

## Conformation of a polyelectrolyte complexed to a like-charged colloid

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We report results from a molecular dynamics simulation on the conformations of a long flexible polyelectrolyte complexed to a charged sphere, *both negatively charged*, in the presence of neutralizing counterions in the strong Coulomb coupling regime. The structure of this complex is very sensitive to the charge density of the polyelectrolyte. For a fully charged polyelectrolyte the polymer forms a dense two-dimensional “disk,” whereas for a partially charged polyelectrolyte the monomers are spread over the colloidal surface. A mechanism involving the *overcharging* of the polyelectrolyte by counterions is proposed to explain the observed conformations.

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Polyelectrolytes in polar solvents are polymers carrying dissociated ionic groups. When a polyelectrolyte is in the vicinity of a charged colloidal particle, both may coagulate leading to *charge complexation*. Studying this process is motivated by many sources. The presence of polyelectrolytes has important effects on the stabilization of colloidal suspensions [1]. Besides that, for polyelectrolytes such as DNA the interaction with the interface of charged membranes or charged particles (histones) is crucial for many biophysical properties [2]. Finally long-range Coulomb interactions represent a theoretical challenge, especially for the understanding of effective attractions between like-charged bodies [3–6].

The adsorption of polyelectrolytes onto an *oppositely* charged spherical particle has recently been experimentally extensively studied [2,7–9]. Various authors have also investigated this phenomenon theoretically [10–16] and by numerical simulations [17–19]. However, much less is known concerning the complexation of a charged sphere with a like-charged polyelectrolyte. To our knowledge there has been no study in this direction until now.

In this paper, we report the rather unexpected complexation between a charged sphere and a long flexible polyelectrolyte, both like (here negatively) charged. This paper constitutes an attempt to elucidate this striking phenomenon. We present results of molecular dynamics (MD) simulation of the two macroions taking into account the counterions explicitly, but add, for simplicity, no salt. We propose a mechanism stemming from the polyelectrolyte overcharging to explain the complexation structure as well as the observed polyelectrolyte conformations.

The MD method employed here is based on the Langevin equation and is the same as the one employed in previous studies [20]. Consider within the framework of the primitive model one spherical macroion characterized by a radius  $r_0$  and a bare charge  $Q = -Z_M e$  (where  $e$  is the elementary charge and  $Z_M > 0$ ) surrounded by an implicit solvent of relative dielectric permittivity  $\epsilon_r$ . The polymer chain is

made up of  $N_m$  monomers of diameter  $l$ . Both ends of the chain are always charged. The monomer charge fraction is  $f$  (i.e., every  $1/f$  monomer is charged) so that the chain contains  $N_{cm} = (N_m - 1)f + 1$  charged monomers. The monomer charge is  $q_m = -Z_m e$  (with  $Z_m > 0$ ). To ensure global electroneutrality we added  $N_c$  small counterions of diameter  $\sigma$  and charge  $+Z_c e$  (with  $Z_c > 0$ ). The whole system is confined in an impermeable spherical cell of radius  $R$ , and the spherical macroion is held fixed at the center of the cell. The dielectric permittivity is the same everywhere, in and outside the cell.

Except for the spherical macroion all particles are mobile. Excluded volume interactions are introduced via a pure short-range repulsive Lennard-Jones potential given by

$$U_{LJ}(r) = 4\epsilon_{LJ} \left[ \left( \frac{\sigma}{r-r_0} \right)^{12} - \left( \frac{\sigma}{r-r_0} \right)^6 \right] + \epsilon_{LJ} \quad (1)$$

for  $r - r_0 < 2^{1/6}\sigma$ , and 0 otherwise. We have set  $r_0 = 7\sigma$  for the macroion-counterion interaction, and  $r_0 = 0$  otherwise. The length and energy simulation units are defined by  $\sigma$  (counterion diameter) and  $\epsilon_{LJ}$ , respectively. The closest center-center distance of the ions to the spherical macroion is  $a = r_0 + \sigma = 8\sigma$ . The macroion volume fraction is defined as  $f_M = (a/R)^3$  and was fixed with  $R = 40\sigma$  to  $8 \times 10^{-3}$ .

The electrostatic interaction between any pair  $ij$ , where  $i$  and  $j$  denote either a macroion or a charged microion (counterion or charged monomer), reads

$$\frac{U_{coul}(r)}{k_B T} = l_B \frac{Z_i Z_j}{r}, \quad (2)$$

where  $l_B = e^2/4\pi\epsilon_0\epsilon_r k_B T$  is the Bjerrum length. To link this to experimental units and room temperature we denote  $\epsilon_{LJ} = k_B T$  ( $T = 298$  K). Being interested in the strong Coulomb coupling regime we choose the relative permittivity  $\epsilon_r = 16$ , corresponding to  $l_B = 10\sigma$  (with  $\sigma = 3.57$  Å), divalent microions ( $Z_m = Z_c = 2$ ) and  $Z_M = 180$ .

The polyelectrolyte chain connectivity is modeled by using a standard anharmonic finitely extensible nonlinear elastic (FENE) potential in good solvent (see, for example, Ref. [21]), which reads  $U_{FENE}(r) = -\frac{1}{2}\kappa R_0^2 \ln[1 - r^2/R_0^2]$ , where  $\kappa$

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TABLE I. Simulation parameters for runs *A*, *B*, *C*, and *D*.  $f$  denotes the charge fraction,  $N_m$  the total number of chain monomers,  $N_{cm}$  the number of charged chain monomers, and  $N_c$  the total number of counterions.

Run	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
$1/f$	1	2	3	5
$N_m$	256	257	256	256
$N_{cm}$	256	129	86	52
$N_c$	346	219	176	142

is the spring constant chosen as  $1000k_B T/\sigma^2$  and  $R_0 = 1.5\sigma$ . These values lead to an equilibrium bond length  $l = 0.8\sigma$ .

Four different parameter combinations, denoted by run *A*, *B*, *C*, and *D*, were investigated and are summarized in Table I. Going from run *A* to *D* we decreased the charge fraction  $f$  from 1 to 0.2, and thereby decreased the linear charge density  $\lambda_{PE}$  of the polyelectrolyte. The contour length of the chain is much larger than the colloidal particle diameter [ $N_m l / (2r_0) \approx 14$  times], so that in principle the chain can wrap around the colloidal particle several times.

Figure 1 shows typical equilibrium configurations of the colloid-polyelectrolyte complex. Note that in all reported cases complexation occurs and the polyelectrolyte is completely adsorbed on the colloidal surface. However, the structure of the resulting complexes depends strongly on  $f$ . For the fully charged polyelectrolyte case [see Fig. 1(a) with  $f = 1$ ] the chain monomers are closely packed together with their counterions forming a two-dimensional dense aggregate. This conformation consists of alternating lines made of monomers and counterions, respectively. When the linear charge density is reduced [see Figs. 1(b) and 1(c)], the complex structures are qualitatively different. In these cases the chain monomers are no longer densely packed. For run *B* [Fig. 1(b)], the monomers spread more over the colloidal surface and the polymer chain partially wraps around the sphere suggesting almost a surface pearl necklace structure. For run *C* [Fig. 1(c)], the chain wraps entirely over the colloidal surface, leading to a quasi-isotropic distribution of the monomers around the spherical macroion.

The physical reason of the complex formation is due to the strong counterion mediated attractions. Basically, the charged species is trying to crystallize in a way that is compatible with the topological constraints (here mainly the chain connectivity and the macroion surface).

To quantify the adsorption of the chain monomers and counterions on the macroion surface, we look at the observable  $P(r)$ , being defined as the amount of monomers (counterions) reduced to the total number of monomers ( $N_m$  (the total number of counterions  $N_c$ )) within a distance  $r$  from the spherical macroion center. Results are depicted in Fig. 2, where we observe for all runs that the particles are condensed within a distance of about  $10\sigma$  from the colloid center and more than 80% of the monomers and counterions are within a distance of  $9.3\sigma$  from the colloid center, corresponding roughly to two particle layers. Due to strong electrostatic attraction between the sphere and the counterions and strong electrostatic repulsion between the sphere and the

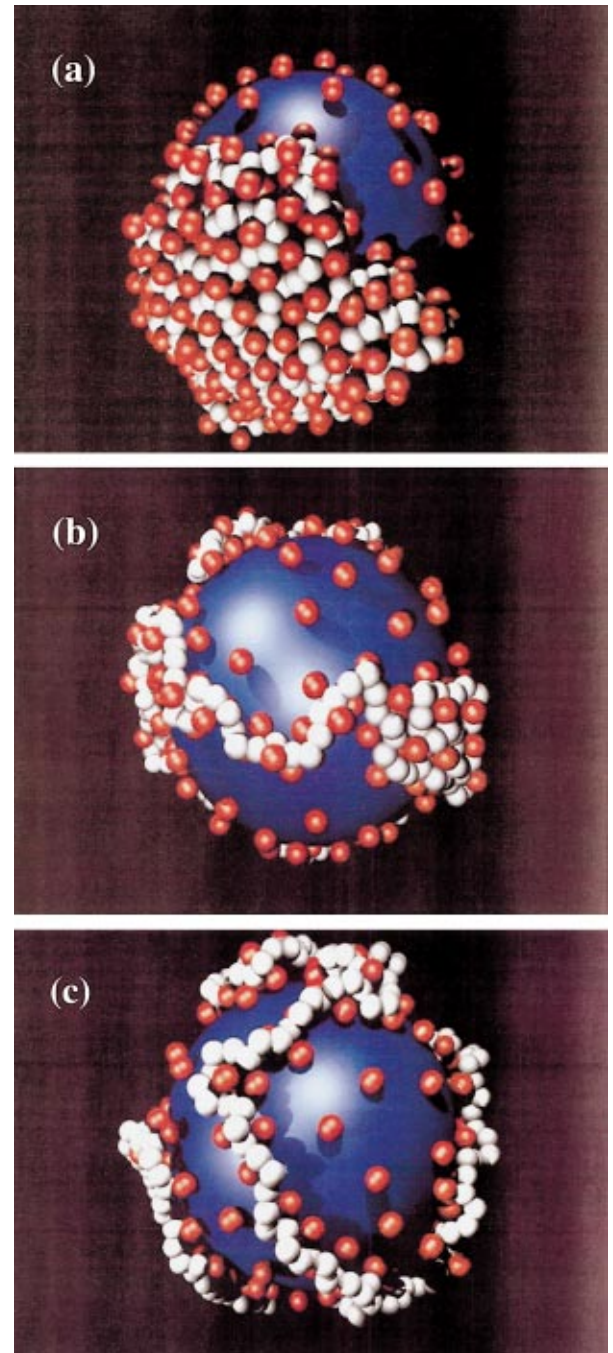


FIG. 1. (Color) Typical equilibrium configurations of the colloid-polyelectrolyte complex for (a) run *A* ( $f = 1$ ), (b) run *B* ( $f = 1/2$ ) and (c) run *C* ( $f = 1/3$ ). Monomers are in white and counterions in red.

charged monomers, the first layer ( $r \sim a = 8\sigma$ ) is exclusively made up of counterions. Note that the monomer depletion in this first layer also concerns *neutral* monomers (runs *B–D*) and this effect is attributed to the chain connectivity. The charged monomers in the second layer repel each other strongly, and keep for high values of  $f$  the chain under tension and, thus, the neutral monomers almost out of the first layer. The second layer consists of both, chain monomers and counterions.

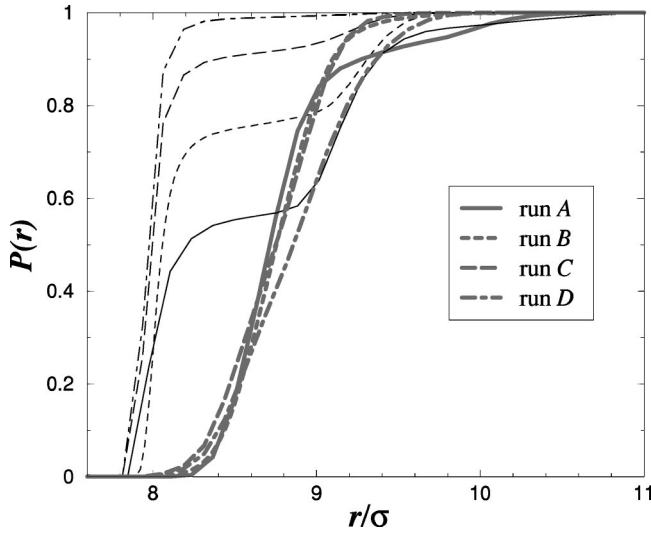


FIG. 2. Fraction of counterions (thin lines) and monomers (thick lines) adsorbed on the spherical macroion as a function of the distance from its center.

Next, we investigate the radius of gyration  $R_g$  (in three dimensions) of the chain in order to gain insight into the spreading of the monomers over the sphere. Results are reported in Fig. 3. It clearly indicates that  $R_g$  increases with increasing  $f$ , which demonstrates that the spreading of the monomers over the macroion surface is enhanced by decreasing the polyelectrolyte charge density. The jump in  $R_g$  is particularly large between the results for  $f=1$  and  $f<1$ . This is in agreement with the visual inspections of the polymer conformations presented in Fig. 1. Moreover, the isotropic case (monomers fully spread over the particle) corresponding to  $R_g \sim a+l=8.8\sigma$  is already reached for  $f=1/2$  (run B).

In the following we are going to argue that the polyelectrolyte *overcharging* is a fundamental key to explaining the observed complex structure. Let  $N_{cd}$  be the number of *con-*

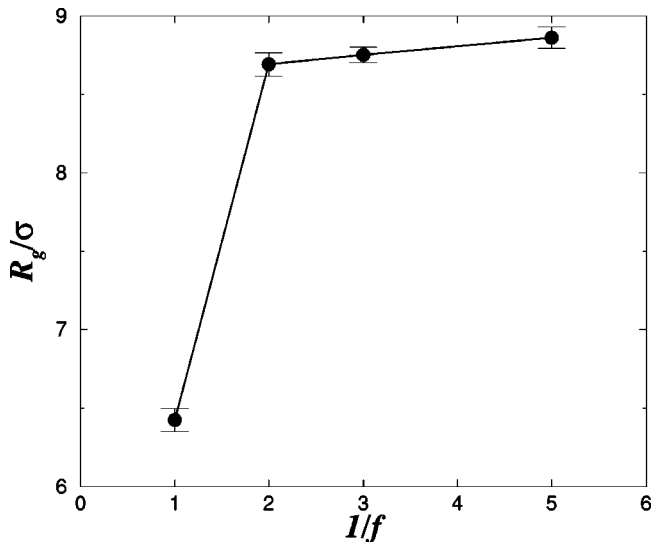


FIG. 3. Radius of gyration of the polymer as a function of the monomer charge fraction  $f$  (runs A–D).

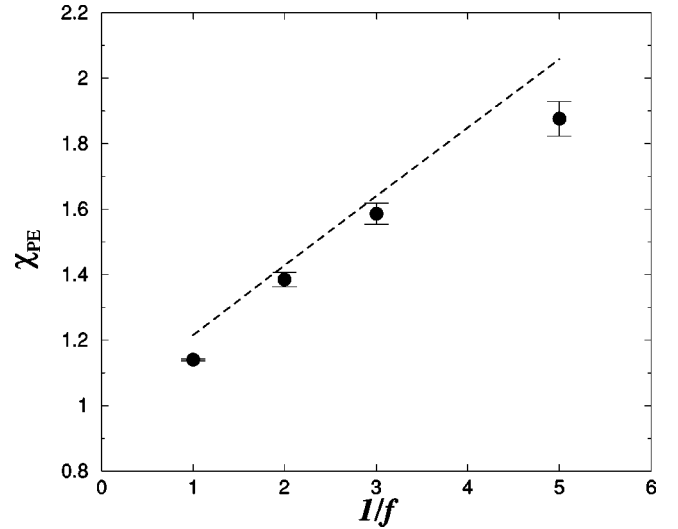


FIG. 4. Polyelectrolyte overcharge as a function of the monomer charge fraction  $f$  (runs A–D). The dashed line corresponds to the theoretical prediction where Eq. (4) was used.

*dened* counterions on the polyelectrolyte where counterions are assumed to be condensed onto the polyelectrolyte when they lie within a distance  $r_c=1.2\sigma$  to the nearest chain monomer. Then the overcharging ratio  $\chi_{PE}$  is defined as

$$\chi_{PE} = \frac{N_{cd}}{N_{cm}}, \quad (3)$$

which is merely the ratio between the amount of the *total* condensed counterion charge (on the chain) and the polyelectrolyte *bare* charge.

This overcharging can also be analytically predicted by the simple assumption that the *uncondensed* counterions, i.e., those who are not “attached” to the chain, have the same *surface* pair distribution as in the case where the polyelectrolyte and its condensed counterions are absent, i.e., where we just have the macroion and its condensed counterions present [23]. This allows us to consider the polyelectrolyte chain as a neutral object, namely the bare charged chain plus its own neutralizing counterions, which then in turn gets overcharged by intercepting all counterions of the macroion which are thought of being uniformly distributed over the macroion surface. We consider counterions as belonging to the chain if their center lies within a ribbon of width  $2r_c$  and area  $A_{rib}=2r_c N_m l$ . If  $c$  is the counterion (of the macroion) concentration then the theoretical overcharge  $\chi_{th}$  is merely given by

$$\chi_{th} = 1 + \frac{A_{rib}c}{N_{cm}} = 1 + \frac{2r_c N_m l Z_M}{N_{cm} Z_c 4\pi a^2}, \quad (4)$$

and for  $N_m \gg 1$  we have

$$\chi_{th} \sim 1 + C/f, \quad (5)$$

where  $C=2r_c l Z_M / Z_c 4\pi a^2$ .

Results are presented in Fig. 4. It indicates that in all



cases overcharging is present (i.e.,  $\chi_{PE} > 1$ ), and that  $\chi_{PE}$  increases with decreasing polyelectrolyte charge density. We have excellent agreement (less than 10% difference) between the simulational results and our toy model [Eq. (4)]. In turn it explains why  $\chi_{PE}$  varies quasilinearly with  $1/f$ .

The  $f$  dependency of the complexation structure can be explained with this overcharging. Indeed, in terms of many-body physics the *overcharged polyelectrolyte* can be seen as a *dressed* (or *renormalized*) particle [bare particle + clothing] with a new *effective* (or *renormalized*) linear charge density  $\lambda_{PE}^* = -(\chi_{PE} - 1)\lambda_{PE}$ , which has an opposite sign to the bare linear charge density  $\lambda_{PE}$  [24]. In this respect, one can also define a *renormalized* charged monomer of effective charge

$$q_m^* = -(\chi_{PE} - 1)q_m. \quad (6)$$

Using Eq. (6) and the results of Fig. 4 this shows that the absolute value of  $q_m^*$  increases with increasing  $1/f$ , and, therefore, the *renormalized* polyelectrolyte self-interaction leads to a stronger *effective monomer-effective monomer* repulsion, which in turn explains why the chain expands with increasing  $1/f$  (see Figs. 1 and 3 for the corresponding structures) [25].

In summary, we have shown that in the strong Coulomb coupling regime, a charged spherical macroion and a long polyelectrolyte can make a complex even if both carry *many like charges*. The resulting structure of the charge complex depends strongly on the linear charge density of the chain. For a fully charged polyelectrolyte, its chain monomers and condensed counterions are densely packed and the polymer wraps only partially the sphere. By decreasing the linear charge density, the wrapping becomes complete. The resulting polyelectrolyte conformations can be explained by the degree of *overcharging* of the polyelectrolyte, which in turn depends on its linear charge density.

A future study will include many other important effects, such as chain length and flexibility, enlarged permittivity constant (weaker Coulomb coupling), added salts, and microions valence to name just the most important parameters. Nevertheless, our observations should trigger new theoretical and experimental works.

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- [23] This statement mainly holds for the first correlational peak, which is the most important for the present discussion (see Ref. [22] for a detailed study).
- [24] This argument assumes that the ions (charged monomers + condensed counterions) distribution along the chain is uniform. This should be relatively well satisfied since the bare charged monomers are already uniformly distributed.
- [25] This reasoning holds in the strong Coulomb coupling regime where the polymer conformation is essentially dictated by the charged (effective) monomers.