

Charged Polymer/Nanoparticle Mixtures: Monte Carlo Simulations

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Abstract: We used Monte-Carlo simulations to study the formation of complexes between charged polymers (or polyelectrolytes) with oppositely charged spherical nanoparticles. We presented the model, the Monte Carlo numerical method and investigated the effects of the ionic concentration of the solution, polyelectrolyte rigidity (or flexibility), linear charge density, and surface charge of the nanoparticles. Polyelectrolyte adsorption is controlled by several competing effects. On the one hand, rigidity and electrostatic repulsion force the polyelectrolyte to adopt extended conformations and limit the number of monomers which may be attached to the nanoparticles. On the other hand, electrostatic attractive interactions between the particle and the polyelectrolyte monomers force the chain to undergo a structural transition and collapse at the particle surface. By increasing the intrinsic rigidity, we observed a transition from disordered and strongly bound complexes to a situation where the polymer touches the particles over a finite length, while passing by the formation of a solenoid conformation. We found that the critical ionic concentration at which adsorption/desorption is observed rapidly increases with the increase of the nanoparticle surface charge density in good agreement with experimental data dealing with the formation of complexes between micelles and oppositely charged polyelectrolytes. Adsorption is also promoted by decreasing the chain stiffness or decreasing the salt concentration for a given chain length.

Keywords: Adsorption · Monte Carlo simulations · Nanoparticles · Polyelectrolytes

1. Introduction

Mixtures of polyelectrolytes (*i.e.* charged polymers) such as synthetic polymers, polysaccharides, DNA, *etc.* and oppositely charged colloids such as organic, inorganic nano-particles, proteins, micelles, vesicles, *etc.* represent key systems in soft condensed science [1], biology [2] and for industrial applications [3]. Applications in the field of water treatment such as flocculating/water insoluble mixtures, adhesion, food technology, powder processing are numerous [4][5] and extension to gene therapy and bioengineering is currently under consideration [6][7]. Intensive research is carried out today in order to get an insight into the mechanisms of condensation and

aggregation of DNA, which both can be induced by a variety of positive ions, due to electrostatic interactions with the oppositely charged phosphate groups on the DNA backbone. DNA molecules condense into toroids and rods in the presence of multivalent cations or polyamines [8]. In environmental chemistry, interactions between inorganic colloids and polysaccharides are also expected to control the coagulation of colloidal material in suspension and the fate and transport of trace pollutants associated with them [9]. Nonetheless, the long range attractive and/or repulsive character of electrostatic interactions between polyelectrolytes and oppositely charged colloids, solution chemistry, chemical composition, geometry and concentration of both polyelectrolytes and colloids, *etc.* give these complexes fascinating properties which are only partially understood. Thus, little is known in the rational use of polyelectrolytes with oppositely charged colloidal particles and the structures of the formed complexes are still not well understood at the molecular level.

Owing to the important potential of computer simulations to provide qualitative and quantitative means of understanding

the factors that could influence polyelectrolyte/nano-particle mixtures, we use and develop Monte Carlo simulations to gain insight into the behavior of polyelectrolyte chains in the presence of oppositely charged colloids [10][11]. As the ionic concentration is expected, *via* screening effects, to play a key role in controlling both chain conformation and polyelectrolyte/particle interaction energy we have also focused on this. A primitive model with a uniformly charged hard sphere to mimic a colloidal nanoparticle and a pearl necklace chain consisting of point charges connected to each other is used. Since a Debye-Hückel approach is considered here (which is an established level of description), ions and counterions are implicitly considered. The adsorption/desorption limit which is a key parameter for technical applications of polyelectrolyte/particle mixtures is also investigated. The polyelectrolyte conformations are analyzed prior to and after adsorption, the polymer interfacial structure is investigated as well as the particle surface coverage and the amount of polyelectrolyte adsorbed. Snapshots of equilibrated conformations are also provided to achieve qualitative views of the polymer/particle com-

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plexes. Some aspects of the adsorption of a polyelectrolyte on nanoparticles are presented here with special attention focused on the effect of i) the colloid surface charge density, ii) polymer intrinsic flexibility iii) polyelectrolyte linear charge density and salt concentration on the adsorption/desorption limit and polyelectrolyte–colloid complex conformation.

2. Model Description

Polyelectrolytes are represented here by a class of material with a succession of N freely jointed hard spheres or physical monomers of radius $\sigma_m = 3.57 \text{ \AA}$. The fraction of ionized monomers f is adjustable (by placing negative charges equal to -1 at the center of the monomers) and the bond length is constant and equal to the Bjerrum length $l_B = 7.14 \text{ \AA}$. The nanoparticle is represented as an impenetrable, uniformly charged sphere with a variable radius σ_p so as to gain full insight into particle curvature effects when necessary. The particle surface charge is assumed to be concentrated into a point charge located at its center and adjusted so as to maintain a constant surface charge density representative of real systems. The solvent is treated as a dielectric medium with a relative dielectric permittivity constant ϵ_r taken as that of water at 298 K *i.e.* 78.5. The total energy E_{tot} ($k_B T$ units) for a given conformation is the sum of repulsive electrostatic interactions between monomers, attractive electrostatic interactions between the chain and the particle E_{el} and, E_{tor} the chain stiffness or bending energy. Hard core interactions E_{ev} are also considered to include both monomer and excluded volumes. Hence the total energy E_{tot} is given by

$$E_{tot} = E_{ev} + E_{el} + E_{tor} \quad (1)$$

All pairs of charged monomers within the polyelectrolyte interact with each other *via* a screened Debye–Hückel long range potential,

$$u_{el}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_r \epsilon_0 r_{ij}} \exp(-\kappa r_{ij}) \quad (2)$$

where z_i represents the amount of charge on unit i and r_{ij} the distance between the centers of two monomers.

Monomers interact with the particle according to a Verwey–Overbeek potential,

$$u_{ai}(r_{ij}) = \frac{z_i z_j e^2}{4\pi\epsilon_r \epsilon_0 r_{ij}} \frac{\exp[-\kappa(r_{ij} - \sigma_p)]}{1 + \kappa\sigma_p} \quad (3)$$

Free ions are not included explicitly in the simulations but their overall effects on monomer–monomer and monomer–particle interactions are described *via* the dependence of the inverse Debye screening length κ^2 [m^{-2}] on the electrolyte concentration. It is worth noting here that the entropy of counterion release is only captured on a linear level. The intrinsic chain stiffness is adjusted by a square-potential with variable amplitude to vary its strength. This gives the bending energy

$$E_{tor} = \sum_{i=2}^N k_{ang} (\alpha_i - \alpha_0)^2 \quad (4)$$

where $\alpha_0 = 180^\circ$ and α_i represents the angle achieved by three consecutive monomers $i-1$, i and $i+1$. k_{ang} [$\text{k}_B \text{T}/\text{deg}^2$] defines the strength of the angular potential.

3. Monte Carlo Simulations

Monte Carlo simulations are performed according to the Metropolis algorithm in the canonical ensemble. In this method successive ‘trial’ chain configurations are generated to obtain a reasonable sampling of low energy conformations. After applying elementary movements which are randomly selected, the Metropolis selection criterion is employed to either select or reject the move. The perturbation process is continued a specified number of times (a typical run requires several millions of perturbations) until the conformation is energy minimized and equilibrated. To generate new conformations, the monomer positions are randomly modified by specific movements.

These movements include three ‘internal’ or elementary movements (end-bond, kink-jump and crankshaft respectively), the pivot and the reptation respectively (Fig. 1). The use of all these movements is very important to ensure the ergodicity of the system as well as the convergence toward minimized conformations. One important challenge is to allow the energy of the complex structure to be minimized gradually without trapping the structure in a local energy minimum. This problem is of particular importance when compact conformations have to be achieved or when large polyelectrolyte chains are considered owing to the fact that a few monomer–monomer contacts can lead to the formation of ‘irreversible’ bonds that freeze the complex structure. Some MC refinements are thus necessary to overcome the formation of structures in local minima and increase the chances of success when sampling new conformations [12]. To generate a collapsed chain the combination of reptation and internal movements has been shown to yield good results. On the other hand to obtain extended structures, pivot movements are the more efficient and can be used alone.

To investigate the formation of polyelectrolyte/nanoparticle complexes, the central monomer of the chain is initially placed at the center of a large three-dimensional spherical box and the particle is randomly placed in the cell. The polyelectrolyte and the oppositely charged particle are then allowed to move (a random motion is used to move the particle). The chain has the possibility to diffuse further away and leave the particle surface during a simulation run and so the polyelectrolyte desorption process can be investigated.

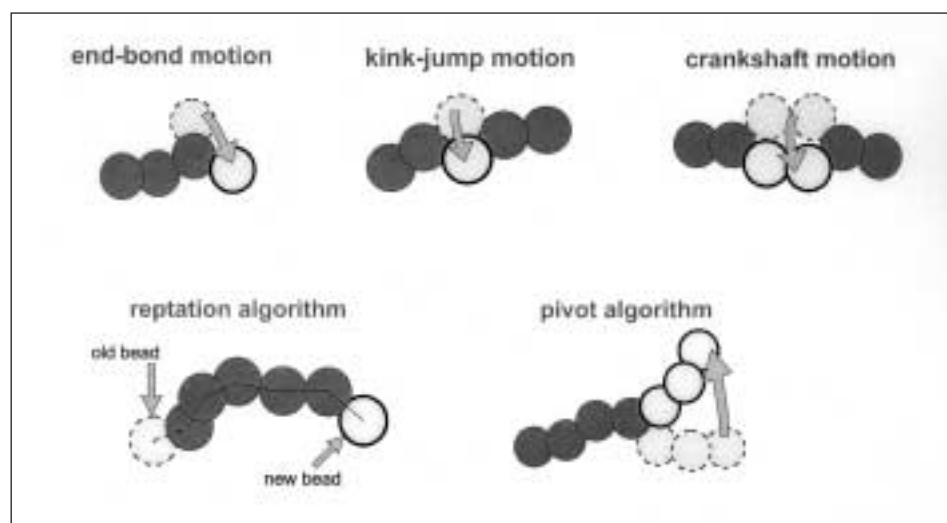


Fig. 1. To generate new conformations, the monomer positions of the polyelectrolyte chains are randomly modified by specific movements. These movements include three ‘internal’ or elementary movements (end-bond, kink-jump and crankshaft respectively), the pivot and the reptation.

4. Polyelectrolyte/Nanoparticle Complexes

4.1. Influence of the Nanoparticle Surface Charge Density

One of the key parameters influencing the interactions between a charged polymer and a nanoparticle is the surface charge density σ of the particle, which is linked in our model to the central charge placed at the particle center and particle radius. In some experimental systems such as micelles, σ is directly related to the protonation or deprotonation of active functions by adjusting the pH of the medium. The presence of charges is expected to control the polyelectrolyte conformation, adsorption–desorption limit, conformation of the adsorbed chains, *etc.* A qualitative picture of polyelectrolyte/particle complexes is usually achieved by representing snapshots of equilibrated structures. They are represented here as a function of σ for a constant ionic strength C_i (Table 1). Increasing σ provokes the adsorption of the polyelectrolyte chain on the particle, the number of adsorbed monomers being proportional to σ . One can note that protruding loops are formed at high σ , *i.e.* when the polyelectrolyte is collapsed at the surface of the particle because of the energy of confinement and electrostatic excluded volume of the polyelectrolyte.

By varying both the ionic strength C_i and σ , we can estimate for each σ value, an adsorption–desorption limit in terms of a critical Debye length. On the one hand, a conformation is considered as ‘adsorbed’ when at least one monomer is positioned in the delimited volume near the surface. On the other hand, during a simulation run, the polyelectrolyte is arbitrarily considered as being adsorbed when the number of ‘adsorbed’ conformations is greater than 50%. In Fig. 2, we estimated the critical Debye-length values for adsorption–desorption at different particle surface charge density σ by varying the ionic concentration. Then we compared them to experimental data corresponding to the simulated system; PVAS chain (poly(vinyl alcohol) partially sulfonated) on an oppositely charged DMDAO micelle (dimethyldodecylamine oxide) [13].

The calculated adsorption–desorption limits determined by MC simulations are in good agreement with the experimental data for this system. Our model seems to capture the physics of the interactions between linear polyelectrolytes and micelles with a regular surface charge distribution. The adsorption–desorption limit is clearly displaced from the higher to the lower ionic strength with decreasing the surface charge density of the micelle.

4.2. Influence of the Chain Rigidity

The chain stiffness k_{ang} which is directly linked to the chain persistence length has also important effects on both the adsorption–desorption limit, conformation of the chain at the surface of the particle and amount of adsorbed monomer on the particle. In Table 2, typical equilibrated conformations of semi-flexible polyelectrolyte/nanoparticle complexes are presented. The same parameters as for the flexible polyelectrolytes are used (Table 1) except for the k_{ang} value which is set to $0.02 k_B T/\text{deg}^2$ (instead of zero). Contrary to the flexible chain, at high σ the chain does not collapse completely on the particle but forms a com-

plex composed of a long tail. Solenoids or toroids as observed for DNA (which is a semi-flexible polyelectrolyte) are achieved at $\sigma = 204 \text{ mC/m}^2$ with no loops. Rigidity hence influences the amount of adsorbed monomer of chain, *i.e.* fewer monomers are adsorbed using rigid chains. The adsorption–desorption limit is also moved and a lower ionic strength is required to adsorb stiff chains.

4.3. Influence of the Linear Charge Density

The linear charge density (LCD), which is related to the charge fraction on the polyelectrolyte backbone is also an important

σ [mC/m ²]	4.5	20.4	204	450
$C_i = 0.04 \text{ M}$				

Table 1. MC equilibrated conformations of flexible polyelectrolyte/nanoparticle complexes at a constant ionic concentration $C_i = 0.04 \text{ M}$ and as a function of the colloid charge density σ . The particle radius σ_p is equal to 2.5 nm , and the central point charge Q of the particle is adjusted so as to vary the surface charge density σ from 4.5 to 450 mC/m^2 . The polymer size is constant and equal to $N = 454$, the monomer radius σ_m is equal to 0.127 nm and the charge to charge distance equal to the Bjerrum length 0.714 nm . Linear charge density LCD of the polyelectrolyte is equal to 0.8 .

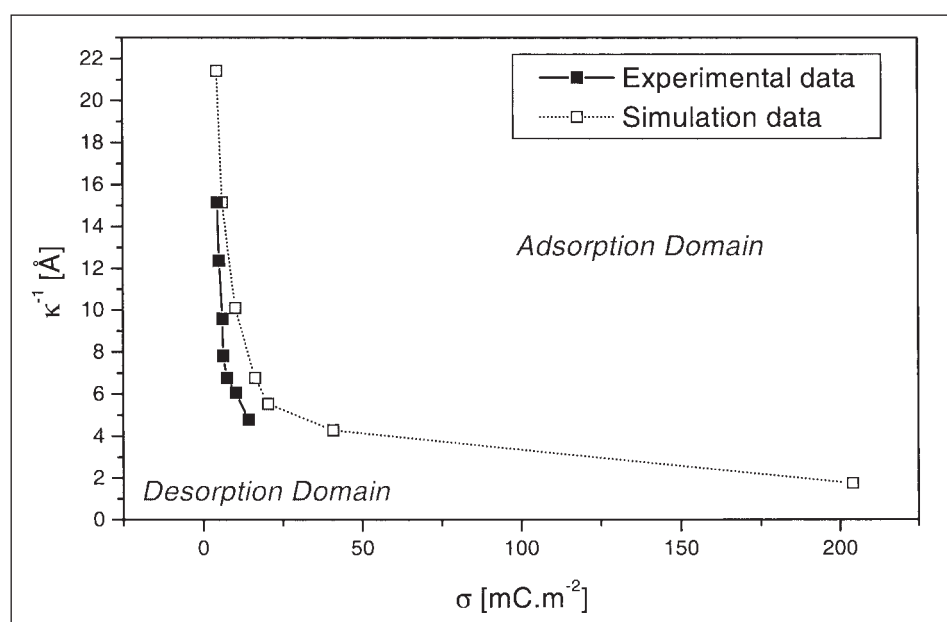


Fig. 2. Comparison of the adsorption–desorption limits of a flexible polyelectrolyte/nanoparticle system between Monte Carlo simulations (Table 1) and experimental data corresponding to [13]; PVAS chain (poly(vinyl alcohol) partially sulfonated) in presence of an oppositely charged DMDAO micelle (dimethyldodecylamine oxide).

Table 2. MC equilibrated conformations of a semi-flexible polyelectrolyte at a constant ionic concentration $C_i = 0.04$ M and as a function of the colloid charge density σ (parameters are similar to Table 1 except for the chain stiffness k_{ang} , which has been introduced and set to $0.02 k_B T / \text{deg}^2$). Compared to the flexible chain, the increase of the chain stiffness revealed the formation of solenoid conformations.

σ [mC/m ²] $k_{ang} = 0.02$ $k_B T / \text{deg}^2$	4.5	20.4	204	450
$C_i = 0.04$ M				

factor controlled in particular by the pH of the medium and the polyelectrolyte concentration. Following the previous approach we have investigated the role of the linear charge density on the formation of a complex between a polyelectrolyte chain and oppositely charged sphere. Variation of the linear charge density was introduced *via* a variable number of uncharged monomers along the chain backbone. The distribution of the charged monomers was always symmetrical, varying from 0.01 to 1 (all monomers ionized). The particle/monomer size ratio was fixed at 10 so that the curvature of the nanoparticle exerts its full effect on polymer adsorption. The central point charge on the colloid was fixed so as to correspond to a surface density of $+100$ [mC/m²].

A qualitative picture of the polyelectrolyte/particle complexes is also presented here by representing some equilibrated structures as a function of C_i and LCD (Table 3). The adsorption-desorption limit is displaced from the higher to the lower ionic strengths with decreasing LCD. Hence, when the linear charge density is small, adsorption is promoted by increasing the attractive interactions between monomers and particle *via* the ionic strength. For example when $C_i = 1.0$ M the polymer is never adsorbed on the colloid whereas when $C_i = 0.1$ M adsorption occurs only when $\text{LCD} > 0.3$. On the other hand, it is also interesting to note the differences in the conformation of the adsorbed chains. For the high values of the LCD the adsorbed structures are more compact and close to the surface of the colloid, whereas in the case of low LCD, the polyelectrolyte chains, even adsorbed, form loops in the solution. We estimated the critical values of adsorption at different ionic concentrations by adjusting the linear charge density. The examination of the probability P_c that a monomer is in contact with the surface of the nano-particle (Fig. 3) presents a sharp transition which seems to be more gradual by increasing the ionic strength.

5. Outlook and Conclusion

Using a Monte Carlo approach, we propose molecular structural models for the determination of the conformation of a polyelectrolyte chain in the presence of oppositely charged particles. The effects of ionic concentration, relative sizes, polyelectrolyte lengths, charge, intrinsic flexibility, *etc.* can be investigated and successfully compared to theory and experiment.

Therefore Monte Carlo simulations constitute a rewarding and invaluable approach and it is shown that computer simulations, theory and experiment can isolate in good agreement the molecular factors that control polyelectrolyte conformations in solution, and at the interfaces, and thus, can be used to address the optimization of nanoparticle-polymer mixtures and guide new experiments. Moreover, these complexes might be used for the development

C_i [M] Linear Charge Density (LCD)	0	0.01	0.1	0.3	1
0.1					
0.2					
0.7					
1.0					

Table 3. Monte Carlo (MC) equilibrated conformations of polyelectrolyte ($N = 100$) nanoparticle complexes as a function of the ionic concentration C_i and polyelectrolyte linear charge density (LCD). Bright monomers represent charged monomers. The LCD is clearly controlling the adsorption/desorption limit and polymer conformation at the particle surface. When screening is important, no adsorption is observed.

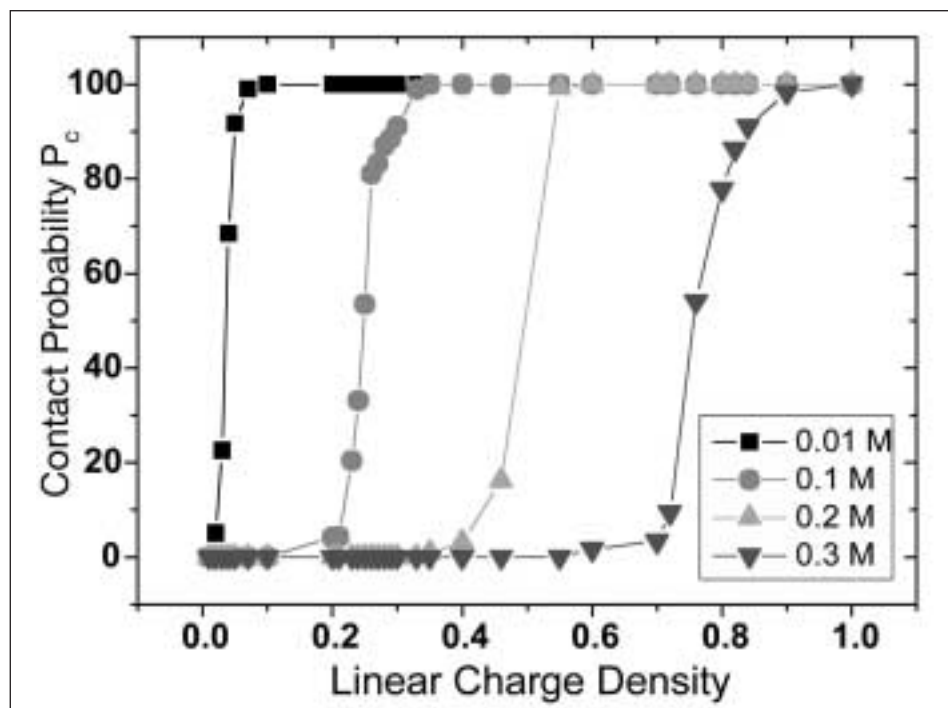


Fig. 3. Contact Probability P_c between the polyelectrolyte and the particle as a function of the linear charge density (LCD). This Fig. demonstrates that the adsorption-desorption limit corresponds to a sharp transition.

of nonviral gene delivery systems and help to optimize the transfection efficiency which depends in particular on the size, charge density of the vector particles.

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