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# Structure and mechanism of formation of polyelectrolyte multilayers

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## Abstract

The mechanism of formation and structure of polyelectrolyte multilayers deposited from salt free solutions on a charged substrate was investigated using MD simulation. The minimum energy configuration of the system was investigated by varying the temperature of deposition and lowering the charge of monomers in the polyelectrolyte chains. The PE molecules in the multilayers were found to be kinetically trapped under influence of strong electrostatic interactions. The multilayered structure composed of seven double layers contained many voids and imperfections resulting from freezing of the structure. Simulation results also show that the resulting structure is truly layered and that the layer thickness is not very different from the thermodynamic equilibrium layer thickness. The structure of the layers is fuzzy in nature and molecules show a high level of interpenetration and disorder.

*Keywords:* Polyelectrolyte; Multilayer; Simulation

## 1. Introduction

Layer by layer (LBL) adsorption of oppositely charged polyelectrolyte (PE) multilayer films has received tremendous attention in recent years because of the versatility and simplicity of the method [1–5]. The technique of polyelectrolyte multilayering has been applied to numerous classes of materials including proteins, synthetic polyelectrolytes, clay minerals, dendrimers, metal colloids and nanoparticles [6–13]. Applications developed using this technology include biosensors, optoelectronic devices, light emitting films, selective membranes, area patterning, catalysis, corrosion protection, encapsulation and gene therapy among many others [14–23]. It is generally believed that the driving force for formation of polyelectrolyte multilayers is electrostatic attraction between the surface and the polyelectrolyte. Experiments have shown that charge overcompensation is necessary for the formation of multilayers [24,25]. The structure of the multilayers depends not only on the type, charge density and molecular weight of the polyelectrolytes being deposited but also on the processing conditions, for example, ionic strength and pH of solution and speed of spinning of solid substrates during deposition. The type of substrate also influences the structure of the deposited layers, however, its effect is limited only to the first three to six layers [26,27].

Analytical models have been developed to describe the formation of polyelectrolyte multilayers on charged surfaces [28–33]. Recent MC and molecular dynamics simulations were devoted to studying different aspects of multilayer formation on spherical, planar and cylindrical surfaces including importance of nonelectrostatic interactions, influence of molecular weight and charge density and effect of the geometry of the substrate on multilayer formation [34–40].

Previous MC and MD simulation studies demonstrated that PE multilayers can spontaneously form from solutions of mixed polyelectrolytes in absence of dissolved salt [25,40]. In this paper, we investigate the molecular mechanism of polyelectrolyte multilayer deposition from salt free solutions using molecular dynamics simulation. Although, both the theoretical study by Solis and Olvera de la Cruz and our MD simulation results demonstrate that PE can form spontaneously from solutions, the question that remains unanswered is that do PE chains in PEM formed experimentally assume their minimum energy conformations or are they kinetically trapped as a result of the strong electrostatic attractions and the high energy barrier that must be crossed by the molecules to change these conformations to the energy minimum [28,40]. We try to get insight into the answer by studying the effect of deposition temperature on conformation of the chains and structure of the multilayers. The purpose of increasing the temperature is to increase the kinetic energy of the molecules so that they can

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cross the electrostatic energy barrier and reach the minimum energy configuration. We also reduce the height of the energy barrier by reducing the charge value to one tenth of the unit charge.

## 2. Simulation details

We conduct coarse grained MD simulation of LBL assembly of polyelectrolyte molecules from dilute solutions. The polyelectrolyte chains consist of Np = 64 monomer beads. A few simulations were carried out with chains consisting of Np = 32. The absolute value of the charge on each charged monomer bead is equal to 1. A coarse grained system was used to reduce the overall number of particles in the system and to subsequently reduce the number of computations per time step. In addition, the overall dynamics of the system is accelerated because the free energy profile in the system is less bumpy [41–43].

Multilayers were deposited on a surface composed of 289 spherical particles that were constrained in place. The dimensions of the surface are 42.8 Å × 42.8 Å. Each bead has a mass of 12 amu. Increasing the mass of each bead to 72 was not found to influence the equilibrium configuration of the system. The surface is located at $Z=0$. The total surface charge is $-144$, corresponding to a negative charge on every other bead. The force field used to model the chains is a simplified form of the PCFF force field and is described by an equation of the form [44,45].

$$\sum_i K_2(b_i-b_0)^2+K_3(b_i-b_0)^3+K_4(b_i-b_0)^4+ \tag{1}$$

$$\sum_i H_2(\theta_i-\theta_0)^2+H_3(\theta_i-\theta_0)^3+H_4(\theta_i-\theta_0)^4+ \tag{2}$$

$$\sum_i V_1\left[1-\cos\left(\varphi_i-\phi_1^0\right)\right]+V_2\left[1-\cos\left(2\phi_i-\phi_2^0\right)\right]$$
$$+V_3\left[1-\cos\left(3\phi_i-\phi_3^0\right)\right]+ \tag{3}$$

$$\sum_{i>j}\frac{q_iq_j}{\varepsilon_r r_{ij}}+\sum_{i>j}\varepsilon_{ij}\left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9-3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] \tag{4}$$

The forcefield employs a quartic polynomial for bond stretching (term 1) and angle bending (term 2) and a three-term Fourier expansion for torsions (term 3). Term 4 is the Coulombic interaction between the atomic charges and term 5 represents the van der Waals interactions. The force field parameters of the chain are given in Table 1 [44,45]. Electrostatic interactions between charged beads are calculated using the Ewald sum method [44]. A relative dielectric constant $\varepsilon_r$ of 80 was used to account for screening of charges by an implicit solvent (water) [44]. Although the beads within a layer are in contact, a high dielectric constant was necessary for the chains to assume realistic conformations in the solution phase. van der Waals cross interaction parameters are calculated using [44,45]:

$$\varepsilon_{ij}=2\sqrt{\varepsilon_i\varepsilon_j}\frac{(\sigma_i^3\sigma_j^3)}{(\sigma_i^6+\sigma_j^6)}$$

$$\sigma_{ij}=\frac{(\sigma_i^6+\sigma_j^6)^{1/6}}{2}$$

Nonbonded van der Waals interactions were calculated with a cutoff distance of $2.5\sigma$, where $\sigma$ is diameter of a chain bead. Standard long range corrections were applied [45]. Simulations were carried out in the NVT ensemble with periodic boundary conditions. A constant temperature was accomplished by linking the system to a Nosé–Hoover thermostat [44]. A simulation time step of 3 fs was used.

Simulations were performed following a method described earlier in detail [37,40]. The procedure resembles experimental deposition of multilayers which proceeds by immersion of a charged substrate in a dilute polyelectrolyte solution followed by a rinsing step to remove excess, unadsorbed molecules and finally immersion in a dilute solution containing the oppositely charged PE followed by a second rinsing step. The charged surface was constructed and its counterions were dispersed throughout the simulation box. A neutral soft repulsive wall was placed at the top of the simulation box to avoid escape of counter ions and chains to the lower side of the charged surface. The upper wall is identical to the lower surface with the exception that it interacts with other particles by a force field that corresponds to the repulsive term of the van der Waals potential described in Eq. (1). A 100 Å thick layer of vacuum was placed on top of the neutral wall to eliminate periodic electrostatic interactions between the charged surface and particles inside the simulation box. A number of positively charged polyelectrolyte molecules were then inserted in the box along with their counter ions. The concentration of chains was kept at $0.03\sigma^{-3}$. The concentration of polymer can be

Table 1
Force field parameters used in the simulation

| | | | | | | |
|---|---|---|---|---|---|---|
| $T$ | 300 K | | | | | |
| Mass | | | | | | |
| All beads | 12.000 | | | | | |
| Bond potential | $b_0$, 1.53 | $K_2$, 299.67 | $K_3$, $-501.77$ | $K_4$, 679.81 | | |
| Angle potential | $\varphi_0$, 112.67 | $H_2$, 39.516 | $H_3$, $-7.443$ | $H_4$, $-9.5583$ | | |
| Torsion potential | $V_1$, 0 | $\phi_1^0$, 0 | $V_2$, 0.0514 | $\phi_2^0$, 0 | $V_3$, $-0.143$ | $\phi_3^0$, 0 |
| van der Waals interactions | $\sigma$ | $\varepsilon$ | | | | |
| All beads | 4.0100 | 0.0540 | | | | |

Units are kcal/mol (energy), Å (distance) and degrees (angle).

considered to be in the dilute regime because the polymer molecules are well dispersed and do not interact with each other in solution. The simulation box was subsequently equilibrated for 20 ns during which equilibration was confirmed by monitoring the total energy and concentration profiles of the various species in the system. After a molecule was absorbed on the surface, the volume of the simulation cell was adjusted so that the concentration of molecules in the solution phase remains constant. In addition, it was observed that the molecules that are close to the surface interact with the surface while molecules that are far away do not feel the presence of the surface. As a result, after adjustment of the volume of the simulation cell, the molecules in the solution phase were redistributed uniformly throughout the solution phase to simulate a real solution in which molecules are uniformly distributed. This process was repeated three or four times until no more absorption was observed indicating equilibrium between the surface and the solution. Unabsorbed polyelectrolyte molecules were then removed along with their counter ions, representing a rinsing step. A number of negatively charged PE molecules were subsequently added to the box along with oppositely charged counterions at a concentration of $0.03\sigma^{-3}$. The system was again equilibrated for 20 ns. The value of thickness increment was subsequently determined. More layers of PE were subsequently added using the same procedure described above. Overall charge neutrality was always maintained in the system using counter ions. After completing the depositions, the system was annealed further for a total of 20 ns. Equilibration was confirmed again by monitoring the energy and concentration profiles in the system. In case of the chains with Np = 32, a total of 14 depositions was carried out.

## 3. Results and discussion

Fig. 1 shows the mechanism of deposition of the PE chains on a previously deposited layer. The deposition proceeds through the following steps. The first step is attraction of part of a PE chain in solution to tail and loop segments of the previously deposited layer. This step is followed by gradual flattening of part of the newly deposited chain to become part of the second layer. The other part of the newly deposited chain extends into solution forming the segments that overcompensate the charges. In addition, it is observed that chains of the new layer penetrate deep into the first layer and form a molecular multilayer that is one atom thick. Furthermore, adsorption of the new layer results in rearrangement of the previous layer. A dominant form of rearrangement is folding of the tail segments as shown in Fig. 1. Tail segments from the first layer that protruded out of the surface before deposition flatten and become oriented parallel to the surface. The tail segments from the first layer fold over the oppositely charged chains to contribute to formation of a new layer. The deposition of the second and third layers proceeds via similar mechanisms. In all cases, the underlying layer undergoes rearrangement upon deposition of the subsequent layer to form a molecularly thin layer. Experimental measurements of layer thickness of PE layers deposited from salt free solutions indicate that the layers are monomolecular and are around 3 Å thick [46]. This is at least true for the first few layers. Deposition of subsequent layers follows a similar mechanism. In addition, the system reaches constant energy and constant number of adsorbed particles very fast (after 0.2 ns). Fig. 2(a) shows the structure of the multilayer after a series of six depositions (three deposition cycles). It can be clearly seen that the resulting structure contains many defects and voids. The multilayers are not densely packed. Fig. 3 shows the concentration profiles of the cationic chains after the series of six depositions. There are many interesting observations. First, the concentration profiles are not uniform. They clearly show a high level of disorder in the multilayers. They also show that beads of the PE chains are not all layered in a monolayer fashion except in the first layer. The thickness of the first layer is around 4 Å which corresponds to the van der Waals diameter of a chain bead. Subsequent layers have

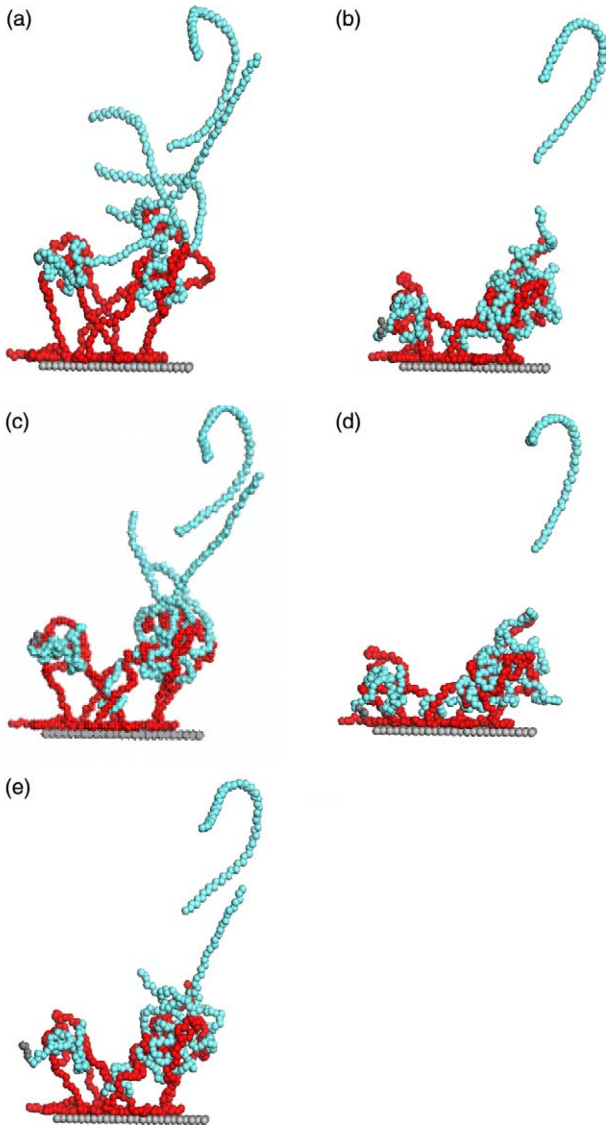

Fig. 1. Mechanism of adsorption of PE molecules on a previously deposited layer.

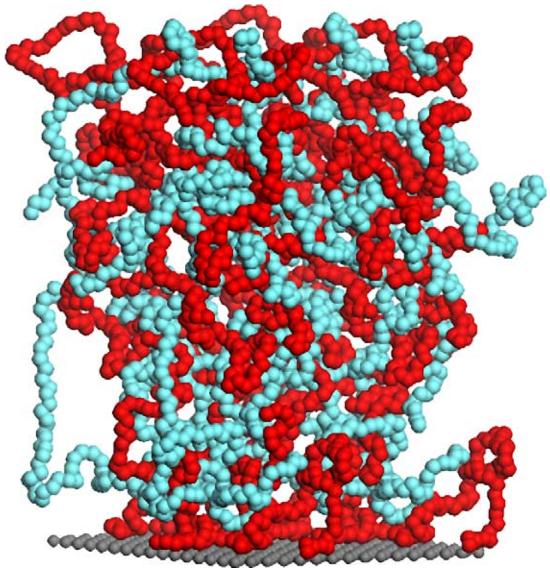

Fig. 2. Configuration of the multilayers with bead charge = 1.

an average thickness of 4.5–5 Å which is slightly higher than the van der Waals diameter of the beads indicating that the beads are not perfectly aligned in a layer. The second observation is that the multilayers show a three zone structure as described by Decher [4]. The first zone in the structure is composed of the first two double layers. The first zone is characterized by sharp concentration peaks and slightly thinner layers. This indicates more ordered and more packed layers. Structure of the first two layers is influenced strongly by the flat rigid substrate, which induces order into the adjacent layers. The second zone is composed of four double layers. These layers are less ordered, less packed and slightly thicker than the layers in zone 1. These layers form the bulk of the multilayer structure and they form once the influence of the rigid substrates disappears. The third zone is a highly disordered region near the interface with the solution. This layer has a thickness of nearly 30 Å and is characterized by a high level of disorder, absence of clear layering and presence of chains extended into solution.

Another observation is that although the total number of depositions was 6, nearly 6–7 double layers formed indicating that more than one layer is formed per deposition. This indicates that chains from one deposition are involved in the formation of many layers. It is worth mentioning here that this phenomenon might be a result of the small width of the simulation box compared to the length of the chain. The fact that chains from one deposition cycle penetrate and participate in the formation of many layers is shown in Fig. 4 which displays the concentration profiles of molecules adsorbed in deposition cycles 1–3 (Fig. 4(a)) and deposition cycles 4–6 (Fig. 4(b)). Chains deposited in one cycle can rearrange and be part of as many as four layers. The concentration profiles of Fig. 4 display the strong interpenetration of the cationic and anionic PE molecules and intermixing of the layers. Except for the first two layers (zone 1), concentration peaks are not very sharp. This result is consistent with the work of Jonas and co-workers who experimentally investigated the internal structure

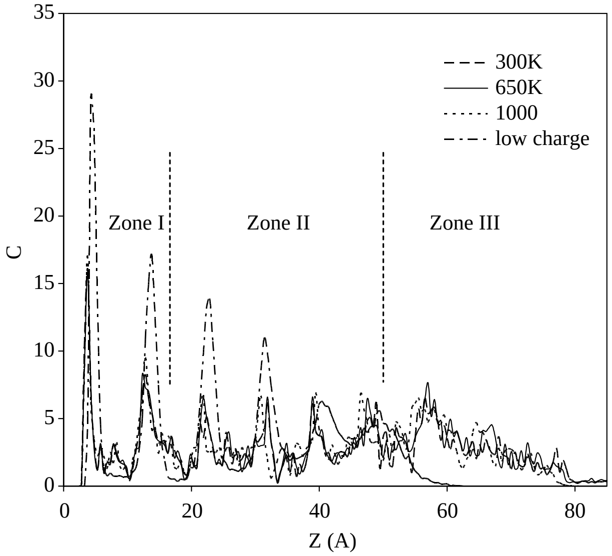

Fig. 3. Concentration profiles of the cationic copolymer at different simulation temperatures and with a charge of 0.1 and temperature of 300 K.

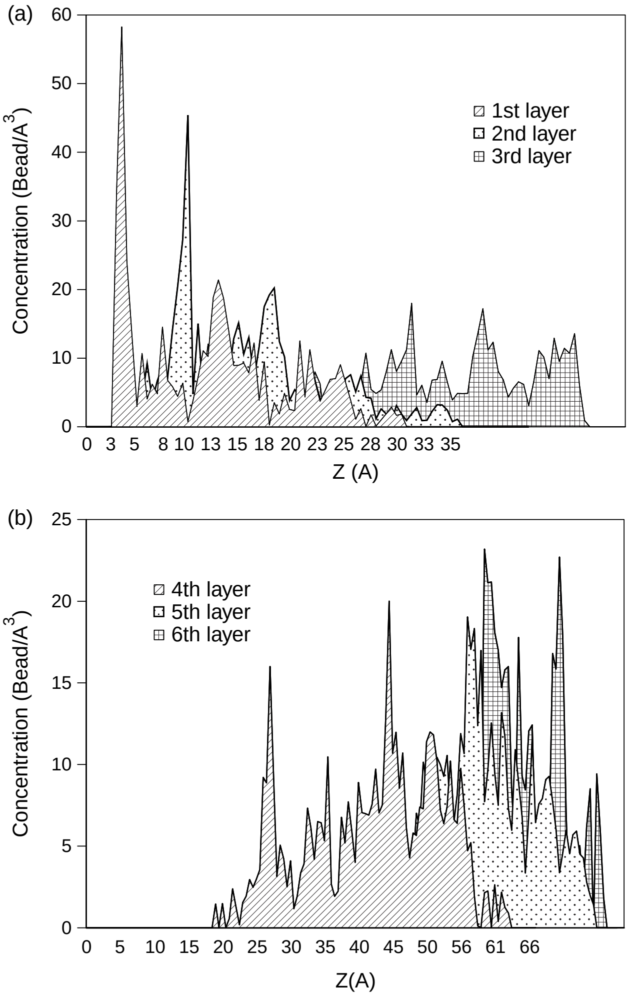

Fig. 4. Concentration profiles of individual layers: (a) depositions 1–3 and (b) depositions 4–6.

of PE multilayers and found that for most PE systems formed using flexible chains; well defined strata are not formed [47].

The highly disordered, defect containing nature of the formed multilayers indicates that the structure of the multilayers formed might not be the optimum thermodynamic equilibrium structure. In order to elucidate the lowest energy equilibrium structure of the multilayers, we try three different approaches. The first approach was to deposit the multilayers at higher temperatures of 650 and 1000 K in order to increase the thermal energy of the system so that it can overcome the electrostatic attractive potential barrier. The resulting multilayer structures were not very different from the structure of the multilayers deposited at 300 K. This is displayed by the concentration profiles of the layers deposited at 650 and 1000 K shown in Fig. 3. The similarity can be understood, because it is clear that increasing the temperature to 1000 K is not sufficient to overcome the electrostatic energy barrier. The second approach was to lower the charge per bead to 0.1 and deposit the layers at a temperature of 300 K. This approach was attempted to lower the energy barrier and allow thermal fluctuations to overcome electrostatic attractions. The resulting multilayer structure is shown in Fig. 5. A well layered and densely packed structure results from this simulation. The new structure is assumed to be the true equilibrium structure if chains were not trapped by the electrostatic attractions. The concentration profile of the cationic PE with low charge is also shown in Fig. 3. Comparing this profile with those of the multilayers with fully charged chains, one can observe differences in order and density of the two systems. The low charge system is more densely packed and has a smaller overall thickness for the same number of beads. The peaks are higher for the low charge system indicating higher bead concentration per layer. However, it is interesting to observe that the layer thickness was not very different from that of the fully charged system. The three zone structure can also be observed in the low charge system, however, the main difference is that the effect of the surface on layer thickness was longer in range, i.e. the concentration of the layers decreased steadily for the five layers shown. Unlike the system with charge 1, steady layer thickness was not attained and more depositions are probably needed to reach that state.

The multilayers formed using the low charge polymers are more densely packed and more highly ordered. But is this the structure that will be assumed by the multilayers if they could overcome the high electrostatic energy barrier? In order to answer this question, we take the final configuration of the low charge multilayers, increase the charge of all beads from 0.1 to 1 and calculate the total and nonbonded energy of the system (system b). Subsequently, we compare the energy of system b with that of multilayers deposited sequentially using polymers with a bead charge of 1 (system a). The energies of systems a and b are shown in Fig. 6. It can be clearly seen in that the energy of system b is lower than that of system a indicating that the energy of system a is at a local minimum and that the system is not at true equilibrium because it is kinetically trapped.

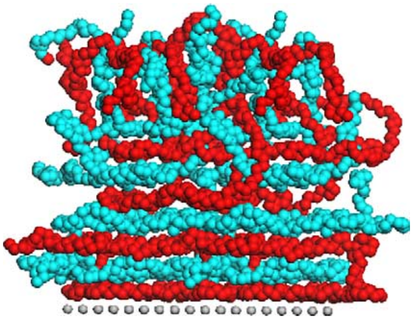

Fig. 5. Configuration of the multilayers with bead charge = 0.1.

The third approach we attempted was to take the final configuration of the high charge multilayers, change the charge of each bead to 0.1 and equilibrate the system for 20 ns. Analyzing the final configuration of the system resulted in a structure that is very similar and has the same energy as the low charge system. The concentration profile of the cationic chains could not be distinguished from that of the low charge chains deposited from solution. This indicates that the high energy chains rearrange to assume an energetically more favorable structure once the high electrostatic energy barrier is overcome. The conclusion that can be made here is that, the high energy chains cannot assume their minimum energy configuration and are trapped by strong electrostatic forces. This is evidenced by presence of a lower energy structure of the multilayers.

Fig. 7 shows a comparison of the intermolecular pair correlation functions of the systems with charge 1 and charge 0.1. The correlation function of the oppositely charged groups indicates higher order and higher correlation and density as expected and has been indicated by the concentration profiles. However, the layer thickness indicated by the distance between minima is almost the same in both cases (slightly thicker for the low charge PE).

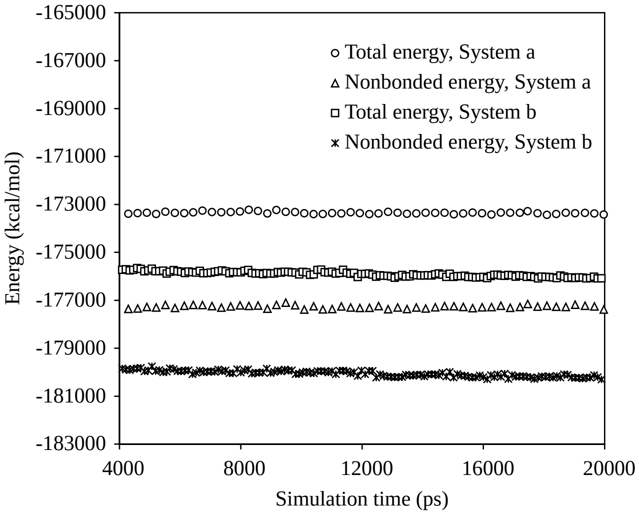

Fig. 6. Total and nonbonded energies per mol for systems a and b. System a: multilayers deposited sequentially from dilute solution with bead charge = 1. System b: multilayers deposited sequentially from solution with bead charges = 0.1. After equilibration, the bead charge was increased to 1 and the energies were calculated with charge 1 and charge 0.1.

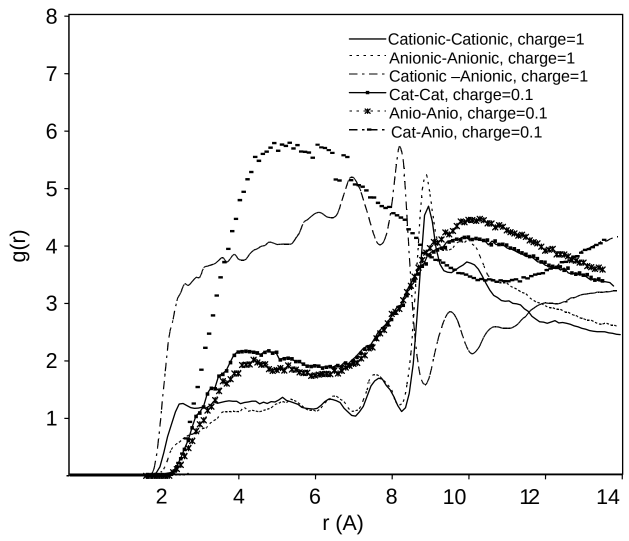

Fig. 7. Comparison of the intermolecular pair correlation functions of the systems with charge 1 and charge 0.1.

We try to answer one final question in this study, that is, what happens to the structure of a layer once more molecules are deposited? To answer this question, we make as many as 14 deposition of the chains with Np = 32 on the negatively charged substrate and observe changes in the structure of the 9th layer as more layers are deposited on top of it. The ninth layer is part of zone 2 in the Decher model. Fig. 8 shows the concentration profile of the 9th layer before and after deposition of further layers. Initially, when the chains are part of zone 3, the concentration profile of the layer is broad and extends from $Z = 35$ to 65 Å. Once more depositions are made; it is observed that the concentration profile becomes sharper and narrower indicating substantial rearrangement of the chains in this zone. It is interesting to observe that chains from the ninth deposition that penetrated deep into underlying layers and extended into the solvent rearranged to be part of the bulk of the layer resulting in the narrower and sharper distribution.

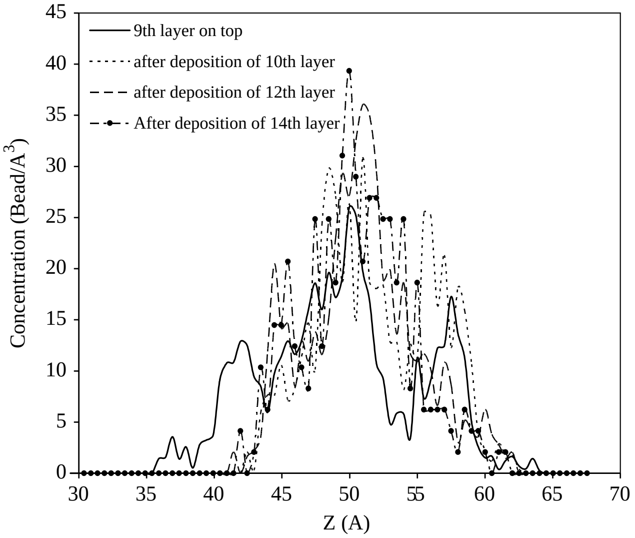

Fig. 8. Change in the concentration profile of the ninth layer before and after deposition of more layers.

## 4. Conclusions

This study shows that the structure of PE multilayers is trapped and is not the lowest energy structure that can be attained if the molecules in the oppositely charged layers are freed from the strong electrostatic attractions. However, this study also shows that the resulting structure is truly layered and that the layer thickness is not very different from the thermodynamic equilibrium layer thickness. The structure of the layers is fuzzy in nature and molecules experience a high level of interpenetration and disorder. There main zones could be distinguished in the structure of the multilayers. The first zone is composed of the 2–3 layers that are next to the surface and is characterized by a high level of order and narrow thickness. Zone three is the interfacial region in contact with the solvent and is characterized by low level of order and presence of chains extended into the solvent. Zone 2 forms the bulk of the layers. In addition, the multilayered structure contains many voids and imperfections resulting from freezing of the structure under the influence of strong electrostatic interactions. Layers in the third zone of the multilayers undergo substantial rearrangement upon deposition of further layers resulting in narrower and sharper distribution.

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