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Monte Carlo simulation of polyampholyte-nanoparticle complexation

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Abstract

The complexation between a polyampholyte and a charged particle was investigated via Monte Carlo simulations on an off-lattice. The simulations revealed that there are three regions for the conformation of the complex formed between a positively charged particle and a polyampholyte chain. When the charge density and the size of the particle were small, the chain adsorbed on the particle surface maintained to a large extent its configuration from the bulk (spherical, dumb-bell, necklace or rod-like). By increasing the charge density and the particle size, the polyampholyte chain has collapsed on the surface. Further increases of the charge density and size of the particle caused a segregation of the beads of the sub-chains with mostly positive charges from those with mostly negative charges, those richer in positive charges being repelled by the particle. The simulation results are compared with some analytical results.

Keywords: Polyampholyte; Nanoparticle; Monte Carlo simulation

1. Introduction

According to their charges, the electrically charged polymers can be classified into polyelectrolytes with a single kind of charge and polyampholytes with both positive and negative charges. The former are encountered in numerous materials, DNA and RNA, whereas the latter are particularly encountered in proteins [1–3]. The conformational changes in solution of the charged polymers have been comprehensively investigated [4–6]. Due to the complexity of the polyelectrolytes which contain hydrophobic and hydrophilic moieties and of the polyampholytes which contain both positive and negative charges, it is difficult to develop theoretical approaches regarding their configurations. On the other hand, by combining a coarse-grained model with a molecular simulation technique, many researchers obtained useful information about the conformation of charged polymer systems [3,4,7–10].

For polyelectrolyte systems, Chodanowski and Stoll investigated, using off-lattice Monte Carlo simulations, the conformations of quenched chains in poor solvents [4]. The Lennard–Jones and Debye–Hückel potentials have been employed to represent the short-range hydrophobic and long-range electrostatic interactions between monomers. In their simulations, they noted that, depending upon the strength of the short-range forces and electrolyte concentration, a globular, cigar-shape or pearl necklace conformation was generated. The complexes of the polyelectrolytes with oppositely charged particles were studied in some detail using simulations [8,9,11–14]. They can be regarded as models for the understanding of (i) the treatment of suspensions in water purification, (ii) the powder processing and (iii) the interaction between DNA and charged leptosomes. Chodanowski and Stoll investigated by Monte Carlo simulations confined in a cell [11,12] the influence of the intrinsic polyelectrolyte rigidity, particle size and ionic concentration on the adsorption/desorption, interfacial structure of the adsorbed layer, and amount of adsorbed polymer. As shown by them, the polyelectrolyte adsorption is controlled by the competing interactions noted above. The rigidity and electrostatic repulsions between monomers led to the extension of the polyelectrolyte chains and limited the number of beads adsorbed on the particle. In contrast, the electrostatic attractive interactions between particle and monomers stimulated the collapse of the polyelectrolyte chain on the particle surface. Similarly, Akinchina and Linse investigated, also by Monte Carlo simulations [13], the effects of the flexibility of the chain, of the fraction of the charged monomers and particle size on

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the properties of the polyelectrolyte-particle complexes. The radial distribution functions, the polyion beads complexation probabilities, and the conformation and energetic characteristics have been determined. Using periodical boundary conditions and the integrated simulation package MOLSM, containing Monte Carlo/molecular dynamics/Brownian dynamics simulations, Jönsson and Linse examined the structure of the complexes formed between a single linear flexible polyelectrolyte and multi-particles with an opposite charge [8,9]. In their simulations, instead of the Debye–Hückel approach, the Ewald summation technique was adopted by them to handle the long range interactions. Carlsson, Linse and Malmsten examined by Monte Carlo simulation the complexes formed between a single polyelectrolyte and a single globular protein molecule with electrostatic charges distributed discretely and non-uniformly on its surface [14]. Ellis, Kong and Muthukumar studied the adsorption of a uniformly charged polyelectrolyte onto a heterogeneously charged surface by Monte Carlo simulations [15]. They found that a polyelectrolyte can be adsorbed on a surface with a net surface charge density of the same sign because of the local attractive regions caused by the spatial inhomogeneity of the surface charge.

Concerning the polyampholytes, the investigations have been mostly focused on their conformation in the bulk [3,16–20]. The behavior of the random polyampholytes is largely determined by the net charge i.e. the difference between the numbers of cationic and anionic groups of the chain. A spherical globule is formed when the chain is neutral or the numbers of positive and negative charges are near to one another. The chain becomes elongated or even acquires a necklace shape, like the polyelectrolytes with a single type of charge, when the net charge becomes of the order or greater than $\sqrt{N}$ (N being the number of charged monomers) [21]. Combining variational mean field calculations with Monte Carlo simulations, Bratko and Chakraborty examined the structure of isolated polyampholyte chains in dilute solutions [17]. Using molecular dynamics simulations [3,20], Tanaka et al. investigated the freezing transition of compact polyampholytes, for both single and multi-chains. They have shown that at high temperatures, the size of a multi-chain system per chain is much greater than that of a single chain system, due to the creation of large void spaces among the chains. At intermediate temperatures, they observed a continuous association and dissociation, and at very low temperatures, they noted an ordered local structure, namely a bcc one. Srivastava and Muthukumar examined the effect of the sequence of charges on the conformation of a polyampholyte in the bulk [21]. Twenty randomly charged neutral copolymers containing 50 monomers have been investigated in their simulations. They have shown that the distribution of charges affected in a major way the configuration.

The adsorption of polyampholyte on charged particles was much less studied than the complexes formed between polyelectrolytes and particles. Dobrynin et al. developed a scaling theory for the adsorption of a randomly charged polyampholyte chain on a charged plane [22]. They found that there are three regimes: the pole, the fence and the pancake ones, which are determined by the surface charge density of the plane. They concluded that even a polyampholyte which has an excess charge of the same sign as the charged plane can be adsorbed by the latter. Netz and Joanny examined the polyampholyte adsorption on charged objects of different shapes, such as the plane, cylinder and sphere [23]. Applying the Debye–Hückel theory, Dobrynin et al. investigated the interaction between two identically charged surfaces immersed in a polyampholyte solution [24]. For symmetric neutral polyampholytes, the results were similar to those in electrolyte solutions. Dobrynin et al. examined the detailed structure of the adsorbed layers and the adsorption isotherms by combining the scaling and the self-consistent field theories [25]. Khan, Åkesson and Jönsson investigated the adsorption of a flexible polyampholyte on a charged plane using Monte Carlo simulations [26].

In the present paper, Monte Carlo simulations will be used to examine the adsorption of a single polyampholyte on a single nano-particle. Different radii of the particles, surface charge densities and ratios between the positive and negative charges in the polyampholyte chain will be considered. The paper is organized as follows: In Section 2, the model and the Monte Carlo algorithm will be described. In Section 3, the main results will be presented. Section 4 contains a comparison with other theories and Section 5 will emphasize the conclusions.

2. Model and Monte Carlo algorithm

In this paper, the polyampholyte chain is represented as a succession of N freely jointed spheres with a radius r_B equal to 3.57 Å. The nano-particles are homogenously charged hard spheres with particle to bead radii r_P/r_B of 5, 10 and 25. The degree of dissociation of the polyampholyte f is taken to be unity. The positive and negative charges are distributed randomly along the chain and the fraction of positive charges varies in most cases between 0.0 and 0.5. In order to examine the effect of charge distribution on the chain configuration, block copolymers and alternative polyampholyte chains are also considered. For a few systems, the polyampholyte chains have net charges of the same sign as that of the particle. The surface charge density of the particles was taken 100, 1000 and 100,000 mC/m^2 (or 6.25×10^{17}, 6.25×10^{18} and 6.25×10^{20} e/m^2). The solvent is assumed a continuum dielectric with the dielectric permittivity of water at 298 K.

The interaction potential between polyampholyte beads is considered as the sum of a short and a long range one

$$E_{B-B}(r_{ij}) = E_S(r_{ij}) + E_L(r_{ij}) \quad (1)$$

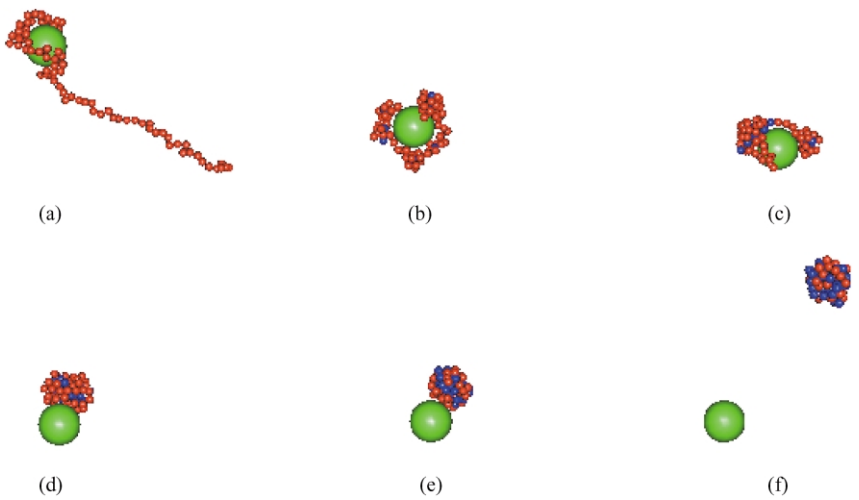

Fig. 1. The conformations of the complexes formed between a charged (100 mC/m^2) particle of small size ($r_P = 17.85$ Å, $r_P/r_B = 5$) and a polyampholyte chain, for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$. The positive beads are blue and the negative ones are red.

where r_{ij} is the distance between the centers of two beads. For the short range interaction E_S, the Lenard–Jones potential is used

$$E_S(r_{ij}) = \varepsilon\left(\left(\frac{2r_B}{r_{ij}}\right)^{12} - 2\left(\frac{2r_B}{r_{ij}}\right)^{6}\right) \tag{2}$$

where r_B is the radius of the beads and ε is a constant taken equal to 2.0. For the long-range interaction E_L, the Debye–Hückel expression for the electrostatic interaction is selected

$$E_L(r_{ij}) = \frac{z_i z_j e^2}{4\pi\varepsilon_0\varepsilon_r r_{ij}}\exp(-\kappa r_{ij}) \tag{3}$$

where e is the protonic charge, ε_0 is the dielectric permittivity of the vacuum, ε_r is the relative dielectric permittivity, and z_i represents the charge number of a bead i and κ is the reciprocal Debye length, given by the expression

$$\kappa^2 = 1000e^2 N_A \frac{C}{\varepsilon_0\varepsilon_r k_B T} \tag{4}$$

where N_A is the Avogadro number, C is the electrolyte concentration which is taken 0.001 M, k_B is the Boltzmann constant, and T is the temperature in K. Consequently, the Debye length at 298 K is equal to 96 Å.

For the interaction between one bead and a particle

$$E_{B-P}(r_{ij}) = E'_S(r_{ij}) + E'_L(r_{ij}) \tag{5}$$

where $E'_S(r_{ij})$ is the excluded volume interaction between a bead and a particle (hard core repulsion), which is equal to 0 for $r_{ij} > r_B + r_P$ and ∞ for $r_{ij} \le r_B + r_P$, where r_P is the radius of the particle.

For $E'_L(r_{ij})$, the following Debye–Hückel expression for the electrostatic interaction will be used:

$$E'_L(r_{ij}) = \frac{z_i z_P e^2}{4\pi\varepsilon_0\varepsilon_r r_{ij}}\frac{\exp(-\kappa(r_{ij} - r_P))}{(1 + \kappa r_P)} \tag{6}$$

where z_P is the charge number of a particle.

The overall effect of the free ions is taken into account via the Debye screening length κ^{-1}.

In the simulation, a particle and a polyampholyte chain were randomly located in a cubic box with a side length $L = 600$ Å, and the traditional motions which account for the kink-jump, tail rotation and reptation were applied by considering an off-lattice at each step. In addition, periodic boundary conditions were employed, and the interactions were truncated using the minimum image convention. After equilibration in 10^6 cycles, the system information was recorded for every 1000 cycles. Due to computer time limitation, the polyampholyte chain was considered to contain only 80 monomer units.

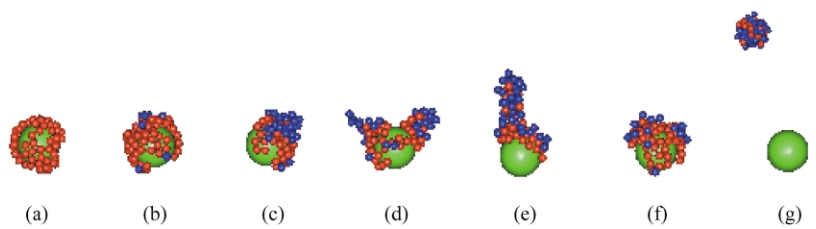

Fig. 2. The conformations of the complexes formed between a charged (1000 mC/m^2) particle of small size ($r_P = 17.85$ Å, $r_P/r_B = 5$) and a polyampholyte chain, for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

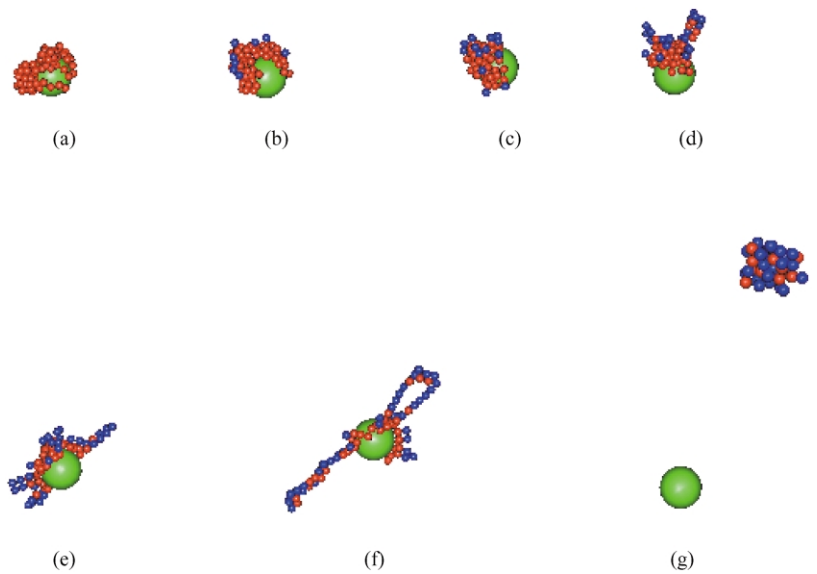

Fig. 3. The conformations of the complexes formed between a charged (100,000 mC/m^2) particle of small size (r_P = 17.85 Å, r_P/r_B = 5) and a polyampholyte chain, for various positive charge fractions (f_P) of the chain. (a) f_P = 0.0, (b) f_P = 0.1, (c) f_P = 0.2, (d) f_P = 0.3, (e) f_P = 0.4, (f) f_P = 0.5, (g) f_P = 0.6.

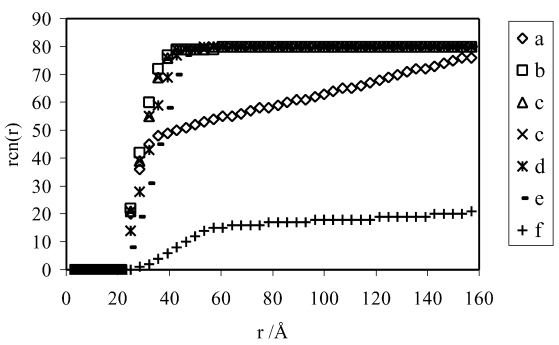

Fig. 4. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100 mC/m^2) particle (r_P = 17.85 Å, r_P/r_B = 5), for various positive charge fractions (f_P) of the chain (a) f_P = 0.0, (b) f_P = 0.1, (c) f_P = 0.2, (d) f_P = 0.3, (e) f_P = 0.4, (f) f_P = 0.5.

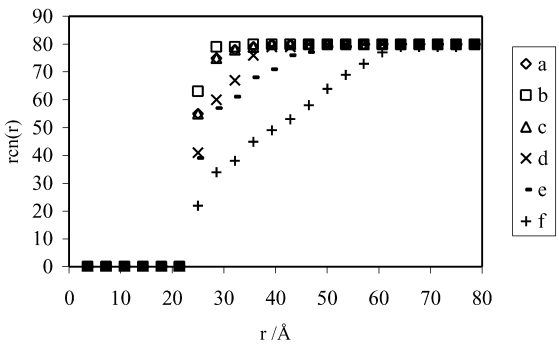

Fig. 5. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (1000 mC/m^2) particle (r_P = 17.85 Å, r_P/r_B = 5), for various positive charge fractions (f_P) of the chain (a) f_P = 0.0, (b) f_P = 0.1, (c) f_P = 0.2, (d) f_P = 0.3, (e) f_P = 0.4, (f) f_P = 0.5.

3. Results and discussions

3.1. Polyampholyte conformation on a charged particle surface

3.1.1. Small particle with a radius r_P17.85Å and r_P/r_B5

The behavior of the polyampholyte in the bulk was found to be mainly controlled by the net charge, the difference between the numbers of positive and negative charges of the chain. As already reported [21], a spherical globule is generated when the net charge of the chain is near neutral, but the polyampholyte becomes elongated or even acquires a necklace shape when the net charge is greater than $\sqrt{N}$ (N being the number of monomers of the polyampholyte chain). In a system formed of a small particle and a polyampholyte chain, the adsorption on a weakly charged particle changes slightly the configuration of the free polyampholyte chain. As shown in Fig. 1, when the surface charge density σ of the particle is equal to 100 mC/m^2, the

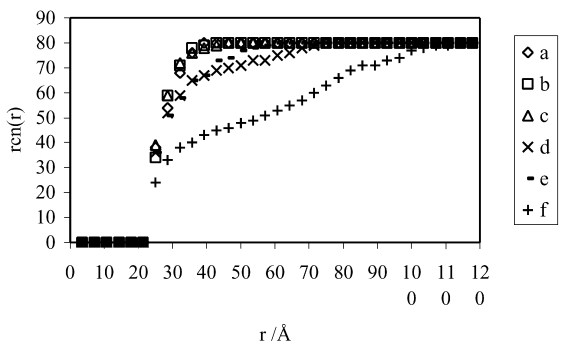

Fig. 6. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100,000 mC/m^2) particle r_P = 17.85 Å, r_P/r_B = 5), for various positive charge fractions (f_P) of the chain (a) f_P = 0.0, (b) f_P = 0.1, (c) f_P = 0.2, (d) f_P = 0.3, (e) f_P = 0.4, (f) f_P = 0.5.

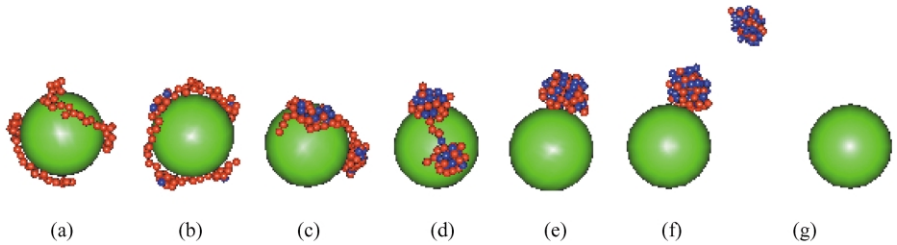

Fig. 7. The conformations of the complexes between a charged (100 mC/m^2) particle of middle size ($r_P = 35.7$ Å, $r_P/r_B = 10$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

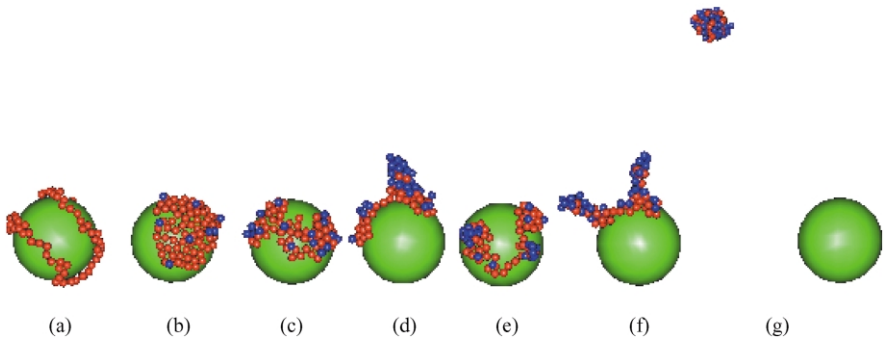

Fig. 8. The conformations of the complexes between a charged (1000 mC/m^2) particle of middle size ($r_P = 35.7$ Å, $r_P/r_B = 10$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

polyampholyte chain acquires, successively, a spherical, dumb-bell, necklace and rod configuration as its positive charge fraction f_P decreases. Because of a weak electrostatic adsorption, the polyampholyte chain with a neutral net charge does not stick in a stable manner to the particle. For $f_P = 0.4$ and $f_P = 0.3$, the chain is adsorbed on the particle surface. The chain acquires a dumb-bell conformation for $f_P = 0.2$ and a necklace one for $f_P = 0.1$. When the fraction of positive charges decreases to zero, the polyampholyte chain reduces to a polyelectrolyte chain with a negative charge [11–13]. In this case, there are also attractive electrostatic interactions between the particle and the chain, but the chain is not completely adsorbed on the particle surface because the latter is weakly charged. The fraction of polyelectrolyte which is not adsorbed on the surface, is extended away from the particle because of the strong repulsive interactions between its beads.

If the charge density on the surface σ is increased to 1000 mC/m^2, the polyampholyte chain collapses on the particle surface for $f_P \leq 0.5$ (Fig. 2), because the particle

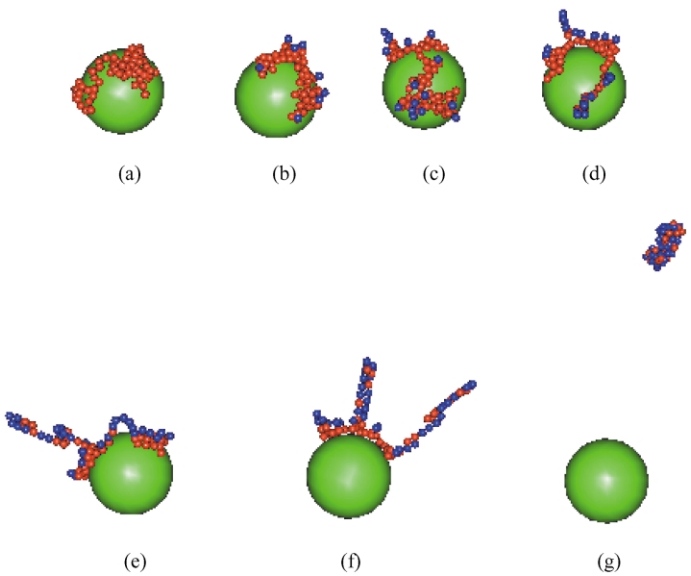

Fig. 9. The conformations of the complexes between a charged (100,000 mC/m^2) particle of middle size ($r_P = 35.7$ Å, $r_P/r_B = 10$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

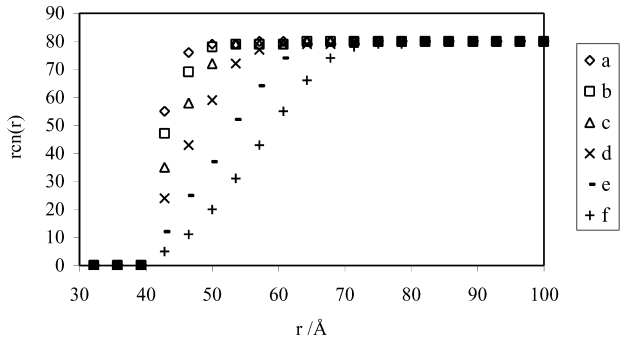

Fig. 10. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100 mC/m^2) particle ($r_P = 35.7$ Å, $r_P/r_B = 10$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$.

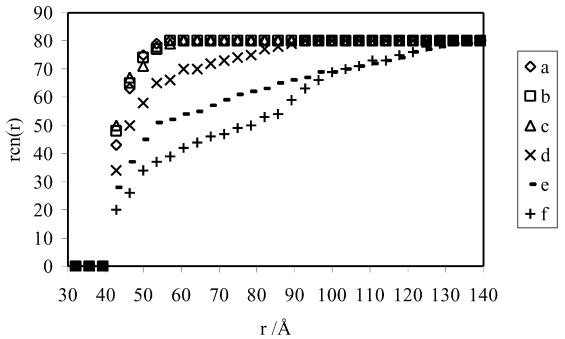

Fig. 12. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100,000 mC/m^2) particle ($r_P = 35.7$ Å, $r_P/r_B = 10$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$.

attracts the beads with negative charges. The beads with positive charges are, however, repelled from the region near the surface, but are not far away because the attractive interactions between the positive and negative charges of the chain are stronger than the repulsive interactions between the positively charged particle and the beads with the same kind of charge. By increasing the fraction of positive charges of the polyampholyte chain f_P to 0.6, the latter is repelled from the surface of the particle. By increasing the charge density on the particle surface σ to 100,000 mC/m^2, the negatively charged beads are compacted more closely to the surface, due to the stronger interactions, but the beads with positive charges are repelled further away from the particle (Fig. 3).

Figs. 4–6 present the accumulations of the polyampholyte beads between the center of the particle and the distance r from this center, the so-called running coordination number, rcn(r), for a small particle of 17.85 Å. As shown in Fig. 4, for a surface charge density $\sigma = 100$ mC/m^2, all the beads are adsorbed near the particle for $f_P = 0.1$–0.4. However, for $f_P = 0.0$, the accumulation is not completed near the particle and some beads are extended into the bulk. This occurs because the repulsive interactions between the

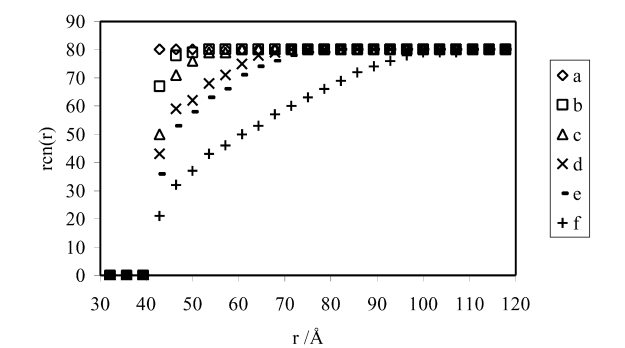

Fig. 11. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (1000 mC/m^2) particle ($r_P = 35.7$ Å, $r_P/r_B = 10$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$.

beads are stronger than their attraction by the weakly charged particle. Although for $f_P = 0.5$ the chain cannot be adsorbed in a stable manner on the particle surface, Fig. 4 shows that there is still a small chance for the chain to approach the particle, because of the weak attractive interactions between the latter and the negatively charged beads of the chain.

Figs. 5 and 6 show that there is a similar tendency for the accumulations of polyampholyte beads along the radius for $\sigma = 1000$ mC/m^2 and $\sigma = 100,000$ mC/m^2. Because of the stronger repulsion between the positively charged beads and the particle at $\sigma = 100,000$ mC/m^2, the accumulation of all the beads is completed at larger values of r in the latter case.

3.1.2. Middle size particle of radius r_P35.7Å and r_P/r_B10

When the r_P/r_B ratio is increased to 10, the total charge of the particle surface becomes large enough to adsorb the beads of the polyampholyte chain for $f_P = 0.5$ even at the weak charge density of $\sigma = 100$ mC/m^2. The chain collapses more completely on this particle surface than on the smaller size one because the total charge of the particle is larger (Fig. 7).

For a charge density on the particle surface of $\sigma = 1000$ mC/m^2 and $f_P \leq 0.5$, the attractive interactions between the particle and the negatively charged beads and those between the beads of different charges are responsible for the configurations of the complexes formed between the chain and particle. The positively charged beads are more compact near the particle than for $\sigma = 100$ mC/m^2, but the negatively charged ones are located near the surface (Fig. 8).

By increasing the charge density on the particle surface to $\sigma = 100,000$ mC/m^2, the interactions between the beads of different charges lose their dominant status (Fig. 9). The attractive interaction between the particle and the beads with negative charges and the repulsive interactions between the particle and the beads with positive charges segregate the chain into two distinct parts, a positive and a negative one. For chains with $f_P = 0.4$ or 0.5, the

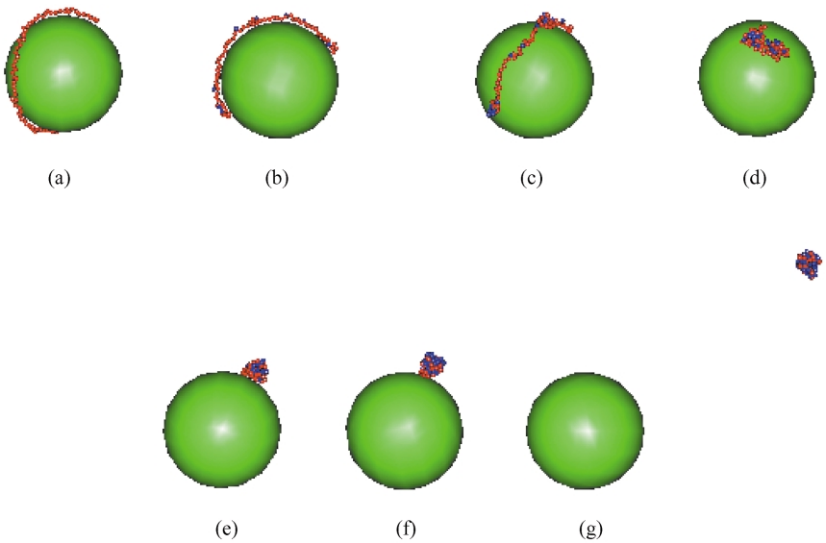

Fig. 13. The conformations of the complexes between a charged (100 mC/m^2) particle of large size ($r_P = 89.25$ Å, $r_P/r_B = 25$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

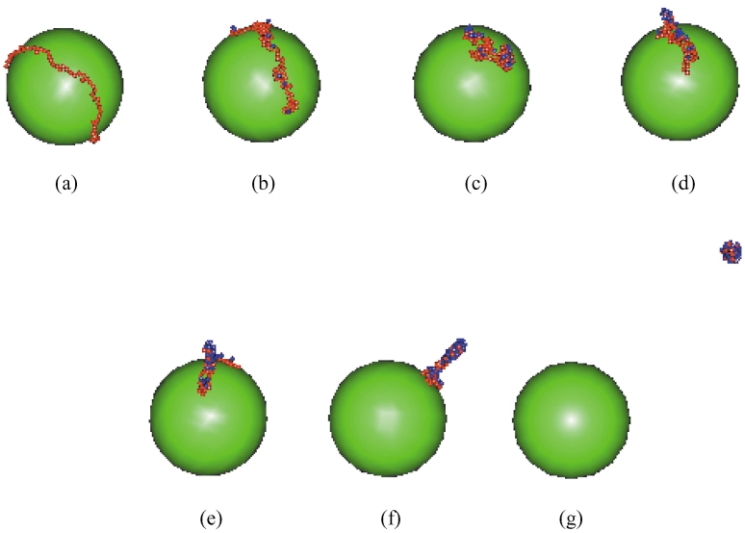

Fig. 14. The conformations of the complexes between a charged (1000 mC/m^2) particle of large size ($r_P = 89.25$ Å, $r_P/r_B = 25$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

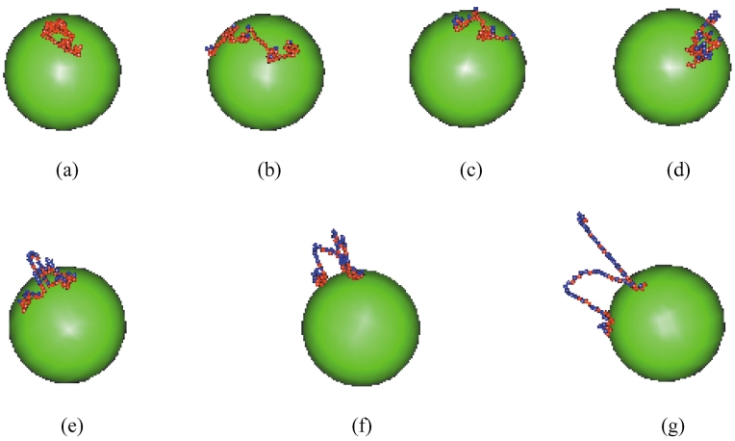

Fig. 15. The conformations of the complexes between a charged (100,000 mC/m^2) particle of large size ($r_P = 89.25$ Å, $r_P/r_B = 25$) and a polyampholyte chain for various positive charge fractions (f_P) of the chain. (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

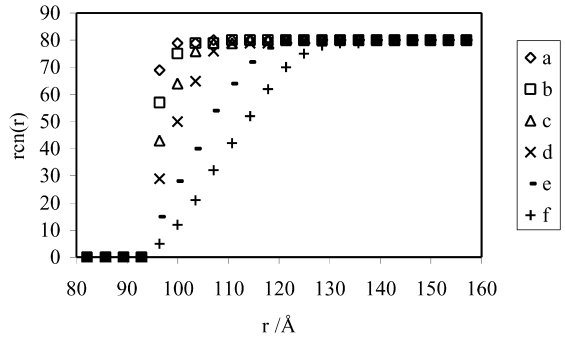

Fig. 16. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100 mC/m^2) particle ($r_P = 89.25$ Å, $r_P/r_B = 25$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$.

conformation of the chains adsorbed on the particle surface is determined largely by the charge distribution along the chain. As shown in Fig. 9(e) and (f), the parts of the chains with a larger number of positively than negatively charged beads are repelled by the particle. The chain with $f_P = 0.6$ cannot be adsorbed on the particle surface in a stable manner and remains in the bulk as a globule.

Figs. 10–12 present the accumulation of polyampholyte beads between the center of the particle and a distance r from its center, for a particle of 35.7 Å size. Comparing Figs. 10–12, one can observe that the final accumulation radius becomes larger with increasing charge density on the particle surface. This occurs because the particle repels the positively charged beads. When the charge density on the particle surface $\sigma = 100,000$ mC/m^2, the curvature of rcn(r) for $f_P = 0.5$ exhibits some irregularity due to the non-homogenous local charge distribution.

3.1.3. Large particle with a radius r_P89.25Å and r_P/r_B25

As the r_P/r_B ratio increases to 25, the conformation of the chain becomes much more extended than at smaller r_P/r_B ratios. In contrast to the conformations present in Figs. 1 and 7, the conformation of the chain on the large particle

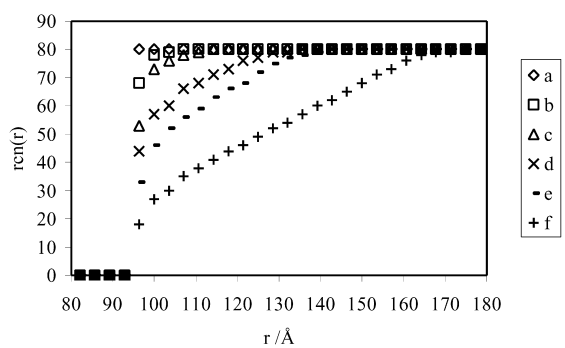

Fig. 17. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (1000 mC/m^2) particle ($r_P = 89.25$ Å, $r_P/r_B = 25$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$.

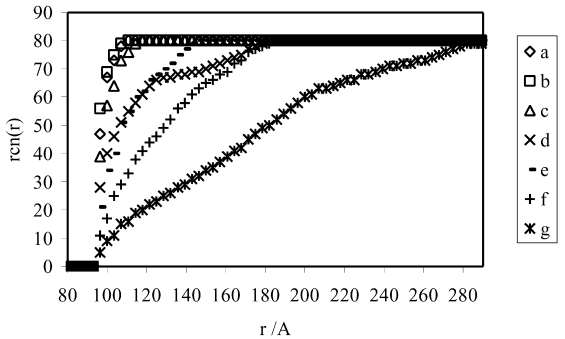

Fig. 18. Running coordination number rcn(r), representing the number of polyampholyte beads within r from the center of a charged (100,000 mC/m^2) particle ($r_P = 89.25$ Å, $r_P/r_B = 25$), for various positive charge fractions (f_P) of the chain (a) $f_P = 0.0$, (b) $f_P = 0.1$, (c) $f_P = 0.2$, (d) $f_P = 0.3$, (e) $f_P = 0.4$, (f) $f_P = 0.5$, (g) $f_P = 0.6$.

changes from a linear to a coil one with increasing f_P, and the dumb-bell and necklace conformations are absent. This happens because of the large charge of the particle even for $\sigma = 100$ mC/m^2 (Fig. 13).

By increasing the charge density on the particle surface σ to 1000 mC/m^2, the chain becomes more compact for smaller values of f_P (Fig. 14). By increasing σ to 100,000 mC/m^2, one can observe that the segregation of charges becomes stronger (Fig. 15). It is interesting to note that the polyampholyte chain with a net charge of the same kind as that of the particle can be adsorbed on the particle (Fig. 15(g)). The local charge distribution rather than the net charge is responsible for this adsorption, those parts of the chain with more negative charges being adsorbed on the particle surface.

As shown in Figs. 16–18, the trend of the rcn(r) behavior with changes in the charge density on the particle surface is the same as in Sections 3.1.1 and Section 3.1.2. The accumulations of beads for large values of σ become complete at larger values of r than for small values of σ. Because the local charge distribution along the chain affects the adsorption and conformation of the random polyampholyte, the rcn(r) curve is not completely smooth (Fig. 18).

3.2. The effect of charge distribution

Srivastava and Muthukumar [21] have examined the effect of the sequence of charges on the conformation of polyampholytes in a bulk. In Section 3.1, some examples were given which showed that the charge distribution along the chain affected the conformation. In this section, the conformations of neutral polyampholytes of the block chains $P_{40}N_{40}$, $(P_{20}N_{20})_2$, $(P_{10}N_{10})_4$, and $(P_4N_4)_{10}$, alternative chain $(PN)_{40}$ and three random chains with different random numbers are investigated (Fig. 19). Fig. 19 shows that the radius of the largest extension of the chain decreases with increasing number of blocks of the chain. It is of interest to note that the tail block with a positive charge is more extended into the bulk for a multi-block polyampholyte

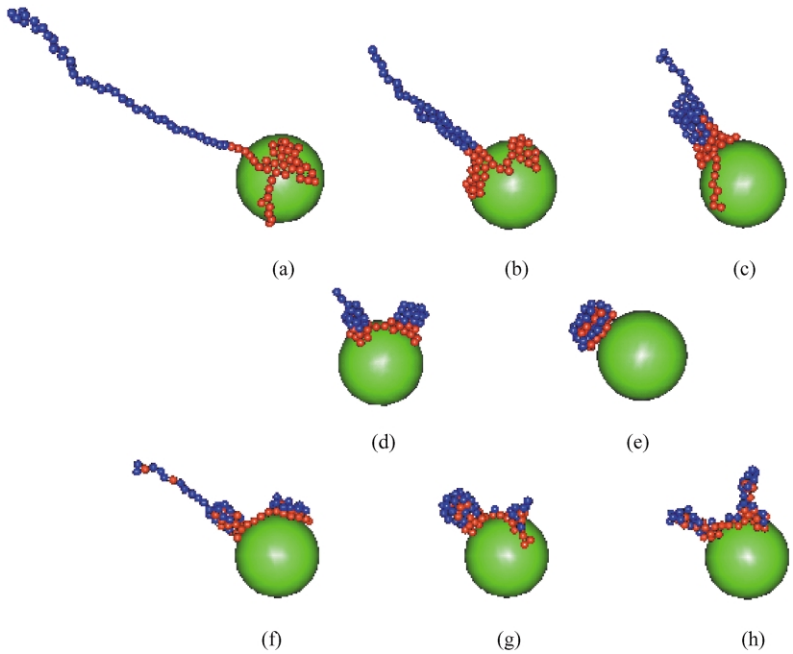

Fig. 19. The configurations of the complexes between a charged particle ($\sigma = 1000$ mC/m^2, $r_P = 35.7$ Å, $r_P/r_B = 10$) and a polyampholyte with various charge distributions. (a) Block polyampholyte chain $P_{40}N_{40}$, (b) block polyampholyte chain $(P_{20}N_{20})_2$, (c) block polyampholyte chain $(P_{10}N_{10})_4$, (d) block polyampholyte chain $(P_4N_4)_{10}$, (e) alternative polyampholyte $(PN)_{40}$, (f) random polyampholyte denoted 1, (g) random polyampholyte denoted 2, (h) random polyampholyte denoted 3. The charge distribution along the random neutral chain denoted 1 is: PNNNNPPNNNPNNPNNPNPNPPN-PNPNNPNNNNNPNPPNPPPPNNNNPNPPPNNPNPPNNPPPNNNNPPPPPPNPPPNPP. The charge distribution along the random neutral chain denoted 2 is: NNPPPNPPNPPPNPNNPPPPNNPPNNPNNPNNNNNPNPNNNNPPPPNPPNPNPPPPPPNPNNPNNPNNPPNNNPPPNNNN. The charge distribution along the random neutral chain denoted 3 is: NNNNPNNPPNPPPPNNPNNPNNNNPNNNPPPPPNNPPPPPNNNNPPNPNPNPNPPNPNPPNNNPNPPPN-PNPPPPPNNNPN. P: Positive charge; N: negative charge.

system because it has only one end which is connected to a block with a negative charge. Regarding the alternative polyampholyte chain, the charge distribution along the chain generates a compact, alternative structure (Fig. 19(e)). As shown in Fig. 19(f)–(h), even for neutral random polyampholytes, there are differences in the conformations for different charge distributions, due to different randomly charged chains.

4. Comparison with theory

Dobrynin et al. investigated theoretically the adsorption of a random polyampholyte chain with a zero net charge on a positively charged planar surface [22]. As noted in their paper, by increasing the charge density of the surface, the neutral random polyampholyte chain passed through three conformations: the pole, the fence and the pancake conformation. As shown in Fig. 2 of their paper, the thickness decreased from the pole to the pancake configuration. Our simulations, with the random number denoted 3 in Fig. 20, show that, because of the stronger interactions between the beads and a particle with a higher charge, a larger separation between the positive and negative groups occurs. Fig. 21 also shows that the thickness becomes greater as the charge density on the particle surface increases.

However, the configuration of an asymmetrical random polyampholyte chain with $f_P = 0.1$ is different from that of a neutral one. As shown in Fig. 22, there is a minimum in the thickness with increasing surface charge density on the particle. This can be explained as follows. The attractive interactions between the particle and the negatively charged beads, and between the positively charged beads and the negatively charged ones determine the beads positions. By increasing the surface charge density on the particle, the positively charged beads collapse together with the more numerous of negative ones on the particle surface. By increasing further the charge density on the particle surface, the repulsive interactions between the particle and the more positively charged sub-chains become stronger and they are pushed away from the particle.

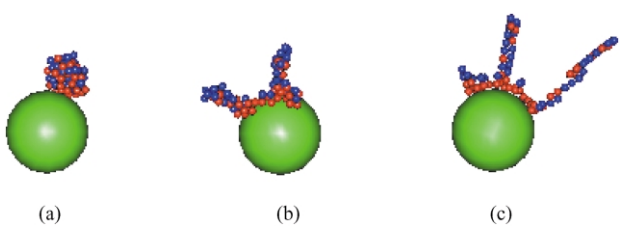

Fig. 20. The configurations of the complexes formed between a neutral random polyampholyte chain and a particle for various surface charge densities on the particle. (a) $\sigma = 100$ mC/m^2, (b) $\sigma = 1000$ mC/m^2, (c) $\sigma = 100,000$ mC/m^2.

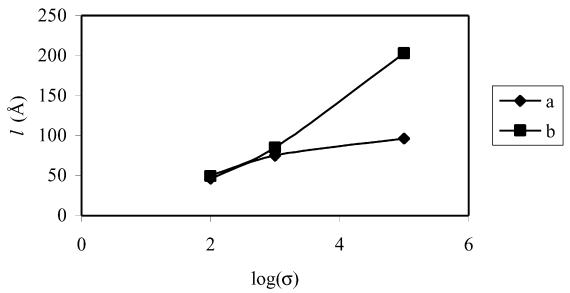

Fig. 21. Dependence of the thickness of a neutral polyampholyte chain on particles for various surface charge densities expressed in mC/m^2 and sizes. (a) $r_P = 35.7$ Å, (b) $r_P = 89.25$ Å.

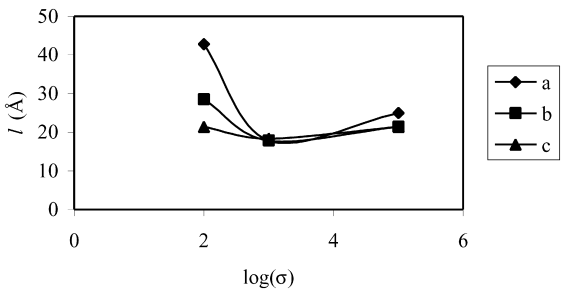

Fig. 22. Dependence of the thickness of an asymmetric polyampholyte chain ($f_P = 0.1$) on particles for various surface charge densities expressed in mC/m^2 and sizes. (a) $r_P = 17.85$ Å, (b) $r_P = 35.7$ Å, (c) $r_P = 89.25$ Å.

In addition, Dobrynin, Rubinstein and Joanny's theoretical results [22] and Lesins and Ruckenstein's experimental finding [27,28] showed that the adsorption of a polyampholyte on a charged surface can occur even when both the polyampholyte and the surface had the same sign of the net charge. A similar result was obtained by us for a polyampholyte chain with $f_P = 0.6$ and a large particle size ($r_P = 89.25$ Å) with $\sigma = 100,000$ mC/m^2 (Fig. 15(g)).

5. Conclusions

In this paper, the conformations of the complexes formed between a polyampholyte and a charged particle were investigated via Monte Carlo simulations on an off-lattice.

The simulations revealed that there are three conformation regimes of the complex. When the charge density is small and the particle size is also small, the chain keeps largely the configuration of a sphere, dumb-bell, necklace or rod which it would have had when alone in the bulk. By increasing the charge density and the particle size, the polyampholyte chain collapses on the surface of the particle and the conformations acquired in the bulk are no longer maintained. A further increase of the charge density on the particle surface and of its size, strengthen the influence of the charged particle leading to a separation between the sub-chains with positive and negative charges. Under the latter conditions, the local charge distribution influences the sub-chain positions, the sub-chains with more positive than negative charges being repelled by the particle surface.

For the adsorption of a random polyampholyte chain with a zero net charge on a charged surface, it was shown that with increasing charge density on the surface of the particle, the thickness of the adsorbed polyampholyte increases. On the other hand, for an asymmetrical polyampholyte chain with more negative than positive charges, the thickness exhibits a minimum. When the net charge of the polyampholyte has the same sign as that of the particle, there are conditions under which the former is adsorbed.

References

[1] Hara M. Polyelectrolytes. New York: Marcel Dekker; 1993.
[2] Candau F, Joanny JF. In: Salomone JC, editor. Encyclopedia of polymeric material, vol. 7. Boca Raton: CRC; 1996.
[3] Tanaka M, Yu Grosberg A, Tanaka T. J Chem Phys 1999;110:8176.
[4] Chodanowski P, Stoll S. J Chem Phys 1999;111:6069.
[5] Strauss UP. Macromolecules 1982;15:1567.
[6] Napper DH. Polymeric stabilization of colloidal dispersions. New York: Academic; 1983.
[7] Kong CY, Muthukumar M. J Chem Phys 1998;109:1522.
[8] Jönsson M, Linse P. J Chem Phys 2001;115:3406.
[9] Jönsson M, Linse P. J Chem Phys 2001;115:10975.
[10] Lyulin AV, Dünweg B, Borisov OV, Darinskii AA. Macromolecules 1999;32:3264.
[11] Chodanowski P, Stoll S. J Chem Phys 2001;115:4951.
[12] Stoll S, Chodanowski P. Macromolecules 2002;35:9556.
[13] Akinchina A, Linse P. Macromolecules 2002;35:5183.
[14] Carlsson F, Linse P, Malmsten M. J Phys Chem B 2001;105:9040.
[15] Ellis M, Kong CY, Muthukumar M. J Chem Phys 2000;112:8723.
[16] Pande VS, Yu Grosberg A, Joerg C, Kardar M, Tanka T. Phys Rev Lett 1996;77:3565.
[17] Bratko D, Chakraborty AK. J Phys Chem 1996;100:1164.
[18] Baumketner A, Shimizu H, Isobe M, Hiwatari Y. J Phys: Condens Matter 2001;13:10279.
[19] Shaffer JS. Macromolecules 1995;28:7447.
[20] Tanaka M, Tanaka T. Phys Rev E 2000;62:3803.
[21] Srivastava D, Muthukumar M. Macromolecules 1996;29:2324.
[22] Dobrynin AV, Rubinstein M, Joanny JF. Macromolecules 1997;30:4332.
[23] Netz RR, Joanny JF. Macromolecules 1998;31:5123.
[24] Dobrynin AV, Rubinstein M. J Chem Phys 1998;109:9172.
[25] Dobrynin AV, Zhulina EB, Rubinstein M. Macromolecules 2001;34:627.
[26] Khan MO, Åkesson T, Jönsson B. Macromolecules 2001;34:4216.
[27] Lesins V, Ruckenstein E. Colloid Polym Sci 1988;266:1187.
[28] Lesins V, Ruckenstein E. J Colloid Interface Sci 1989;132:566.