. This simple result is a consequence of the entropic repulsion of the hard wall at small distances. It is obtained for a neutral chain close to a surface when $z\ll R_g$. On the other hand, at large distances, when $\tilde{z}\rightarrow\infty$ at fixed $\tilde{N}$, the force applied at one end of the chain to keep it at a fixed position tends to a constant $F^0(z,N)=NqE_0$, which corresponds to the Coulomb force.

(ii) When $\tilde{N}\ll 1$, electrostatic effects are unimportant and the polyelectrolyte molecule merely behaves as a neutral chain entropically repelled by a hard wall [15]: $F(z)\simeq -k_BT/z$ for $z\ll R_g$ and $F(z)\simeq NqE_0$ for $z\gg R_g$. When $\tilde{N}\gg 1$, the ground state dominance approximation is correct for $z\ll z_0$, while $F(z)\simeq NqE_0$ for $z\gg z_0$.

Using Eq. (8), we obtain the ground state dominance approximation for the force

$$F_{\mathrm{GSD}}(z)=-\frac{k_BT}{\delta}\frac{\mathrm{Ai}'(\tilde{z}-\lambda_1)}{\mathrm{Ai}(\tilde{z}-\lambda_1)}. \tag{10}$$

At small distances, when $z\ll\delta$, we retrieve $F_{\mathrm{GSD}}\simeq -k_BT/z$; for $z\gg\delta$ a simple and nontrivial regime is obtained:

$$F_{\mathrm{GSD}}(\tilde{z}\gg 1)\simeq\frac{k_BT}{\delta}\sqrt{\frac{z}{\delta}}=NqE_0\sqrt{\frac{z}{z_0}}. \tag{11}$$

Note that $F_{\mathrm{GSD}}(z)=NqE_0$ when $z=z_0$. In Fig. 1, the force profile $F(z)$ is shown for $\tilde{N}\gg 1$.

A simple understanding of these results can be achieved by using scaling arguments. The electrostatic field applied on a polyelectrolyte molecule is significant if $NqE_0R_g\gg k_BT$, which can be rewritten $\tilde{N}\gg 1$. In that case, the chain tends to get confined close to the surface, within a layer of thickness $H_c\ll R_g$. The value of H_c is obtained by minimizing its energy [2], which is a sum of the confinement and of the electrostatic energies

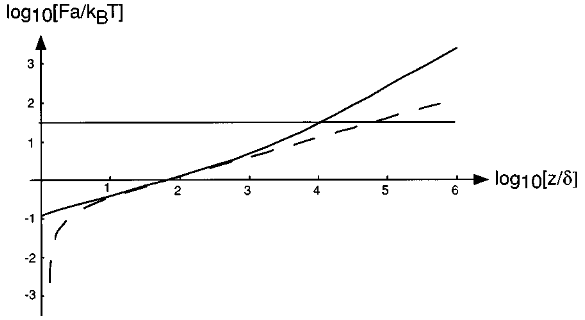

FIG. 1. The force profile of a chain adsorbed at an oppositely charged surface in an unscreened electrostatic field. The dashed line shows the ground state dominance approximation. The full line shows the model of a freely jointed chain. Its slope crosses over from 1/2 to 1, corresponding to the crossover from the Gaussian regime to the non-Gaussian regime. The horizontal line corresponds to the Coulombic force at the plateau. The plot corresponds to $a/\delta\simeq\sqrt{6}/20$ and $z_g=1600$ nm. The plateau value corresponds to $Nfx=10\sqrt{6}/8$. These values are obtained, for instance, when $a=0.2\sqrt{6}$ nm, $f=0.1$, $N=10^5$, and $x=(\sqrt{6}/8)10^{-3}$, leading to $\delta=4$ nm. At short distances, the force profile is best approximated by the ground state dominance approximation, diverging in the logarithmic plot for $z\simeq\delta$, when $F(z)=0$. At intermediate distances, when $F\gg k_BT/a$, the model of the freely jointed chain is more adapted. The crossing point between the full line and the horizontal line indicates the detachment of the chain. It occurs here at $z\simeq 10^4\delta\simeq Na$.

$$W_c(H_c)\approx k_BT\frac{Na^2}{H_c^2}+NqE_0H_c. \tag{12}$$

The value of the thickness where $W(H_c)$ is minimized is $H_c\approx\delta$. Hence, δ can be interpreted as the thickness of the freely adsorbed chain. The thickness δ is independent of the size of the chain R_g. On the other hand, if the chain has one of its end points fixed at a given position very far from the surface, it stretches in the direction parallel to the electric field $\vec{E}_0$, with a length $H_s\gg R_g$. The value of H_s is also obtained by minimization of the free energy of the chain, including an entropic elasticity and an electrostatic contribution

$$W_s(H_c)\approx k_BT\frac{H_s^2}{Na^2}-NqE_0H_s. \tag{13}$$

This leads to $H_s\approx z_0$. Namely, the distance at which the chain leaves the surface when one of its ends is pulled away corresponds to the length of the chain in the bulk, away from the surface. The force $F(z)$ is dominated by the entropic repulsion of the wall for $z\ll\delta$; this effect being independent of R_g, the only relevant length is z and, consequently, $F(z)\simeq -k_BT/z$. This result holds as long as $z\gg a$ and is characteristic of a Gaussian structure (see Appendix D for a rodlike structure). On the other hand, when $z\gg z_0$, the only contribution to the force is the Coulomb force $F(z)=NqE_0$.

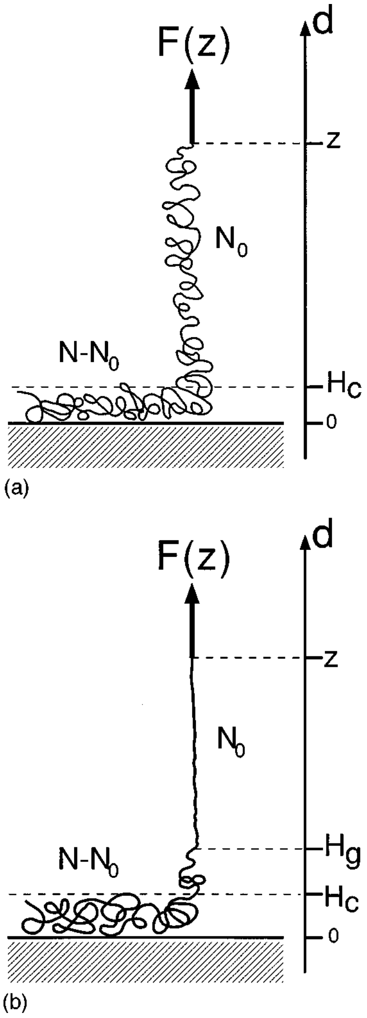

FIG. 2. A schematic view of a chain adsorbed at an opposite surface with one end fixed at a distance z from the surface. N_0 monomers are desorbed from the surface. In (a), the chain remains Gaussian. In (b), the chain exhibits a nonlinear elasticity for $z \gg H_g$.

At $\delta \ll z \ll z_0$, we divide the chain into two sections, N_0 monomers are desorbed from the surface, and $N - N_0$ monomers are still confined close to the surface [see Fig. 2(a)]. The force is $F(z) = N_0 q E_0$. For $z < z_0$, the scaling expression for the number of desorbed monomers is written as a power law

$$N_0(z) \simeq N(z/z_0)^{\nu}. \tag{14}$$

The exponent α is found by imposing that $N_0(z)$ be independent of N for $z < z_0$, giving $\nu = 1/2$, and we find again Eq. (11). $N_0(z)$ can also be obtained by minimizing the free energy of the chain with respect to N_0

$$W(N_0) \approx k_B T \frac{z^2}{N_0 a^2} + N_0 q E_0 z. \tag{15}$$

Note that $F(z = \delta) \approx N q E_0 (\delta / z_0)^{1/2} = k_B T / \delta$, in agreement with the continuity of the force over the whole range of values for z.

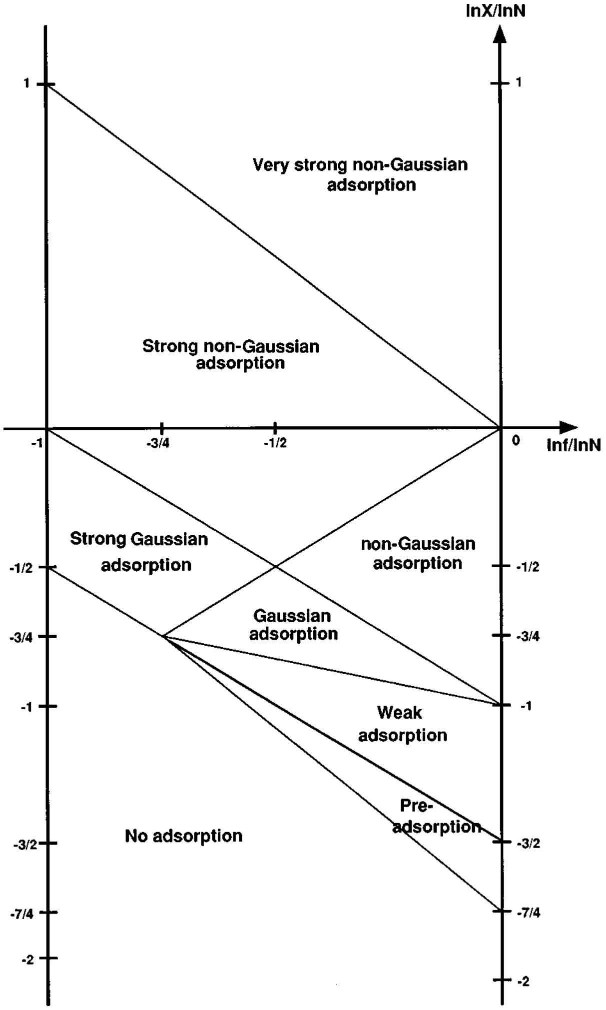

FIG. 3. The different regimes of adsorption for a polyelectrolyte chain in an unscreened field, in the limit $N \rightarrow \infty$.

In Fig. 3(a), we represent the different regimes of adsorption of a polyelectrolyte chain in an unscreened field, depending on the strength of the electrostatic field x and on the fraction of charged monomers f. When $x \ll f^{-1} N^{-3/2}$ ($\tilde{N} \ll 1$), electrostatic interactions between the surface and the monomers have little effect on the chain [regions of no adsorption and of preadsorption; see Fig. 3(a)]. On the other hand, when $x \gg f^{-1} N^{-3/2}$, adsorption is expected to take place, and $H_s > H_c$.

B. Stretching of a freely jointed chain

We have assumed above that the polyelectrolyte molecule could be modeled as a Gaussian chain. This assumption clearly breaks down if the chain stretching becomes too important: A real chain cannot be longer than its contour length Na. When the Gaussian chain theory predicts $z_0 > Na$, it is therefore outside its range of validity. This occurs when $x > f^{-1} N^{-1}$. In order to investigate this situation, it is more realistic to model the macromolecule as a freely jointed chain. The energy of the chain under a tension $\vec{F}$ is $-\vec{F} \cdot \vec{R}$, where $\vec{R}$ is the end-to-end vector of the chain. For a freely jointed chain, an exact counting of the conformations is possible and shows, in analogy with the average dipole moment of a dipolar material in an electrostatic field [12], that the relation between the magnitude of the average end-to-end vector, R, and F is given by

$$F=\frac{k_BT}{a}\left[\mathcal{L}_g^{-1}\left(\frac{R}{Na}\right)\right], \tag{16}$$

where $\mathcal{L}_g(y)=\coth(y)-y^{-1}$ is the Langevin function. For small values of F, the Gaussian behavior is recovered: $F=3k_BTR/(Na^2)$. As the chain is strongly stretched, it can be characterized by the average position of monomer s, ignoring the fluctuations around its average conformation. Using Eq. (16), we write the local force balance on the monomers located in the desorbed part of the chain, $0<s<N_0$ [see Fig. 2(b)]. On the chain segment between s to $s+ds$

$$\frac{k_BT}{a}\left[\mathcal{L}_g^{-1}\left(\frac{1}{a}\frac{dz}{ds}\right)(s+ds)-\mathcal{L}_g^{-1}\left(\frac{1}{a}\frac{dz}{ds}\right)(s)\right]$$
$$=qdsE_0 \tag{17}$$

leading to

$$\frac{k_BT}{a}\mathcal{L}_g^{-1}\left(\frac{1}{a}\frac{dz}{ds}\right)(s)=qE_0s-F(z). \tag{18}$$

For $s=N_0$, the left-hand side vanishes in Eq. (18) and we obtain $F(z)=N_0qE_0$. After integration of Eq. (18), the tension along the chain is obtained. In particular, the tension at the fixed end, $s=0$, is

$$F(z)=N_0(z)qE_0=\frac{k_BT}{a}k^{-1}\left(\frac{z}{z_g}\right), \tag{19}$$

where $k(y)\equiv\ln[\sinh(y)/y]$ and $z_g\equiv a/fx=k_BT/(qE_0)$. When $z\ll z_g$, Eq. (19) gives the Gaussian chain result, Eq. (11). On the other hand, when $z\gg z_g$, $F(z)\gg k_BT/a$ and the relation between the force $F(z)$ and z is given by

$$F(z)-\frac{k_BT}{a}\ln\left(\frac{2F(z)a}{k_BT}\right)=qE_0\frac{z}{a}. \tag{20}$$

Namely, $F(z)\approx qE_0z/a$ for $z\gg z_g$. Hence, since H_g is the distance above which the chain is no longer Gaussian, in the freely jointed chain model, $H_g=z_g$. Consequently, the Gaussian model can be used when $z_g\gg z_0$, i.e., $x\ll f^{-1}N^{-1}$. Note that this condition is equivalent to $z_0\ll Na$. The opposite case, $z_0\gg Na$ (or, equivalently, $z_0\gg z_g$), is characterized by a non-Gaussian entropic elasticity of the chain, and we call it the non-Gaussian regime. Regions designed as non-Gaussian adsorption, strong non-Gaussian adsorption and very strong non-Gaussian adsorption in Fig. 3(a) correspond to the non-Gaussian regime.

These results can be interpreted in terms of simple scaling arguments. Close to the surface, the chain remains Gaussian and $F(z)\approx NqE_0\sqrt{z/z_0}$. The distance at which the chain becomes fully stretched, $F(z)=k_BT/a$, is found to be $z=z_g$. For $z\gg z_g$, the desorbed part of the chain is a rod, and the number of desorbed monomers is $N_0(z)\simeq z/a$ [(see Fig. 2(b)]. Hence, $F(z)\simeq qE_0z/a$ for $z\gg z_g$. When $x\gg f^{-1}$, note that $\delta\ll a$ and $z_g\ll a$. In this regime [regime of very strong non-Gaussian adsorption in Fig. 3(a)], the chain is fully stretched at all distances z and $F(z)=qE_0z/a$.

C. Effects of intramolecular electrostatic repulsions

A polyelectrolyte chain is stretched by internal electrostatic repulsions when $f\gg N^{-3/4}$. In this situation, different regimes of adsorption have been defined by Borisov [2]. When $NqE_0H_0\ll k_BT$, or equivalently $x\ll N^{-2}f^{-5/3}$, the effect of the electrostatic field on the molecule is negligible [region of no adsorption in Fig. 3(a)]. When $NqE_0R_g\ll k_BT\ll NqE_0H_0$, i.e., $N^{-2}f^{-5/3}\ll x\ll f^{-1}N^{-3/2}$, the molecule, keeping its natural conformation, comes in contact with the surface and starts to orient parallel to the surface; it gets confined within a distance $H_c\simeq a/(fNx)$ from the surface. This regime was named as the preadsorption regime [see Fig. 3(a)] [2]. For $x\gg f^{-1}N^{-3/2}$, the chain adsorbs and it is confined within a distance $H_c=\delta$ from the surface. The size of confinement δ is independent of the length of the chain, which is characteristic of a ''real'' adsorption, in contrast with the pre-adsorption. When $f^{-1}N^{-3/2}\ll x\ll f$ [regions of weak, Gaussian, and non-Gaussian adsorption in Fig. 3(a)], $\delta\gg\xi$: the chain of blobs is stretched but it retains its internal structure at length scales smaller than ξ [2]. When $x\gg f$ [regions of strong Gaussian adsorption, strong non-Gaussian adsorption and very strong non-Gaussian adsorption in Fig. 3(a)], $\delta\ll\xi$, and each individual blob is strongly adsorbed on the surface [2].

We now consider the situation where one end of the chain is pulled at a distance z from the surface. When there is no adsorption, the chain can be modeled as a rigid charged rod of size H_0. In this situation $H_i=+\infty$ and $H_s=H_0$. An energetic cost is associated to the loss of entropy of the rod for being confined close to the surface, $W_{\text{rod}}^c=-k_BT\ln\Omega$, where Ω is the solid angle including all the orientations for the rod forbidden by the presence of the surface. When $z>H_0$, $\Omega=0$. When $z<H_0$, $\Omega=2\pi(1-z/H_0)$, hence the solid angle corresponding to the configurations allowed by the presence of the surface is $\Omega_c=4\pi-\Omega=2\pi(1+z/H_0)$. The force profile is consequently $F(z)=-k_BT/(z+H_0)$ for $z<H_0$ and $F(z)=NqE_0$ when $z>H_0$. The statistical physics of a charged rod at an oppositely charged surface are presented in Appendix D. Note that the chain can be modeled as a rod only at length scales larger than the lateral size of the rod, namely, the radius of gyration R_g, in the case of a polyelectrolyte chain. At short distances, $z\ll\xi$, the polyelectrolyte behaves as a Gaussian chain, $F(z)=-k_BT/z$.

In the preadsorption regime, the chain can still be modeled as a rod. But, in contrast to the previous case of no adsorption, thermal fluctuations are small. The second end of the chain remains at the surface when $z<H_0$ (see Fig. 4), and the chain is parallel to the electric field when $z>H_0$. The force $F(z)$ is dominated by the electrostatic interactions: $F(z)=NqE_0/2$ for $R_g\ll z<H_0$, and $F(z)=NqE_0$ when $z>H_0$ (see Appendix D). This problem is very similar to that of a weightlifter lifting a dumbbell of mass M and of length H_0 by one of its sides. At heights smaller than H_0, the weightlifter has to exert a force $Mg/2$, since it is lifting only half of the dumbbell. At short distances, the situation is similar to the regime of no adsorption: $F(z)=-k_BT/z$ when $z\ll\xi$.

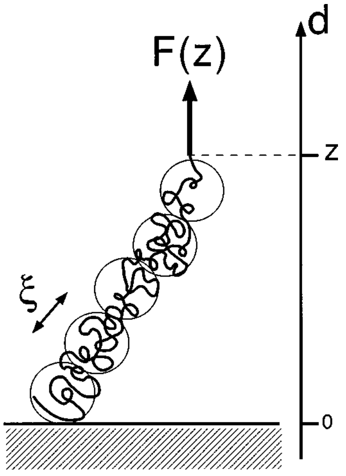

FIG. 4. A chain of electrostatic blobs that remains rodlike when it is detached. The circles picture the blobs.

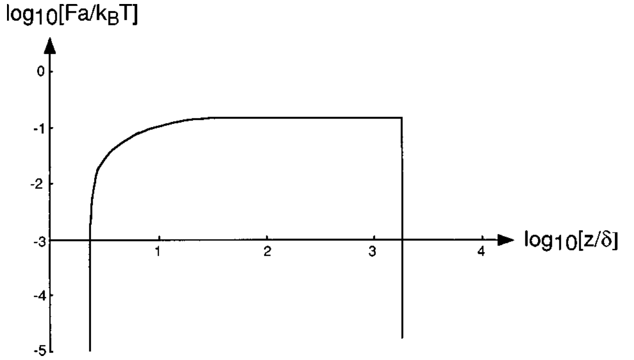

FIG. 5. The force profile $F(z)$ for a chain in a salt solution. Values used in Fig. 1 are kept. The Debye-Hückel length is $\kappa^{-1} = 36$ nm. The first part of the plot, up to the plateau, corresponds to the ground state dominance approximation. The second part of the plot, indicating where the chain detaches, is obtained from previous results on the detachment of neutral chains, and is obtained by continuation of the first part. The chain detaches at $z \simeq 7 \times 10^3$ nm.

When adsorption takes place, the chain is confined within a distance $\delta \ll R_g$ from the surface. When $z \ll \xi$, the entropic repulsion of the wall is again $F(z) = -k_BT/z$. When $z \gg \delta$, several regimes can be obtained. We call the weak adsorption regime the case where H_0 is the distance at which the chain leaves the surface. In this regime, $z_0 \ll H_0$, the stretching of the chain due to the electrostatic field is negligible with respect to the stretching caused by the intramolecular electrostatic repulsions, $H_i = +\infty$, and the chain can still be represented as a rod of length $H_s = H_0$. In addition, the energetic cost for bending the chain and breaking it up in one adsorbed part and one desorbed part, as was represented in Fig. 2, is, neglecting logarithmic contributions, $k_BTN_0f^{4/3}$, where $N_0 = Nz/H_0$ is the number of desorbed monomers. When $z_0 \ll H_0$, this energy is larger than the electrostatic energy NqE_0z of a fully desorbed rodlike chain. Hence, when one of its ends is pulled away from the surface, the chain keeps its rodlike conformation (as represented in Fig. 4). Consequently, when $R_g \ll z < H_0$, $F(z) = NqE_0/2$ and when $z > H_0$, $F(z) = NqE_0$. The force profile in the regime of weak adsorption differs slightly from the force profile in the regime of preadsorption only in the range of distances $\xi \ll z \ll R_g$, which we did not investigate. The weak adsorption regime is shown on Fig. 3(a), where its boundaries are defined by $f^{-1}N^{-3/2} \ll x \ll f^{-1/3}N^{-1}$.

When the electrostatic field is larger than in the weak adsorption regime, the chain bends and breaks up into one desorbed part and one adsorbed part, in order to minimize its electrostatic energy, as represented in Fig. 2. When $\delta \gg \xi$, the adsorption regimes of ''intermediate strengths'' are obtained. Depending on the relative values of z_g and z_0, the non-Gaussian elasticity plays a role at large distances or not [regimes of Gaussian and non-Gaussian adsorption in Fig. 3(a)]. On the other hand, at short enough distances, the desorbed part of the chain keeps its structure in terms of electrostatic blobs. The number of desorbed monomers is then $N_0(z) = Nz/H_0$ and the force is dominated by the intramolecular electrostatic repulsions. Its component on the d axis is $F(z) \approx k_BTf^{2/3}/a$. This expression for $F(z)$ is valid as long as $\delta \ll z \ll z_1 \equiv af^{1/3}/x$. When $z \gg z_1$, the electrostatic energy due to the field dominates over the intramolecular repulsions, and we can use the results of the previous section: $F(z) = NqE_0\sqrt{z/z_0}$ for $z \ll z_g$ and $F(z) = NqE_0z/a$ for $z \gg z_g$. Note that $z_1 \gg \delta$ when $\delta \gg \xi$, i.e., $x \ll f$. The adsorption regimes of ''intermediate strengths'' correspond to $H_c = \delta \ll z_1 \ll H_0, z_0$. In these regimes, $H_i = z_1$ and, since $z_1 < z_g$, $H_i < H_g$.

In the regimes of strong and very strong adsorption, $z_1 \ll \delta \ll \xi$, the effects of intramolecular repulsions are negligible, $H_i = 0$. In the strong Gaussian adsorption regime, $F(z) = -k_BT/z$ for $z \ll \delta$, $F(z) = NqE_0\sqrt{z/z_0}$ for $\delta \ll z \ll z_0$ and $F(z) = NqE_0$ for $z \gg z_0$. In the strong non-Gaussian adsorption regime, the non-Gaussian elasticity, $F(z) = NqE_0z/a$, is observed for $z_g \ll z \ll Na$. In the very strong adsorption regime, the Gaussian behavior disappears, $z_g \ll \delta \ll a$.

In conclusion, three main situations are observed:

(i) $H_i = +\infty$, in the regimes of no adsorption, preadsorption, and weak adsorption ($x \ll f^{-1/3}N^{-1}$); the chain can be modeled as a rigid rod of size $H_s = H_0$ as long as $z \gg R_g$, while it is Gaussian for $z \ll \xi$. In these regimes, $F(z) = NqE_0$ for $z > H_0$ and $F(z) = -k_BT/z$ for $z \ll \xi$.

(ii) $H_c = \delta \ll H_i = z_1 \ll H_s = z_0$ or Na. The intramolecular electrostatic repulsions are predominant as long as $z < H_i$.

(iii) $H_i = 0$, when $x \gg f$. The intramolecular electrostatic repulsions can be neglected, as in the previous sections.

D. Limits of validity of the unscreened model

So far, we have neglected all possibilities of screening of the electrostatic field. However, a real water solution contains at least the counterions corresponding to the charges on the surface. The higher the charge on the surface, the larger the number of counterions. The screening of the surface due to the counterions is characterized by the Gouy-Chapman length $\lambda \equiv 2a/x$. In addition to the counterions, there are other free ions in the solution: the counterions of the polyelectrolyte chain, ions due to the dissociation of water, added salt, impurities, etc. These ions, called all together as ''salt,'' also contribute to the screening, with a characteristic length

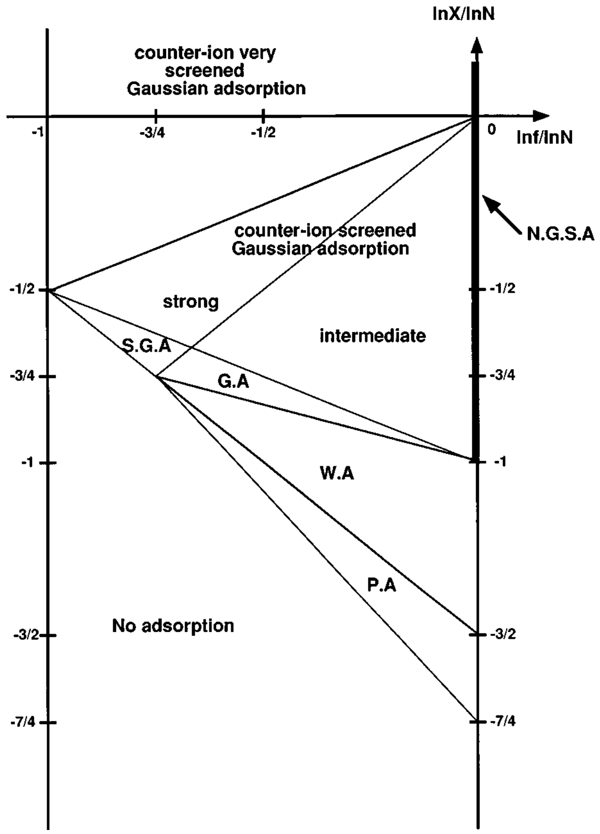

FIG. 6. The different regimes of detachment for a chain, including the effect of the counterions, in the limit $N\rightarrow\infty$. The counterion screened Gaussian adsorption is either intermediate ($H_i>H_c$) or strong ($H_i<H_c$). SGA, GA, WA, and PA refer to strong Gaussian adsorption, Gaussian adsorption, weak adsorption, and preadsorption. NGSA stands for non-Gaussian counterion screened adsorption, and corresponds to values of f of order unity.

scale $\kappa^{-1}\equiv(8\pi l_B n)^{-1/2}$, n being the concentration of salt molecules. The total electrostatic potential profile is $U(z)\equiv V(z)-V_0$, where [13]

$$\tanh\left(e\frac{V(z)}{4k_BT}\right)=\tanh\left(e\frac{V_0}{4k_BT}\right)\exp(-\kappa z). \tag{21}$$

Note that $V(z=0)=V_0$ and $V(z\rightarrow\infty)=0$. The electrostatic potential at infinity $U(z\rightarrow\infty)=-V_0$ is determined by

$$\kappa\lambda\sinh\left(\frac{eV_0}{2k_BT}\right)=1. \tag{22}$$

Two different limits should be distinguished: when the salt concentration is very low, $\lambda\ll\kappa^{-1}$, $E(z)=2k_BTe^{-1}/(z+\lambda)$ for $z\ll\kappa^{-1}$, while $E(z)=(4\kappa k_BT/e)\exp(-\kappa z)$ for $z\gg\kappa^{-1}$. This case is considered in Sec. IV. On the other hand, if the concentration of salt is high, in the Debye-Hückel limit, $\kappa^{-1}\ll\lambda$, a single simple expression is obtained for the electrostatic field: $E(z)=E_0\exp(-\kappa z)$. This situation is investigated in Sec. V. Hence, the electrostatic field is unscreened only up to lengths smaller than λ and κ^{-1}. When the length H_s of the chain extended by the field is small, $H_s\ll\kappa^{-1}$ and $H_s\ll\lambda$, the theory put forward for an unscreened field can be used. The force $F(z)$ reaches a plateau $F(z)=NqE_0$ at $z=H_s$. It then decreases slowly and is proportional to the electrostatic field: $F(z)=NqE(z)$. On the other hand, when $\kappa^{-1}\ll H_s$ or $\lambda\ll H_s$, the screening of the electrostatic field is important. Even in a salt-free solution, this occurs as soon as $\lambda=z_0$, i.e., when $x\gg f^{-1/2}N^{-1}$, because of the presence of the counterions [see Fig. 3(b)].

An important question that we have not considered so far is the screening of the charge of the surface by the charged monomers of the chain itself. This problem is very difficult to handle exactly since it would involve a self-consistent calculation of the partition function. We expect, however, that the screening due to the chain is negligible when the electrostatic field at the surface is large enough, namely, when the charge on any given area of the surface is larger than the charge contained within the part of the chain that adsorbs above this given part of the surface. For a Gaussian chain confined within a distance δ from the surface, this condition is fulfilled when $x\gg f$. On the other hand, if the electrostatic field is low, the screening effects due to the chain charges may become important. However, we saw that when $x\ll f$, $\delta\gg\xi$ and the internal structure of the chain in terms of electrostatic blobs is not modified by the field, even when it is unscreened. Therefore we expect that the scaling results obtained for the unscreened field are not modified when a single chain is considered. However, even in a dilute solution, polyelectrolyte chains may adsorb at an oppositely charged surface and form a nondilute adsorbed layer. Hence, situations where the screening of the electric field by the chains cannot be neglected may occur even when $x\gg f$. However, we did not investigate this problem here.

IV. SALT-FREE SOLUTION

Even in the absence of salt, the electrostatic field is screened by the counterions of the surface and by the chain. The Gouy-Chapman length $\lambda\equiv 2a/x$ is associated with the screening due to the counterions. The electrostatic field is $E(z)\simeq E_0$ for $z\ll\lambda$ and $E(z)\simeq 2k_BT/(ez)$ for $z\gg\lambda$. Different adsorption regimes are obtained depending on the fraction of charged monomers f and on the intensity of the field x and are presented in Fig. 6. As shown in Sec. III A, the electrostatic interactions are expected to be unimportant when $x\ll f^{-1}N^{-3/2}$; this corresponds to regions of no adsorption and preadsorption in Fig. 6. For a Gaussian chain, the theory of the unscreened Gaussian chain is straightforwardly generalized when $\lambda\gg z_0$, i.e., when $x\ll f^{-1/2}N^{-1}$ (regions of Gaussian and strong Gaussian adsorption in Fig. 6). On the other hand, when $f^{-1/2}N^{-1}\ll x$, the simple scaling approach of a Gaussian chain in an unscreened field breaks down as soon as $z>\lambda$. Note that, since $z_1<\lambda$ ($f<1$), the effect of intramolecular repulsions is negligible at the length scales where the screening of the field by the counter-ions becomes important.

We first consider the case where $\lambda>\delta$ ($x\ll f^{1/2}$). In this situation a polyelectrolyte chain adsorbed at a charged surface is confined within a layer of thickness $H_c=\delta$. When the chain is pulled away from the surface, it remains Gaussian as long as $z\ll H_g$. If the fraction of charged monomers f is of order unity (along the vertical axis in Fig. 6), $H_g\approx z_g=a/fx\simeq\lambda$ (see Sec. II B). For $z(s)\ll H_g$ the chain has

Gaussian elasticity, the electric field is unscreened, and results of Sec. II A are valid, while for $z(s) \gg H_g$ the chain is rodlike and the electric field is screened; $N_0 \simeq z/a$ and $F(z) \simeq 2(k_BT/a) f \ln(z/\lambda)$. On the other hand, if $f \ll 1$ (we define this as the region of counter-ion screened Gaussian adsorption in Fig. 6), $H_g \gg \lambda$. For $\lambda \ll z \ll H_g$, the chain is Gaussian and the electric field is screened. In this limit, we write the local mechanical equilibrium of the chain, as in Sec. II B. Equation (17) reads, for a Gaussian chain in a screened electrostatic field,

$$\frac{3k_BT}{a^2}\left(-\frac{dz}{ds}(s+ds)+\frac{dz}{ds}(s)\right)=-\frac{3k_BT}{a^2}\frac{d^2z}{ds^2}(s)ds=-ds\frac{dU}{dz}. \tag{23}$$

Integrating Eq. (23) yields an expression for the tension along the chain:

$$\frac{3k_BT}{a^2}\frac{dz}{ds}(s)=-\sqrt{F^2(z)-6\left(\frac{k_BT}{a}\right)^2\frac{U(z)-U(z(s))}{k_BT}}. \tag{24}$$

At $s=N_0$, $z(s=N_0)=0$, $U(z(s))=0$ and the left hand-side in Eq. (24) vanishes, leading to

$$F(z)=\frac{k_BT}{a}\sqrt{6\frac{U(z)}{k_BT}}. \tag{25}$$

The expression for the tension of the chain is simplified

$$\frac{3k_BT}{a^2}\frac{dz}{ds}(s)=-\frac{k_BT}{a}\sqrt{\frac{6U(z(s))}{k_BT}}. \tag{26}$$

Equations (25) and (26) are correct when $z, z(s) \gg H_c$. They apply for any form of the electrostatic potential. The case of a salt solution is presented in Appendix C. For an electrostatic field screened by counterions, we obtain

$$F(z)=\frac{k_BT}{a}[12f\ln(1+z/\lambda)]^{1/2}. \tag{27}$$

There is no plateau for the force, in contrast with the situation of an unscreened electrostatic field, but the dependence of the force with z is weak (logarithmic), and the order of magnitude of $F(z)$ is constant, $F(z) \approx f^{1/2}k_BT/a$. The distribution of the monomers along the chain is obtained by integration of Eq. (26):

$$s=\frac{12}{\sqrt{3}}f^{-1/2}x^{-1}\int_{u(z(s))}^{u(z)}du\exp(u^2), \tag{28}$$

where $u(z(s)) \equiv [\ln(1+z(s)/\lambda)]^{1/2}$. When $z \ll \lambda$, we get back the results of an unscreened Gaussian chain. The position of monomer s is given by

$$z(s)=z\left(\frac{N_0(z)-s}{N_0(z)}\right)^2. \tag{29}$$

As expected, Eq. (29) shows that the monomers are not homogeneously distributed, in contradiction to what was assumed in the simple scaling arguments developed so far. However, the scaling results are not affected. On the other hand, when $z \gg \lambda$, the results corresponding to a screened field are obtained. In particular, the number of desorbed monomers is

$$N_0(z)=\sqrt{3}f^{-1/2}\frac{z}{a}[\ln(z/\lambda)]^{-1/2}. \tag{30}$$

Note that the scaling form of Eqs. (27) and (30) can be obtained by ignoring the inhomogeneity of the distribution of the monomers and equilibrating the elastic force and the electrostatic force acting on the desorbed part of the monomer

$$3\frac{k_BTz}{N_0a^2}=\int_0^{N_0}dN(z')qE(z')=2k_BTf\frac{N_0}{z}\ln(z/\lambda). \tag{31}$$

Equation (27) shows that $H_g \approx \lambda \exp(1/f)$. The chain remains in contact with the surface until the end point is at a distance H_s, obtained from Eq. (30). Assuming Gaussian elasticity, $H_s \simeq Naf^{1/2}$, up to a logarithmic correction. At large distances, when the chain is detached $(z \gg H_s)$, the force decreases logarithmically. Note that the value of H_g is strongly increased, as a consequence of the screening of the electrostatic field by the counterions, and $H_g \gg H_s$ for $f \ll 1$. Hence, the chain remains Gaussian, even at strong values of the electrostatic field, when $f \ll 1$.

We now consider the case where $\lambda \ll \delta$ $(x \gg f^{1/2})$. The confinement layer reaches a minimal value $H_c = af^{-1/2}$, independent of the field strength x, as can be shown by a minimization of the free energy $W(H_c)$ of a chain homogeneously confined within a layer of thickness H_c, with

$$W(H_c)=k_BT\frac{Na^2}{H_c^2}+\frac{N}{H_c}qE_0\lambda\int_0^{H_c}dt\ln(1+t/\lambda). \tag{32}$$

When f is of order unity, H_c is of the order of the monomer size. Hence $H_g \approx H_c$. The desorbed part of the chain is rodlike, $N_0 = z/a$ and $F(z) \simeq 2(k_BT/a) f \ln(z/H_c)$ (along the vertical axis in Fig. 6). When $f \ll 1$ (region of counterion very screened gaussian adsorption in Fig. 6), the chain is Gaussian and the results of the region of counterion screened Gaussian adsorption are generalized as soon as $z \gg H_c$ by replacing λ by H_c in Eqs. (27)–(31). A more precise approach, however, should take into account the inhomogeneity of the chain within the layer of confinement.

These results hold as long as there is no salt in the solution. If salt is added or naturally present in the solution, they are modified at distances larger than the Debye-Hückel length $\kappa^{-1} = (8\pi l_B n)^{-1/2}$, n being the concentration of salt molecules. The polymer has a Gaussian elasticity ($H_g \to \infty$) as soon as $\kappa^{-1} \ll z_g$, independent of the charge fraction f. The force reaches a plateau value for $z \gg \kappa^{-1}$: $F(z) \simeq (k_B T/a)[12 f \ln(1+\kappa^{-1}/\lambda)]^{1/2}$ if $\lambda \ll \kappa^{-1}$ and $F(z) \simeq (k_B T/a)(3 f \kappa^{-1}/\lambda)^{1/2}$ if $\kappa^{-1} \ll \lambda$. This last result is discussed in greater detail in the following section. The size of full extension is increased by the presence of salt: when $\kappa^{-1} \gg \lambda$ this effect is negligible, but when $\kappa^{-1} \ll \lambda$ and $\kappa^{-1} \ll z_0$, $H_s \approx N a f^{1/2} (\kappa^{-1}/\lambda)^{1/2}$.

V. SCREENING OF THE ELECTROSTATIC FIELD BY THE SALT

We now consider in more detail the case where the screening is dominated by the salt ions. When $\kappa^{-1} \ll \lambda$, Eqs. (21) and (22) give a simple expression for the electrostatic potential: $V(z) = E_0 \kappa^{-1} \exp(-\kappa z)$ and $U(z) = -E_0 \kappa^{-1}[1 - \exp(-\kappa z)]$. The Green function $G(z,N)$ for a Gaussian chain is solution of Eq. (2). We define

$$G_1(z,N) \equiv G(z,N) \exp\left(\frac{N q E_0 \kappa^{-1}}{k_B T} \right). \tag{33}$$

$G_1(z,N)$ is the Green function of the chain with a potential $V(z)$, instead of $U(z)$. Rescaling lengths in units of $2\kappa^{-1}$, the convenient reduced variables are $z^+ \equiv \kappa z/2$ and $N^+ \equiv R_g^{+2} \equiv \kappa^2 R_g^2/4$. We also define $\alpha \equiv 2(\kappa\delta)^{-3/2}$. $G_1(z,N)$ is a solution of

$$\frac{\partial G_1}{\partial N^+}(z^+,N^+) = \frac{\partial^2 G_1}{\partial z^{+2}}(z^+,N^+) + \alpha^2 G_1(z^+,N^+) \times \exp(-2z^+). \tag{34}$$

The solution of Eq. (34) can be expanded in terms of the eigenfunctions of Eq. (34) [6]. It can easily be checked that the positive real numbers form a continuous set of eigenvalues. In addition, there may be a finite number of negative eigenvalues forming a discrete set. To a negative eigenvalue $-\beta^2$, we associate an eigenvector $u_0(z^+) \propto J_\beta(\alpha e^{-z^+})$, where $J_\beta(y)$ is the Bessel function of order $\beta > 0$ [10]. The possible values of β are restricted by the hard-wall boundary condition $J_\beta(\alpha) = 0$. The Bessel functions J_β have an infinite number of positive zeros, and we denote as $j_{\beta,n}$ the nth zero of J_β. The value of $j_{\beta,n}$ increases when β increases. Hence, the maximal possible value for β, denoted from now on as β_0, is determined by the condition $j_{\beta_0,1} = \alpha$. It corresponds to the ground state, where the eigenvalue $-\beta_0^2$ is minimal. The next possible value for β is obtained from the equation $j_{\beta,2} = \alpha$, the third one by $j_{\beta,3} = \alpha$, and so on. Note that the number of zeros of J_0 smaller than α is equal to the number of negative eigenvalues. When the salt concentration increases, α decreases and the number of negative values diminishes. Eventually, the last negative eigenvalue disappears when α becomes equal to the first zero of J_0. The adsorption threshold is defined by $\alpha_{ads} = j_{0,1} \simeq 2.4048\ldots$, i.e.,

$$\delta_{\rm ads} = (2/j_{0,1})^{2/3} \kappa^{-1}. \tag{35}$$

In terms of electric field, it corresponds to a critical value above which there are bound states and the chain is adsorbed. Below the critical field, the ground state dominance approximation can be justified when $N^+ \to \infty$ at a given value of z. In this limit, the ground state eigenvalue is $-\beta_0^2$ and

$$G_{\rm GSD}(z,N) = C(\alpha) J_{\beta_0}[\alpha \exp(-z^+)] \exp[N^+(\beta_0^2 - \alpha^2)], \tag{36}$$

where $C(\alpha)$ is a normalization constant, which depends only on α. When $\alpha \to \infty$, $\beta_0 \approx \alpha - c\alpha^{1/3}$, with $c \approx 1.855\,75$ [10], and we obtain the result of the ground state dominance approximation for the Green function of a polyelectrolyte chain at a charged unscreened surface. The force $F(z)$, defined by Eq. (9), is given by

$$F_{\rm GSD}(z) = \frac{1}{2} k_B T \alpha \kappa \exp(-z^+) \frac{J'_{\beta_0}[\alpha \exp(-z^+)]}{J_{\beta_0}[\alpha \exp(-z^+)]}. \tag{37}$$

Note that $G_{\rm GSD}(z=0,N) = 0$, as required by the hard wall condition. For a given value of $\alpha > j_{0,1}$, $G_{\rm GSD}(z,N) \propto z$ when z is small enough, leading to $F_{\rm GSD}(z) = -k_B T/z$. At large distances, the Green function also vanishes: $G_{\rm GSD}(z \to \infty) \propto \exp(-\beta_0 z^+)$. Hence

$$F_{\rm GSD}(z \to \infty) = k_B T \beta_0 \kappa/2. \tag{38}$$

Equation (38) shows that the force $F(z)$ reaches a plateau value at large distances. When $\alpha \gg 1$ (i.e., $\delta \ll \kappa^{-1}$), well above the adsorption threshold, the plateau value is equal to $F(\infty) \simeq k_B T \kappa^{-1/2} \delta^{-3/2} = (k_B T/a)\sqrt{6 f x \kappa^{-1}/a}$. This result can be related to the case of a neutral chain close to a surface, with short-ranged interactions between the surface and the monomers of the chain [14,15]. In our case, the range of the interaction is of order κ^{-1}. At distances much larger than κ^{-1}, our model can be mapped onto a short-ranged interaction model, monomers being attracted to the surface by an attractive potential $U(z) = -(\beta_0/12) k_B T \kappa a^2 \delta(z)$, where $\delta(z)$ is the Dirac function, by imposing that the force has the same value. Using the results of Refs. [14,15], the ground state dominance result can be extended at large distances. We obtain the length H_s at which the chain jumps away of the surface in order to minimize its elastic energy: $H_s = (1/12)\beta_0 \kappa N a^2$. When $\alpha \gg 1$, this simplifies to $H_s = \kappa^{-1/2} \delta^{-3/2} N a^2/6 = (f x \kappa^{-1}/6a)^{1/2} N a$. An example for the whole force profile is shown on Fig. 5.

These results can be interpreted with scaling arguments. A simple model consists in considering that, due to the exponential character of the screening, it is legitimate to approximate the electrostatic field by a step function $E(z) = E_0$ for $z < \kappa^{-1}$ and $E(z) = 0$ for $z > \kappa^{-1}$. The theory for unscreened fields can be used for $z < \kappa^{-1}$. But for $z > \kappa^{-1}$, there is no field and the force $F(z)$ is a constant. It should be noted that as soon as $\kappa^{-1} \ll z_g$ the chain always shows Gaussian elasticity. The plateau value for the force is $F(\infty) = F(\kappa^{-1}) = NqE_0 \sqrt{\kappa^{-1}/z_0} = (k_B T/a)\sqrt{6 f x \kappa^{-1}/a}$. The number of desorbed monomers is obtained by minimizing the free energy of the chain $W(N_0) \approx N_0 q E_0 \kappa^{-1} + k_B T z^2/(N_0 a^2)$, and we obtain $N_0 = z/a \sqrt{a/f x \kappa^{-1}}$. The stretched length of the chain, assuming that it does not jump away from the surface, is $H_s' = Na\sqrt{f x \kappa^{-1}/a}$. Note that H_s' scales as H_s. It is shown in Appendix C that $H_s = H_s'/2$. For a non-Gaussian chain or for a chain stretched by intramolecular electrostatic repulsions, the same rule $F(\infty) = F(\kappa^{-1})$ can be applied to obtain the order of magnitude of the value of the plateau. This explains for instance the last result of Sec. IV.

VI. CONCLUSION

We have discussed theoretically the detachment of a polyelectrolyte chain when it is pulled away from a charged surface carrying charges with opposite sign to that of the polymer. The force that is necessary to maintain one of the end points of the chain at a fixed distance z from the surface increases with the distance and then reaches a plateau where it is approximately constant. The chain detaches from the surface when the end point is at a finite distance in the regime where the force has reached a plateau.

The applied external force balances the electrostatic force on the desorbed monomers. At short distances the chain is only weakly stretched and the force increases as $F \propto z^{1/2}$. At larger distances, the force becomes large and in some cases the nonlinear stretching elasticity of the chain must be taken into account; this leads to a faster increase of the force $F \propto z$. If the electric field of the charged surface is not screened, the saturation value of the force is the total Coulomb force on the chain $F = NqE_0$. If the electric field is screened either by the counterions or by added salt, the value of the force on the plateau (or the pseudoplateau where the force increases only logarithmically with distance) is independent of molecular weight and decreases with the screening (the ionic strength). The distance where the chain detaches from the surface grows linearly with the molecular weight.

All these results have been obtained with several levels of approximation. In certain cases we were able to consider the chain as a Gaussian and to calculate explicitly the partition function. When the chain is highly stretched a classical approximation that amounts to writing a local force balance on the monomers turns out to be a good approximation. In all cases the results can be explained in terms of simple scaling laws. We also have discussed in detail the limits of validity of our approach. A difficulty with polyelectrolytes is that the exact effects of the electrostatic interactions on the structure of a chain in solution are still badly understood at distances larger than κ^{-1} [7,8]. Hence the criterion obtained in Sec. III C telling when these interactions can be neglected ($x \gg f$ or $z \gg z_1$) may be of interest. However, it should be noted that only the structure of the chain at distances smaller than the screening length κ^{-1} is important in this work, since at larger length scales the electrostatic field is screened.

The results obtained in this paper have been compared to recent AFM experiments performed in Strasbourg by diMeglio and Senden [3]. In the performed experiments, loops are pulled instead of the end of the chain. Several loops may be pulled together, but since the loops have different lengths, they detach sequentially and their contributions can be separated in the force profile. Pulling one loop is merely like pulling two ends. We estimated that their system corresponded to the non-Gaussian counterion screened adsorption regime (see Fig. 6) with a Debye-Hückel length $\kappa^{-1} \simeq 47$ nm. A plateau in the force profile due to the screening by the salt is obtained in the experiment by Senden and di Meglio and its value, of the order of 10^{-10} N, is in good agreement with our predictions.

Some of the hypotheses of our model remain, however, too rough to allow for a quantitative comparison between theory and experiment. For instance, the surface is, in real samples, never homogeneously charged. Some elementary charges are spread over the surface with an average distance separating them. This average intercharge distance is of the order of a few nanometers, for mica in pure water [16,17]. When z is smaller than this characteristic distance, our results are dubious and the discrete nature of the charges must be explicitly taken into account. Similarly, it may not always be correct to assume that the charge is uniformly spread along the chain, in particular when $f \ll 1$. And for annealed polyelectrolytes (polyacids or polybases for example, the average charge per monomer depends on local properties such as the local electrostatic potential. We did not consider in details annealed polyelectrolytes in this paper. Another assumption of our model is that the solution behaves as a θ solvent. Taking into account the excluded volume and the short-ranged interactions between the monomers and the surface makes the problem more complex, but, in a poor solvent, interesting predictions might be obtained, with a possible nonmonotonous force profile [18,19]. Another improvement of the model could consist in taking into account the local variations of the dielectric constant, in particular at the surface, where image charge effects can be of some importance.

This work could be extended in two directions. The AFM experiments are also able to probe the dynamical behavior of a chain adsorbed on a surface. It would thus be interesting to make a theoretical study of the dynamical behavior of an adsorbed polyelectrolyte chain responding to an oscillatory force $F(z)$.

The situation where many chain adsorb at the surface was only introduced briefly. We expect a quite rich variety of behaviors to occur, depending on the density of the chains at the surface and on their average charge. In the case where the chains are densely packed and highly charged, they might be considered as grafted by the electrostatic attraction.

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APPENDIX A

We present here the calculation of the Green function of a Gaussian polyelectrolyte chain in infinite space in the presence of a constant electrostatic field $\vec{E}_0$. The plane where the electrostatic potential is zero is set to coincide with the plane $z=0$. The properties of the chain are invariant by translation: if a given conformation of the chain in the integration domain of Eq. (1) is shifted by a given vector $\vec{r}$, the corresponding term in the summation is multiplied by a factor $\exp(-Nq\vec{E}_0\cdot\vec{r}/k_BT)$ depending on the translation vector but independent of the conformation, which can therefore be extracted from the integral. Using this property, it follows that

$$G^0(z,N)=h(N,fx)\exp\left(-\frac{NqE_0z}{k_BT}\right). \qquad \text{(A1)}$$

Equation (3) is valid for the Green function $G^0(z,N)$ for all values of z, and it leads to a simple differential equation for $h(N,fx)=h(\tilde{N})$:

$$\frac{dh}{d\tilde{N}}=\tilde{N}^2h. \qquad \text{(A2)}$$

Equation (A2) is easily solved. Taking into account the boundary condition $G^0(z,N=0)=1$, obtained from Eq. (1), we retrieve Eq. (7). Note that the energy of the chain is proportional to $\tilde{N}^3$. This result is also obtained by using Eq. (13) with $H_s=z_0$.

APPENDIX B

The Laplace transform, with respect to the variable $\tilde{N}$, of the Green function of a single polyelectrolyte chain in a constant field in infinite space, Eq. (7), is not defined. However, this is not the case for a single polyelectrolyte chain in semi-infinite space, attracted to the surface, as is shown by Eq. (8). Hence, we introduce the Laplace transform $\overline{G}(\tilde{z},p)$ of $G(\tilde{z},\tilde{N})$:

$$\overline{G}(\tilde{z},p)=\int_0^\infty d\tilde{N}\ G(\tilde{z},\tilde{N})\exp(-\tilde{N}p). \qquad \text{(B1)}$$

By taking the Laplace transform of Eq. (2), a second order linear differential equation for $\overline{G}(\tilde{z},p)$ is obtained. For $\tilde{z}>0$,

$$\frac{\partial^2\overline{G}}{\partial\tilde{z}^2}(\tilde{z},p)-(\tilde{z}+p)\overline{G}(\tilde{z},p)=-1. \qquad \text{(B2)}$$

A particular solution of Eq. (B2) is given by the Wronskian of the integrals of the Airy functions $Gi(\tilde{z}+\tilde{p})$ [10], given by

$$\mathrm{Gi}(y)=\pi^{-1}\int_0^\infty dt\ \sin(t^3/3+yt). \qquad \text{(B3)}$$

The general solution of the homogeneous equation associated to Eq. (B2) is the set of the linear combinations of the Airy functions $\mathrm{Ai}(\tilde{z}+p)$ and $\mathrm{Bi}(\tilde{z}+p)$. Using the boundary conditions $\overline{G}(\tilde{z}=0,p)=0$ and $\overline{G}(\tilde{z},p)$ bounded,

$$\overline{G}(\tilde{z},p)=\frac{1}{Ai(p)}[\mathrm{Ai}(p)\mathrm{Gi}(\tilde{z}+p)-\mathrm{Gi}(p)\mathrm{Ai}(\tilde{z}+p)]. \qquad \text{(B4)}$$

Denoting the inverse Laplace transform operator as $\mathcal{L}^{-1}$, we define

$$K(\tilde{z},\tilde{N})\equiv\frac{\mathcal{L}^{-1}\left[Gi(p)\dfrac{Ai(\tilde{z}+p)}{Ai(p)}\right](\tilde{N})}{\mathcal{L}^{-1}[Gi(p)](\tilde{N})}. \qquad \text{(B5)}$$

The Green function is expressed as

$$G(z,N)\propto[\exp(-\tilde{N}\tilde{z})-K(\tilde{z},\tilde{N})]. \qquad \text{(B6)}$$

APPENDIX C

For a solution containing salt, such that $\kappa^{-1}\ll\lambda$, Eq. (25) is written as

$$F(z)=\frac{k_BT}{a}\sqrt{\frac{6fx\kappa^{-1}}{a}[1-\exp(-\kappa z)]}. \qquad \text{(C1)}$$

Below the temperature of adsorption, when $\delta\ll\kappa^{-1}$, we expect Eq. (C1) to be correct as soon as $z\gg\delta$. For $z\gg\kappa^{-1}$, the plateau value predicted by the ground state dominance approximation is obtained. An integration of Eq. (26) yields the expression of the tension and of the distribution of the monomers along the chain

$$3\frac{k_BT}{a^2}\left(\frac{dz}{ds}\right)(s)=-\frac{k_BT}{a}\sqrt{\frac{6fx\kappa^{-1}}{a}}\left[\frac{\sqrt{1-\exp(-\kappa z)}-\tanh(s\sqrt{fx\kappa a/6})}{1-\sqrt{1-\exp(-\kappa z)}\tanh(s\sqrt{fx\kappa a/6})}\right], \qquad \text{(C2)}$$

$$z(s)=-\kappa^{-1}\ln\left[1-\left(\frac{\sqrt{1-\exp(-\kappa z)}-\tanh(s\sqrt{fx\kappa a/6})}{1-\sqrt{1-\exp(-\kappa z)}\tanh(s\sqrt{fx\kappa a/6})}\right)^2\right]. \qquad \text{(C3)}$$

The number N_0 of desorbed monomers is obtained from Eq. (49):

$$N_0=(fx\kappa a/6)^{-1/2}\tanh^{-1}[\sqrt{1-\exp(-\kappa z)}]. \qquad \text{(C4)}$$

When $z\ll\kappa^{-1}$, these results match with those of the unscreened field. When $z\gg\kappa^{-1}$, the relation between $z(s)$ and s is linear, in agreement with the constant value of the tension at large distances.

$$z(s)\simeq z-s\sqrt{2fx\kappa^{-1}a/3}. \tag{C5}$$

The point where the chain jumps away from the surface can be obtained by calculating the free energy of the stretched chain, including its electrostatic and its entropic contributions, and comparing it with the energy of a desorbed chain. The electrostatic energy is equal to the entropic energy. We find that the free energy of the adsorbed polyelectrolyte molecule is

$$W(z)=k_BT\frac{\kappa^{-1}}{a}\sqrt{6fx}\left[\ln\left(\frac{1+\sqrt{1-\exp(-\kappa z)}}{1-\sqrt{1-\exp(-\kappa z)}}\right)-2\sqrt{1-\exp(-\kappa z)}\right]. \tag{C6}$$

When $z\gg\kappa^{-1}$, $W(z)\simeq 2N_0(z)qE_0\kappa^{-1}$. When z is large enough, the criterion for the chain to jump away from the surface is $W(z)>NU(z)\simeq NqE_0\kappa^{-1}$. The chain leaves the surface before it is fully extended, when $N_0=N/2$, i.e., when $z=H_s=Na\sqrt{fx\kappa^{-1}/6a}$, as was predicted in Sec. III. Hence $H_s=H_s'/2$.

APPENDIX D

The partition function of a rigid charged rod with one end fixed at a distance z from an oppositely charged surface is

$$Z(z)=\begin{cases}\dfrac{4\pi a}{NfxH_0}\left[\exp\left(-\dfrac{Nfxz}{2a}\right)-\exp\left(-\dfrac{Nfx(2z+H_0)}{2a}\right)\right], & z<H_0\\[2ex] \dfrac{8\pi a}{NfxH_0}\sinh\left[\dfrac{NfxH_0}{2a}\right]\exp\left(-\dfrac{Nfxz}{a}\right), & z>H_0.\end{cases} \tag{D1}$$

This leads to a force $F(z)=NqE_0$ when $z>H_0$, while when $z<H_0$,

$$F(z)=NqE_0(1-\tfrac{1}{2}\{1-\exp[-Nfx(z+H_0)/2a)\}^{-1}). \tag{D2}$$

In the regime of no adsorption ($NfxH_0/a<1$), Eq. (D2) simplifies as $F(z)\simeq -k_BT/(z+H_0)$, while in the situation of preadsorption or weak adsorption ($NfxH_0/a>1$), $F(z)\simeq NqE_0/2$. The average position of a free rod close to a charged surface can also be calculated:

$$\langle z\rangle=\frac{a}{Nfx}\left\{2-Nfx\frac{H_0}{2a}\left[\exp\left(\frac{NfxH_0}{2a}\right)-1\right]^{-1}\right\}. \tag{D3}$$

In the regime of no adsorption, Eq. (D3) yields $\langle z\rangle\simeq a/(Nfx)\gg H_0$; in the regime of preadsorption, $R_g\ll\langle z\rangle\simeq 2a/(Nfx)\ll H_0$.

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