

POLYMÈRES AUX INTERFACES
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Polyelectrolyte adsorption

David ANDELMAN^a, Jean-François JOANNY^b

^a School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, 69978 Ramat Aviv, Israel

^b Institut Charles-Sadron, 6, rue Boussingault, 67083 Strasbourg cedex, France

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Abstract. The problem of charged polymer chains (polyelectrolytes) as they adsorb on a planar surface is addressed theoretically. We review the basic mechanisms and theory underlying polyelectrolyte adsorption on a single surface in two situations: adsorption of a single charged chain, and adsorption from a bulk solution in θ solvent conditions. The behavior of flexible and semi-rigid chains is discussed separately and is expressed as function of the polymer and surface charges, ionic strength of the solution and polymer bulk concentration. We mainly review mean-field results and briefly comment about fluctuation effects. The phenomenon of polyelectrolyte adsorption on a planar surface as presented here is of relevance to the stabilization of colloidal suspensions. In this respect we also mention calculations of the inter-plate force between two planar surfaces in presence of polyelectrolyte. Finally, we comment on the problem of charge overcompensation and its implication to multi-layers formation of alternating positive and negative polyelectrolytes on planar surfaces and colloidal particles. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

polyelectrolyte / adsorption / colloidal particles / multilayers

Adsorption de polyélectrolytes

Résumé. *Nous discutons les approches théoriques qui permettent d'étudier les polymères chargés qui s'adsorbent sur une surface plane dans deux situations : l'adsorption d'un polymère isolé et l'adsorption à partir d'une solution lorsque le solvant est un solvant θ . Nous considérons séparément le comportement de polymères rigides et flexibles en fonction de divers paramètres physicochimiques comme la charge du polymère, la charge de la surface, la force ionique de la solution et la concentration en polymère. Nous décrivons essentiellement les modèles de type champ moyen, mais nous discutons aussi brièvement l'effet des fluctuations. L'adsorption de polyélectrolytes est capitale pour l'étude de la stabilité de suspensions colloïdales. Dans cette optique, nous mentionnons aussi des études sur les forces entre deux surfaces planes en présence de polyélectrolytes. Enfin, nous présentons le problème de l'inversion de charge et son application à la formation de multicouches polyélectrolytes sur des surfaces planes et des particules colloïdales. © 2000 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS*

polyélectrolyte / adsorption / particules colloïdales / multicouches

Note présentée par Guy LAVAL.

1. Introduction

Polymers are often used as chemical additives to control the stability or tune the viscoelastic properties of colloidal suspensions. In these applications the interaction between polymers and colloidal particles in solution plays a major role. Neutral polymers are mostly used in organic solvents. Their interaction with colloidal particles has been studied in great details, both theoretically and experimentally, and their adsorption behavior is rather well understood [1–4]. Because polymer additives are often charged in aqueous solvents, it is of great importance to understand quantitatively their interaction with colloidal particles.

In this short review we try to give an overview of the adsorption behavior of charged polymers (polyelectrolytes) on colloidal particles. We focus on the limit where the polymer size is much smaller than the particle size. Hence, it is sufficient to study the adsorption of polyelectrolyte chains on flat surfaces. Although no complete description of polyelectrolyte adsorption exists at present, some important results have recently been obtained using mean-field theory and other approximations. These theoretical results seem to be in good agreement with the experimental observations. One of the points that we would like to highlight is the possibility of surface charge inversion. A charged polymer adsorbing on an oppositely charged surface can overcompensate the original surface charge. Because the polyelectrolyte creates a thin adsorbing layer adjacent to the surface, the overall charge of the surface combined with the adsorbing polymer can have an opposite sign than the original surface charge.

Let us start by considering single chain behavior in a dilute aqueous solution of polyelectrolytes [5]. At this low concentration limit, the polyelectrolyte chains only weakly interact with one another and can be considered as isolated chains dispersed in solution. For simplicity we consider as a reference only neutral polymers in a θ solvent, where the chain conformation obeys Gaussian statistics. The end-to-end distance of a neutral chain of N monomers is $R_0^2 = 2Nal_0$, where a is the monomer size and l_0 the persistence length. Charged chains are highly stretched as compared to neutral chains with the same chemical composition but with no dissociated charged groups. The repulsive interaction energy between two charged monomers at a distance r can be written as $e^2/4\pi\epsilon r = k_B T l_B/r$, where $l_B = e^2/4\pi\epsilon k_B T$ is the Bjerrum length, ϵ is the dielectric constant of the aqueous medium, and $k_B T$ the thermal energy. For water with $\epsilon \approx 80\epsilon_0$ and at room temperature, $l_B \approx 7 \text{ \AA}$. When salt (electrolyte) is added to the solution, the electrostatic interaction is screened over the Debye length $\kappa^{-1} = (8\pi n l_B)^{-1/2}$, where n is the salt concentration.

Let us now consider two types of polyelectrolytes: flexible and semi-rigid chains. If the polymer backbone is semi-rigid or if the polymer is highly charged, the main effect of the electrostatic interaction is to increase the persistence length [6]. The effective persistence length due to electrostatic interaction is $l_\tau = l_0 + (\tau^2 l_B)/(4\kappa^2)$, where $\tau = f/a$ is the charge density per unit length and $0 \leq f \leq 1$ is the fraction of charged monomers on the chain. In the limit of low ionic strength the polymer becomes very stiff and behaves as a rigid rod ($R = Na$).

If the polymer backbone is flexible, or the polymer is only weakly charged, the statistics of polymer conformation is Gaussian at small length scales but the chain is stretched at larger length scales. A simple way to describe the chain conformation is shown in *figure 1* and uses the so-called ‘electrostatic blob’ model [7]. The chain can be viewed as a fully stretched chain of Gaussian subunits (called the electrostatic blobs) of size $\xi_{el} \approx a(a/f^2 l_B)^{1/3}$ and each containing g monomers. Within each blob the chain segment

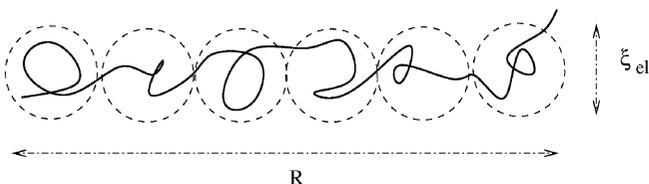


Figure 1. A polyelectrolyte is represented as a rod-like chain of electrostatic blobs. Inside each blob of size ξ_{el} , the chain obeys Gaussian statistics. The chain end-to-end distance is R .

obeys Gaussian statistics, $g \approx (\xi_{el}/a)^2$. The blob size ξ_{el} is obtained by equating the electrostatic interaction of fg charged monomers inside the blob with the thermal energy $k_B T$. The size of the entire chain is then $R \approx Na^{2/3}(f^2 l_B)^{1/3}$. The crossover between the rigid and the flexible polyelectrolyte behaviors occurs when $a^2 > f^2 l_B l_0$.

In the remaining of the paper we review the adsorption of flexible and semi-rigid polyelectrolyte chains on planar surfaces. We discuss the adsorption of a single polyelectrolyte chain on a charged surface of opposite charge. Section 3 is devoted to the mean-field theory of multi-chain polyelectrolyte adsorption on a charged surface. We first summarize the results obtained analytically by asymptotic methods and then present some scaling arguments based on numerical studies of the mean-field equations. In Section 4, we comment on correlation effects of semi-rigid (rod-like) and charged polymers. The last section is devoted to two specific examples: (i) interactions between surfaces coated by an adsorbed polyelectrolyte layer, and (ii) polyelectrolyte multilayers.

2. Single chain adsorption

In this section we discuss the adsorption of an isolated polymer chain on an oppositely charged surface. First we consider flexible and weakly charged chains and then semi-rigid chains.

2.1. Flexible and weakly charged chains

When a flexible polyelectrolyte is attracted by an oppositely charged surface with surface charge density (in units of number per unit area) σ , the polymer adsorbs and forms a thin layer of thickness δ adjacent to the surface. This is shown schematically on *figure 2*. The chain thickness results from a balance between the attractive electrostatic interaction and the repulsive confinement force due to the Gaussian chain entropic elasticity [8]. The thickness resulting from the minimization of the adsorbed chain free energy is:

$$\delta = (a^2 / f \sigma l_B)^{1/3} \quad (1)$$

This result is valid at sufficiently large σ where the thickness δ is smaller than the Gaussian end-to-end distance R_0 . At lower values of σ , the chain of blobs retains its conformation upon adsorption and is only weakly adsorbed (see Ref. [8] for more details). Another polymer-surface interaction originates from the dielectric discontinuity between the surface and the aqueous solution. The dielectric discontinuity can be understood in terms of repulsive image charges that cause repulsive interaction at surfaces having a dielectric constant lower than that of the bulk solution. This interaction competes with the adsorption mechanism but is rather weak for moderately high σ and can be ignored in most situations.

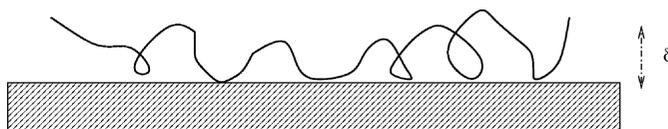
When salt is added to the aqueous solution the electrostatic interaction close to the surface is screened. The conformation of the adsorbed chain does not change as long as the Debye screening length is larger than the thickness, $\kappa^{-1} > \delta$. If the screening length becomes shorter than δ , the chain no longer adsorbs [9]. This gives the criterion for adsorption: $\sigma > \kappa^3 a^2 / (f \sigma l_B)$. The last result can be understood also by considering the screening effect on the free energy of the adsorbing chain.

2.2. Semi-rigid chains

Using similar arguments it is possible to describe the adsorption of semi-rigid chains on planar surfaces. The force that opposes confinement does not originate from the Gaussian chain elasticity but is due to bending fluctuations of semi-rigid chains [10]. The adsorption thickness of the adsorbed chain is:

Figure 2. A chain adsorbed on a flat solid surface is schematically drawn.

The adsorption thickness is δ .



$$\delta = (l_B \sigma \tau l_{\text{eff}}^{1/3})^{-3/5} \quad (2)$$

The effective persistence length of the chain l_{eff} includes both the electrostatic and the bare bending contributions. The electrostatic contribution to the persistence length does not reduce here to the contribution calculated by Odijk [10] because the length scales involved in the adsorption can be shorter than the screening length. This is the reason why we introduce here an effective persistence length [5]. This has been discussed in detail in Ref. [11]. When image charge effects are taken into account, the relevant persistence length is always the bare persistence length l_0 . When salt is added, a semi-rigid chain also desorbs when the screening length is of the order of the chain thickness i.e., if $\sigma \approx \kappa^{5/3} / (\tau l_{\text{eff}}^{1/3} l_B)$.

Although it is difficult to perform experiments for very dilute polyelectrolyte solutions in the bulk, single chain manipulations are possible at surfaces. Conformations of individual adsorbed chains can be probed by pulling a single chain off the surface with the tip of an atomic force microscope (AFM). These experiments measure the interplay between the chain elasticity and the surface-chain electrostatic interaction [12]. The signature of the electrostatic interaction is an increase of the force with the distance from the surface up to distances comparable to the Debye screening length. For larger distances the force profile reaches a plateau.

2.3. Counterion release

When a strongly charged polyelectrolyte adsorbs on an oppositely charged surface, the counterions that neutralize the chain charges play an important role. Above a critical charge per unit length, $\tau_c = 1/l_B$, some of the counterions condense on the polymer and the polyelectrolyte together with the condensed counterions has an effective charge (per unit length) τ_{eff} lower than its nominal τ value and approximately equal to the critical condensation charge $\tau_{\text{eff}} \simeq \tau_c = 1/l_B$. This phenomenon is known as counterion or Manning condensation [13].

When the chain is adsorbing on an oppositely charged surface, the condensed counterions can be released into the solution, because their release leads to a big increase in counterion translational entropy. The corresponding free energy gain can be as large as the direct electrostatic interaction and, thus, is a major driving force for the adsorption. For a semi-rigid polyelectrolyte adsorbing on a flat surface, counterion release has recently been studied [14]. The main result is that a complete counterion release occurs only for very large surface charges.

3. Mean-field theory of polyelectrolyte adsorption

3.1. The adsorption profile equation

The simplest approach to study the adsorption of a multi-chain polyelectrolyte solution on a solid surface is to use a mean-field theory in analogy to what has been done for the adsorption of neutral polymers [15]. The polymer conformation is calculated in a mean-field potential due to the interactions with the surface and the other polymer chains, $U(z)$, and is described by ϕ , the so-called order parameter. This order parameter is related to the local concentration of monomers $c(z)$ at a distance z from the surface by $\phi(z) = \sqrt{c(z)}$. Next, for long enough chain, $N \gg 1$, it is possible to employ the ground state dominance approximation. Corrections beyond the ground state dominance are important if the chain tails have important contribution to the adsorption energetics. These corrections are not important when the adsorbing layer is thin and dense, as is the case for polyelectrolytes. The equation governing the order parameter is the standard Edwards equation:

$$-\frac{a^2}{6} \frac{d^2 \phi}{dz^2} + (U(z) - E) \phi = 0 \quad (3)$$

where E is the ground state free energy and can be calculated by equating the polymer chemical potential in the adsorbed layer and in the bulk. The mean-field potential U includes both the local electrostatic

potential and the excluded volume interaction with the other monomers. For simplicity, we consider here only the case of a θ solvent where the second virial coefficient exactly vanishes $v = 0$, and write $U(z) = -f\psi(z) + w^2c^2(z)/2$, where w^2 is the third virial coefficient for the (repulsive) interactions between monomers, $c = \phi^2$ is the monomer concentration and ψ the dimensionless electrostatic potential (rescaled by $e/k_B T$). We choose the zero of electrostatic potential so that far from the surface, $\psi = 0$, and discuss the case where the polymer is negatively charged and the surface is positive. The electrostatic potential ψ satisfies a generalized Poisson–Boltzmann equation:

$$\frac{d^2\psi}{dz^2} = \kappa^2 \sinh \psi + 4\pi l_B f \phi^2 \quad (4)$$

The above equation is the Poisson equation relating the Laplacian of the electric potential to the total charge in the system, which is the sum of the small ionic charges (satisfying the Boltzmann distribution) and the polymer charges. In addition, we need to specify the boundary conditions for ψ and ϕ . The electrostatic boundary condition is $d\psi/dz|_0 = -4\pi l_B \sigma$ because the surface charge density is fixed, and the ϕ boundary condition can be expressed in terms of the short range non-electrostatic interactions between the polymer and the surface $\phi^{-1} d\phi/dz|_0 = -1/d$. We note that this boundary condition is often used in problems of polymer adsorption. It conveniently depends only on one parameter d . The extrapolation length d is inversely proportional to the short range interaction between the polymer and the surface. It is positive and of the order of a molecular size if the polymer-surface interaction is attractive and of order $k_B T$ per monomer. The length d is negative if the chains are repelled by the surface and it vanishes for an impenetrable surface (a hard wall) where $\phi(0) = 0$. We will also consider an indifferent surface for which $1/d$ vanishes; it is a surface at the transition between adsorption and depletion (ignoring electrostatic effects).

This set of equations (3)–(4) can be used to calculate the mean field adsorption profiles. The profile equations have been solved either numerically [16,17] or using asymptotic analysis [18]. Related discrete lattice models have also been developed [5]. We summarize below the main findings, starting with the case of adsorption on non-charged surfaces.

3.2. Adsorption on electrically neutral surfaces

We first consider an electrically neutral surface in the limit of very small ionic strength ($\kappa^{-1} \rightarrow 0$). For example, this can be the case of polyelectrolyte adsorption at liquid–air or liquid–liquid interfaces. The polymer chains are attracted to the surface by non-electrostatic interactions as is parameterized by the length d , and form a thin layer on the surface. Only a small fraction of the counterions are localized in this layer as can be checked a posteriori. To a good approximation, the electrostatic problem can be solved by considering the dense adsorbed polymer layer by itself as a charged surface with a charge density $\sigma = f\Gamma$, where Γ is the monomer surface coverage (per unit area):

$$\Gamma = \int [c(z) - c_{\text{bulk}}] dz \quad (5)$$

The electrostatic potential is obtained by solving the standard Gouy–Chapman problem for the counterion charge density in presence of a charged surface. At length scales smaller or comparable with the adsorbed layer thickness, the electrostatic potential, is constant $\psi = 2 \log(\kappa \lambda_{GC})/2$, where the Gouy–Chapman length is defined as $\lambda_{GC} = 1/(2\pi l_B \sigma) = 1/(2\pi l_B f \Gamma)$.

Close to the surface, the excluded volume interaction dominates and the monomer concentration decays as a power law:

$$c(z) \approx 1/(z + d/2) \quad (6)$$

The electrostatic potential creates a strong barrier against adsorption that starves the adsorbed layer and reduces the adsorption when the charge of the polymer increases. At large distances (though smaller than λ_{GC}), the concentration decays exponentially $c(z) \approx \exp(-2z/\delta_n)$ where the layer thickness is $\delta_n = a/\sqrt{-6f\psi}$. Because $\Gamma \approx a^{-2}$, the thickness is indeed much smaller than the Gouy–Chapman length and the counterions are not localized inside the adsorbed polymer layer in consistence with our assumptions. The strong adsorption limit requires that $\delta_n > d$. This indeed fixes the minimum strength of the attractive short range potential. Note also that the adsorption on a charged surface having the same sign as the polymer charge can be treated in a similar way, but then the effective charge of the surface is $f\Gamma + \sigma$.

3.3. Adsorption on oppositely charged surfaces: charge inversion

When the polymer adsorbs on a charged surface with an opposite charge, and in the limit of low ionic strength, the polymer essentially neutralizes the charge of the surface or even slightly overcompensates it. The effective charge of the surface coated by the adsorbed polymer layer is low and, as a first approximation, the Poisson–Boltzmann equation can be linearized. The polymer forms a very thin and dense adsorbing layer on the surface almost free of counterions. An asymptotic expansion of the mean-field equations can be carried out [18] ignoring the role of the counterions in the adsorbed layer. If the surface charge is low, excluded volume interactions are negligible and the thickness of the adsorbed layer remains comparable with the thickness of a single adsorbed chain, δ , given by equation (1). The polymer charge always overcompensates the surface charge by a small amount, $\Delta\sigma/\sigma \approx \kappa\delta(1 + \delta^2/\xi_{el}^2)$, where the overcharging parameter is defined as $\Delta\sigma = f\Gamma - \sigma$.

At higher values of the surface charge, $\sigma > \sigma_c \sim f$, excluded volume becomes important and the thickness δ_{ev} of the adsorbed layer increases with the surface charge $\delta_{ev} \simeq \xi_{el}^2/\delta$. In this regime as well, the surface charge is weakly overcompensated. In the limit of high ionic strength, the electrostatic interaction is short range and essentially contributes to the excluded volume interaction. The properties of the adsorbed layer strongly depend on the short range interaction between the polymer and the surface. If the adsorbing surface is an ideal impenetrable surface (with no other interactions), there is no adsorption just like the case for a single chain. If the surface is indifferent, i.e., if the short range attraction exactly compensates the impenetrable surface repulsion yielding $1/d = 0$, the overcompensation can be quite large, $\Delta\sigma = 2\sigma$.

Numerical studies of the mean-field equation allow an explicit calculation of the polymer concentration profiles. In [17] polyelectrolyte adsorption is investigated using different boundary conditions from the one discussed above. The results are interpreted in terms of scaling laws. The polymer concentration was fixed to be zero on the surface, which effectively means that the adsorption length d vanishes. The electrostatic boundary condition is chosen to be either a fixed surface potential $\psi_s = \text{const}$ or a fixed surface charge $\sigma = \text{const}$. The numerical results [17] for different surface boundaries, different monomer sizes and polymer charges indicate that, to a good approximation, the adsorption can be characterized by a single adsorption length scale, D .

For low salt concentration, $D \ll \kappa^{-1}$ and for a constant ψ_s :

$$D \sim f^{-1/2}\psi_s^{-1/2} \quad (7)$$

In this limit, $\psi_s \sim \sigma D l_B$, and these results are in agreement with the asymptotic analysis discussed above, $D \sim \delta$. The polymer surface excess Γ can also be obtained by scaling arguments and is equal to:

$$\Gamma \sim \psi_s^{3/2} f^{-1/2} \sim \sigma f^{-1} \quad (8)$$

The asymptotic analysis predicts in this case a weak charge inversion, which is consistent with this scaling result. The overcompensation is observed numerically by calculating the electrostatic potential which is non monotonic. Namely, at some distance from the surface the electric field is zero: $d\psi/dz = 0$.

In high salt conditions, the salt screens all electrostatic interactions including the repulsive monomer–monomer interactions and the attractive surface–monomer interactions. The characteristic size of the adsorbed polyelectrolyte layer D now depends on κ :

$$D \sim \frac{\kappa}{f\psi_s} \quad (9)$$

Using the appropriate relation between ψ_s and σ : $\psi_s \sim \sigma l_B / \kappa$, the scaling with σ is:

$$D \sim \frac{\kappa^2}{f\sigma} \quad (10)$$

Because of the Debye screening, the electrostatic interaction generates a positive electrostatic contribution to the second virial coefficient $v_{\text{elec}} \sim f^2 \kappa^{-2}$ even when the solvent is a θ solvent. For large enough values of the polymer charge f , the surface excess is:

$$\Gamma \sim \frac{\kappa\psi_s}{f} \sim \frac{\sigma}{f} \quad (11)$$

At high salts, the overcompensation is not universal and strongly depends on the system parameters such as d . It is thus difficult to compare the numerical results to the asymptotic results presented above in very specific conditions. One of the ways to cause overcompensation is to change the solvent quality. For a polymer in a good solvent, the overcompensation decreases with the excluded volume parameter v (the second virial coefficient). For $v \leq v_{\text{elec}}$ a strong overcompensation is expected. This indeed was obtained in [17] from the numerical solution of the mean-field profile equations.

3.4. Adsorption from dense solutions

The structure of an adsorbed polyelectrolyte layer strongly depends on the concentration of the bulk solution. The main feature of semi-dilute or dense solutions is that the structure factor $S(q)$ has a strong peak at a wavenumber $q^* > 0$ indicating that concentration fluctuations decay in an oscillatory manner. Any perturbation of the otherwise homogeneous solution creates a spatial modulation in the polymer concentration profile with a period $2\pi/q^*$. This phenomenon also manifests itself for adsorbing polyelectrolytes. Damped oscillations of the concentration profile have been explicitly calculated in [19] using a Debye–Hückel (linearized) theory and treating the adsorbing surface as a perturbation. The modulations exist at weak ionic strength, while the concentration profile becomes monotonically decreasing for large ionic strength, ($\kappa > q^*$). It is conceivable to assume that these damped oscillations occur also beyond the validity of the linear Debye–Hückel regime. They can be related to oscillatory forces measured in thin film balance with soap films containing polyelectrolytes [20].

4. Adsorption of semi-rigid polyelectrolytes: correlation effects

The main assumption of mean-field theory is that only the average concentration is treated while neglecting concentration fluctuations. Because electrostatic interactions between adsorbed chains are very strong, they can lead to pronounced correlations. In particular, it is important to consider concentration fluctuations in the direction parallel to an adsorbing surface. A general treatment of concentration fluctuations is not yet available for flexible chains. For semi-rigid polymers, a rough approximation is to assume that semi-rigid polyelectrolytes adsorbed on a surface of opposite charge form a perfect two-dimensional smectic phase where the all the rods are parallel to one of the surface directions and equally spaced in the other direction [11]. A large charge overcompensation is found under certain ionic strength conditions. The total adsorbed polymer charge is $f\Gamma = \tau\kappa / \log(\tau\sigma^{-1}\kappa)$. Charge inversion is thus found at

large enough ionic strength for $\tau\kappa > \sigma$. This model has been extended to highly charged polymers taking into account counterion condensation by Shklovskii and collaborators [21].

For weakly charged polyelectrolytes, concentration fluctuations certainly play an important role and the chains adsorbed on the surface can similarly show a smectic or nematic order. A model where the flexible polymers are treated as rods formed by chains of blobs is presented in [22]. The main result is a strong charge overcompensation obtained in the intermediate ionic strength regime.

5. Concluding remarks

We have described in this short review some of the basic properties of polyelectrolytes adsorbing on planar surfaces at thermodynamic equilibrium. Assuming that the system is in thermodynamic equilibrium is certainly a strong assumption. The electrostatic interaction between chains is strong and the relaxation towards the equilibrium state may be very slow in certain experiments. The adsorbed polyelectrolyte layer can then be trapped in a metastable state. A nonequilibrium theory taking into account adsorption kinetics is needed to understand these experiments. We hope that it will be addressed in future works.

Because polyelectrolyte adsorption is of great importance in more complex situations, we would like to briefly discuss two types of experimental setups. In the first the interactions between surfaces (or large colloidal particles) is mediated by polyelectrolytes, whereas in the second a multilayered adsorption of alternating positive and negative polyelectrolytes is considered.

5.1. Polyelectrolyte adsorption and inter-colloidal forces

The interactions between two planar surfaces coated by polyelectrolytes have been studied using a mean-field approach and scaling arguments by Borukhov et al. [23], and Monte-Carlo simulations by Woodward et al. [24]. Within mean-field theory, a general contact theorem can be obtained and leads to an expression for the inter-surface force in this system. The force is calculated numerically from polyelectrolyte concentration profiles and analytically, in some limits. The principal result shows that overcompensation of surface charges by the polyelectrolyte can lead to effective attraction between two equally charged surfaces.

At low salt concentration, depicted on *figure 3*, strong repulsion between the two surfaces results from depletion of the polyelectrolyte from the inter-surface gap at short separations. At larger separations when the two polyelectrolyte adsorbing layers on each of the surface have a strong overlap, the inter-surface force becomes attractive. The magnitude of this attraction scales as $f^{1/2}$ and its characteristic length scale scales as $l_0/f^{1/2}$. At large inter-surface separations the two surfaces interact only via weak electrostatic repulsion.

At high salt concentration and for highly charged polyelectrolyte $f \lesssim 1$, the polymer contribution to the attraction at short distances scales as f/κ and the characteristic length scale is $\kappa l_0^2/f$. An example is shown on *figure 4*. In the other limit of weakly charged polyelectrolytes, $f \ll 1$, the interaction is repulsive for all surface separations and decays exponentially with a decay length equal to κ^{-1} .

It is worth mentioning that irreversible effects play an important role on inter-surface forces because of very slow kinetics in the process of polyelectrolyte adsorption. In many situations it is a good approximation to consider that the surface excess of adsorbed polyelectrolytes remains constant as the distance between the two plates is varied. In [23] it was shown that attractive forces can be obtained for irreversible adsorption and that their magnitude is larger than the ones corresponding to equilibrium processes.

5.2. Polyelectrolyte multilayers

Polyelectrolyte multilayers are obtained by consecutive adsorption of positively and negatively polyelectrolytes either on a flat surface or on a colloidal particle [25]. If the process is initiated from a charged planar surface, the surface charge can be inverted by adsorption of the first polyelectrolyte layer (of opposite charge) as discussed in the previous sections. The second polyelectrolyte layer is bound to the first layer by polyelectrolyte complexation. A simple Debye–Hückel model has recently been proposed in [26]. This

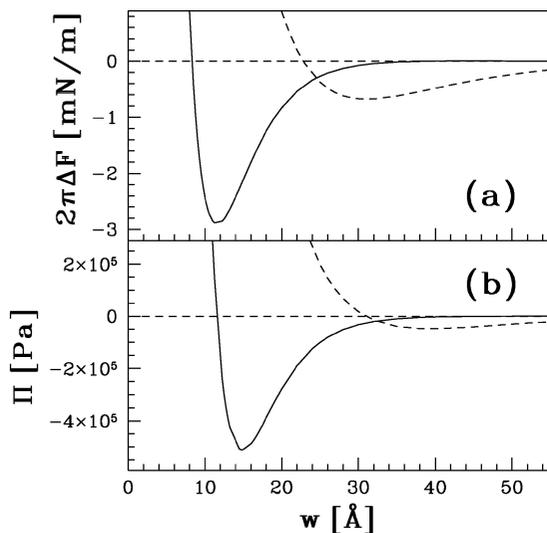


Figure 3. Inter-surface interactions for a polyelectrolyte solution between two surfaces held at a constant potential, $\psi_s = 2$, and in low salt condition, $n = 10^{-6}$ M. (a) The surface free energy $2\pi\Delta F$ as a function of the inter-surface separation w . (b) The force per unit area $\Pi = -\partial\Delta F/\partial w$ between the two surfaces as a function of the separation w . The different curves correspond to different polymer charge: $f = 1$ (solid curve) and $f = 0.2$ (dashed curve). The parameters used for this and the following figures are: non-zero second virial coefficient $v = 50 \text{ \AA}^3$, $a = 5 \text{ \AA}$, and polymer concentration in the bulk 10^{-6} \AA^{-3} . Adapted from [23].

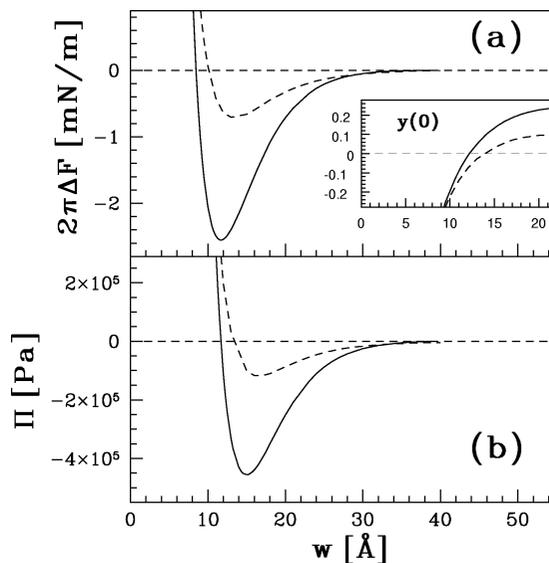


Figure 4. Inter-surface interactions for highly charged polyelectrolytes ($f = 1$) at high salt concentration. (a) The surface free energy $2\pi\Delta F$ as a function of the inter-surface separation w . (b) The force per unit area $\Pi = -\partial\Delta F/\partial w$ between the two surfaces as a function of the separation w . The salt concentration is $n = 0.1$ M (solid curve) and $n = 1$ M (dashed curve). The inset shows the mid-plane values of the electrostatic potential $y(0) = \psi(w/2)$ as a function of w . Adapted from [23].

model predicts charge inversion after adsorption of the second layer, and allows the built-up of alternating positively and negatively charged polyelectrolyte layers by successive complexations. The Debye–Hückel approach is a high temperature approximation which ignores strong association between ions. An alternative approach considering explicitly the formation of ion pairs has recently been proposed by Zeldovich and Khokhlov [27].

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