Adsorption of charged polymers

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Abstract. We review some of the theoretical results that we have obtained recently on the adsorption of polyelectrolytes on surfaces of opposite charge. We consider two problems, the formation of polyelectrolyte multilayers and the formation of complexes between rigid polyelectrolytes and small spheres.

For polyelectrolyte multilayers, the overcompensation of the adsorbing surface charge and the anchoring between consecutive layers are studied.

For polyelectrolyte–sphere complexes, the wrapping of the polymer on the sphere is shown to occur continuously at low ionic strength and discontinuously at high ionic strength.

The findings of some recent experiments are briefly compared with our results.

1. Introduction

Polyelectrolytes are polymers carrying ionizable groups. In a polar solvent such as water, due to the gain in translational entropy, the counterions are released and the polymer chain becomes electrically charged. The long-range character of the electrostatic interaction and the presence of free or almost free counterions lie at the origin of the very specific properties of polyelectrolyte solutions, which have been extensively studied over recent years [1]. In a water solvent the properties of a charged polymer chain can be even more complex, as they also depend on very specific short-range interactions (hydrogen bonding, the hydrophobic effect). These complex effects often induce a local collapse of the polymer chains [2] and will be ignored throughout this paper.

Most water-soluble polymers are in fact polyelectrolytes and polyelectrolytes are therefore an essential component in most problems of the chemistry of formulation in water. They then interact with other components such as colloidal particles or surfactant aggregates. It is of utmost importance to understand in detail the adsorption behaviour of the polyelectrolyte on the particle or aggregate surface, as it governs the complexation between the polyelectrolyte and the various colloidal objects. Polyelectrolytes can be used to monitor either the phase behaviour or the rheology of the solution. Typical examples are paints, for which the rheology is often adjusted by addition of water-soluble polymers, and waste-water treatment, where polyelectrolytes are used to control the flocculation of colloidal particles.

The other important area where polyelectrolytes play an important role is that of biomolecules. Most biopolymers are polyelectrolytes (DNA being a typical example) and the physical description of many biological processes requires the understanding of the interaction between biopolymers and objects of colloidal size such as proteins. Electrostatic interactions often also play a major role here.

In this context, in this short paper, we summarize some of our recent theoretical work on the behaviour of polyelectrolytes at an interface between the water solvent and a solid

surface. We describe two problems, one involving flexible polyelectrolytes—the formation of polyelectrolyte multilayers—and one involving rigid polyelectrolytes—the complexation of small spherical objects by rigid polyelectrolytes.

Polyelectrolyte multilayers, first studied experimentally by Decher, are formed by successive adsorption of positively charged and negatively charged polyelectrolyte from a water solution onto a solid surface. Alternating layers of opposite charges form and one can pile up to 50 layers on the surface. Polyelectrolyte multilayers have a number of potential applications in such areas as non-linear optics or catalysis [3]. The experiments raise a number of interesting fundamental questions such as the possibility of inversion of the charge of a surface by adsorption of a polyelectrolyte with a charge opposite to that of the surface and the complexation between polyelectrolytes of opposite signs that holds consecutive layers in the multilayer. These problems are discussed in the following section using simple mean-field approaches. We find in particular that at low ionic strength the charge of a solid surface can always be inverted by adsorption of a polyelectrolyte of opposite charge; at high ionic strength the possibility of charge inversion depends on the short-range interaction between the monomers and the surface.

The interaction between polyelectrolytes and small spheres of opposite charge is of interest for many problems such as the interaction between polyelectrolytes and spherical surfactant micelles or the formation of the nucleosomal complex between DNA and histone proteins. This question has been extensively studied recently both experimentally and theoretically [5–8]. The aim of our work has been to try to investigate, in the case where the polymer is rigid, the importance of various physicochemical parameters such as ionic strength, the charge and the radius of the sphere, the stiffness and the charge of the polymer. This work is summarized in section 3.

In all of this work, we use the simplest possible model for the electrostatic interactions and our calculations often remain at the Debye–Hückel level. This is a valid approximation for polymers and charged objects with a low charge density but it neglects phenomena such as Manning condensation of the counterions at large charge densities. It will thus not provide a quantitative description of many experiments but we believe that this simplification gives a good insight into the physical mechanisms involved.

2. Polyelectrolyte multilayers

In this section, we discuss the formation of polyelectrolyte multilayers by flexible poly-electrolytes. We first discuss the adsorption of a single chain on a solid surface of opposite charge, then discuss charge inversion in the first layer and finally the formation of the following layers.

The conformation of flexible polyelectrolytes is conveniently described in terms of a blob model. The chain has N monomers of size a and a small fraction f of the monomers carry a charge. The Coulombic interaction between two charges at a distance r is written as $v(r) = kT\ell_B/r$ where ℓ_B is the so-called Bjerrum length (equal to 0.7 nm in water). At short length scales, the electrostatic interactions are not important and the chain remains Gaussian. At large length scales, the electrostatic interactions dominate and the chain is stretched. The average chain conformation can then be viewed as a linear array of Gaussian electrostatic blobs. The size of the blob ξ is fixed by the fact that the electrostatic interaction between two neighbouring blobs is of order kT, $\xi \simeq 1/(f^2\ell_B)^{1/3}$. Each blob contains $g \simeq (\xi/a)^2$ monomers and the radius of the chain is $R = (N/g)\xi \simeq Nf^{2/3}$.

In the vicinity of a surface carrying σ charges per unit area with sign opposite to that of the polymer, the polymer chain is strongly attracted and is confined in a layer of thickness δ

which at high enough surface charge is smaller than the blob size. This thickness results from the balance between the attractive electrostatic force NfE ($E = 4\pi\sigma\ell_B$ being the surface electric field) and the confinement force of the Gaussian blobs [9]. One finds

$$\delta = 1/(4\pi f\sigma\ell_B)^{1/3} \tag{1}$$

where $a/6^{1/2}$ is chosen as the unit of length.

The first layer of a polyelectrolyte multilayer is formed by adsorption of a dilute polyelectrolyte solution on a surface of opposite charge. The layer is dense and can be studied using the standard methods developed to study polymer adsorption. Within the framework of a mean-field theory, the chain conformation is described by the Edwards order parameter $\psi(z)$, related to the local monomer concentration $c(z)$ at a distance z from the adsorbing surface by $c = \psi(z)^2$. The order parameter satisfies the Edwards mean-field equation for a Gaussian chain in an effective external potential:

$$0 = -\frac{\partial^2\psi}{\partial z^2} + (fV(z) + \epsilon)\psi. \tag{2}$$

ϵ is a Lagrange multiplier related to the bulk chemical potential of the chains and V the mean-field potential seen by the chains, i.e. the local electrostatic potential. The electrostatic potential is given by the Poisson–Boltzmann equation which we write in the Debye–Hückel approximation:

$$\frac{\partial^2 V}{\partial z^2} = \kappa^2 V - 4\pi\ell_B f\psi^2. \tag{3}$$

We have supposed here that there is a finite concentration of added salt n and that the inverse square screening length is $\kappa^2 = 8\pi n\ell_B$. The mean-field Edwards equation is based on the so-called ground-state dominance approximation for the conformation of the polymer chains. It thus implicitly assumes that the structure of the adsorbed layer is dominated by the loops that the chains form on the solid surface and it ignores the role of the two tails of the chains. As discussed below, adsorbed polyelectrolyte layers have a very small thickness in most cases and one can check explicitly that the tails play no role, unlike in the case of neutral polymer layers.

This set of two equations has been solved numerically by several authors [10, 11]. We have looked for analytical solutions using asymptotic matching [4]. In the limit where the salt concentration is very low, the thickness of the adsorbed layer is proportional to the single-chain thickness δ. The amount of adsorbed polymer per unit area Γ slightly overcompensates for the solid surface charge $\Gamma = (\sigma + \delta\sigma)/f$, where the charge overcompensation is $\delta\sigma/\sigma \propto \kappa\delta$. In this limit, the mean-field approach always predicts a small charge inversion and the charge inversion vanishes when there is no added salt. When the inverse screening length κ vanishes, the electrostatic free energy of this two-dimensional problem is infinite if the effective surface charge (surface + adsorbed layer) is non-zero and we thus expect exact charge compensation. At finite but very small ionic strength, the charge inversion is due to the formation of loops that maintain some of the charges away from the surface. If the salt concentration is high ($\kappa\delta \gg 1$) the electrostatic interactions are screened and can be described by an effective excluded volume. The monomer concentration in the adsorbed layer decreases then as a power law as for neutral polymer adsorption. The amount of adsorbed polyelectrolyte depends strongly on the short-range non-electrostatic interaction between the polymer and the adsorbing surface. If this surface is a hard wall (infinitely repulsive), there is no adsorption and $\Gamma = 0$. If it shows a short-range attraction which is just at the transition between adsorption and depletion for the monomers (an 'indifferent' surface or, in statistical mechanics language, at the special transition), there is a strong adsorption and overcompensation of the charges, $\Gamma = 2\sigma/f$. In

the following, we consider this case of high ionic strength only. Polyelectrolyte adsorption can thus overcompensate for the surface charge but only if there exist strong enough attractive short-range interactions. The charge inversion allows us then to build up the other layers. The charge overcompensation by an exact factor of 2 is predicted only for an 'indifferent' surface and we do not have any qualitative explanation for the precise value of this factor. In practice, it is better to use a more strongly attractive surface onto which the monomers are adsorbed; the charge overcompensation is then by a factor larger than 2.

After the formation of the first layer, the polyelectrolyte solution (say anionic) is washed off and replaced by another polyelectrolyte solution of opposite sign (say cationic). We will assume that the adsorption is irreversible and that the amount of adsorbed anionic solution remains constant. The formation of the second layer then proceeds by formation of a polyelectrolyte complex. When two polyelectrolytes of opposite charges are mixed, they phase separate in water and form a dense complex. The attractive electrostatic energy can be calculated using the random-phase approximation and a one-loop calculation for the free energy [12]. In the limit of very high ionic strength, for symmetric polymers the complex is neutral, and the concentrations of the two polyelectrolytes are identical and equal to [13]

$$c_K = \frac{3\pi \ell_B^2 f^2}{4\kappa w^2}. \tag{4}$$

The complex is stabilized at the θ-point by the three-body interactions and w^2 is the corresponding third virial coefficient (w is a volume of the order of the monomer volume). The concentration in the complex increases with polymer charge and decreases with ionic strength. Note however that the polymer charge f must remain small—otherwise the Debye–Hückel approach is certainly not valid; at high charges one can expect an ordering of the charges in the complex similar to that in a NaCl crystal.

In the multilayer, a neutral complex is formed between each layer and the consecutive one and the local concentration is c_K. However, if the amount of polymer due to the last adsorption is fixed because of the irreversible adsorption, the new adsorbing polyelectrolyte is at equilibrium with the complex layer and can form loops dangling into the solution outside the complex layer. As the complex is neutral, these loops create the charge inversion that allows for the formation of the following layer. The density in these loops decays as in a neutral polymer adsorbed layer, $c(z) \propto 1/z^2$, and the amount of polymer in one layer is

$$\Gamma_l = \int \mathrm{d}z \, c(z) \propto (\kappa \ell_B)^{1/2}. \tag{5}$$

The amount of polymer in one layer thus increases very weakly with the salt concentration. This is in qualitative agreement with recent experiments performed by means of optical reflectometry [15].

3. Complexation between stiff polyelectrolytes and small spheres

Another parameter that plays a major role in determining the conformation of a polyelectrolyte chain is the stiffness of the chain as characterized by its persistence length. If the bare persistence length ℓ_0 (at very high ionic strength) is smaller that the electrostatic blob size, the chain can be considered as flexible (with a Kuhn length larger than the monomer size, though). If the persistence length is larger than the electrostatic blob size ξ, the chain is rigid and has locally a rodlike behaviour (radius proportional to the number of monomers). It is then more convenient to use the contour length s to describe the chain conformation and to introduce the charge per unit length $\tau = f/a$; the total contour length is denoted by L. The chain is weakly charged and no Manning condensation occurs when $\tau \ell_B \ll 1$.

At finite ionic strength the screened Coulomb interaction between monomers $v(r) = kT(\ell_B/r)\exp{-\kappa r}$ makes the chain stiffer. At large distances the total persistence length is the sum of the bare persistence length and an electrostatic persistence length calculated first by Odijk, Skolnick and Fixman, $\ell_p = \ell_0 + \tau^2\ell_B/(4\kappa^2)$. In fact, the persistence length depends on the length scale: it is the bare persistence length at short length scales and the electrostatic persistence length ℓ_p at large distances. The crossover between these two behaviours occurs for a length scale $s_c = \tau^{-1}(\ell_0/\ell_B)^{1/2}$. The variation of the persistence length with the length scale (or the associated wave vector) has been calculated in reference [1].

Although polyelectrolyte multilayers can also be formed with rigid polyelectrolytes [16], we do not discuss them here; we only consider the interaction between a rigid polyelectrolyte and a sphere of size D smaller than the total persistence length and of opposite charge Z [17] (the other limit of a sphere larger than the persistence length has been studied in [5, 7]).

In the absence of salt, the adsorption of a rigid polyelectrolyte on a planar surface can be studied on the basis of a Flory-like argument. The attractive electrostatic free energy of the chain with a thickness δ, $F_{el}/kT = 4\pi\ell_B\sigma\delta\tau L$, is balanced by the loss of entropy due to the confinement of the bending fluctuations [14], $F_{conf}/kT = L(\delta^2\ell_{eff})^{-1/3}$, where ℓ_{eff} is the relevant persistence length. A more detailed analysis shows that ℓ_{eff} is the bare persistence length ℓ_0. The thickness of the adsorbed chain is

$$\delta = (\sigma\tau\ell_B\ell_0^{1/3})^{-3/5}. \tag{6}$$

For reasonable values of the parameters, this thickness is small—of the order of a monomer size—and in a first approximation the chain lies flat on the surface. If salt is added to the solution, a discontinuous desorption occurs when the screening length is of order δ.

When the polyelectrolyte chain interacts with a sphere of opposite charge Z and size D smaller than its persistence length, it bends in order to wrap around the sphere. If the sphere charge is small enough, the polymer bends only weakly and the total energy of the sphere complex can be expanded in powers of the local curvature $\rho(s)$. We use here a two-dimensional geometry and the Fourier variable q conjugate to s:

$$F/kT = \int \frac{dq}{2\pi}\left(\frac{1}{2}\ell_p(q)\rho(q)^2 - g(q)\rho(q)\right). \tag{7}$$

$\ell_p(q)$ is the persistence length at a wave vector q and g is the first-order expansion of the electrostatic interaction between the sphere and the polymer. Both of these functions are known. The shape of the polymer is obtained by minimization of the free energy and Fourier inversion. It is a hump shape with an inflection point and the two arms of the chain bending away from the sphere at low ionic strength $\kappa D \ll 1$ since the two arms of the polymer strongly repel each other. At high ionic strength the two arms do not interact and the polymer bends towards the sphere. As the charge of the sphere increases, the curvature at the point where the polymer touches the sphere becomes equal to the inverse sphere radius and the polymer must then touch the sphere over a finite length. We call this the touching transition. At weak ionic strength ($\kappa D \ll 1$), the touching transition is obtained from the free energy (7); the threshold is $Z_t \propto (\ell_0/\ell_B)^{1/2}$ if $D > s_c$ and $Z_t = \ell_0/(\tau\ell_B D)$ if $D < s_c$ where s_c is the contour length where the effective persistence length crosses over from the bare value ℓ_0 to the Odijk value dominated by electrostatics. Note that as this transition involves bending at short distances, it depends strongly on the bare persistence length. Above the touching transition the complex is roughly neutral and the polymer length that touches the sphere is $\ell = Z/\tau$.

When the charge of the sphere is further increased, the polymer wraps around the sphere completely; we consider that it wraps when the polymer length in contact with the sphere ℓ is of the order of the sphere radius D. At low ionic strength, the wrapping transition occurs roughly

for $Z_w \propto \tau D$. Formulating a more complete theory is difficult, as it must take into account the detailed conformation of the chain on the sphere and its three-dimensional character. However, the wrapping transition can be obtained from a simple heuristic argument at high ionic strength. If a length ℓ of polymer touches the sphere, the free energy of the complex is the sum of a bending energy $F_B/kT = \ell\ell_p/D^2$ and the electrostatic energy, which in the Debye–Hückel approximation can be written as $F_{el}/kT = 4\pi\ell_B\kappa^{-1}Z\tau\ell/D^2$. These two contributions to the free energy increase linearly with ℓ and the wrapping transition is obtained when the free energy becomes negative, i.e. for a sphere charge

$$Z_w = \frac{\kappa\ell_p}{\tau\ell_B}. \tag{8}$$

Note that the wrapping threshold Z_w is a non-monotonic function of the inverse screening length κ when the persistence length is given by the Odijk–Skolnick–Fixman relation. The minimum occurs for $\kappa^{**} \propto 1/s_c \propto \tau(\ell_B/\ell_0)^{1/2}$.

The phase diagram of the complex including the touching and wrapping transitions is displayed in figure 1 in the limit where the polymer is not too rigid, $\ell_0 \ll \tau^2\ell_B D^2$. There are two characteristic values of the inverse screening length, κ^{**} and $\kappa^{***} \propto (\tau^2\ell_B/\ell_0 D)^{1/3}$. One of the central results is that if $\kappa > \kappa^{***}$, then the wrapping transition pre-empts the touching transition and the wrapping of the sphere by the polymer is a first-order discontinuous transition.
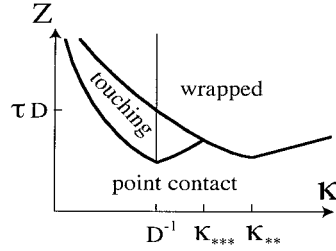

Figure 1. The phase diagram for the complex between a polyelectrolyte and a small sphere. Z is the charge of the sphere and κ the inverse electrostatic screening length.

4. Concluding remarks

We have presented here simple electrostatic models to study two problems associated with polyelectrolyte adsorption on a surface of opposite charge.

We predict that a flexible polyelectrolyte weakly overcompensates for the surface charge upon adsorption at low ionic strength. At high ionic strength charge inversion is obtained only if the polymer has a strong enough attractive interaction with the surface. These predictions were obtained from a mean-field theory that considers only electrostatic interactions. It will be necessary in the future to investigate the roles of both the lateral concentration fluctuations in the layer and the excluded volume. We have also studied here just the asymptotic limits of high and low ionic strength; it is important to study the intermediate range that corresponds to many experiments.

The mechanism that we invoke for the anchoring of the layers in the polyelectrolyte multilayers is the formation of polyelectrolyte complexes. We have discussed it only for very high ionic strength; we predict an amount adsorbed in each layer (or equivalently a thickness of each layer in the dried state after evaporation of the solvent) that increases weakly with the

ionic strength as $\kappa^{1/2}$. We are currently investigating the complex formation and multilayers over the whole range of ionic strength.

Nevertheless, our results seem to be in qualitatively good agreement with recent experiments on polyelectrolyte multilayers [15]. The first layer must be strongly attracted towards the solid surface and our model for the polyelectrolyte complexation seems to reproduce the main experimental results.

The formation of complexes between rigid polyelectrolytes and small spheres has been studied by ignoring the bending fluctuations of the polymer and mostly using a two-dimensional chain conformation. This has allowed us to determine the phase diagram of the complex. Our results are confirmed by a recent numerical minimization of the complex free energy by Kunze and Netz [18], who did not make these approximations. Some effects however still need to be considered, such as image charge effects and non-linear electrostatics. If the charges are so high that the electrostatics becomes non-linear, counterions can strongly condense on the sphere and on the polymer. Upon adsorption, condensed counterions are released and gain a large entropy. In the linear approximation, at low charges, the counterion release is a small effect, but at high charges it can become a dominant effect.

Our results allow the explanation of some of the properties of nucleosome complexes. The nucleosome complex is known experimentally to be stable under physiological conditions but to be unstable against both increase and decrease of ionic strength. This is consistent with the phase diagram of figure 1 which predicts, starting from the wrapped phase, a continuous destabilization of the complex with decreasing ionic strength and a discontinuous destabilization with increasing ionic strength.

Acknowledgment

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