Theor Chem Acc (2003) 110: 126–129
DOI 10.1007/s00214-003-0466-y

Theoretical
Chemistry Accounts

Regular article

Nonlinear electric response of polyampholytes

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Received: 22 March 2002 / Accepted: 11 July 2002 / Published online: 16 September 2003

Abstract. The behavior of polyampholytes (PAs) in electric fields is investigated by Monte Carlo simulations. In bulk it is found that the response of the PA depends on the charge sequence. For small repeating units of positive and negative charges the response is linear, while bigger units results in a nonlinear response in both the induced dipole moment and the resulting polymer conformation. This is reflected in how PAs modify colloidal suspensions, and while PAs always decrease the repulsion between charged colloidal particles, some net-neutral PAs can even induce an effective attraction between the colloidal particles.

Keywords: Polyampholytes – Monte Carlo simulations – Colloidal stability – Linear response

Polymers with a large response to an external electric field are of great interest in many areas of nanoscale sciences. In this article we describe charged polymers, so-called polyampholytes (PAs), which have this attractive feature. Computer simulations show that when a PA is exposed to an electric field it can display a very large and nonlinear conformational response. This property could be used to convert electrical energy into mechanical energy, which is essential when designing molecular machines, for example motors and artificial muscles [1, 2]. Furthermore, the same type of polymer can be used as a field sensor [3], as these easily detectable size changes will arise from variations in the electrochemical environment. In addition to reporting general properties of PAs in electric fields, we also describe how structural features of PAs can be used to great effect in colloidal chemistry.

PAs are charged polymers with both positively and negatively charged monomers. This class of polymers is widely used as modifiers of colloidal stability in, for example, the photographic, pharmaceutical and food industries. Competition between the different charges on the polymer gives them a rich phase behavior [4]. The polymer conformation not only depends on electrostatic parameters, such as the net charge and the charge distribution, but also on common polymer properties, such as chain size, stiffness, hydrophobicity [5, 6, 7, 8, 9, 10, 11]. Another interesting characteristic of PAs is that charged surfaces attract net-neutral PAs, and even PAs with a net charge of the same sign as the surface [10, 12, 13, 14, 15].

In the work presented here, PAs are modeled as N charged hard-sphere monomers, with a diameter d, connected by springs with a force constant K. Two sets of Monte Carlo (MC) simulations were performed. One with a single PA in an external electric field and one with PAs together with colloidal particles. All the simulations were carried out in the so-called primitive model whereby the solvent is described by the dielectric constant ϵ_r.

The total energy for the system is given by

$$U_{\text{tot}} = U_{\text{bond}} + U_{\text{el}} + U_{\text{hc}} + U_{\text{ext}} \tag{1}$$

where $U_{\text{bond}} = \sum_{i=1}^{N-1} \frac{K}{2} |\mathbf{r}_i - \mathbf{r}_{i+1}|^2$ comes from the harmonic springs and $|\mathbf{r}_i - \mathbf{r}_{i+1}|$ is the distance between consecutive monomers. $U_{\text{el}} = \sum_{i<j}^{N} \frac{q_i q_j e^2}{4\pi\epsilon_r\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|}$ is the electrostatic energy between the monomers, q_i is the valency of monomer i and e is the elementary charge. U_{hc} is a hard-core cutoff given by

$$U_{\text{hc}} = \begin{cases} 0, & |\mathbf{r}_i - \mathbf{r}_j| \geq d \\ \infty, & |\mathbf{r}_i - \mathbf{r}_j| < d \end{cases} \tag{2}$$

and U_{ext} is the energy due to interactions with an external electric field.

In the case with added colloidal particles, the system, consisting of two charged colloids, their counterions and a PA chain, is confined to a spherical cell and no interactions are allowed outside the cell. Thus, the cell radius R_c determines the concentration of the solution.

In the simulations reported here the following parameters were used: $N = 40$, $d = 4$ Å, $K =$

Contribution to the Björn Roos Honorary Issue

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14×10^{-3} N/m and $\epsilon = 78$ (the value for water at 298 K). All monomers have a charge of either +1 or −1 and the total chain charge is zero. The colloidal particles have a radius of 10 Å and charge, Q, of −10, −15 or −20. The cell radius was chosen to be 100 Å. The simulations were carried out in the canonical ensemble. All the particles were displaced randomly, except for the colloids, which were moved symmetrically along a central axis through the cell. The energies were computed from Eq. (1) and moves were accepted according to the Metropolis MC scheme [16, 17].

When such a PA is placed in an electric field, a dipole moment is induced. This is shown for PAs with different types of charge sequences in Fig. 1. For the chain with a sequence of alternating positive and negative charges, the induced dipole moment responds linearly to the field at all strengths. For the chains with a larger block size, the linear response only holds at low field strengths. At a critical value of the applied field, the induced dipole moment undergoes a transition, whereby it will increase manyfold. Figure 1 shows that the bigger the block size the smaller is the critical field strength at which this transition appears. The increase of the induced dipole moment is also larger and rapider for large block sizes. The initial regime of linear response to the applied field defines the polarizability of the PA.

Accompanying the sudden increase in the induced dipole moment at the critical field strength is a dramatic change of the PA conformation. Snapshots of a PA in electric fields of different strengths are shown in Fig. 2. It is clear that in a weak electric field the PA maintains a globular structure with only a modest induced dipole moment (Fig. 2b), while above the critical field strength the PA is dramatically unfolded (Fig. 2c).

The unfolding of both the triblock PA (+10, −20, +10) and the alternating PA with a block size of 10 (+10, −10, +10, −10) seems to take place in distinct steps as indicated from the curves in Fig. 1. We can speculate that these steps can be made more distinct and tailored to specific electric field strengths by varying parameters such as the line charge density or the polymer stiffness.

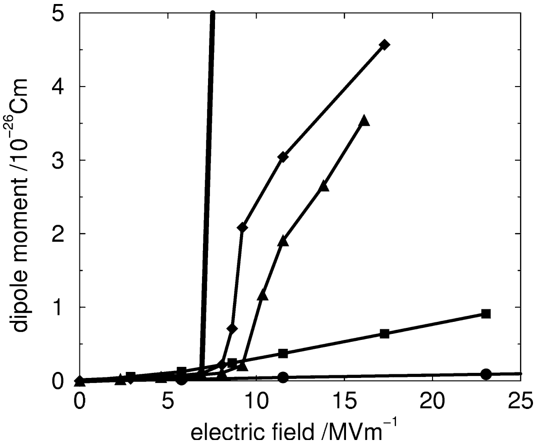

Fig. 1. The induced dipole as a function of an external electric field for different polyampholytes (PAs) with a chain size $N = 40$. The chains are: an alternating chain with a block size of 1 (+1, −1, +1, −1, ...) (*circles*), an alternating chain with a block size of 4 (+4, −4, +4, −4, ...) (*squares*), a triblock chain (+10, −20, +10) (*triangles*), an alternating chain with a block size of 10 (+10, −10, +10, −10) (*diamonds*) and a diblock chain (+20, −20) (*thick line*)

Another interesting question is how the nonlinear response of PAs will affect interactions in colloidal dispersions. This problem can be studied qualitatively with simulations of a simple model system consisting of two charged spherical colloids with neutralizing counterions and a PA chain. The most important result from the simulations is the free energy of interaction between the two colloidal particles as shown in Fig. 3.

In general it is found that addition of PAs will reduce the double-layer repulsion between the colloidal particles. With a few exceptions, the lowering is more significant for PAs with large block sizes. For weakly charged colloids, where the electric field experienced by the PA is lower than the critical value, the reduction of the double-layer repulsion is related to the linear PA polarizability. If the colloid charge is increased, standard Derjaguin–Landan–Verwey–Overbeck theory [18, 19] would predict a stronger repulsion. However, in the presence of PAs, the opposite is found and, in some cases, there is even an effective attraction between the colloids. For example, in the presence of a diblock PA the free energy of interaction between the two charged colloids becomes more attractive the higher the colloidal charge is (Fig. 3a). This behavior is a direct consequence of the "unfolding" seen in Fig. 2c.

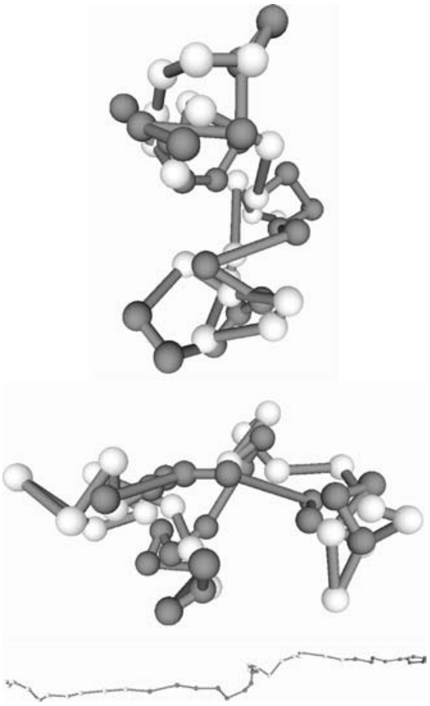

Fig. 2. Snapshots from Monte Carlo simulations of an alternating PA with a block size of 10, $N = 40$ and bond length of 10 Å at different electric fields: **a** $E = 0$ V/m, **b** $E = 7$ MV/m and **c** $E = 17$ MV/m. The pictures are drawn to different scales as the monomer size indicates. The pictures were produced with GISMOS [22]

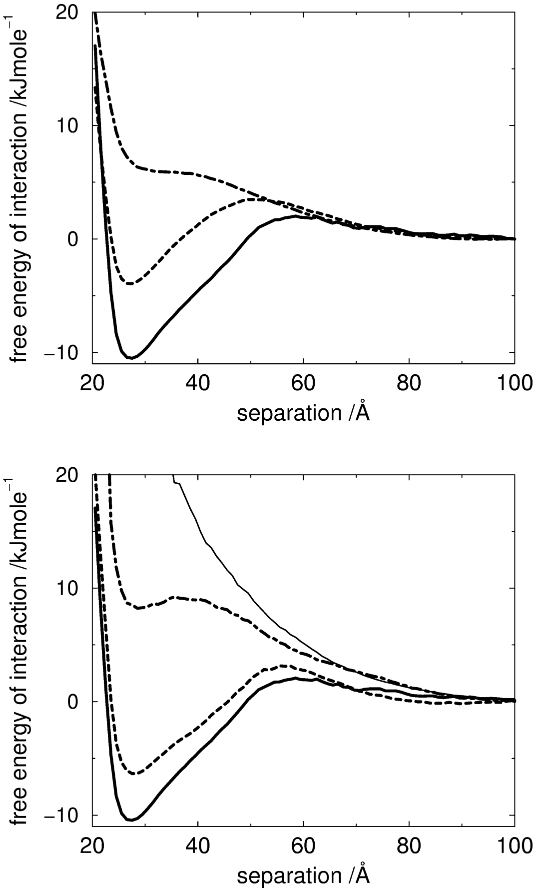

Fig. 3. The free energy of interaction between charged spheres in the presence of a PA with $N = 40$. **a** A diblock chain with colloids of charge $Q = -10$ (*dot-dashed line*), $Q = -15$ (*dashed line*) and $Q = -20$ (*solid line*). **b** The high surface charge case, $Q = -20$, with the following chains: diblock (*solid line*), "reversed" triblock $(-10, +20, -10)$ (*dashed line*), "normal" triblock with $(+10, -20, +10)$ (*dot-dashed line*) and counterions only (*thin solid line*)

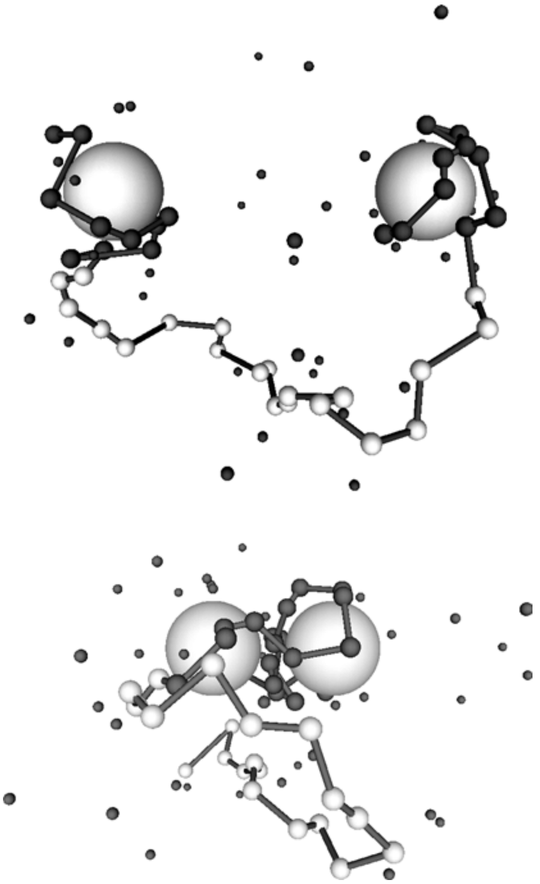

Fig. 4. Snapshots from simulations of a PA with $N = 40$ and two colloidal particles, each with $Q = -20$. The *top picture* shows a typical case of a triblock adsorbing to the two colloids. The chain is not under tension, hence no attractive force is found. The *bottom picture* displays a diblock that adsorbs to both colloids pulling them to a surface–surface separation of about a bond length. Counterions and positively charged monomers are shown in *dark grey* and negatively charged monomers in *light grey*. The pictures were produced with the software package GISMOS [22]

Whether or not attraction occur is also depends on the PA charge sequence and, for example, the triblock PA induces a significant reduction in the double layer repulsion, but not any attraction. When studying snapshots from this system (Fig. 4a) many configurations where the two ends of the PA bridge the two large particles are found. Even though these are common they do not give rise to a net attraction since the bonds are not sufficiently stretched to create a strong chain tension. Rather, bridging attraction is found at distances of the order of the bond length in the PA, as is shown for a diblock PA $(+20, -20)$ in Fig. 4b. This is in agreement with results for polyelectrolytes [20, 21], which have only one kind of charge, in the presence of surfaces with opposite charge. The mechanism behind attraction induced by PAs and polyelectrolytes is most likely of the same origin.

To conclude, the Figs. 1 and 2 show conclusively that for some PAs there exists a critical field strength at which the PA unfolds and which leads to a huge increase in the induced dipole moment of the PA. It is also shown that a net neutral PA reduces the repulsion and in some cases even induces an attraction between two macromolecules of the same charge. This attraction is intimately coupled to the nonlinear response to the electric field generated by the macromolecules. The mechanism of attraction is the same as for polyelectrolytes and is active at separations on the order of the monomer–monomer distance.

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