Adsorption of Polyelectrolyte onto a Colloid of Opposite Charge

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We study theoretically an idealized model for the adsorption of a weakly charged polyelectrolyte chain onto an oppositely charged colloidal particle. Within the framework of the self-consistent field theory, and using an analogy with the quantum theory of the atom, we show that the connectivity between the charges of the polymer leads to an "overcharge" of the colloidal particle, which can adsorb a chain of total charge up to $15/6$ times its own charge. [S0031-9007(98)08181-2]

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The motivation for studying the interaction between polyelectrolytes and colloidal particles stems from many sources. First, the presence of polymers, in many cases charged, has a salient effect on the stabilization of colloidal suspensions [1,2]. Industrial applications range from stabilization of ink to wasted water treatment and paper making [1,3]. On the other hand, charged polymers, as building blocks of living matter, are of fundamental importance in biology and biochemistry [4]. Most proteins and nucleic acids, and more generally hydrosoluble macromolecules are charged and their interactions in the intercellular fluid affect the behavior of the cell. Third, the understanding of the interactions between charged chains and another charged object presents a certain theoretical challenge. Despite important efforts [5,6], the understanding of charged systems, which exhibit very distinct properties than neutral polymers, is still largely unsatisfactory. The main complexity introduced by the presence of charges on the chain is the long-range nature of the Coulombic interaction, complicated by such phenomena as the counter-ion condensation [7] and screening effects [8]. For neutral polymers, the interactions are usually short range and scaling or self-consistent field approaches have proved their efficiency [9,10]. For charged chains, on the other hand, even asymptotic results are often model dependent.

The adsorption of polyelectrolytes onto a charged surface has already been actively studied in the past [11,12]. More recently, the self-consistent field approaches were adopted to describe the adsorption of a polyelectrolyte chain onto a flat charged surface. The nonlinear Poisson-Boltzmann equation determining the polymer concentration profile and the amount of polymer adsorbed onto the surface was solved either numerically [13] or after linearization in the limit of weak absorption analytically [14]. The attraction between two like-charged particles via polyelectrolyte adsorption has been investigated as well [15]. The specific problem of the overcompensation of a surface charge by adsorption of polyelectrolyte, namely, the fact that a charged surface may attract a polymer of total charge higher than its own, is nowadays actively studied, either in spherical [16,17] or planar [18] geometries. In those studies, the overcharging is the result of particular configurational considerations [16], and of counter-ion/salt effects [17,18].

In this Letter, we address the problem of the adsorption of a weakly charged chain onto a small colloidal particle of opposite charge. We consider the limit of strong dilution where the colloids can be considered as independent of one another, and we show how the "three dimensional" (spherical) geometry has crucial effects on the chain-colloid system and brings quite a new physics.

Thanks to the classical work of Debye and Hückel [8], the physics of a charged colloid surrounded by a cloud of pointlike ions is now well understood [19]. As is shown below, the most striking effect of the connectivity between the charges of the polyelectrolyte chain is that colloidal particle of charge $-Qq$ is able to absorb a chain of size N and charge fraction f such that at least

$$\frac{fN}{Q} = \frac{15}{6}. \tag{1}$$

The small colloidal particle may thus absorb a chain with a larger total charge than its own, and this charged complex is thermodynamically stable. To prevent any misunderstanding we note that the total neutrality of the system is, of course, preserved by counter-ions in solution. The system is assumed to be very dilute, so that the concentration of counter-ion around the colloid is very low.

As will be developed below, the problem can be thought of as an analog of the Hartree calculation of atomic structures [20]. The result of Eq. (1) has been obtained using a restricted class of trial functions to describe the configuration of the polyelectrolyte chain. A more careful analysis, such as the numerical determination of the distribution function, could show only a larger overcharging effect.

Let us consider a pointlike colloidal particle of charge $-Qq$ in contact with a weakly, homogeneously charged polyelectrolyte chain of N monomers, a fraction f of which carries a charge q. The fraction of charged monomers is supposed to be small enough for the neutral section between the two consecutive charges to be flexible. We also concentrate on the limit of infinite polymer dilution and zero salt concentration, and we neglect any counter-ion effect, the Debye length of the solution being much larger

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than any scale of interest. Such conditions are experimentally accessible [21,22], but they let aside important problems (counter-ions condensation, electrostatic screening, size of the colloidal particle, ...). However, these simplifications allow for a simple analytical treatment of the problem, within the framework of a self-consistent field theory.

The two ingredients of our model polyelectrolyte are the electrostatic interactions and the connectivity between charges. The total electrostatic energy of the charge i located in $\mathbf{r}_i$ consists of two terms: the attraction by the charge $-Q$ of the colloidal particle, and the repulsion by the $f(N-1)$ other charges q of the polyelectrolyte chain. The electrostatic potential experienced by the segment i can be written

$$\phi(\mathbf{r}_i) = -\frac{Q}{\epsilon|\mathbf{r}_i|} + \int d\mathbf{r}\, \frac{qc(r)}{\epsilon|\mathbf{r}-\mathbf{r}_i|}, \tag{2}$$

where $c(r)$ is a smoothed number density of (polyelectrolyte) charges at r, and ϵ is the permittivity of the solution. The connectivity between charges is introduced following Edwards' description of a polymer chain, where the polymer order parameter ψ is defined such as $fN|\psi(\mathbf{r})|^2 = c(\mathbf{r})$. In the situation of ground state dominance [9], the free energy per charge reads

$$F = \int d\mathbf{r}\left\{kT\,\frac{a^2}{6}\,|\nabla\psi|^2 + \Phi(\mathbf{r})\,|\psi(\mathbf{r})|^2\right\}, \tag{3}$$

where k is the Boltzmann constant, T the temperature, and a the averaging distance between neighboring charges. The gradient term accounts for the entropy of the chain, and the potential $\Phi(\mathbf{r})$ describes the electrostatic energy due to all the charges of the system,

$$\Phi(\mathbf{r}) = kTl_b\left(-\frac{Q/q}{|\mathbf{r}|} + \frac{fN}{2}\int d^3r'\,\frac{\psi^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right), \tag{4}$$

where $l_b = q^2/(\epsilon kT)$ is the so-called Bjerrum length of the solution. Note that the potential Φ differs from the electrostatic potential Eq. (2) by a factor of one-half in front of the integral, which avoids the double counting of the charge-charge interaction.

The functional minimization of the free energy Eq. (3), with the normalization condition $\int d^3r\,\psi(r) = 1$, leads to a Schrödinger-like equation for ψ: $\hat{H}\psi = \epsilon_0\psi(\mathbf{r})$ with

$$\frac{\hat{H}}{kT} \equiv -\frac{a^2}{6}\nabla^2 + l_b\left(-\frac{Q/q}{|\mathbf{r}|} + fN\int d^3r'\,\frac{\psi^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right). \tag{5}$$

In this equation, $\hat{H}$ is the Hamiltonian operator of the chain, and ϵ_0 plays the role of a chemical potential which ensures the normalization of ψ.

To calculate the distribution of charges around the colloid, one should solve Eq. (5). However, the self-consistency of the electrostatic potential makes this problem quite hard. Instead, we notice that Eq. (5) is reminiscent of the Hartree equation for an atom, where electrons gravitate around a charged nucleus [20], and this equivalence allows us to take advantage of the numerous computations, both numerical and analytical, of the eigenfunction of electrons in atoms. To calculate the free energy of the complex, we use a function resembling the ground state of the hydrogen atom, to which our problem is equivalent if one lets aside the interactions between the charges of the polyelectrolyte. This trial function has been used by Hartree in the case of more complex atoms as well [23],

$$\psi(r) = \frac{z^{3/2}}{\pi^{1/2}}\,e^{-zr}, \tag{6}$$

where z is the trial parameter which will be determined by minimization of the free energy (3).

Insertion of Eq. (6) into Eq. (3) gives the total energy per charge

$$\frac{E(z)}{kT} = \frac{a^2z^2}{6} - Ql_bz + \frac{5}{16}fNl_bz\,. \tag{7}$$

The minimization with respect to z gives $z^* = 3l_b/a^2Q^*$ and the ground state energy

$$E^* = -\frac{3}{2}\,kT\left(\frac{l_b}{a}\,Q^*\right)^2 \quad \text{with } Q^* \equiv Q - \frac{5}{16}fN\,. \tag{8}$$

This is the main result of this paper. It tells us that because of the connectivity of the polyelectrolyte, a colloid of charge $-Q$ may attract a polyelectrolyte of total charge Nf larger (and opposite), and this up to charges $fN = 16/5Q$. This is very different from the natural result $N \le Q$ for nonconnected ions. It is thus possible to form *stable* charged complexes, since a positively charged chain will tend to collapse onto a negatively charged colloid even if the resulting total charge is larger than zero. At this point, it is necessary to stress that the precise form of the trial function, Eq. (6), is *not* crucial to describe the overcharging we observe, but merely influences the numerical factor (16/5 here).

If $fN < 16/5Q$, the distribution of the segment is obtained by inserting z^* in Eq. (6), and leads to the definition of the collapse radius of the complex $R_{\mathrm{colps}} \equiv a^2/(6l_bQ^*)$. The charge distribution decreases exponentially over this length if $Q^* > 0$, and the chain is collapsed onto the colloid. When $Q^* < 0$, the charge of the chain is too large for the polymer to be entirely collapsed. One may then expect the formation of a starlike complex where parts of the chain are collapsed and parts are stretched away from the core, the size of these branches being linear in the number of charges they contain. Our description of the collapsed state does not take into account the hard core repulsion between monomers. It is clear that if the collapse radius R_{colps} is smaller than the radius corresponding to the close packing configuration ($R_{\mathrm{pack}} \propto N^{1/3}b$ where b the monomer size) the latter would better characterize the size of the complex.

At this point, we need to investigate the validity of our treatment. An isolated, weakly charged, flexible polyelectrolyte can be pictured as a "rod" formed by electrostatic blobs of size $\xi = b(f^2 l_b/b)^{-1/3}$ [5]. The chain is Gaussian inside a blob, while the interactions between blobs are essentially electrostatic. The adsorbed polymer chain considered in this work is pictured as wrapped around the colloidal particle, forming a layer of thickness h defined by either R_{colps} or R_{pack}. It is thus necessary that the polymer be flexible (Gaussian) on the scale of the corona. Taking $h = R_{\text{pack}}$ and $b \simeq l_b$, the condition becomes $f \sim 1/\sqrt{N}$. For typical polymer sizes, we obtain $f \sim 5\%$, a fraction accessible experimentally. Furthermore, this constraint is less strong when the radius of the colloid is larger.

The self-consistent field approach is usually valid if the interactions between components are less than the thermal energy kT [9]. This assumption is certainly not valid deep in the core of the colloid-polyelectrolyte complex, where the charges are in close contact, but should be satisfied in the outskirts of the charge distribution for $r \simeq R_{\text{colps}}$. Our treatment should thus enable us to determine whether the polyelectrolyte is in a collapsed (R_{colps} finite) or unbounded state ($R_{\text{colps}} \rightarrow \infty$). A related assumption is the one of the ground state dominance, which requires that the difference between the energies of the first excited state E_1 and of the ground state E_0 of the polymer is much larger than kT. It is reasonable to assume that E_1 is of the same scaling form as $E_0 = fNE^*$, where E^* is given by Eq. (8), which leads to the condition $fNE^* > kT$. In summary, the system should be close enough from the collapse to unbounded transition and the polyelectrolyte should be large enough: $l_b < R_{\text{colps}} < fNl_b$.

Another approximation is the use of a class of trial function instead of the solution of Eq. (5). The validity of this approximation is difficult to estimate without performing the full numerical resolution of Eq. (5). In atomic physics, the chosen trial function turns out to be very close to the solution obtained by numerical minimization of the free energy (see [20] and reference therein). This is a good indication that such a class of trial function is satisfactory for our problem as well. Furthermore, it has already been mentioned that the precise form of the trial function is not crucial. It merely influences the numerical factor (16/5 here; see next paragraph). One effect not taken into account by the use of a smoothly varying distribution function is the existence of large loops in the polyelectrolyte configuration, which may stretch away from the charged complex. However, even if such loops exist for a polymer in the bound state, one can expect that they do not participate in the electrostatic balance, and can only increase the overcharging effect.

A major approximation of this work is the pointlike nature of the colloidal particle. This is a sensitive point since the overcharging effect does not exist for a flat surface (it can arise due to the counter-ions [18]), which indicates that a crossover must exist for a finite particle radius. The use of the wave function of the electron in an hydrogen atom in the $2p$ state [24] can give indications on the influence of the radius of the colloid [25]. It defines the lowest energy state of the hydrogen atom which has a zero probability at the origin. For a colloidal particle of radius R, we write it $\psi_2 = \alpha(r - R)e^{-z(r-R)}$, where α is a normalization factor. If $R = 0$, we obtained the same results as before, with $Q^* = Q - 93/256fN$ and $E^* = -9/8(l_b/aQ^*)^2$ instead of Eq. (8). We can thus qualitatively describe the overcharging effect with this trial function as well. We have studied the variation of the free energy Eq. (3) and the optimum inverse decay length z^* [Eq. (8)], with the radius of the colloid. The main effect of an increase of the colloid radius is to decrease the energy scale. Hence, we have defined the maximum radius for which the overcharging effect can still be observed, by the radius for which the minimum of energy for $N = Q + 1$ is of order k_BT. One can easily show that this criterion gives a maximum radius $R_{\max} = \beta Q l_b$, beyond which there is no overcharging (β is a numerical factor which is equal to $1/2$ with this given trial function). Interestingly, this condition is reminiscent of the condition for the condensation of counter-ions onto a charged sphere, to within a factor which contains the logarithm of the counter-ion concentration [26]. One can thus expect an interesting competition between counter-ion condensation and overcharging due to polyelectrolyte adsorption in less dilute colloidal solutions. One should notice that if the charge of the colloid is mostly located at its surface, the charge and the size of the particle are related by $Q \sim (R/b)^2$ where b is a molecular size, and the condition for overcharging becomes $R > b^2/l_b$.

The previous description should hold as long as the colloid can be considered as a sphere for the polymer adsorption. When the thickness of the adsorbed layer becomes of the order of the radius of the colloid ($R \sim R_{\text{colps}} = bN^{1/3}$), the behavior of the adsorbed chain should cross over smoothly to the behavior of a polyelectrolyte adsorbed onto a charged flat surface. Hence, the overcharging effect should be present for $b^2/l_B < R < bN^{1/3}$, which defines a very large range of radii. Note that the upper bound is probably much higher than computed above, where we have supposed a close packing situation in the adsorbed corona.

Several extensions of this work could be of interest. Upon increasing the concentration of colloids, one may wish to investigate the creation of bridges formed by a polyelectrolyte chain adsorbed onto several particles [15]. This bridging effect, of crucial importance for colloid-colloid interaction and the stabilization of colloidal suspension, could be investigated using the Hartree formalism. If one assumes that the form of the polymer distribution function around a colloid is only weakly affected by the presence of other colloids, one can associate the formation of bridges with the overlapping of the distribution functions around two colloids. It is not clear how well the chosen trial function could describe the bridged state, and this question is currently under investigation.

Another effect in more concentrated systems is the screening of the electrostatic interactions due to the increase of the counter-ion concentration around the charged complex. Such a screening can also be observed by the adjunction of salt in the solution. The simplest way to deal with the screening is to substitute the Yukawa screened electrostatic potential to the simple $1/r$ potential in Eqs. (2) and (4). However, such a procedure would not describe properly a possible rearrangement of the polymer layer. The electrostatic repulsion felt by a given monomer when the colloid is overcharged would be screened by the counter-ions if this monomer is beyond the screening length. This would lead to an increase of the total charge of the complex. We have seen that the reversal of the colloid charge, and the counter-ion condensation onto the colloid are related effects. A loop in the polymer distribution might lead to the condensation of counter-ions. The effective charge of the colloid, along with the charge reversal, would then be reduced. In summary, the presence of a second length (the Debye length λ_D) leads to a much more complex situation. If this length is much larger than the collapse radius, the present description is correct. If $\lambda_D \ll R_{\text{colps}}$ on the other hand, the interaction potential will be the Yukawa potential, and the overcharging effect is weakened. The most complex and interesting case arises when both lengths are of the same order. This situation necessitates a much more thorough study, beyond the scope of the present work.

Finally, we have seen that the geometry of the colloidal particle is of great importance in this problem. It would be enlightening to derive the polymer distribution function for any size of the colloidal particle radius. This way, we could describe more rigorously the crossover sketched above, between a small spherical colloid with an important charge reversal, and the limit of a flat surface, where no overcharging is observed.

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