# Entropy and enthalpy of polyelectrolyte complexation: Langevin dynamics simulations

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# Entropy and enthalpy of polyelectrolyte complexation: Langevin dynamics simulations

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We report a systematic study by Langevin dynamics simulation on the energetics of complexation between two oppositely charged polyelectrolytes of same charge density in dilute solutions of a good solvent with counterions and salt ions explicitly included. The enthalpy of polyelectrolyte complexation is quantified by comparisons of the Coulomb energy before and after complexation. The entropy of polyelectrolyte complexation is determined directly from simulations and compared with that from a mean-field lattice model explicitly accounting for counterion adsorption. At weak Coulomb interaction strengths, e.g., in solvents of high dielectric constant or with weakly charged polyelectrolytes, complexation is driven by a negative enthalpy due to electrostatic attraction between two oppositely charged chains, with counterion release entropy playing only a subsidiary role. In the strong interaction regime, complexation is driven by a large counterion release entropy and opposed by a positive enthalpy change. The addition of salt reduces the enthalpy of polyelectrolyte complexation by screening electrostatic interaction at all Coulomb interaction strengths. The counterion release entropy also decreases in the presence of salt, but the reduction only becomes significant at higher Coulomb interaction strengths. More significantly, in the range of Coulomb interaction strengths appropriate for highly charged polymers in aqueous solutions, complexation enthalpy depends weakly on salt concentration and counterion release entropy exhibits a large variation as a function of salt concentration. Our study quantitatively establishes that polyelectrolyte complexation in highly charged Coulomb systems is of entropic origin. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2178803]

## I. INTRODUCTION

Electrostatic attraction between two oppositely charged polyelectrolytes results in polyelectrolyte complexes widely used for flocculation, coating, and coacervation.[1] Recently, polyelectrolyte complexes have attracted considerable interest in the design of cationic polymers as nonviral synthetic vectors for gene therapy purposes.[2,3] Cationic polymers ("vectors") interact electrostatically with negatively charged DNA molecules, condensing them into a globule that facilitates the transportation to targeted cells. Another rapidly growing use for polyelectrolyte complexes has been to fabricate multilayered functional materials by sequentially adsorbing positive and negative charged polymers on charged surfaces of different geometries.[4]

A lot of experimental investigations have focused on the structural characteristics of polyelectrolyte complexes and their stability in response to environmental changes such as temperature and solution ionic strength.[5–13] In general, the morphology of a polyelectrolyte complex resembles a compacted globule, with an interpenetrating internal structure of no apparent long-range order. A polyelectrolyte complex usually has 1:1 stoichiometry of positive and negative charged polymers, regardless of their molecular characteristics such as charge density and chain length.[1,5,6] As such, a

complete exclusion of counterions of both signs is expected in a polyelectrolyte complex. Stability studies of polyelectrolyte complexes have shown that complexes made of highly charged polymers such as double-stranded DNA (dsDNA) are typically stable to the change of solution ionic strength while those from weak polyelectrolytes such as polyacrylic acid could undergo complete dissociation at elevated salt concentrations.[10] In contrast to intensive studies in structure-property relationship of polyelectrolyte complexes, the energetics of polyelectrolyte complexation has received much less attention.[14–18] In titration microcalorimetry study of polycation-DNA interactions, it was concluded that electrostatic interaction constitutes approximately 90% of total binding free energy at low salt concentration.[16] Moreover, a small positive enthalpy was reported in a study of DNA complex with a cationic copolymer,[14] while a negative one was measured in complexation of DNA with another cationic copolymer.[17] In both cases, polyelectrolyte complexation was driven by a large entropy gain, presumably due to the release of adsorbed counterions.[18] Salt effects on the enthalpy and entropy of polyelectrolyte complexation were also investigated.[19–22] It was observed that the driving force for polyelectrolyte complexation tends to decrease with salt concentration. But the enthalpy and entropy components respond differently to the addition of salt: a weak salt dependence for the enthalpy of complexation and a large variation in the entropy with salt concentration.

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Theoretical and simulation efforts were also made to study the formation and structural characteristics of polyelectrolyte complexes. Theories on polyelectrolyte complexation have dealt primarily with weakly charged polyelectrolytes; free energy of complexation was formulated and phase diagrams of polyelectrolyte complexes were constructed.[23–26] Monte Carlo simulation was first applied to study the interpenetrating aggregates formed by two oppositely charged polymers; the radii of gyration of a chain in an aggregate and of aggregates were examined at different chain lengths.[27] Similar system was later investigated by molecular dynamics simulation; the radii of gyration and the densities of the polyelectrolyte complexes were discussed at different Coulomb interaction strengths.[28] Polyelectrolyte complexes formed in solutions of multiple chains were recently systematically studied on effects of asymmetric chain lengths[29–31] and different salt contents.[32] Simple rules for cluster formation by oppositely charged polymers were proposed. Lately, Monte Carlo and molecular dynamics simulations were also applied to study the multilayering of oppositely charged polyelectrolytes at charged surfaces of different geometries.[33,34] Globules of oppositely charged polymers were obtained in the first few layers,[33] while strongly intermixing structures were observed for multilayers when adsorbed chains were allowed to equilibrate for a long period of time.[34]

Most of the theoretical and computational studies above have so far focused on different structures of polyelectrolyte complexes. A systematic study of energetics for polyelectrolyte complexation is lacking. Experimental works have, however, provided a wealth of enthalpy data for complex formation by polyelectrolytes of vastly different molecular characteristics, but they were often compounded by contributions from hydrophobic interaction, hydrogen bonding, hydration force, etc., making it hard to discern from others the electrostatic contribution, which is of foremost interest for any charged systems. It is desirable to have a prior knowledge of how the electrostatic interaction will affect complexation behavior before designing new polyelectrolyte architectures. In this paper, by using Langevin dynamics simulation, we attempt to systematically examine the energetics profile of complex formation by two oppositely charged polyelectrolytes in both weakly and strongly interacting systems and with different salt concentrations.

We model uniformly charged flexible polymers of $N$ monomers immersed in a dielectric continuum characterized by dielectric constant $\epsilon$. In salt-free solutions, $N/Z_c$ counterions each with valency of $Z_c$ are included for electrostatic neutrality. Variation of salt concentrations is made through addition of a given amount of salt cations and anions into the solution.

The paper is organized as follows. Section II describes the simulation method. The results and discussion are given in Sec. III. Equilibrium properties of isolated polyelectrolytes are first presented. The enthalpy and entropy of polyelectrolyte complexation are reported for both salt-free solutions and solutions with different salt contents. In the end, we summarize the major conclusions.

## II. SIMULATION METHOD

In the current study, flexible polyelectrolytes are modeled as freely jointed chains; each chain has $N$ spherical beads connected by a harmonic stretching bond. Each bead carries charge of either $e$ or $-e$ where $e$ is unit electric charge. The counterion is treated as a sphere with point electric charge of either 1 or $-1$. The salt ions are chosen to be made of the same positive and negative counterions of polyelectrolyte chains used. Two oppositely charged chains together with their neutralizing counterions and prescribed amount of salt ions are placed in a dielectric medium of uniform dielectric constant $\epsilon$. The system is taken to be a cubic box of volume $L^3$ with periodic boundary conditions in all three dimensions.

In our system, two consecutive beads in each chain are connected by a harmonic stretching spring whose potential is taken to be

$$U_{\text{bond}} = k_b(l - l_0)^2, \tag{2.1}$$

where $l$ is the bond length and $l_0$ is the equilibrium bond length. We have used $l_0$ as the unit of length throughout the simulations. The spring constant $k_b$ is chosen to be high enough (i.e., $5000\epsilon_{\text{LJ}}/l_0^2$) to allow fluctuation of the bond length within 10% of $l_0$. Consecutive bonds are freely jointed together and the polyelectrolyte chain is intrinsically flexible in the current study.

The excluded volume interaction between nonbonded beads of the chain is taken as a purely repulsive Lennard-Jones potential

$$U_{\text{LJ}} = \begin{cases} \epsilon_{\text{LJ}}\left[\left(\dfrac{\sigma}{r}\right)^{12} - 2\left(\dfrac{\sigma}{r}\right)^{6} + 1\right], & r \leq \sigma \\ 0, & r > \sigma, \end{cases} \tag{2.2}$$

where $\epsilon_{\text{LJ}}$ is the interaction strength, $\sigma$ is the distance at which the potential is zero, and $r$ is the distance between two particles. $\epsilon_{\text{LJ}}$ is used as the unit of energy in our system. Same form of potential is used for the excluded volume interactions of polymer beads-ions and ions-ions where ions are either counterions or salt ions. So we have simulated charged polymers in a good solvent condition. The values of $\sigma$ are taken as $1.0l_0$, $0.8l_0$, and $0.6l_0$ for bead-bead, bead-ion, and ion-ion, respectively. Here, the choices of $\sigma$ are considered only as a model system due to the lack of complete knowledge on sizes of hydrated ions near charged polymers.

The electrostatic interaction among charged beads and ions follows the Coulomb law

$$U_C(r_{ij}) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 \epsilon r_{ij}}, \tag{2.3}$$

where $r_{ij}$ is the distance between charged species $i$ and $j$ and $Z_k$ is the valency of the $k$th ion ($Z_k = Z_p$ for the polymer bead, $Z_k = Z_c$ for counterion, and $Z_k = Z_s$ for salt ion). $\epsilon_0$ is the permittivity of vacuum and $\epsilon$ is the relative dielectric constant of the medium. We have adopted Ewald summation technique[35] to compute the electrostatic interaction potential $U_C$.

In current simulations, the strength of electrostatic interaction among charged groups is parameterized by the Coulomb strength parameter $\Gamma$ defined as

$$\Gamma = \frac{l_B}{l_0}, \tag{2.4}$$

where $l_0$ is the charge separation distance along a chain or, in uniformly charged chains, the equilibrium bond length and $l_B$ is the Bjerrum length defined by

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon k_B T}, \tag{2.5}$$

with $k_B T$ being the Boltzmann constant times the absolute temperature $T$. In the following results, temperature appears only through $\Gamma$ with the multiplicative combination of $T$ and the temperature dependent $\epsilon(T)$ which is characteristic of specific solvent used. For instance, in the case of water and dsDNA ($l_0 = 0.17$ nm), $\Gamma$ increases from 4.18 at 20 °C to 4.81 at 70 °C. In experimental systems, $\Gamma$ could be tuned continually by changing charge separation distance $l_0$, e.g., using polymers of different charge densities.

The solvent of uniform dielectric constant $\epsilon$ is modeled as a Langevin thermostat. The dynamics of the $i$th particle (either bead or ion) is given by the Langevin equation

$$m\frac{d^2\mathbf{r}_i}{dt^2} = -\zeta\mathbf{v}_i - \nabla_{\mathbf{r}_i}U + \mathbf{F}_i(t), \tag{2.6}$$

where $m$ and $\zeta$ are the mass and the friction coefficient, respectively, of the $i$th particle. The mass of polymer beads is set as unit mass, and that of counterions and salt ions is half unit mass. Friction coefficient is chosen as constant $\tau^{-1}$ where $\tau = \sqrt{m\sigma^2/\epsilon_{\rm LJ}}$ is the unit of time in the system. In defining this time unit, $m = 1$ and $\sigma = l_0$. $\vec{r}_i$ and $\vec{v}_i$ are the position and velocity vector of the $i$th particle, respectively. $U$ is the total potential energy ($U = U_{\rm bond} + U_{\rm LJ} + U_C$) acting on the $i$th particle. $\vec{F}_i(t)$ is the random force from the solvent acting on the $i$th particle and satisfies the following fluctuation-dissipation theorem:

$$\langle\mathbf{F}_i(t)\cdot\mathbf{F}_j(t')\rangle = \delta_{ij}6k_B T\zeta\delta(t - t'). \tag{2.7}$$

To integrate Eq. (2.6), we have used the velocity-Verlet finite-differencing scheme. The integration time step $\delta t$ is set at 0.001 in units of $\tau$. Different values of $\delta t$ from 0.0001 to 0.01 were found to give equivalent results for radius of gyration, Coulomb energy, etc. The only place where the choice of $\delta t$ affects is the initial time for the approach of equilibrium. The total duration of each simulation run takes from $10^6$ to $10^7$ time steps, depending on the choices of system parameters such as $\Gamma$ and salt concentration.

The ranges of values studied in current work are $N = 60$, $Z_c = 1$, $L = 129$, and $\Gamma = 0.01$–6.0. From Eqs. (2.4) and (2.5), a low value of $\Gamma$ could be due to high dielectric constant, high temperature, or large charge separation distance as with polymers of low charge density. We have investigated polyelectrolyte complexation in a wide range of $\Gamma$ to cover both weakly and strongly interacting Coulomb systems. The concentration of salt is varied from $0.1M$ to $0.5M$ by adding corresponding amount of salt ions to the system. Simulations

on systems with even higher salt concentrations are presently hindered by prohibitively long computational time required for large Coulomb systems.

A typical simulation protocol is as follows: Two oppositely charged chains are first randomly generated in a large simulation box, the distance between them being half of the length of the simulation box. Counterions and salt ions are randomly distributed throughout the rest of the simulation box. In the first stage, Langevin dynamics simulation is carried out for prescribed time steps, ensuring that each chain reaches its equilibrium state. In the second stage, the pre-equilibrated chains together with their adsorbed counterions are translated to a center-of-mass separation distance of twice the average radius of gyration of each chain and Langevin dynamics simulation is further carried out. During each simulation, the position and velocity data of each particle are stored every 1000 time steps, from which physical quantities such as radius of gyration and Coulomb energy are computed and analyzed.

## III. RESULTS AND DISCUSSION

### A. Properties of isolated polyelectrolyte chains

Before considering the energetics of polyelectrolyte complexation, we first note the reference properties of isolated polyelectrolytes. The dynamics and structures of polyelectrolytes in solutions have been the subjects of intense research in the past few decades.[36–46] Here, we will focus on only two aspects: chain configuration as measured by its radius of gyration $R_g$ and the interaction of single polyelectrolyte chain with its counterions, i.e., counterion adsorption. Here, we simulated single polyelectrolyte in salt-free solution at different Coulomb interaction strengths $\Gamma$.

#### *1. Radius of gyration*

A polyelectrolyte chain differs considerably from its neutral analog because of its highly charged backbone and long-ranged nature of electrostatic interaction.[36–38,42–44] The size and shape of a polyelectrolyte chain depend on the strength of electrostatic interaction, which in the current study is characterized by a Coulomb interaction strength $\Gamma$. We have simulated polyelectrolyte chains at a broad range of $\Gamma$, in efforts to study the behavior of a polyelectrolyte chain in both weakly and strongly interacting systems. As a measure of chain configuration, the average radius of gyration of a polyelectrolyte chain, $R_g$, is monitored as a function of $\Gamma$ in Fig. 1. A nonmonotonic dependence on $\Gamma$ is apparent for $R_g$: At the lowest range of $\Gamma$ where Coulomb interaction is considerably weaker than thermal energy, a polyelectrolyte chain behaves more like a neutral self-avoiding chain; with increasing $\Gamma$, intrachain monomer-monomer repulsion becomes stronger and chain size expands to minimize the repulsion; at high enough $\Gamma$, there is increasing attraction between counterions and charged monomers, and chain size starts to fall down when $\Gamma > 1.0$; finally, at the highest value of $\Gamma$, $R_g$ is comparable to that at the lowest $\Gamma$ value. Previous simulation studies have also observed similar behavior of radius of gyration of single polyelectrolyte.[28,44,46,47]
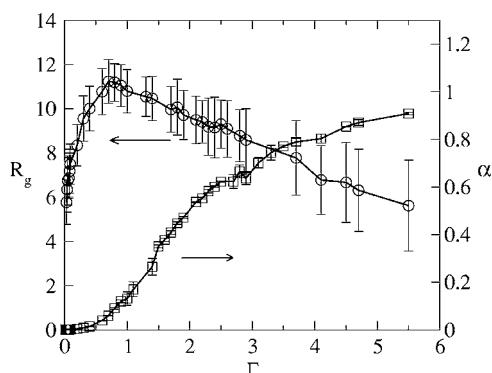
FIG. 1. Radius of gyration $R_g$ and fraction of adsorbed counterions $\alpha$ as functions of Coulomb interaction strength $\Gamma$ in salt-free solutions. Chain length $N=60$ and counterion valency $Z_c=1$.

## 2. Counterion adsorption

The highly charged backbone of a polyelectrolyte chain creates a considerable attraction for its counterions. According to polyelectrolyte theories,[48,49] such attraction amounts to territorially adsorbing a fraction of counterions onto the chain when $\Gamma$ becomes large enough, e.g., $\Gamma > 1.0$. In the current simulation study, a counterion is considered as adsorbed if it falls within a cutoff distance ($l_0$) to the chain backbone. The choice of the cutoff distance is to ensure that the Coulomb attraction experienced by a counterion at that distance is equal to or larger than thermal energy $k_B T$. It is also evident from direct visualizations of chain and counterion configurations that at large enough $\Gamma$, there are some certain numbers of counterions clustering around the chain. The total number of such adsorbed counterions is counted and averaged over different configurations after the chain establishes its equilibrium state. The fraction of adsorbed counterions is plotted as a function of $\Gamma$ in Fig. 1 for a single polyelectrolyte. It assumes a sigmoidal shape: the fraction of adsorbed counterions is negligible until $\Gamma$ reaches about 1, after which it increases steadily and saturates toward 100% at the highest $\Gamma$ studied. It shall be pointed out that $\Gamma$ in aqueous solutions is 2.8 and 4.1 for sodium polystyrene sulfonate (NaPSS) and dsDNA, respectively; in other words, for these highly charged polyelectrolytes, over 70% of charges are already neutralized by monovalent counterions at room temperature. It is no wonder that the actual charges of a strong polyelectrolyte in aqueous solutions could be significantly lower than that from its chemical structure. By associating with charged monomers, adsorbed counterions neutralize intrachain monomer-monomer repulsion. Such counterion-monomer association, however, does not resemble frozen ion pairs as found in ionic crystals; it is, in fact, very dynamical in nature: adsorbed counterions are able to move along the contour length of the chain and frequently exchange with free counterions in the solution (see Refs. 45 and 47).

## B. Polyelectrolyte complexation in salt-free solutions

We first examine the complex formation by two oppositely charged polymers in salt-free solutions where only polymers and their exact number of neutralizing counterions
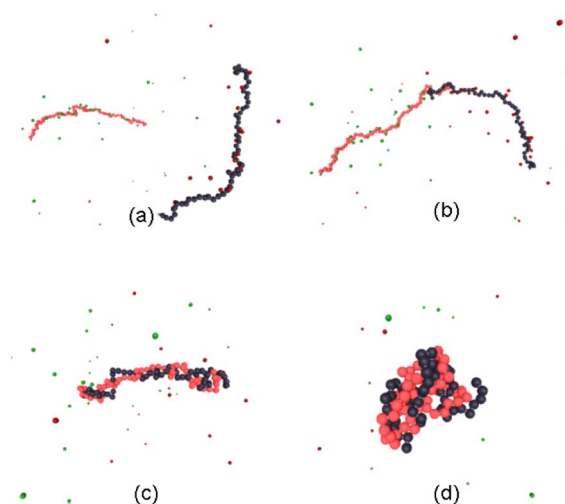


FIG. 2. Snapshots of chain configurations at different stages during the complexation between two oppositely charged polymers in salt-free solutions. The gray bead represents a positively charged chain and the dark one is a negatively charged chain. Positive and negative counterions are shown as gray and dark dots, respectively. Chain length $N=60$, counterion valency $Z_c=1$, and $\Gamma=2.0$. (a)–(d) represent simulation time units of 71, 501, 811, and 966, respectively.

are present. Two oppositely charged chains are first introduced in a dilute solution where the distance between these two chains is much larger ($\sim 10R_g$) than either their radii of gyration or Debye screening length. These individual chains are equilibrated for a sufficiently long period of time during which each chain could have diffused a distance of the length of a simulation box without encounter with each other. Chain size, counterion adsorption, and Coulomb energy of the system are monitored at the same time to ensure that polyelectrolyte chains indeed reach their equilibrium states. After the equilibration stage, two chains are translated, together with their adsorbed counterions, to a center-of-mass separation distance of $2R_g$. This translation is used only to facilitate the encounter between two otherwise widely separated chains; we have systematically experimented with different separation distances and found the same results as obtained from the situation where two chains freely diffuse into each other. The close encounter of two oppositely charged chains typically leads to a fast overlapping and complexation. The resultant complex is further allowed to equilibrate with the rest of the solution until the Coulomb energy of the system stabilizes.

## 1. Kinetics and structures of polyelectrolyte complexes

Figure 2 shows snapshots from computer simulations of typical chain configurations at different stages during the complexation between two oppositely charged polymers at $\Gamma=2.0$. From Fig. 2, two significant changes are obvious: Those counterions which are previously associated with polyelectrolyte chains are displaced during the course of complexation, and extended chains collapse into a compacted globule after complexation. These changes have to do with the cooperative interaction between two oppositely charged polyelectrolytes whose topologically connected charged monomers present a stronger affinity to its analog of
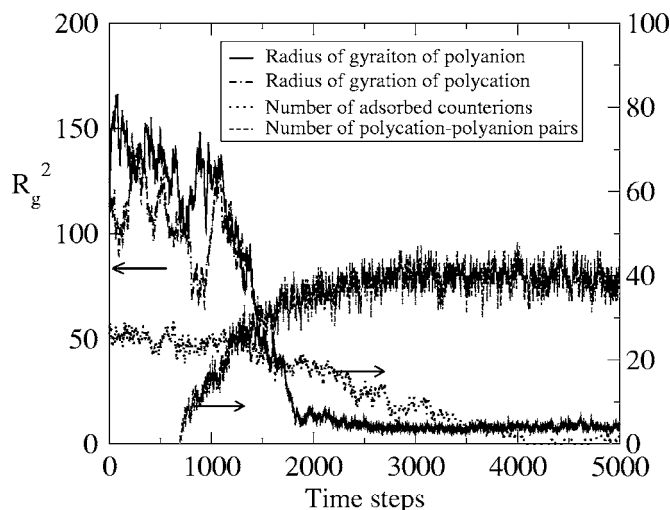
FIG. 3. The time evolution of the radii of gyration for positively and negatively charged chains during the complex formation and the time evolution of the numbers of adsorbed counterions and polycation-polyanion pairs during the complex formation. Chain length $N=60$, $Z_c=1$, and $\Gamma=2.0$.

opposite sign than discrete counterions do. The solution after polyelectrolyte complexation consists of counterions of both signs and a complex made of two oppositely charged chains. In experiments, mixing of solutions containing oppositely charged polymers often leads to a macrophase separation of polyelectrolyte complexes from the rest of the solution, or precipitation. In the current study, the interaction between solvent molecules and polyelectrolyte beads is not explicitly accounted for; polyelectrolytes are envisaged to be in a good solvent condition by ascribing a purely repulsive excluded volume interaction between two polymer beads (see Sec. II). So, polyelectrolyte complexation studied here would correspond to that in dilute solutions with good solvent, and the resultant polyelectrolyte complex is in equilibrium with the rest of the solution, without precipitation.

Figure 3 follows dynamic evolution of the radii of gyration for both positive and negative polyelectrolyte chains participating in complexation. Upon approaching, two oppositely charged chains quickly overlap with each other in a cooperative fashion as seen in a quick drop of chain size. Similar observations were made in Monte Carlo[27] and molecular dynamics[28] simulations on complexation of two oppositely charged polymers.

We have shown in the previous section that counterion adsorption on isolated polyelectrolytes is common, especially at large $\Gamma$. Also plotted in Fig. 3 are the evolutions in the number of adsorbed counterions and polycation-polyanion pairs during the complex formation between two oppositely charged chains. At $\Gamma=2.0$, there are about 30 adsorbed counterions on each chain at the start of complexation. During complexation, these counterions are progressively displaced by polycation-polyanion pairs. The final complex is deprived of any counterion of both signs. This counterion release phenomenon is more prominent at even larger $\Gamma$, i.e., $\Gamma>3$ where over 70% of counterions are associated with polyelectrolyte chains before complexation. Counterion release has been indirectly measured from complexation in solutions,[18] and a complete exclusion of coun-
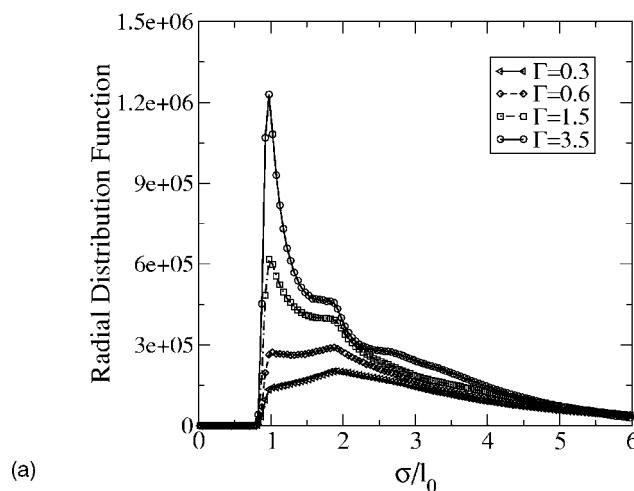


(a)
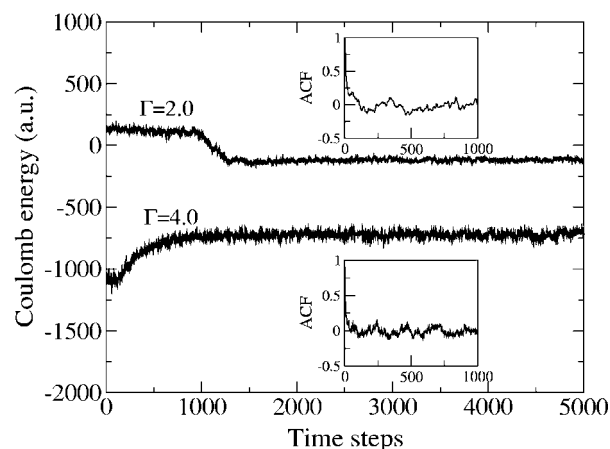


(b)

FIG. 4. (a) Radial distribution function of two oppositely charged chains within a polyelectrolyte complex at different Coulomb interaction strengths. (b) The time evolution of Coulomb energy of the system during the complex formation at $\Gamma=2.0$ and 4.0. Autocorrelation functions for the plateau regimes are plotted in the inset. Chain length $N=60$ and $Z_c=1$.

terion was observed inside a multilayered film made by alternative adsorption of oppositely charged polyelectrolytes. In the following sections, we will examine the enthalpy and entropy consequences of such ionic exchange processes.

The internal structure of a polyelectrolyte complex after it reaches the equilibrium state (see discussions below) is characterized by radial distribution function between oppositely charged monomers as shown in Fig. 4(a). The correlation between oppositely charged monomers within a polyelectrolyte complex is weak and broad at small $\Gamma=0.3$ where two oppositely charged chains are seen to undergo dynamical complexation-dissociation throughout simulation. The sharp peak of radial distribution function at $\sigma=1.0l_0$ (the diameter of polymer bead used in simulations) at larger $\Gamma>1.0$ reflects a close pairing between oppositely charged monomers. Direct visualizations of the complex from simulations reveal a collapsed interpenetrating globule. This is consistent with the general observation in experiments where the so-called scrambled egg morphology of polyelectrolyte complexes is typically found. More complicated structures such as toroids and folded chains may result from stiff polyelectrolytes such as dsDNA.[11,46]
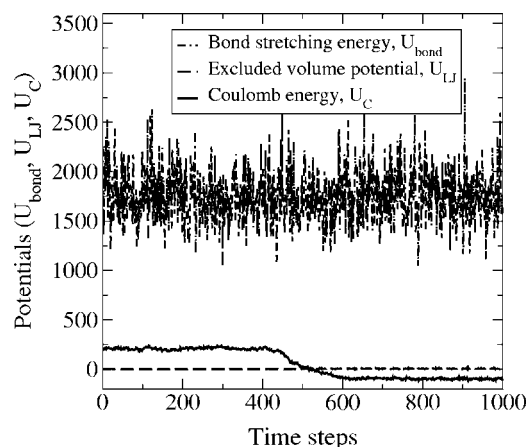
FIG. 5. The changes in bond stretch energy, Lennard-Jones interaction, and Coulomb energy during the complex formation between two oppositely charged polymers. Chain length $N=60$, counterion valency $Z_c=1$, and $\Gamma=2.0$.

Overall, thanks to the intrinsic flexibility of polyelectrolyte chains in the current modeling, a polyelectrolyte complex formed at $\Gamma>1.0$ is a collapsed globule with interpenetrating chains that are closely paired locally between two oppositely charged monomers. Figure 4(b) depicts the time evolution of Coulomb energy of the system for $\Gamma=2.0$ and $\Gamma=4.0$. In both cases, the Coulomb energy of the system levels off after the formation of polyelectrolyte complexes and the autocorrelation functions of the plateau regime (see inset) clearly indicate that the fluctuation of Coulomb energy at this stage is completely random, that is, polyelectrolyte complexes are in their equilibrium states.

### 2. Coulomb energy change of polyelectrolyte complexation

According to the model described in Sec. II, the total internal energy of a system consists of three parts: bond stretching energy, Lennard-Jones excluded volume interaction, and Coulomb interaction. As an example, Fig. 5 compares the contributions from all the three parts during the complex formation at $\Gamma=2.0$. All but Coulomb energy show little change in going from the isolated to the complexed state. This is due to the fact that we are simulating freely jointed chains which could adjust their conformations to accommodate close pairing without significant monomer overlapping or bond distortion. Thus, the enthalpy of polyelectrolyte complexation is directly equal to the Coulomb energy difference $\Delta E$ between that before and after complexation [see Fig. 4(b)]. Figure 6 shows $\Delta E/T$ at different $\Gamma$ along with the respective Coulomb energies before and after complexation. Similar to the shape of $R_g$ in Fig. 1, the Coulomb energy of the system before complexation is a nonmonotonic function of $\Gamma$, going through a maximum before rapidly decreasing when the attraction between counterions and polyelectrolytes becomes stronger. $\Delta E$ is negative and small in the very low limit of $\Gamma$, e.g., $\Gamma<0.3$, when the net attractive energy between two oppositely charged chains is small. This attractive energy becomes larger with $\Gamma$, resulting in a more negative $\Delta E$ of complexation. The Coulomb energy change is the most negative around $\Gamma=1.0$, after which it gets less
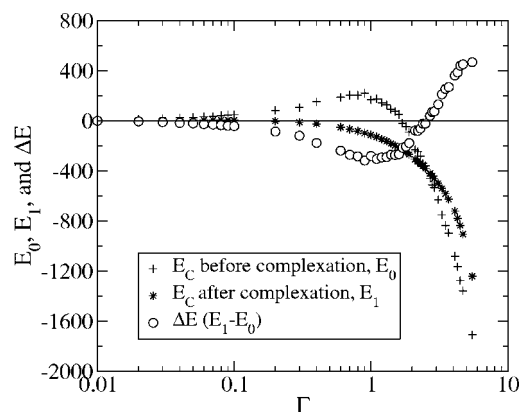


FIG. 6. Coulomb energy of a system before complexation and after complexation and net Coulomb energy gain for the complex formation between two oppositely charged polymers at different $\Gamma$ values. Chain length $N=60$ and counterion valency $Z_c=1$.

negative, and at $\Gamma>2.5$, starts to turn positive. This positive Coulomb energy change, however, does not increase infinitely with $\Gamma$; it starts to level off at the highest $\Gamma$ studied. It is expected that at even higher values of $\Gamma$, Coulomb energies of isolated and complexed states shall converge since all the charges in the system, either monomers or counterions, will be completely neutralized by ion pairing. We have not been able to explore even higher range of $\Gamma$ because at that stage, nearly all the counterions are adsorbed on polyelectrolyte chains and isolated polyelectrolyte chains are significantly compacted, making it impossible to observe complexation (if it does happen) between two collapsed chains within reasonable simulation time.

The fact that negative Coulomb energy change $\Delta E$ reaches its minimum around $\Gamma=1.0$ is closely related to the amount of adsorbed counterions shown in Fig. 1. At $\Gamma<1.0$, only a few percent of total counterions adsorb on a chain and leave most of polymer charges un-neutralized. Such highly charged state is alleviated when two oppositely charged chains complex in such a fashion that most of their charges are now neutralized, resulting in a net Coulomb energy gain. At large $\Gamma$, such favorable Coulomb energy change (negative $\Delta E$) is diminished when more and more chain charges are already neutralized by adsorbed counterions before complexation, and it is energetically less favorable to displace counterions-monomers interaction by polycation-polyanion interaction. $\Gamma$ for commonly investigated polyelectrolytes is in the range of 2–4 (e.g., for sodium polystyrene sulfonate and dsDNA, $\Gamma$ is 2.8 and 4.1, respectively, in aqueous solutions at room temperature.). As seen in Fig. 6, in this range, $\Delta E$ can be either negative or positive depending on the Coulomb interaction strength of a particular system, as found in complexation of DNA with different cationic copolymers.[14,17] Matulis *et al.* have applied electrostatic binding model to study the energetics and its temperature dependence for DNA complexation with multivalent cationic species and found a small positive enthalpy that is increasing with temperature.[50] This could be explained by an increase of $\Gamma$ with temperature in aqueous solutions, e.g., for dsDNA, $\Gamma$ increases from 4.2 at 20 °C to 4.8 at 70 °C, which leads to a more positive $\Delta E$ of polyelectrolyte complexation, as revealed in Fig. 6.

We must point out that the enthalpy of complexation measured in experiments is often complicated by unknown contributions from hydrogen bonding, hydrophobic interaction, and hydration force, making it difficult to discern the significance of electrostatic contribution that is of most interest to a charged system. Our simulations on simple polyelectrolyte systems have clearly demonstrated an intriguing behavior of Coulomb energy change accompanying polyelectrolyte complexation across different electrostatic interaction strength regimes.

### 3. Counterion release entropy of polyelectrolyte complexation

In complexation with another oppositely charged chain, the configuration, translational, and rotational entropies of a polyelectrolyte chain are reduced, the extent of which depends on how compact the chain is within the complex. More important, as evident in Fig. 6, the complex formation is accompanied by a concomitant release of adsorbed counterions, increasing the system entropy. To quantify these entropy changes upon complexation, we have resorted to two different approaches:

(1)  Free energy of polyelectrolyte complexation is first obtained by Eq. (3.1), and the entropy of complexation is then calculated by subtracting the free energy from the enthalpy of complexation, $T\Delta S = \Delta E - \Delta F$.

$$\frac{\Delta F}{T} = -\int_{T_{ref}}^{T} \frac{\Delta E}{T'^2} dT', \tag{3.1}$$

where $T$ is the temperature of interest and $T_{ref}$ is the reference temperature which in the current study is taken to be the temperature when $\Gamma$ is the smallest (e.g., 0.01). To carry out the above integration, $\Delta E/T$ in Fig. 6 was first fitted by a smooth fifth order polynomial function of $\Gamma$, $\Delta E/T = f(\Gamma) = \sum_{i=1}^{5} A_i \Gamma^i$ where $A_i$ is the coefficient for the $i$th power term. Next, $dT'/T'$ and the limits of integration in Eq. (3.1) need to be expressed in the $\Gamma$ space. From its definition in Eqs. (2.4) and (2.5), the relation between $\Gamma$ and $T$ is specific to the solvent (and $T$ dependence of $\epsilon$) and the charge separation $l_0$ on the polymer. However, the practical range of $\Gamma$ available for a specified solvent is very narrow, as already pointed out after Eq. (2.5). Therefore, we adopt the procedure of changing $\Gamma$ over a wider range by tuning the charge separation length (i.e., the "charging" procedure) but by fixing $T$ for a given solvent. This is performed by defining $\Delta F/T$ as $\Gamma\Delta F'$,

$$\Gamma\Delta F' = -\ln\left[\mathrm{Tr}\,\exp\left(-\frac{1}{T}\mathcal{H}\right)\right] = -\ln[\mathrm{Tr}\,\exp(-\Gamma\mathcal{H}')], \tag{3.2}$$

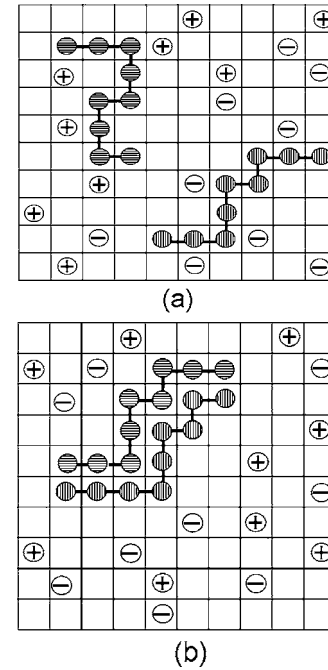where $\mathcal{H}$ is the Hamiltonian of the system and Tr gives the partition sum. Now, we get exactly



FIG. 7. Lattice model representations of polyelectrolyte chains and counterions (a) before polyelectrolyte complexation and (b) after polyelectrolyte complexation. The chain with beads of vertical stripes is positively charged, and the chain with beads of horizontal ones is negatively charged.

$$\frac{\Delta F}{T} = \int_{\Gamma_{ref}}^{\Gamma} \frac{f(\Gamma')}{\Gamma'} d\Gamma'. \tag{3.3}$$

This is a general result valid for any solvent at a given temperature.

(2)  By using a mean-field lattice model [see Figs. 7(a) and 7(b)], we can explicitly write down the formulas for the entropy of the system before and after complexation. At each $\Gamma$, based on counterion adsorption results in Fig. 3, a certain number of counterions are assigned to each chain. Since these adsorbed counterions are strongly attracted to the chain, their mobility is highly retarded and much smaller than that in the free states. So we did not include the configuration entropy of adsorbed counterions in the following calculations. From Fig. 7(a), the entropy for the isolated polyelectrolytes and their counterions is

$$
\begin{aligned}
S_0 = {}& n_{+,p}\ln\phi_{+,p} + n_{-,p}\ln\phi_{-,p} \\
& + (1-\alpha_+)n_{+,c}\ln(1-\alpha_+)\phi_{+,c} \\
& + (1-\alpha_-)n_{-,c}\ln(1-\alpha_-)\phi_{-,c},
\end{aligned} \tag{3.4}
$$

where $n_{+,i}$ and $n_{-,i}$ are the numbers of positive and negative species $i$ (chain, $i=p$; counterion, $i=c$), respectively. Similarly, $\phi_{+,i}$ and $\phi_{-,i}$ are the volume fractions of positive and negative species $i$ (chain, $i=p$; counterion, $i=c$) and $\alpha_+$ and $\alpha_-$ are the fractions of adsorbed counterions for positive and negative counterions. The first two terms in Eq. (3.4) are the configuration entropies for positive and negative charged chains and the last two terms represent the translational entropies of unadsorbed counterions of both signs. In a similar fashion, the entropy of the system after the
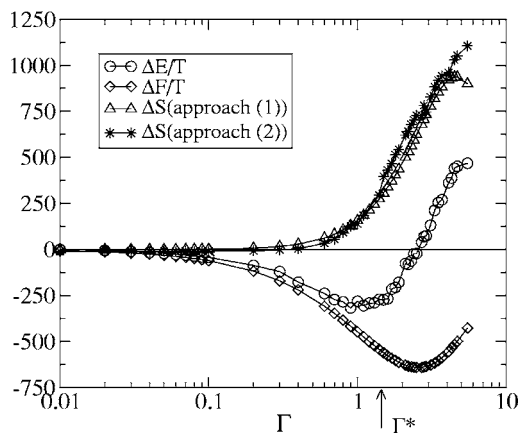
FIG. 8. Comparison of the counterion release entropy of polyelectrolyte complexation determined by two different approaches defined in the text. Approaches 1 and 2 use Eqs. (3.1) and (3.6), respectively. Chain length $N$ =60 and counterion valency $Z_c$=1.

complex formation can be approximated by

$$S_1 = n_\pm \ln \phi_\pm + n_{+,c} \ln \phi_{+,c} + n_{-,c} \ln \phi_{-,c}, \qquad (3.5)$$

where $n_\pm$ and $\phi_\pm$ are the number and volume fraction of the complex, respectively. Here, we treated the polyelectrolyte complex of oppositely charged chains as a new chainlike object with $\phi_\pm$ volume, and the released counterions are free to explore the whole volume. From Eqs. (3.4) and (3.5), the net entropy change resulting from polyelectrolyte complexation is

$$\Delta S = S_1 - S_0$$
$$= -\left\{ n_\pm \ln \frac{2}{\phi_p} + 2N \ln \phi_c - 2(1-\alpha)N \ln \alpha\phi_c \right\},$$
$$\qquad (3.6)$$

where we have used the following equalities: $\phi_{-,p} = \phi_{+,p} = \phi_p = 0.5\phi_\pm$, $n_{+,p} = n_{-,p} = n_\pm = 1$, $\phi_{-,c} = \phi_{+,c} = \phi_c$, $n_{+,c} = n_{-,c} = N$, and $\alpha_- = \alpha_+ = \alpha$. In Eq. (3.6), when the fraction of adsorbed counterions, $\alpha$, approaches 1 at a high Coulomb interaction strength (see Fig. 3), the second term in Eq. (3.6) with its $N$ dependence dominates over the first term, i.e., counterion release entropy contributes the most to the entropy of polyelectrolyte complexation.

Figure 8 compares the results from the above two approaches. Entropies calculated by two independent ways are in good agreement with each other across a large range of $\Gamma$. The entropy of complexation is negligible at lower range of $\Gamma$, e.g., $\Gamma < 1.0$, but quickly increases afterwards. The biggest discrepancy between the two approaches appears at the highest value of $\Gamma$ studied; while the entropy from approach (1) starts to go down, that from the mean-field calculation continues to increase. The difference can be attributed to the assumption used in the mean-field approach, that is, released counterions can explore the whole solution volume to maximize their entropy, which is not particularly true at high Coulomb interaction strengths where ion pairing is prevalent. Except for this minor discrepancy at very large values of $\Gamma$, the agreement of these two approaches throughout most of

Coulomb interaction strengths demonstrates that counterion release entropy is the dominant contribution to the entropy of polyelectrolyte complexation for $\Gamma > 1.0$.

Taking Coulomb energy change and counterion release entropy together, free energy of polyelectrolyte complexation takes on a concave-up function of $\Gamma$ as shown in Fig. 8. It closely follows the decreasing negative $\Delta E$ for $\Gamma < 1.0$, and at $\Gamma = 1.0$ the entropy contribution kicks in and continually lowers free energy until $\Gamma = 2.5$. At $\Gamma \geqslant 2.5$, the magnitude of negative free energy of complexation starts to reduce due to the fact that the Coulomb enthalpy now becomes increasingly positive.

If we define $\Gamma^*$ as the Coulomb interaction strength where the magnitudes of the enthalpy $\Delta E$ and the entropy $T\Delta S$ equal each other, Fig. 8 can be divided into two regimes at $\Gamma^* = 1.5$: Below $\Gamma^*$, polyelectrolyte complexation is driven by the negative Coulomb energy change derived from electrostatic attraction between two oppositely charged polymers, while the counterion release entropy only plays a subsidiary role; above $\Gamma^*$, the counterion release entropy contributes significantly. Especially at the high range of $\Gamma$ where the Coulomb energy change is positive and opposes polyelectrolyte complexation, it is the large counterion release entropy that actually drives polyelectrolyte complexation. As already mentioned above, for highly charged polyelectrolytes, e.g., NaPSS and dsDNA in aqueous solutions, $\Gamma$ is in the range of 2.0–4.0 where, according to Fig. 8, the counterion release entropy is expected to contribute significantly to the driving force of complexation involving these polyelectrolytes. This is not to rule out the possible contributions of nonelectrostatic origin, such as hydrophobic interaction and hydration force, but to denote the critical role of counterion release entropy played in the free energy change of complexation by highly charged polyelectrolytes.

## C. Polyelectrolyte complexation in the presence of salt

The presence of salt is ubiquitous in most experiments on polyelectrolyte complexation. Salt ions screen the electrostatic interaction among charged particles, and depending on salt concentrations used, the ionic strength of a solution can be readily tuned. In this section, we seek to understand the effect of varying ionic strength on the energetics of polyelectrolyte complexation, i.e., the effects on the Coulomb energy change and counterion release entropy. Three different salt concentrations have been used: $0.1M$, $0.25M$, and $0.5M$. Simulations on even larger salt concentrations are presently hindered by the prohibitively long computational time required for large Coulomb systems. Also, only monovalent salt is considered in the current study.

### 1. Salt effect on Coulomb energy change of polyelectrolyte complexation

Polyelectrolyte complexation between two oppositely charged polymers is carried out in three salt concentrations, and Fig. 9 compares their respective Coulomb energy change $\Delta E$ with the one in the salt-free solution. The salt effect on $\Delta E$ manifests itself very differently in different Coulomb interaction strength ranges. At $\Gamma < 3.0$, $\Delta E$ in the solution with
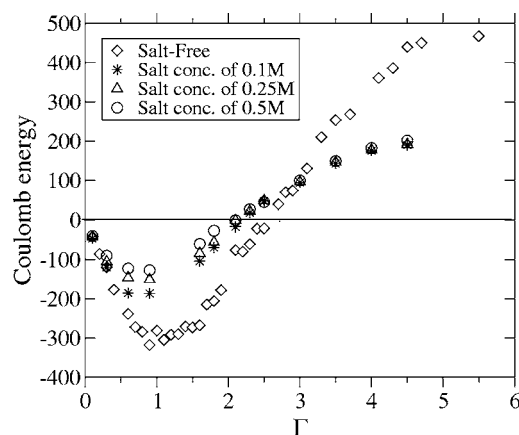
FIG. 9. Salt effects on the Coulomb energy change of polyelectrolyte complexation. Three different salt concentrations are studied, $0.1M$, $0.25M$, and $0.5M$. Monovalent salt is used. Chain length $N=60$ and counterion valency $Z_c=1$.



FIG. 10. Salt effects on energy of complexation at $\Gamma=2.0$ and $\Gamma=4.0$. The salt concentration is $0.5M$. Chain length $N=60$ and $Z_c=1$.

a salt concentration, e.g., $0.1M$, either becomes less negative ($\Gamma<2.0$) or even changes from negative to positive ($2.0<\Gamma<3.0$), in comparison with that in salt-free solutions. In other words, at $\Gamma<3.0$, polyelectrolyte complexation in the presence of salt has a less favorable $\Delta E$ than that in the salt-free solution. By contrast, at $\Gamma>3.0$, $\Delta E$ in salty solutions is always less positive than the one in salt-free solutions, suggesting that in this high Coulomb interaction strength range, the energy barrier (positive $\Delta E$) is lower for polyelectrolyte complexation in the presence of salt. Also, in the weak Coulomb interaction range, $\Gamma<2.0$, $|\Delta E|$ decreases notably with salt concentrations, but it becomes almost invariant to the changes in salt concentrations at $\Gamma>2.0$ where experiments on highly charged polyelectrolytes in aqueous solutions are of interest. Such a weak dependence of $\Delta E$ on salt concentration in high Coulomb interaction strength range has been observed in experiments on DNA binding with cationic polymers,[14,16] oligometric lysines and arginines,[19] multivalent cationic species,[15] as well as proteins.[20] Despite the fact that $\Delta E$ only weakly depends on salt concentrations in those experiments, the free energy of polyelectrolyte complexation would decrease readily with the salt concentration used. This suggests that in these strongly interacting systems, ionic screening effect alone cannot adequately explain the reduction of the driving force for polyelectrolyte complexation due to the addition of salt.

To elucidate the salt effects on $\Delta E$ in different Coulomb interaction strength regimes, it is instructive to understand how the salt addition influences the interactions among charged groups in the system. There are three pairwise interactions that make up the Coulomb energy of the system: polyion-polyion, polyion-counterion, and counterion-counterion. If we further differentiate the polyelectrolyte chains together with their adsorbed counterions from the free counterions, these pairwise interactions can be artificially grouped into two distinct contributions: Contribution I which includes both the interactions among polyions (with adsorbed counterions) and the interaction between these polyions and free counterions, and contribution II that only involves the interaction among free counterions. The salt
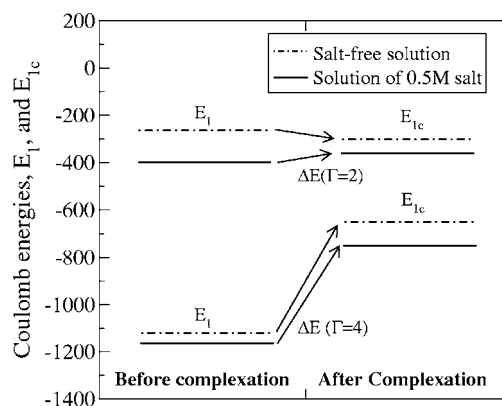
effects on these two distinct contributions to the overall Coulomb energy are illustrated at $\Gamma=2.0$ and $4.0$ in Fig. 10, as examples for polyelectrolyte complexation in two different Coulomb interaction strength regimes. Let $E_1$ and $E_2$ be these two contributions prior to complexation. After complexation, the corresponding values are $E_{1c}$ and $E_{2c}$. The values of these energies are computed by taking the time average in the isolated and complexed states.

For $\Gamma=2.0$, the values of $E_1$ and $E_{1c}$ are $-250$ and $-300$, respectively, for the salt-free case, while $E_2$ and $E_{2c}$ are essentially zero. In the presence of $0.5M$ monovalent salt, the values of $E_1$ and $E_{1c}$ are $-400$ and $-350$, respectively. $E_2$ and $E_{2c}$ are essentially about $-600$ for $0.5M$ salty solution. Thus, the energy of complexation, dominated by contribution I, is exothermic and endothermic for the salt-free and salty cases, respectively. The exothermicity for the salt-free case implies that for complexation at $\Gamma=2.0$, the replacement of polyion-counterion interactions by polycation-polyanion interactions is favorable in energy, as already shown in Fig. 9. By adding salt ions to the system before complexation, polyion-counterion interaction is strengthened (by screening the repulsion among those un-neutralized chain charges), and consequently $E_1$ is significantly more negative in comparison with the salt-free case. Since $E_{1c}$ is essentially the same in the final complexed states, the complexation process is less exothermic in the salty case. In fact, for the values of the parameters used here, the process is actually slightly endothermic. It is to be noted that $E_{1c}$ is slightly more negative for the salty case in comparison with the salt-free case. This is due to the interaction of the polyelectrolyte complex with the surrounding counterions of both signs, although the interior of the complex is essentially deprived of counterions.

For $\Gamma=4.0$, $E_1$ and $E_{1c}$ are $-1100$ and $-650$, respectively, for the salt-free case. The corresponding values for the solution of $0.5M$ monovalent salt are $-1150$ and $-750$. The second contribution is around zero and $-750$ for the salt-free and salty cases without any significant change during complexation. So, at $\Gamma=4.0$, the endothermicity of polyelectrolyte complexation is reduced in the presence of $0.5M$ salt. The calculated endothermicity for both salt-free and salty cases at $\Gamma=4.0$ is due to the fact that the polyelectrolyte chains are already neutralized by counterion adsorption before complexation at these high $\Gamma$ values. In general the role
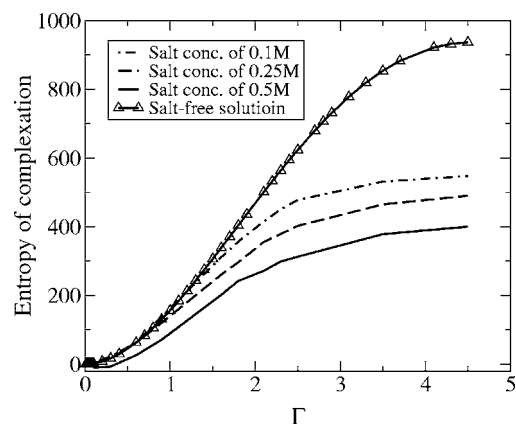
FIG. 11. Salt effects on the counterion release entropy of polyelectrolyte complexation. Three different salt concentrations are studied, $0.1M$, $0.25M$, and $0.5M$. Chain length $N=60$ and $Z_c=1$.

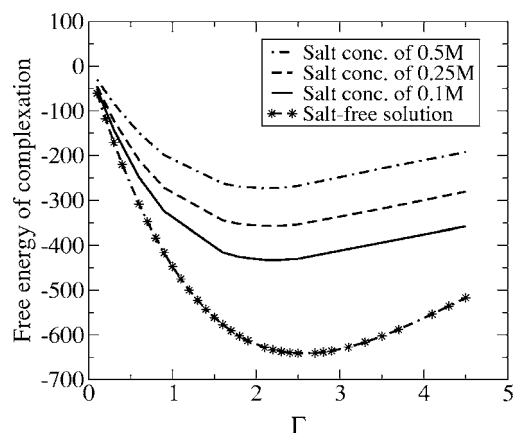

FIG. 12. Salt effects on the free energy of polyelectrolyte complexation. Three different salt concentrations are studied, $0.1M$, $0.25M$, and $0.5M$. Chain length $N=60$ and $Z_c=1$.

of salt is to make the complexation process more endothermic, as is evident in Fig. 10. Furthermore, our simulation results, at $\Gamma \sim 0.1$ show that complexes dissociate at higher ionic strengths. It is therefore envisaged that complexes at higher $\Gamma$ values may require much higher salt concentrations to lose their stability.

### 2. Salt effect on counterion release entropy of polyelectrolyte complexation

Counterion release entropy of polyelectrolyte complexation at different salt concentrations is calculated from approach (1); the result is compared with that in salt-free solutions in Fig. 11. In the lowest salt concentration, counterion release entropy does not deviate much from that in salt-free solutions until $\Gamma=1.8$ after which the reduction in entropy is very significant. There is also a big difference in $\Delta S$ for low and high salt concentrations. At $\Gamma=1.8$, $\Delta S$ in salt concentration of $0.5M$ is about 40% smaller than that in salt concentration of $0.1M$. Such a large difference in $\Delta S$ persists into the higher range of $\Gamma$. We have also monitored the fraction of adsorbed counterions at different salt concentrations; in the range of ionic strength studied here, the number of adsorbed counterions only slightly increases from that in salt-free solution, e.g., at $\Gamma=4.0$, $\alpha$ is 0.80 and 0.87 for salt-free solutions and salt concentration of $0.5M$, respectively. So, the large reduction of counterion release entropy in the presence of salt cannot be attributed to the changes in the number of adsorbed counterions but rather to the counterion osmotic pressure changes induced by increasing salt concentration. The entropy gain for adsorbed counterions to be released from polyelectrolyte chains is reduced when there are already plenty of free counterions present in the solution. The suppression of counterion release entropy $\Delta S$ by the addition of salt is consistent with what has been observed in studies of DNA binding with cationic species.[14,16,19,20,50]

Combining $\Delta S$ and $\Delta E$, it is clear that the addition of salt decreases the free energy for polyelectrolyte complexation as shown in Fig. 12. Such reduction, however, takes on very different origins at low and high Coulomb interaction strengths. As an example, in solutions with salt concentration of $0.1M$, at $\Gamma<1.8$ the reduction of $\Delta F$ is mainly due to the

fact that $\Delta E$ is now much smaller than that in salt-free solutions, while at higher range of $\Gamma$, especially when $\Gamma>3.0$, polyelectrolyte complexation is actually helped by a less positive Coulomb energy change compared to that in salt-free solution, and the reduction in $\Delta F$ is brought about by a strong suppression of counterion release entropy as shown above. There are ongoing debates in literature on the salt effect on polyelectrolyte complexation.[19,20] A predominantly entropic effect in salt-dependent electrostatic contribution to the free energy of polyelectrolyte complexation is inferred from the counterion adsorption theory.[20] It is also argued that addition of salt mainly acts to screen the Coulomb interaction in the system, resulting in a weaker tendency for polyelectrolyte complexation. Our systematic simulations on polyelectrolyte complexation at different salt concentrations and Coulomb interaction strengths have shown that the exact nature of salt effects on the driving force of polyelectrolyte complexation has to do with the strength of Coulomb interaction at which the complexation is carried out. In the weakly interacting regime, ionic screening effect is manifested in a strong reduction in Coulomb energy change of complexation. In the strongly interacting regime, the strong suppression of counterion release entropy results in a weaker driving force for polyelectrolyte complexation.

## IV. CONCLUSIONS

The energetics of complexation by two oppositely charged polymers were studied in both weakly and strongly interacting Coulomb systems and at different salt concentrations. Using a simple model of polyelectrolyte with explicit counterions and salt ions, the Coulomb energy change and entropy of polyelectrolyte complexation were clearly defined. Distinct energy and entropy contributions to complexation of oppositely charged polyelectrolytes were differentiated at weak and strong Coulomb interaction strengths. In a weakly interacting system, polyelectrolyte complexation is driven by negative Coulomb energy change derived from electrostatic attraction between two oppositely charged chains. Because of the weak Coulomb interaction strength, there are only a small amount of counterions adsorbed on a polyelectrolyte chain, and consequently a less counterion re-

lease entropy is obtained. In a strongly interacting system, polyelectrolyte chains attract a large number of counterions. As such, the complex formation is driven by a large entropy gain due to counterion release upon complexation while opposed by a positive Coulomb energy change.

Addition of monovalent salt is found to strongly affect the energetics of complex formation. Compared to salt-free solutions, the Coulomb energy change of polyelectrolyte complexation, negative or positive, is reduced by ionic screening effect across all the Coulomb interaction strengths studied. The counterion release entropy of complexation decreases with salt concentration as well, but significant reduction only appears at strong Coulomb interaction strength. Taken together, at the weak interaction strength, the decreases of both negative Coulomb energy change and positive entropy result in a weaker tendency for polyelectrolyte complexation. At the strong interaction strength, a less positive Coulomb energy change in the presence of salt actually decreases the positive Coulomb energy change for complexation but this is counteracted by an even stronger suppression of counterion release entropy. Overall, the driving force for complexation weakens with salt concentration at all Coulomb interaction strengths. Also, in the range of Coulomb interaction strength of interest in experiments ($\Gamma = 2-4$), the Coulomb energy change of complexation is only a weak function of salt concentration, which is in contrast to the large variations in counterion release entropy as a function of salt concentrations. Our result leads to the notion that the salt effect on polyelectrolyte complexation in those highly charged systems is of entropic origin. Our simulation study on a simple model of polyelectrolyte complexation is in qualitative agreement with many available experimental observations and provides insight into fundamental forces behind complexation among polyelectrolytes.

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