

Molecular Dynamics Simulations of Electrostatic Layer-by-Layer Self-Assembly

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Electrostatic assembly of multilayered thin films through sequential adsorption of polyions in layer-by-layer fashion utilizes the strong electrostatic attraction between oppositely charged molecules. We perform molecular dynamics simulations of multilayers of flexible polyelectrolytes around a charged spherical particle. Our simulations establish that the charge reversal after each deposition step is a crucial factor for the steady layer growth. The multilayers appear to be nonequilibrium structures.

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Electrostatic interactions between macroions play an important role in different areas ranging from materials science to biophysics [1]. For example, electrostatic interactions between multivalent metal ions and double stranded DNA molecules, actin filaments, tobacco mosaic viruses are responsible for their assembly into compact bundle structures [2]. The packaging of DNA into chromosomes is also driven by strong electrostatic interactions between negatively charged DNA and positively charged histones [3]. The complexation of DNA with positively charged polyelectrolytes, dendrimers, or liposomes facilitates the DNA uptake through the negatively charged cell membrane and was used for gene therapy [4]. Electrostatic interactions are also important for understanding the effective attraction between like-charged macroions in a variety of colloidal systems including solutions of charged micelles, dendrimers, and polyelectrolytes [5,6]. In all these systems the electrostatic interactions are so strong that they can effectively be considered at low temperature limit that leads to strong correlations in position and orientation of macroions [1,7,8]. In strongly correlated ionic systems the charge inversion (overscreening or overcharging) becomes possible. In this case, the effective charge (for example, the charge of DNA-polyelectrolyte complex) that is seen from outside by the test charge could be opposite in sign.

Charge inversion [1] plays a central role in electrostatic assembly technique that allows the fabrication of multilayer films from synthetic polyelectrolytes, DNA, proteins, nanoparticles, etc. (see [9] for examples). The key to successful deposition of multilayer assemblies in a layer-by-layer fashion is the inversion and subsequent reconstruction of surface properties. A typical experimental procedure involves immersing a solid substrate into dilute solutions of anionic or cationic polyelectrolytes for a period of time optimized for adsorption followed by a rinsing step to remove any loosely adsorbed material. Further film growth is achieved by alternating the deposition of polyanions and polycations from their aqueous solutions. After a few dipping cycles, experiments show a linear increase of multilayer thickness, indicating that the system reaches a stationary regime.

Charge reversal is necessary for the steady layer growth after each deposition cycle, but it is not sufficient to explain the appearing multilayered structures. An important question that one has to ask is what role the kinetics of complexation between macroions plays in their stratification in the layered fashion. Is multilayered structure a true equilibrium state or is it just one of the possible intermediates that the system visits during its quest toward complete equilibrium? To answer these questions, in this Letter, we study the kinetics of multilayer assembly of oppositely charged polyelectrolytes at a charged spherical particle by molecular dynamics (MD) simulations. We establish that the stratified multilayered structure around adsorbing particle only appears for short simulation runs when adsorbed chains do not have enough time to intermix between different layers. This is an indication of the nonequilibrium nature of multilayer electrostatic assembly.

The MD simulations of multilayer assembly were performed from solutions of polyelectrolytes consisting of $N_p = 32, 16$, and 8 monomers. For each chain length the fraction of charged monomers on a chain is equal to $f = 1, 0.5$, and 0.25 corresponding to every, every second, and every fourth bead carrying a charge. Multilayers were formed around a charged spherical particle that has $N_s = 80$ negatively charged Lennard-Jones beads with a diameter σ . The central particle has 80 overlapping beads on its surface and has a bucky ball structure of C80. The radius of the particle, measured as the distance between the center of the bucky ball and centers of mass of the forming particle beads, is equal to 1.5σ . Such a structure of the central particle prevents penetration of adsorbed chains into its interior.

Polyelectrolyte chains are modeled as bead spring chains of N_p monomers. The connectivity of beads in the chains is maintained by the finite extension nonlinear elastic (FENE) potential [10], with the spring constant $k_s = 15k_B T / \sigma^2$, where k_B is the Boltzmann constant and T is the absolute temperature, and the maximum bond length $R_{\max} = 2.0\sigma$. Counterions were explicitly included in our simulations. Electrostatic interaction between any two charged particles bearing charge valences q_i and q_j , and separated by a distance r_{ij} is given by the Coulomb

potential:

$$U_{\text{Coul}}(r_{ij}) = k_B T \frac{l_B q_i q_j}{r_{ij}}. \quad (1)$$

All charged particles are monovalent ions with $q_i = \pm 1$. The strength of the electrostatic interactions is described by the Bjerrum length $l_B = e^2/\epsilon k_B T$, defined as the length scale at which the Coulomb interaction between two elementary charges e in a dielectric medium with the dielectric constant ϵ being equal to the thermal energy $k_B T$. In our simulations, the value of the Bjerrum length l_B is equal to 1.0σ . The particle-particle particle-mesh (PPPM) method implemented in the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [11] has been used to calculate the electrostatic interactions with all periodic images of the system. Also, all the charged and uncharged particles in this system interact through the truncated-shifted Lennard-Jones (LJ) potential. The cutoff distance of $r_c = 2.5\sigma$ was chosen for the macroion/polymer-polymer and $r_c = 2^{1/6}\sigma$ for polymer-counterion as well as counterion-counterion interactions. The interaction parameter was set to $\epsilon_{LJ} = 0.75k_B T$ for all the pairs. The combination of FENE and LJ potentials prevents the chains from crossing each other during the simulation run.

Simulations were carried out in a constant number of particles, volume, and temperature ensemble (NVT) with periodic boundary conditions. The constant temperature is achieved by coupling the system to a Langevin thermostat. In this case, the equation of motion of i th particle is

$$m \frac{d\vec{v}_i}{dt}(t) = \vec{F}_i(t) - \xi \vec{v}_i(t) + \vec{F}_i^R(t), \quad (2)$$

where \vec{v}_i is the bead velocity and \vec{F}_i is the net deterministic force acting on i th bead of mass m . \vec{F}_i^R is the stochastic force with zero average value $\langle \vec{F}_i^R(t) \rangle = 0$ and δ -functional correlations $\langle \vec{F}_i^R(t) \vec{F}_i^R(t') \rangle = 6\xi k_B T \delta(t - t')$. The friction coefficient ξ was set to $\xi = m/\tau_{LJ}$, where τ_{LJ} is the standard LJ time $\tau_{LJ} = \sigma(m/\epsilon_{LJ})^{1/2}$. The velocity-Verlet algorithm with a time step $\Delta t = 0.01\tau_{LJ}$ was used for integration of the equations of motion (2).

Simulations were performed by the following procedure. The spherical particle remains fixed at the center of a cubic simulation box with the box size $L = 26\sigma$ during the whole simulation run. Counterions from the charged particle were uniformly distributed over the box volume. Then M_1 positively charged polyelectrolytes, together with their counterions, were added to the simulation box constituting the first deposition step. (For our longest chains with $N_p = 32$ there were 16 chains in the simulation box.) During each deposition step, for chains of different lengths, we have maintained the same polymer concentration, $c = 0.03\sigma^{-3}$, of newly added polyelectrolyte chains. After completion of the first simulation run (dipping cycle), unadsorbed polyelectrolyte chains were removed (rinsing step). To separate the adsorbed chains from the rest of polyelectrolytes, we used a cluster algo-

rithm [12] with a cutoff radius equal to σ . After each simulation run, only the counterions needed for compensation of excess charge of the particle-adsorbed chains aggregate, were kept in the simulation box to maintain the system electroneutrality.

At the beginning of the second step, the simulation box is refilled with $M_2 = M_1$ oppositely charged polyelectrolytes together with their counterions. This is followed by another simulation run. We repeated these dipping and rinsing cycles to simulate the buildup of nine layers and performed two different simulations with durations of 2×10^5 and 2×10^6 integration steps for every deposition cycle. Before collecting the data, the system was allowed to equilibrate for a half time of the total simulation run in each dipping cycle.

Figure 1 shows the sequential deposition process of fully charged polyelectrolytes with 32 monomers. Nine simulation layers have been adsorbed and snapshots (a)–(f) represent the first five layers. Each layer of oppositely charged polyelectrolytes has been displayed in a different shading (color) for clarity. Starting with the 80 negative beads on the spherical particle, the adsorbed first layer [snapshot (b)] brings in four chains consisting of 128 charged monomers. Thus, an excess of 48 charges is accumulated around the sphere and allows further adsorption of oppositely charged polyelectrolytes. The ensuing simulation led to the deposition of the second layer [snapshot (c)]. Further dipping cycles are repeated [snapshots (d)–(f)] to assemble layers of polyelectrolytes onto one another.

The number of chains in the layers increases with the deposition cycles. This can be seen by plotting the number of adsorbed monomers during the assembly as a function of the number of deposition cycles (Fig. 2). The increase in the number of adsorbed monomers, as evident from Fig. 2, is dependent on the degree of polymerization and

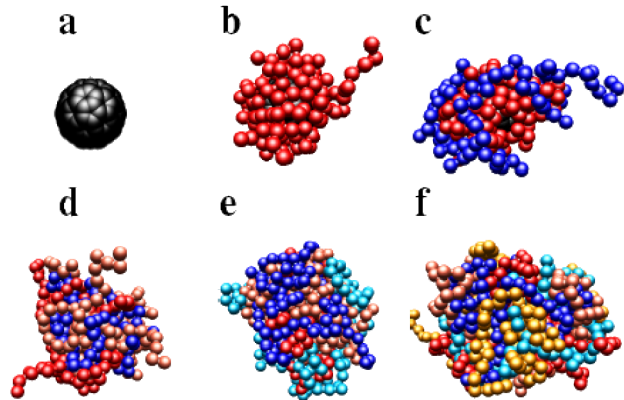


FIG. 1 (color online). Sequential evolution of the layer structure around the spherical macroion during the adsorption of fully charged ($f = 1$) polyelectrolytes, with number of monomers $N_p = 32$. Snapshots taken after the completion of deposition cycles from 1 through 5 with time duration 2×10^5 MD steps per each deposition step. (a) Macroion is shown in black; (b)–(f) Buildup of layers 1 to 5.

the fraction of charged monomers. The adsorbed amount is consistently high for chains with $N_p = 32$ ($f = 1$ and 0.5) followed by $N_p = 16$ ($f = 1$) over others. Simulations of much longer durations (2×10^6 MD steps each) result in similar overcharging and layer buildup. For chains with degrees of polymerization $N_p = 8$ ($f = 1$) and $N_p = 16$ ($f = 0.5$), the number of adsorbed chains is significantly less and seems to approach a steady state as the number of deposition cycles increase. An initial repetitive pattern of adsorption and desorption with no gain in the number of adsorbed chains is found for these chains. In the case of $N_p = 8$ ($f = 0.5$) as well as weakly charged chains with $f = 0.25$ for all the chain lengths ($N_p = 32, 16$, and 8), although the first layer is formed, it falls short of charge reversal precluding further layer growth. This trend can be understood by considering the concept of charge over-compensation due to charge fractionalization [1]. When a polyelectrolyte chain adsorbs electrostatically on a charged surface, the stoichiometry is greater than 1:1, more often than not, with the formation of loops and tails. The charge on these loops and tails builds up the excess charge essential for the growth of the multilayers. This effect is more pronounced in longer chains, with higher charges than in the ones that are either short or partially charged. In the case of shorter chains, the loose ends that form tails or loops are less probable and in chains that are not fully charged, the residual charge is less even if loops and tails are formed.

The adsorption of new layers is also accompanied by the desorption of chains from previous layers in exchange for newer chains being adsorbed. For example, six deposition cycles of polyelectrolyte chains with degree of polymerization $N_p = 16$ ($f = 1$), have 496 monomers. In the seventh layer, there are a total of 608 monomers adsorbed, out of which the contribution of the first five layers is only 464 monomers. This loss of two chains was indeed an exchange that took place between polyelectro-

lytes of similar charge, while the total number of adsorbed chains increased substantially. This dynamic exchange has occurred during the assembly indicating the accessibility of interior layers to the newly adsorbed chains. This happens more frequently in the longer simulation runs. It is worthwhile to note that Schlenoff and co-workers reported slow displacement or exchange of adsorbed chains along with kinetically irreversible nature of the deposited layers [13]. Thus, desorption or process of chain exchange evidenced in this simulation closely resembles what happens in an actual experiment and indicates the dynamic nature of the assembly process.

The radial density distribution function $\rho(r)$, for the multilayer assembly during short deposition cycles lasting 2×10^5 MD time steps, is shown in Fig. 3. The inset in Fig. 3 shows the difference in radial density distribution of positively and negatively charged chains, $\Delta\rho(r) = \rho_+(r) - \rho_-(r)$, in a multilayer arrangement. These distribution functions were averaged separately for each deposition step after the formation of all the adsorbed layers. This separate data collection allowed us to analyze the evolution of the multilayer structure and the interpenetration of the layers during the deposition process. The plots clearly indicate a layered distribution of the polyelectrolyte chains around a spherical particle of radius 1.5σ . The first layer has more monomers present in it and hence the sharp peak in the density profile. A decrease in density of the subsequent layers is associated with the increase of the effective radius of the adsorbing aggregate. Also, the appearance of chains from the 5th and 9th layers around the central particle can be attributed to the asymmetric layer growth and the “mistakes”

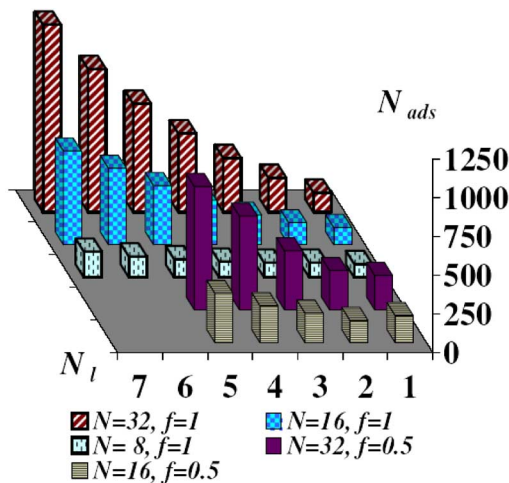


FIG. 2 (color online). Dependence of the number of adsorbed monomers (N_{ads}) on the number of deposition cycles (N_l) for the time duration of 2×10^5 MD steps per each deposition cycle.

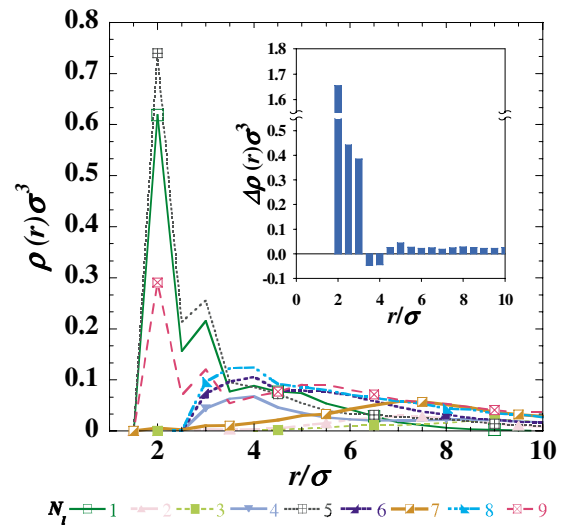


FIG. 3 (color online). Density profiles of the fully charged ($f = 1$) polyelectrolyte chains with $N_p = 32$ after completion of nine deposition cycles (N_l) with a duration of 2×10^5 MD steps each. Inset shows the difference between the corresponding radial monomer densities of positively and negatively charged chains, $\Delta\rho(r) = \rho_+(r) - \rho_-(r)$.

propagating as the deposition proceeds. On the other hand, when the simulations were performed for 2×10^6 MD steps (~ 10 times longer), the chains have enough time to rearrange. Chains with like charges from different deposition cycles do exchange places. This exchange is limited to immediate neighbors in the shorter simulation runs. The penetration is almost complete in the longer simulation run (2×10^6 MD steps).

The reason for slow intermixing between the layers is the formation of ionic pairs between oppositely charged monomers. Such ionic pairs act as effective friction centers slowing the motion of polymer chains. The polymer dynamics in this case is controlled by association and dissociation of the ionic pairs and can be described in the framework of the sticky Rouse model for short chains, and by the sticky reptation model for chains above the entanglement threshold [14]. Our simulations show that the formation of ionic pairs could lead to an increase of the chain relaxation time in the adsorbed layer in comparison with that of a chain in a solution. Based on this, the multilayered structure can be understood as a kinetically trapped nonequilibrium state and given sufficient time, the multilayers would eventually condense to the bilayer structure. Thus, multilayer formation can be seen as a special case en route to the more stable bilayer formation. In a recent study [15], polyelectrolyte multilayering was studied using the Monte Carlo simulations based on the assumption that multilayering occurs whether one proceeds in a stepwise fashion as envisaged in a real experiment or when the oppositely charged polyelectrolytes are added together. In such a situation, it was noted that the polyelectrolyte bilayering on a spherical surface requires a sufficiently strong extra short-ranged interaction between the macroion and the polyelectrolyte.

The theoretical models of electrostatic assembly based on the notion of thermodynamic equilibrium during polymer adsorption process were proposed by Netz and Joanny [16] for a system of semiflexible polymers and by Mayes *et al.* [17] for multilayers of flexible polymers. In these models, each new growing layer was assumed to be in thermal equilibrium with surrounding solution during the deposition step. After the deposition was complete the layer structure was fixed providing a solid charged substrate for the next layer. The idea of a frozen layer structure contradicts the results of our simulations. In our simulations, we found a strong intermixing of the layers even in the case of short deposition cycles. The intermixing between polyelectrolyte chains deposited during different deposition cycles continues during the whole simulation run. Thus, the assumption of the frozen layer structure should be reconsidered to obtain a sound theoretical model of the electrostatic assembly.

In conclusion, in our MD simulations we have reconstructed the experimental situation of multilayer assembly around charged spherical particle. The multilayer formation was found to be a nonequilibrium state ap-

peared only in short simulation runs. When the system was allowed to equilibrate during each deposition step for longer period of time the multilayered structure was reduced to bilayer. The exchange of chains indicative of a nonfrozen inner layering and the resulting interdiffusion of layers recreate an experimental situation. Another important feature of multilayer assembly is the ion pair formation between oppositely charged polyions. The discreteness of charge pair interactions lays emphasis on the critical charge threshold required to build the layers. Only strongly charged chains were able to regenerate the surface properties and to produce steady buildup of multilayers. Finally, the nonequilibrium nature of polyelectrolyte multilayering certainly leaves scope for further theoretical work. The successful theory of multilayer assembly should explicitly take into account the dynamic nature of chain adsorption.

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