Simulations of Polyelectrolyte Adsorption to a Dielectric Like-Charged Surface

Alexandre P. dos Santos,* Matheus Girotto,* and Yan Levin*

Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, CEP 91501-970 Porto Alegre, RS, Brazil

ABSTRACT: We explore, using the recently developed efficient Monte Carlo simulation method, the interaction of an anionic polyelectrolyte solution with a like-charged dielectric surface. In addition to polyelectrolytes, the solution also contains salt with either monovalent, divalent, or trivalent counterions. In agreement with recent experimental observations, we find that multivalent counterions can lead to strong adsorption of polyelectrolytes onto the surface. On the other hand, addition of a 1:1 electrolyte diminishes the adsorption induced by the multivalent counterions. Dielectric discontinuity at the interface is found to play only a marginal role in polyelectrolyte adsorption.

INTRODUCTION

Charged polymers are ubiquitous in biology and chemistry. In industry, they are used as purifying agents and superabsorbents. The strong electrostatic attraction between charged impurities, induced by the oppositely charged polyelectrolytes, can lead to flocculation and precipitation of suspensions. Polyelectrolytes are also used in medical applications as antibiotics and in diagnostics as chemical sensors. For amphiphilic polyelectrolytes the antimicrobial behavior appears to be related to the electrostatic interactions between the negative charges of the cell membrane and positively charged sites of the polyelectrolyte, as well as the hydrophobic interactions with the phospholipids and polyelectrolytes. Under physiological conditions, DNA is a negatively charged polyelectrolyte that can interact with positively charged liposomes or proteins. A number of groups have studied charged polymers interacting with oppositely charged surfaces, with special attention given to the curvature effects. Ionic specificity, the so-called Hofmeister effect, was observed in the interaction between polyelectrolytes and hydrophobic surfaces. Other authors have investigated the effective attraction induced by multivalent counterions between like-charged polyelectrolytes. This attraction was found to be short-ranged and to depend strongly on the concentration of multivalent counterions and monovalent salts present in the solutions. The attraction appeared as a consequence of strong positional correlations between the condensed counterions surrounding the polyelectrolytes. Recently, some groups conducted studies on the interaction between polyelectrolytes and like-charged membranes, which is also the topic of the present paper. In the present work, we will explore the effect of dielectric contrast and the concentration of both multivalent and monovalent electrolytes on the interaction of polyelectrolytes with a like-charged surface.

Simulations of Coulomb systems are difficult because of the long-range nature of Coulombic forces. In a slab geometry, the complexity increases further because of the reduced symmetry, which complicates the implementation of periodic boundary conditions using standard Ewald summation techniques. Different methods have been devised to overcome these difficulties. Recently, we introduced a new method that allowed us to efficiently perform simulations of systems with an underlying slab geometry. The method was developed specifically to study inhomogeneous Coulomb systems near charged surfaces, such as electrodes, membranes, or large colloidal particles. The idea of the new approach is to separate the electrostatic potential produced by the uniformly charged surface from the other electrostatic interactions, treating it as an external potential acting on ions and polyelectrolytes. The difficulty, however, is that such a separation results in a non-neutral Coulomb system that, when treated using regular Ewald summation, leads to infinite electrostatic self-energy. Nevertheless, we were able to show that this infinite contribution can be renormalized away, resulting in a well-defined finite electrostatic energy that can be used within the Metropolis algorithm to very efficiently perform Monte Carlo (MC) simulations. A similar approach was also recently proposed in refs 43, 44 in which the regularization was done by introducing a uniform background. In the present article, we will show how to modify the energy expressions derived in ref 42 to study systems with dielectric discontinuities.

A particularly interesting application of the new algorithm, presented in the present article, is to explore the adsorption of polyelectrolytes onto a like-charged dielectric surface, which could
Correspond to a phospholipid cell membrane, in an electrolyte solution containing multivalent and monovalent counterions. We will show how such systems can be efficiently simulated using the new algorithm based on the non-neutral three-dimensional (3D) Ewald summation method. In particular, we will explore the effects of dielectric surface polarization, multivalent counterions, and monovalent salts on the interaction between an anionic polyelectrolyte and a like-charged membrane. In the following sections, we will present the computational details, results, discussions, and conclusions of the present study. All technical details of the derivations will be provided in the Appendix.

Computational Details

Our system consists of a negatively charged surface with surface charge density $\sigma$, an anionic polyelectrolyte, and a dissolved salt. The simulation box has sides $L_x = 160.1 \, \text{Å}$, $L_y = L_w$, and $L_z = 4L_w$. The electrolyte is confined in $-L_y/2 < x < L_y/2$, $-L_z/2 < y < L_z/2$, and $0 < z < L_z$, where $L = 250 \, \text{Å}$, whereas empty space is maintained in the complementary region, $L < z < 4L_w$. The charged surface is located at $z = 0$. The primitive model is considered. The polyelectrolytes are modeled as flexible linear chains of $N_w$ spherical monomers of charge $-q$ adjacent to each other, where $q$ is the proton charge. Besides ions from the $\alpha$:1 salt at concentration $\rho_w$, where $\alpha$ is the cationic valence, additional monovalent counterions of charge $q$ that neutralize the polypeptide and surface charge are also present. The effective diameter of all ions and monomers is set to $4 \, \text{Å}$. Water is a continuum medium of dielectric constant $\varepsilon_w = 80\varepsilon_c$, where $\varepsilon_c = 1$ is the dielectric constant of vacuum. The Bjerrum length, defined as $\kappa_b = \sqrt{\varepsilon_w k_B T}$, is set to $7.2 \, \text{Å}$, the value for water at room temperature. In the region of empty space, $z < 0$, we consider that the medium is a continuum with dielectric constant $\varepsilon_w$, modeling a cell membrane. The total energy of the system is given by

$$U = U_0 + U_{\text{elf}} + U_L + U_{\text{cor}} + U_p + U_{\text{pol}} \quad (1)$$

In the present method, the details of which are presented in the Appendix, the electrostatic interaction energy between an infinite charged dielectric surface and all of the charged particles is calculated explicitly and is given by

$$U_0 = -\frac{2\pi}{\varepsilon_w} (1 + \gamma) \sum_{i=1}^{N_w} q_i z_i \sigma \quad (2)$$

where $\gamma = (\varepsilon_w - \varepsilon_m)/\varepsilon_w + \varepsilon_m$. The rest of the polyelectrolyte–dielectric system, which in the absence of the surface charge accounted for by eq 2 is no longer charge-neutral, is treated using our modified periodic 3D Ewald summation method. The Coulomb potential is split into short-range and long-range contributions. The short-range part can be studied using simple periodic boundary conditions, whereas the long-range contribution can be efficiently evaluated in the reciprocal Fourier space. The short-range electrostatic energy is

$$U_0 = (1/2) \sum_{i=1}^{N} q_i \phi_i(r) \quad (3)$$

where $\phi_i(r)$ is

$$\phi_i(r) = \sum_{j=1}^{N} \frac{\text{erfc}(\kappa_i |r - r_j|)}{\varepsilon_w |r - r_j|} + \sum_{j=1}^{N} \frac{\gamma q_j}{\varepsilon_w [r - r_j]} \quad (4)$$

where $N$ refers to all of the charges in the simulation box, except the wall charge; $r_i$ is the position of charge $q_i$; and $r_j = r_j - 2z_j \hat{z}$ is the position of image charge $\gamma q_j$. The prime on the summation means that $j \neq i$. The damping parameter is set to $\kappa_s = 4/L_w$. The self-energy contribution is

$$U_{\text{elf}} = -\frac{\kappa_s}{\varepsilon_w \sqrt{|r_i|}} \sum_{i=1}^{N} q_i^2 \quad (5)$$

The long-range electrostatic energy is

$$U_L = \sum_{k \neq 0} \frac{2\pi}{\varepsilon_w V |k|} \left[ \left( -\frac{|k|^2}{4\kappa_s^2} \right) \times [A(k)^2 + B(k)^2] + A(k) C(k) + B(k) D(k) \right] \quad (6)$$

where

$$A(k) = \sum_{i=1}^{N} q_i \cos(k \cdot r_i)$$

$$B(k) = -\sum_{i=1}^{N} q_i \sin(k \cdot r_i)$$

$$C(k) = \sum_{i=1}^{N} \gamma q_i \cos(k \cdot r_i')$$

$$D(k) = -\sum_{i=1}^{N} \gamma q_i \sin(k \cdot r_i')$$

The number of vectors, $k$, defined as $k = (2m/L_x, 2m/L_y, 2m/L_z)$, where $m$’s are integers, is set to around 400 to achieve convergence.

The correction, which accounts for the conditional convergence of the Ewald summation appropriate for the slab geometry, is derived in the Appendix. It is given by

$$U_{\text{cor}} = \frac{2\pi}{\varepsilon_w V} [M_z^2 (1 + \gamma) - G_z Q_z (1 + \gamma)] \quad (7)$$

where

$$M_z = \sum_{i=1}^{N} q_i z_i, \quad G_z = \sum_{i=1}^{N} q_i z_i^2, \quad \text{and} \quad Q_z = \sum_{i=1}^{N} q_i \quad (8)$$

Note that this correction depends on the net charge, $Q_0$, present inside the simulation cell, without including the surface charge of the membrane, which has already been accounted for in $U_p$.

The monomers that compose a polyion interact via Coulomb potential and a simple parabolic potential $\kappa_b^4 a^2 r^2$, that models stretching of molecular bonds

$$U_{\text{pol}} = \sum_{a, \text{mon.}} \frac{A}{2} (r - r_0)^2 \quad (9)$$

The sum is over the adjacent monomers, where $r$ is the distance between the adjacent monomers, $A = 0.97\kappa_b T$, and $r_0 = 5 \, \text{Å}$.

The simulations are performed using the Metropolis algorithm, with $10^6$ MC steps for equilibration. The profiles are calculated with $5 \times 10^4$ uncorrelated states, each obtained with 100 trial movements per particle. Polyions can perform rotations and reptation moves. In addition, polyion monomers can attempt short displacements, whereas ions can perform both short- and long-distance moves.
RESULTS AND DISCUSSION

First, we explore the effect of dielectric discontinuity on the interaction of a polyelectrolyte with a surface. We consider two cases: \( \epsilon_m = \epsilon_0 \) and \( \epsilon_m = \epsilon_w \). The effect of surface polarization on the ionic double layer was extensively studied for different geometries.\(^{48-57} \) In Figure 1, the polyion center of mass (PCM) distribution is shown as a function of the distance from the surface, with \( \epsilon_m = \epsilon_0 \) and \( \epsilon_m = \epsilon_w \), corresponding to the absence of polarization. Surface charge density \( \sigma = -0.1 \text{ C/m}^2 \), the number of polyions in the simulation box is 20, \( N_m = 18 \), \( \alpha = 3 \), and the salt concentration is 60 mM.

![Figure 1. Comparison between the PCM concentration and the distance from the surface, obtained with \( \epsilon_m = \epsilon_0 \) and \( \epsilon_m = \epsilon_w \) corresponding to the absence of polarization. Surface charge density \( \sigma = -0.1 \text{ C/m}^2 \), the number of polyions in the simulation box is 20, \( N_m = 18 \), \( \alpha = 3 \), and the salt concentration is 60 mM.](image)

The adsorption is a consequence of many body interactions between the surface-condensed counterions and the polyelectrolyte monomers. For the \( \alpha = 3 \) electrolyte, there is a significant adsorption of polyions onto a like-charged membrane, as was also observed in the experiments and simulations.\(^{34} \) Next, we consider the \( \alpha = 2 \) electrolyte. Increasing the concentration of the \( \alpha = 1 \) electrolyte enhances the electrostatic screening, decreasing the repulsion, leading to a small adsorption at a high salt concentration, in agreement with the recent experimental results.\(^{34} \) The adsorption is a consequence of the trends between the nonlinear effects of counterion correlations and “linear” Debye screening, which decreases all electrostatic interactions. We expect the same behavior to occur for 2:1 electrolytes but at concentrations higher than the ones investigated in the present article. A similar effect has been found for colloidal systems, for which the effective colloidal charge was predicted to first decrease, and sometimes even become reversed, with increasing concentration of electrolyte, with the trend reversing at larger multivalent salt concentrations.\(^{58} \) Finally, in Figure 4, we explore the effect of addition of a 1:1 electrolyte to a polyelectrolyte solution containing the \( \alpha = 3 \) electrolyte at 60 mM concentration. We see that the addition of the 1:1 electrolyte screens the electrostatic interactions, diminishing the adsorption of polyions onto a like-charged surface.\(^{58} \)

The mechanism responsible for the attraction of the polyion to a like-charged membrane was partially attributed to hydrophobic interactions between the charged polymers and the surface, for moderate trivalent salt concentrations.\(^{34} \) However, here, we see that purely electrostatic interactions, without any specific hydrophobic effects, already result in a like-charge attraction. It was also suggested\(^{34} \) that the charge inversion of the polyion–cation complex is responsible for the polyion condensation onto a like-charged surface. However, our simulations show that, in general, this is not the case. In the presented model, the polyions are not sufficiently charged to result in a charge reversal of the polyion.\(^{58} \) In simulations, we see that the attraction is a consequence of strong electrostatic correlations between the adsorbed multivalent ions\(^{31,59,60} \) and the polyion monomers. Electrostatic correlations have been previously found to also be responsible for the reversal of electrophoretic mobility\(^{61,62} \) and attraction between like-charged colloidal particles.\(^{31,63} \)
CONCLUSIONS

We have presented MC simulations of polyelectrolyte solutions interacting with like-charged surfaces. The simulations were performed using a recently developed algorithm that allows us to efficiently study inhomogeneous Coulomb systems with a planar charged interface. The effect of membrane polarization, which results in an induced surface charge, has been taken into account using image charges. The adsorption has been characterized by the PCM distribution. Surprisingly, we find a small adsorption of polyions onto a like-charged membrane even for the $\alpha = 1$ electrolyte at a sufficiently high concentration. In this case, the electrostatic correlations do not play any significant role and the attraction is a consequence of steric and depletion interactions. For the $\alpha = 2$ electrolyte, under all of the conditions studied in the article, adsorption increased with salt concentration; however, we expect this trend to reverse at concentrations higher than the ones explored in the present article, similar to that observed for trivalent counterions. For the $\alpha = 3$ electrolyte, the polyion adsorption was found to first increase with the concentration of the multivalent salt and then decrease. Addition of a 1:1 electrolyte to a polyelectrolyte solution containing multivalent counterions decreased the polyion adsorption. All of the results are consistent with the recent experimental observations.

Figure 3. PCM concentration vs distance from the surface, obtained for different salt concentrations. The parameters are the same as those in Figure 1, except $\alpha$ and salt concentrations. The valence of the $\alpha$:1 electrolyte is indicated in the panels.

Figure 4. Comparison between the PCM density and distance from the surface, obtained with and without the addition of a 1:1 salt. The concentration of the 3:1 electrolyte is fixed at 60 mM. The parameters are the same as those in Figure 1.
APPENDIX

Energy Calculations

We consider a system of \( N \) charged particles, with charges \( q_j \) located at \( r_j \), bounded by a dielectric wall at \( z = 0 \). The simulation box has sides \( L_x, L_y, L_z \) and volume \( V = L_x L_y L_z \). The electrolyte is confined in \(-L_x/2 < x < L_x/2, -L_y/2 < y < L_y/2, \) and \( 0 < z < L \). In general, the system is not charge-neutral.

To take into account the long-range nature of Coulombic forces, we replicate the system periodically in all directions. The ions in the main simulation cell interact with all other ions in the cell and also with all periodic replicas. We define a vector \( r_{\text{rep}} \) as \((n_1 L_x, n_2 L_y, n_3 L_z)\), where \( n_i \)'s are integers. To correctly simulate the system, we have to consider the polarization of the dielectric wall, which can be done by introducing image charges. The potential due to the real and image charges at an arbitrary position, \( r \), inside the main simulation cell is

\[
\phi_i(r) = \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j(s) - \rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s + \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s
\]

where \( \rho_j(s) = q_j \delta(s - r_j) \) is the charge density of ion \( j \) and its infinite replicas and \( \rho_j^G(s) = q_j \delta(s - r_j - r_{\text{rep}}) \) is the image charge density of ion \( j \) and its infinite replicas. The prime over the summation means that \( j \neq n \) for \( n = (0, 0, 0) \). Constant \( \gamma \) assumes the value \( \gamma = (\varepsilon_w - \varepsilon_m)/(\varepsilon_w + \varepsilon_m) \), where \( \varepsilon_m \) is the dielectric constant of the surface medium and \( \varepsilon_w \) is the dielectric constant of the medium in which the real charges are. Vector \( r' \) is the position of the image charges defined as \( r' = r_j - 2a \hat{z} \). Vectors \( n = (n_x, n_y, n_z) \) represent the different replicas.

We use the 3D Ewald technique to efficiently sum over the replicas. The potential has the form

\[
\phi_i(r) = \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j(s) - \rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s + \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s
\]

\[
= \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s + \sum_{n} \sum_{j=1}^{N} \int \frac{\rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s
\]

\[
- \int \frac{\rho_j^G(s)}{e \varepsilon_k |r - s|} \, d^3 s
\]

(11)

where

\[
\rho_j^G(s) = \rho_j \left( \kappa^2 / \sqrt{\pi} \right) \exp(-\kappa^2 s - r_j - r_{\text{rep}}^2)
\]

\[
\rho_j^G(s) = \gamma \rho_j \left( \kappa^2 / \sqrt{\pi} \right) \exp(-\kappa^2 s - r_j - r_{\text{rep}}^2)
\]

and \( \kappa \) is a damping parameter. The first two terms of eq 11 define a short-range potential, \( \phi_i^S(r) \)

\[
\phi_i^S(r) = \sum_{j=1}^{N} \frac{q_j \text{erfc}(\kappa s |r - r_j|)}{e \varepsilon_k |r - r_j|} + \sum_{j=1}^{N} \frac{q_j \text{erfc}(\kappa s |r - r_j|)}{e \varepsilon_k |r - r_j|}
\]

(13)

Notice that we can exclude the summation over \( n \)'s in the short-range potential, adopting the usual minimum image convention, \( n = (0, 0, 0) \). This is appropriate because of the exponentially fast decay of erfc(x) with increasing x. The total short-range interaction energy is then

\[
U_i^S = (1/2) \sum_{j=1}^{N} q_j \phi_i^S(r_j)
\]

The last term of eq 11 is added to remove the prime over the summation in the third term of eq 11 and corresponds to the potential produced by the \( i \)th Gaussian charge

\[
\phi_i^{\text{G}}(r) = \frac{q_j \text{erfc}(\kappa s |r - r_j|)}{e \varepsilon_k |r - r_j|}
\]

(15)

The total self-energy is

\[
U_{\text{self}} = -\frac{1}{2} \sum_{j=1}^{N} q_j \phi_i^{\text{G}}(r_j) = -\frac{\kappa}{\varepsilon_k \sqrt{\pi}} \sum_{j=1}^{N} q_j^2
\]

(16)

The third and fourth terms of eq 11 define the long-range potential, \( \phi_i^L(r) \)

\[
\phi_i^L(r) = \sum_{n} \sum_{j=1}^{N} \frac{q_j \text{erfc}(\kappa s |r - r_j - r_{\text{rep}}|)}{e \varepsilon_k |r - r_j - r_{\text{rep}}|}
\]

\[
+ \sum_{n} \sum_{j=1}^{N} \frac{q_j \text{erfc}(\kappa s |r - r_j - r_{\text{rep}}|)}{e \varepsilon_k |r - r_j - r_{\text{rep}}|}
\]

(17)

We can Fourier-transform eq 17, resulting in

\[
\phi_i^L(r) = \frac{4 \pi q_j}{e \varepsilon_k V |k|^2} \left[ \frac{1}{4 |k|^2} + \frac{1}{4 |k|^2} \right] \exp[i \cdot (r - r_j)]
\]

\[
+ \gamma \exp[i \cdot (r - r_j)]
\]

(18)

with \( k = \left( \frac{2 \pi a}{L_x}, \frac{2 \pi a}{L_y}, \frac{2 \pi a}{L_z} \right) \). We note that the term corresponding to \( k = (0, 0, 0) \) is divergent. However, the divergence can be renormalized away by changing the zero point of the potential, as discussed in ref 42. We expand the singular term around \( k = (0, 0, 0) \) and keep the nonvanishing factors

\[
\lim_{k \to 0} \sum_{n} \sum_{j=1}^{N} \frac{4 \pi q_j}{e \varepsilon_k V |k|^2} \left[ \frac{1}{4 |k|^2} + \frac{1}{4 |k|^2} + \gamma \frac{1}{2 |k|^2} \right]
\]

(19)

The first two terms are zero for neutral systems, \( \sum_{j=1}^{N} q_j = 0 \), but diverge for systems with a net charge. However, they are independent of position and can be renormalized away by simply redefining the zero of the potential.\(^42\) The second and third terms are zero, as shown in ref 42. The remaining terms can be calculated taking into account the aspect ratio of the infinite system. For details of the calculations, see ref 42. For a slab geometry, the directions \( \hat{x} \) and \( \hat{y} \) tend to infinity much faster than \( \hat{z} \), resulting in a finite correction potential

\[
\phi_i^{\text{corr}}(r) = -\sum_{j=1}^{N} \frac{2 \pi q_j}{e \varepsilon_k V} \left[ (z - z_j)^2 + \gamma (z - z_j)^2 \right]
\]

(20)

The correction energy is \( U_{\text{corr}} = (1/2) \sum_{j=1}^{N} q_j \phi_i^{\text{corr}}(r_j) \), which after a short calculation reduces to
\[ U_{cor} = \frac{2\pi}{\epsilon_0} \left[ M_z^2 (1 - \gamma) - G_z Q_z (1 + \gamma) \right] \]  

where

\[ M_z = \sum_{i=1}^{N} q_i z_i, \quad G_z = \sum_{i=1}^{N} q_i z_i^2, \quad \text{and} \quad Q_z = \sum_{i=1}^{N} q_i \]

We can now exclude \( k = 0 \) in the long-range potential (eq 18), as it is now accounted for by the correction potential. The long-range energy is given by \( U_L = (1/2) \sum_{i=1}^{N} q_i \phi_i(r) \), which can be written as

\[ U_L = \sum_{k \neq 0} \frac{2\pi}{\epsilon_0} v |k|^2 \exp \left( -\frac{|k|^2}{4\epsilon_c^2} \right) \times \left[ A(k)^2 + B(k)^2 \right] \]

\[ + A(k)C(k) + B(k)D(k) \]

where

\[ A(k) = \sum_{i=1}^{N} q_i \cos(k \cdot r_i) \]

\[ B(k) = -\sum_{i=1}^{N} q_i \sin(k \cdot r_i) \]

\[ C(k) = \sum_{i=1}^{N} y_i q_i \cos(k \cdot r_i') \]

\[ D(k) = -\sum_{i=1}^{N} y_i q_i \sin(k \cdot r_i') \]

In general, charged surfaces also contribute with counterions, which must be included in the main simulation cell. The electrostatic potential produced by the surface acts on all of the charged particles inside the simulation cell and can be added as an external field

\[ \phi_n(r) = -\frac{2\pi}{\epsilon_n} (1 + \gamma) \sigma z \]

where \( \sigma \) is the surface charge density. The total plate ions' interaction energy is \( U_p = \sum_{i=1}^{N} q_i \phi_i(r) \).

The total electrostatic energy is given by a sum of all contributions

\[ U = U_0 + U_{elf} + U_{cor} + U_L + U_p \]

## REFERENCES


(34) Tiraferrì, A.; Maroni, P.; Borkovec, M. Adsorption of Polyelectrolyte to Like-Charged Substrates Induced by Multivalent Counterions as Exemplified by Poly(styrene sulfonate) and Silica. Phys. Chem. Chem. Phys. 2015, 17, 10348−10352.