

Brownian Dynamics Simulations of Rigid Polyelectrolyte Chains Grafting to Spherical Colloid

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Abstract Brownian dynamics simulations are employed to explore the effects of chain stiffness and trivalent salt concentration on the conformational behavior of spherical polyelectrolyte brush. The rigid brush adopts bundle-like morphology at a wide range of trivalent salt concentration. The number variation of bundles pinned on the colloid surface shows a non-monotonic profile as a function of the chain stiffness. The radial distributions of monomers and ions and the charge ratio between condensed ions and monomers are calculated. The charge inversion is observed for the high salt concentration regardless of chain rigidity. Furthermore, the pair correlation functions of monomer-monomer and monomer-salt cation are used to elucidate the aggregated mechanism of the bundle-like structure.

Keywords Brownian dynamics simulation; Spherical polyelectrolyte brush; Chain stiffness; Trivalent salt concentration; Pinned bundle morphology

Citation: Hao, Q. H.; Zheng, Z.; Xia, G.; Tan, H. G. Brownian Dynamics Simulations of Rigid Polyelectrolyte Chains Grafting to Spherical Colloid. Chinese J. Polym. Sci. 2018, 36(6), 791–798.

INTRODUCTION

When polyelectrolyte chains are densely grafted on the surfaces of various geometries, the so-called polyelectrolyte brush is formed. Polyelectrolyte brushes offer inspiring possibilities to tune the surface properties, which are important in many scientific fields including colloid stabilization^[1], lubrication^[2, 3], protective coating^[4], functional layers with switchable adhesion and wetting properties^[5], and so forth. For these reasons, polyelectrolyte brushes have recently received a great deal of attentions by theory, experiments, and simulation studies^[6–9]. However, most of studies concentrate on brushes formed from completely flexible chains. There is limited understanding of grafted semi-flexible or stiff polymers.

Some studies of the polyelectrolyte brushes consisting of semi-flexible or rod-like chains have been carried out^[10–19]. For example, by means of neutron scattering techniques, Guenoun *et al.*^[10] probed the structure of the spherical polyelectrolyte brushes formed by the charged corona and the neutral hydrophobic micelle. A rod-like picture of the arms was observed, which appeared very weakly sensitive to the addition of monovalent salt. Using electrochemical methods, the charging behavior of the semi-flexible single-stranded DNA (ss DNA) planar brush as a function of chain coverage and salt concentration was probed by Shen *et al.*^[11]. Employing the optical tweezer apparatus, Kegler *et al.*^[12]

measured the thickness of the stiff, double-stranded DNA (ds DNA) spherical brush in the monovalent salt solutions. The brush thickness H decreased with $C_s^{-1/3}$ (C_s is the salt concentration), which was in agreement with the prediction of the scaling theories^[1]. On the simulation side, Fazli *et al.*^[13] conducted a Monte Carlo (MC) simulation to study the structure-property relationships of planar rod-like polyelectrolyte brushes in the free salt solutions with monovalent and multivalent counterions. They demonstrated the emergence of surface patterns in the rod conformations, namely, the staggered type for monovalent counterions and the “tepee frameworks” for the trivalent counterions. Likos *et al.*^[14] studied the conformations of the spherical DNA polyelectrolyte brush by means of molecular dynamics (MD) simulations. They pointed out that the shape of the brush was rather insensitive to ionic strength for rigid chains. Wynveen and Likos^[15, 16] performed MD simulations and a theoretical treatment to investigate the combined effects of chain stiffness and salt concentration on the interactions between two opposing flat surfaces sparsely tethered with polyelectrolyte chains. Cao *et al.* presented a series of MD simulation studies to explore the conformation of grafted bottle-brush polyelectrolyte backbone with rigid side chains^[17], the effects of salt concentration and chain stiffness on the responses of planar polyelectrolyte brushes under external electric fields^[18], and the conformational properties of flexible and semi-flexible polyampholyte grafted on the internal surface of the spherical cavity^[19].

Considering the common existence of assemblies of stiff polymers in biological systems, examples including DNA^[12], filamentous actin (F-actin)^[20], and microtubules^[21], it is

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Received August 11, 2017; Accepted September 11, 2017; Published online January 15, 2018

necessary to explore the effect of chain stiffness on the properties of the polyelectrolyte brushes. Unlike the polyelectrolyte brushes formed by the flexible chains, the surface patterns of the grafted polyelectrolyte chains with stiffness have received few attentions so far. Recently, it was reported that the rod-like ungrafted polyelectrolyte chains favored aggregation and formed bundle-like structure in the salt solutions^[22–24]. To understand whether the rigid polyelectrolyte chains grafting on the spherical colloid surface can gather and then emerge the surface patterns is our focus in this work. Furthermore, it is confirmed that the salt concentration can also play an important role on the structure of polyelectrolyte brushes. In addition, the identical curvature of the spherical substrate may introduce more interesting phase behaviors for the tethered polyelectrolyte layers. The MD simulation incorporating with Langevin thermostat is called Brownian dynamics (BD) simulation^[25–27], which is commonly used in studying the properties of polyelectrolyte brushes^[17–19]. Therefore, by means of BD simulations, the effects of chain rigidity and salt concentration on the surface patterns of spherical polyelectrolyte brushes are investigated thoroughly. Specifically, the number of bundles, the brush thickness, the radial distribution profiles, the ratio between charges of condensed ions and the monomers, and the pair correlation functions are calculated. The rest of the paper is organized as follows. The simulation details are described in the next section, followed by the results and discussion as the main part. Brief conclusions are provided in the final section.

SIMULATION DETAILS

The spherical polyelectrolyte brush is modeled as a neutral colloid of radius R_c with $M = 45$ chains. Each chain contains $N = 36$ monomers with diameter σ , which are immobilized by one end at the colloid surface. The radius of the colloid is set as $R_c = 5.0\sigma$. The grafted sites are uniformly distributed on the colloid surface. Every four monomer along the chain carries a negative unit charge $-e$, resulting in a charge fraction $f = 0.25$. Counterions with positive unit charge $+e$ are added to guarantee the charge neutrality in the implicit solvent system. The salt described as trivalent cations $+3e$ and monovalent anions $-e$ is also included. The diameters of counterions and salt ions are also selected as σ . The colloid is situated at the center of the cubic simulation box with a side length of $L = 90\sigma$ and periodic boundaries, which is large enough to avoid interactions between the brush and its periodic image.

The short-range excluded volume interaction between any two beads is described by a truncated-shifted Lennard-Jones (LJ) potential,

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right] & r \leq r_c \\ 0 & r > r_c \end{cases} \quad (1)$$

where r denotes the separation between any two beads. ϵ is the strength of the pairwise interaction and equals $1.0k_B T$ (k_B is Boltzmann constant and T is the desired temperature) regardless of the bead type, r_c is the cutoff radius and is fixed

as follows, $r_c = 2.5\sigma$ is for only monomer-monomer interactions, and otherwise $r_c = 2^{1/6}\sigma$.

The adjacent monomers along the chain are connected via a finite extensible nonlinear elastic (FENE) potential^[28],

$$U_{\text{bond}}(r) = -\frac{1}{2}k_{\text{spring}}R_{\text{max}}^2 \ln \left[1 - \left(\frac{r}{R_{\text{max}}} \right)^2 \right] \quad (2)$$

in which $k_{\text{spring}} = 30.0\epsilon/\sigma$ and $R_{\text{max}} = 1.5\sigma$ are the spring constant and the maximum bond length, respectively.

The chain stiffness is taken into account through using a harmonic angle potential,

$$U_{\text{angle}}(\theta) = \frac{1}{2}k_{\theta}(\theta - \theta_0)^2 \quad (3)$$

where θ is the angle subtended between the neighboring bonds, θ_0 is the equilibrium value of the angle and equals π , the prefactor k_{θ} is the bending energy constant, which is used to modulate the chain rigidity.

The electrostatic interaction between charged particles is described by the usual Coulomb potential,

$$U_{\text{Coul}}(r) = k_B T \frac{\lambda_B q_i q_j}{r} \quad (4)$$

where q_i and q_j are the valences of particles i and j . The Bjerrum length $\lambda_B = e^2/(4\pi\epsilon_0\epsilon_r k_B T)$ is set as 3.0σ , where ϵ_0 and ϵ_r are the vacuum permittivity and the dielectric constant of the implicit solvent. Coulombic interactions are calculated by the particle-particle/particle-mesh (PPPM) algorithm with estimated accuracy 10^{-3} ^[29].

The open-source software LAMMPS^[30] is used to carry out BD simulations in the NVT ensemble. All parameters are dimensionless based on the three basic units (length σ , mass m , and energy ϵ). Constant temperature $T = 1.0\epsilon/k_B$ is maintained by coupling the system to a Langevin thermostat. The equation of motion for bead i is described as

$$m \frac{d^2 \vec{r}_i(t)}{dt^2} = -\nabla_i U - \zeta \frac{d\vec{r}_i(t)}{dt} + \vec{F}_i^R(t) \quad (5)$$

where m is the mass of the bead. The mass $m = 1.0$ is identical for all types of beads. U denotes the total potential energy of the system, namely, $U = U_{\text{LJ}} + U_{\text{bond}} + U_{\text{angle}} + U_{\text{Coul}}$. ζ is the friction coefficient. $\vec{F}_i^R$ is the random force^[31] with zero average value $\langle \vec{F}_i^R(t) \rangle = 0$ and with the correlation function $\langle \vec{F}_i^R(t) \vec{F}_i^R(t') \rangle = 6\zeta k_B T \delta(t - t')$. And the correlation function of the random force is used to couple the system to the heat bath. The value of the friction coefficient is set to $\zeta = 0.143m/\tau$, where τ is the standard LJ-time unit.

A dimensionless parameter in view of the ratio between the total charges of the salt cations and those of the

$$\text{polyelectrolyte chains is defined as } \gamma = \frac{\left| 3e \left(L^3 - \frac{4\pi}{3} R_c^3 \right) C_s \right|}{MNf(-e)},$$

which is used to reflect the effect of the salt concentration on the conformation of the brush. The value of parameter γ is varied from 0.01 to 10.0. And the value of k_θ spans from 5.0 to 100.0 corresponding to different chain stiffness in our simulation. The configurations and velocities of the particles are generated by the velocity-Verlet MD algorithm. The integration time step of $\Delta t = 0.01\tau$ is used. Initially, the polyelectrolyte chains are fully extended along the radial direction. The counterions and salt ions are homogeneously dispersed within the accessible space of the simulation box. The system is equilibrated for 2×10^6 time steps, and then a production run is performed for 3×10^6 time steps. A snapshot from simulations is saved every 2×10^3 time steps and 1501 configurations are collected for analyzing the properties of the spherical brushes by our programs.

RESULTS AND DISCUSSION

In the case of tethered polyelectrolyte chains with stiffness, the spherical brush is inclined to self-assemble into pinned cylindrical bundles pointing along the radial direction of the grafted colloid. A subset of bundle morphologies with different amounts of bundles is illustrated in Fig. 1(a). In experiments, for realistic biomolecules such as DNA, F-actin, and microtubules, the ionic correlations of multivalent counterions together with the stiffness of chains favor bundle formation^[32]. Based on MD simulations, it was reported that the aggregation of similarly charged rod-like polyelectrolyte chains can lead to the formation of finite bundles^[22–24]. For the rigid chains tethered at one end to the colloid surface, it is still observed that the bundle-like morphology is formed in

the confinement associated with grafting. Moreover, the number of pinned bundles can be controlled by salt concentration and chain stiffness.

In order to clarify the influence of chain stiffness on the bundle-like morphology, we plot the number of bundles in one brush as a function of chain stiffness, which is shown in Fig. 1(b). Three typical salt concentrations are provided, namely, the low salt concentration $\gamma = 0.1$, the stoichiometric salt concentration $\gamma = 1.0$, and the high salt concentration $\gamma = 10.0$. When the chain stiffness is weak ($k_\theta \leq 25.0$), the increase of the chain stiffness can lead to an increase in the number of the bundles for all salt concentrations. The electrostatic repulsion between charged monomers combined with the chain stiffness make the chains separate as far as possible, which opposes bundle growth. The addition of multivalent salt will screen the electrostatic repulsion and induce bridging attraction among the charged monomers, which favor aggregation of the polyelectrolyte chains. The balance of the two above-mentioned effects will stabilize the bundle-like structure. Once the chain stiffness parameter exceeds 25.0, the number of bundles is rather insensitive to the chain rigidity. Moreover, for fixed chain stiffness, the number of bundles decreases with the increase of the trivalent salt concentration for $\gamma \leq 1.0$. The trivalent salt ions act as the gluing agent to promote aggregation, which is in agreement with available experiments^[32, 33].

To investigate quantitatively the extension of the brush formed by stiff chains, we calculate the average height of the

grafted layer using the formula $H = \frac{2 \int_0^{\frac{1}{2}} r \rho_m(r) dr}{\int_0^{\frac{1}{2}} \rho_m(r) dr} - R_c$,

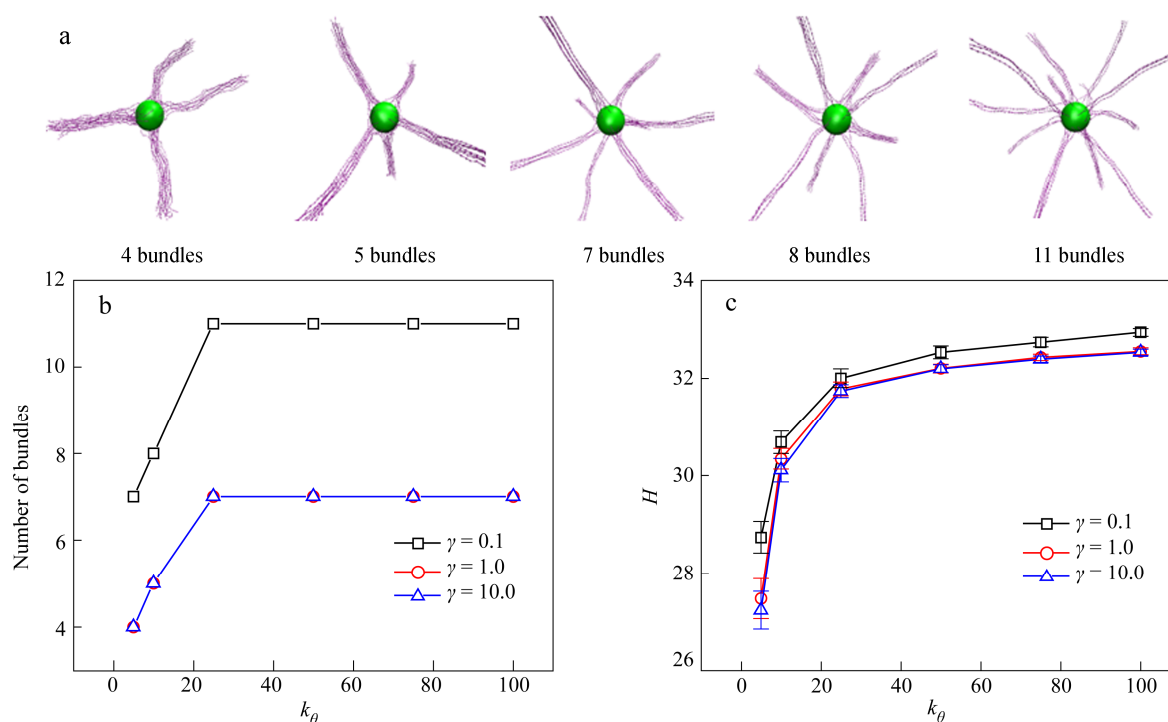


Fig. 1 (a) Snapshots of spherical polyelectrolyte brushes with different numbers of bundles from simulation; (b) The number of bundles tethered on colloid versus the rigidity of the chains; (c) The thickness of the spherical polyelectrolyte brush as a function of the rigidity of the chains

where $\rho_m(r)$ is the radial distributions of the monomers. The brush height H as a function of the chain stiffness for different salt concentrations is illustrated in Fig. 1(c). With the increase of the chain stiffness, the brush height increases obviously due to the strong bending energy of stiff chains. For the strong stiff brush $k_\theta > 25.0$, its height scarcely changes with the chain stiffness, which means that the chains already adopt a strongly extended conformation. Furthermore, for the fixed chain stiffness $k_\theta \leq 5.0$, the brush height decreases with the increasing salt concentration for $\gamma \leq 1.0$, while for high salt concentration $\gamma > 1.0$, the brush height is not affected by the salt concentration. For $k_\theta > 5.0$, the brush height is rather insensitive to the salt concentration, which can be attributed

to the fact that the reduced osmotic pressure is not enough to overcome the bending energy due to the added trivalent salt. When the grafted chains are sufficiently rigid, the independence of the brush height on the salt concentration was also observed by simulation for the planar polyelectrolyte brush^[18].

In order to understand the bundle morphology of the brush, we select three typical stiff chains to calculate the radial distributions of monomers, counterions, salt cations, and end-monomers. The results are depicted in Fig. 2. As shown in upper panels of Fig. 2, the radial distributions of monomers display an oscillatory profile close to the grafting surface. The oscillation decays with the increase of distance r and evolves

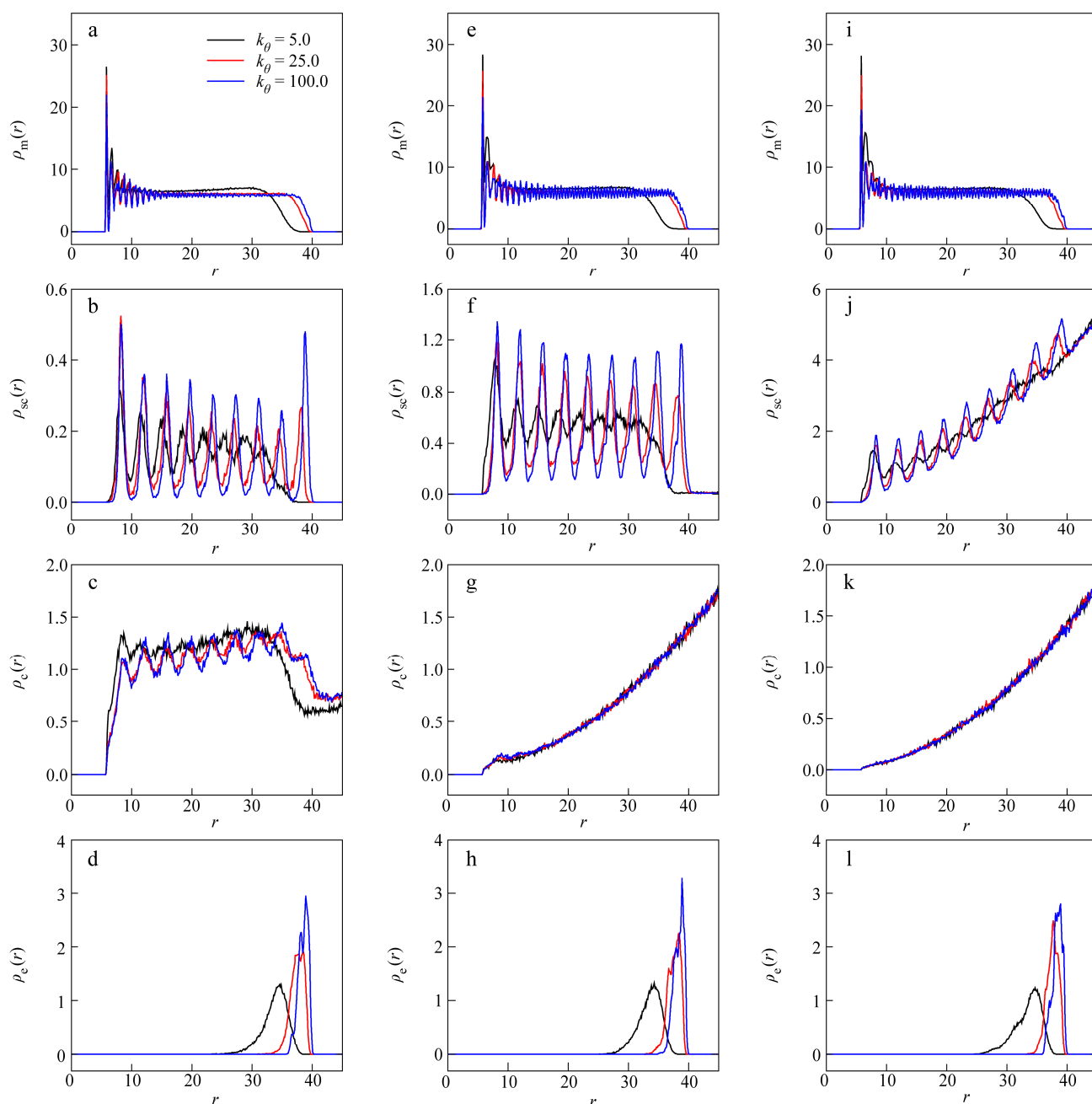


Fig. 2 Radial distributions of monomers ρ_m , salt cations ρ_{sc} , counterions ρ_c , and end-monomers ρ_e with different chain stiffness: (a–d) low salt concentration $\gamma = 0.1$, (e–h) moderate salt concentration $\gamma = 1.0$, and (i–l) high salt concentration $\gamma = 10.0$ (The online version is colorful.)

into a flat profile eventually. We can understand these oscillatory curves by means of analyzing an extreme situation, that is, all the tethered chains are fully stretched along the radial direction. It is imagined that there are 36 (the polymerization degree of the grafted chains) sharp peaks in the radial distribution profile of monomers. The more stretched the chain is, the more pronounced the oscillatory radial distribution profile is. This is not the case for the polyelectrolyte brushes formed by the flexible chains^[34], namely, the magnitude and range of oscillation in the monomer radial distributions are less than those of the rigid brushes. Towards the end of the brush, the enhanced lateral fluctuations of the chains give rise to the flat profile. The oscillatory profile of monomers was also observed for the semi-flexible DNA chains grafted on the spherical surface of the colloids^[14]; however, the bundle-like structure was not observed in their simulation. Furthermore, the oscillatory feature becomes pronounced with the increase of the chain stiffness for all the salt concentrations.

For $\gamma \leq 1.0$ (see Figs. 2b and 2f), the added salt cations are effectively accumulated around the charged monomers due to the strong electrostatic attraction. The profile of the distribution of salt cations shows an oscillatory curve because of the chain rigidity. And the oscillation becomes more pronounced with the increase of chain stiffness. There are nine charged monomers in each chain ($f = 0.25$), and it is worth noting that nine peaks are observed in turn along the radial direction for the distribution of salt cations. Furthermore, the peaks close to the grafting surface and near the chain end are more pronounced than those in the middle part of the brush. We can understand this feature by analyzing the competition between the electrostatic attraction and the translational entropy gain from the lateral fluctuations. Because of the curvature of the spherical grafting surface, the local charge density of the chains close to the grafting surface is higher than that far from the grafted surface, which corresponds to a lower value of the local electrostatic potential. The relatively low Coulomb potential promotes the

added multivalent salt cations accumulation near the grafting surface. The increase of translational entropy from an additional freedom close to the rim of the brush promotes the aggregation of the trivalent salt cations around the terminal monomers. To our knowledge, it is the first time to predict that the multivalent salt ions are accumulated initially both close to the grafting surface and at the end of the brush for the rigid chains grafted on the spherical colloid surface. For $\gamma > 1.0$ (see Fig. 2j), the excessive salt cations dissociate out of the brush and disperse in the solution.

For the low salt concentration $\gamma = 0.1$ (see Fig. 2c), the added salt cations cannot neutralize the charged monomers. Most of the counterions are confined around the charged monomers. Because of the chain stiffness, an obvious oscillation distribution profile for the counterions is observed. For the high salt concentrations $\gamma \geq 1.0$ (see Figs. 2g and 2k), the charged monomers are completely neutralized by the trivalent salt cations. The counterions evaporate away from the charged monomers, which leads to a gradually increasing curve for the radial distribution of the counterions. The single peak profile of the end-monomers (see Figs. 2d, 2h, and 2l) reveals that the chains with stiffness adopt a stretched conformation in the trivalent salt solutions.

To clarify the aggregated mechanism of the bundle-like structure, the ion condensation along the rigid chain is analyzed. If the distance of an ion to any monomer is smaller than λ_B , the ion is considered to be condensed on the chain. The dimensionless parameters ψ_c , ψ_{sc} , and ψ_{sa} are calculated, which are defined as the ratio of condensed charges of counterions, salt cations, and salt anions respectively to the chain bare charges. And the sum $\psi_{tot} = \psi_c + \psi_{sc} - \psi_{sa}$ are also calculated. The condensed charge ratios for chain stiffness $k_\theta = 5.0$ and 25.0 as a function of γ are depicted in Fig. 3. For $k_\theta > 25.0$, the condensed charge ratios remain unchanged with the case of $k_\theta = 25.0$, which are not shown in Fig. 3. As can be seen in Figs. 3(a) and 3(b), for $\gamma = 0.01$, since there is only a small amount of trivalent salt cations in the solution, the

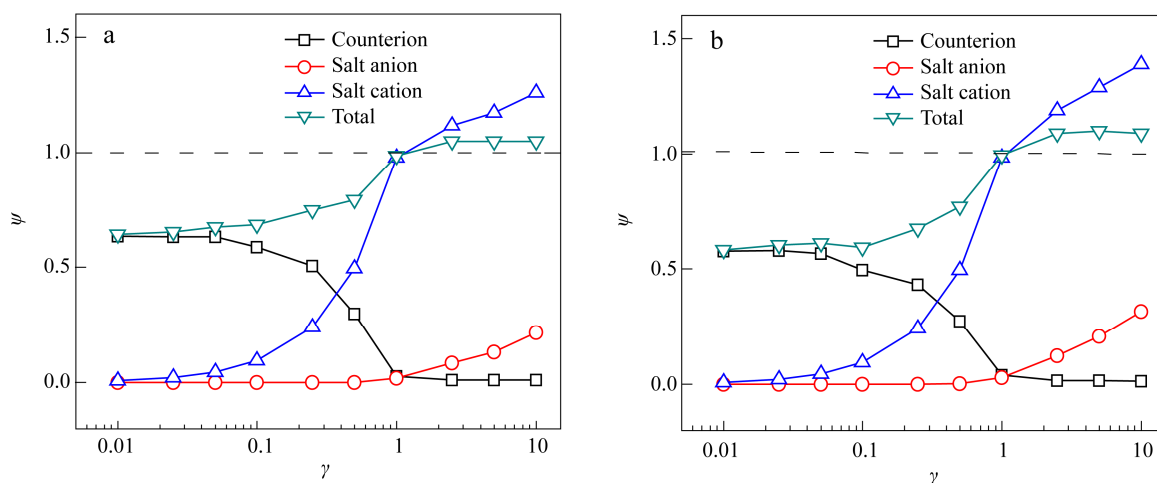


Fig. 3 Ratio of total charge of counterions ψ_c (square), salt anion ψ_{sa} (circle), salt cation ψ_{sc} (upper triangle), and the sum $\psi_{tot} = \psi_c + \psi_{sc} - \psi_{sa}$ (down triangle) to the amount of charges in the brush as a function of γ : (a) $k_\theta = 5.0$, (b) $k_\theta = 25.0$ (The case of brush charge neutralization ($\psi_{tot} = 1.0$) is marked with a dashed line.)

monovalent counterions are still dominant to neutralize the charged monomers. As γ increases ($0.01 < \gamma \leq 1$), once the trivalent salt cations are added in the solution, they replace the condensed monovalent counterions to accumulate around the charged monomers. For $\gamma > 1$, the excess trivalent salt cations together with the monovalent salt anions are condensed on the polyelectrolyte chains. The total condensed ratio ψ_{tot} is slightly greater than the unity, which is considered as the charge inversion phenomenon. The charge inversion becomes obvious when the chain stiffness k_θ changes from 5.0 to 25.0 (see Figs. 3a and 3b). This charge inversion was also observed

for flexible planar polyelectrolyte brush in trivalent salt solution based on MD simulations^[34, 35].

In order to further characterize the bundle morphology of the brush, the pair correlation functions of monomer-monomer $g_{\text{m-m}}(r)$ and monomer-salt cations $g_{\text{m-sc}}(r)$ are calculated and shown in Fig. 4. For clarity, the height of the first peak of $g_{\text{m-m}}(r)$ and $g_{\text{m-sc}}(r)$ is presented in Fig. 5. For a fixed salt concentration, the height of first peak located at $r = 1.0$ in $g_{\text{m-m}}(r)$ decreases with the increase of chain stiffness, which evidences that the intrachain neighbour correlation weakens (see Fig. 5a). However, the other peaks become

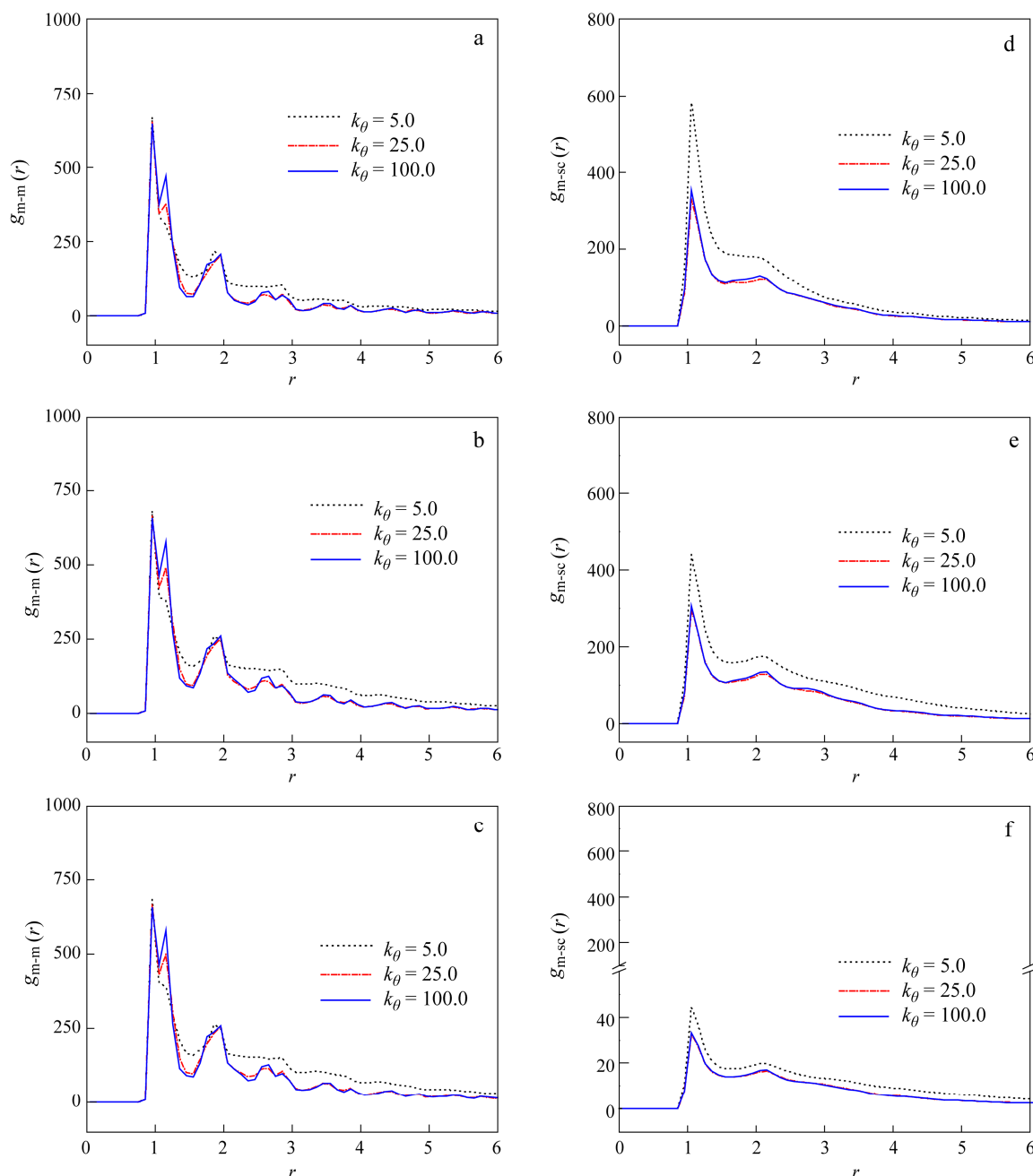


Fig. 4 The pair correlation functions of (a–c) monomer-monomer $g_{\text{m-m}}(r)$ and (d–f) monomer-salt cations $g_{\text{m-sc}}(r)$ for different salt concentrations: (a, d) $\gamma = 0.1$, (b, e) $\gamma = 1.0$, (c, f) $\gamma = 10.0$

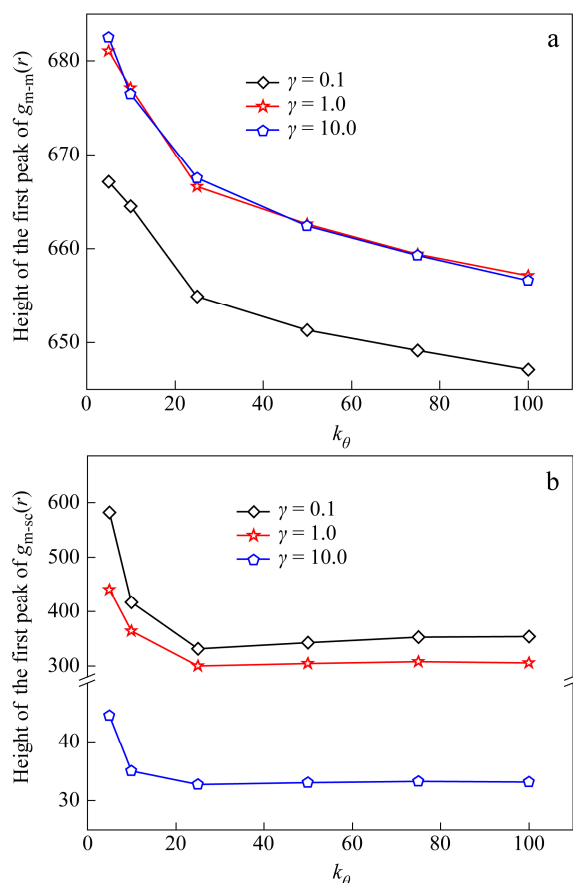


Fig. 5 The height of the first peak of (a) $g_{m-m}(r)$ and (b) $g_{m-sc}(r)$ as a function of the chain stiffness in different salt concentrations

pronounced with the increasing bending rigidity, which corresponds to an increase of interchain correlation. Furthermore, the appearance of long-range structural order in $g_{m-m}(r)$ is represented as the increasing number of bundles with the increasing chain stiffness in Fig. 1(b). The pair correlation $g_{m-sc}(r)$ weakens with the increase of chain stiffness (see lower panels of Fig. 4) for $k_\theta < 25.0$, which can be attributed to the increasing long-range order originated from chain stiffness. For fixed chain stiffness, the value of $g_{m-sc}(r)$ decreases with the increase of the salt concentration, which is distinct from polyelectrolyte brush formed by flexible chains^[35]. Specifically, for the brush formed by flexible chains, the pair correlations between monomers and trivalent salt cations are the strongest at the stoichiometric ratio $\gamma = 1.0$.

CONCLUSIONS

In this work, the effects of chain stiffness and trivalent salt concentration on the conformations of spherical polyelectrolyte brushes are studied using BD simulations. The simulation results are as follows. (1) The stiff brush adopts the bundle-like morphology in the trivalent salt solutions. The amount of bundles per brush firstly increases with the increase of chain stiffness, and then keeps unchanged for further increase of the chain stiffness. (2) The oscillatory profile of the radial distribution of monomers demonstrates

that the grafted chains are in a stretched state. With the addition of the salt, the trivalent salt cations will replace the monovalent counterions and accumulate around the charged monomers. It is interesting to predict that the multivalent ions aggregate firstly in both the inner and the rim parts of the brush. (3) The charge condensed ratio shows a weak responsive magnitude to the chain stiffness. The charge inversion phenomena are observed for $\gamma > 1.0$ regardless of chain rigidity. (4) Interchain correlations increase with the increasing chain stiffness, which is responsible for the decrease of the bundle size. However, correlations between charged monomers and trivalent salt cations weaken with the increasing salt concentration irrespective of the chain rigidity, which is different with the flexible brush.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 21474005) and the Fundamental Research Funds for the Central Universities (No. 3122016L011).

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