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Conformation transitions of a polyelectrolyte chain: A replica-exchange Monte-Carlo study

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The thermodynamic behavior of a strongly charged polyelectrolyte chain immersed in a salt-free solution is studied using replica-exchange Monte-Carlo simulations. The results reveal that the chain can assume a variety of conformations, and it undergoes two phase transitions upon cooling. The first transition is identified as a continuous counterion condensation transition while the second one as a first-order coil-globule transition. In the globular state, the counterions and the charged chain segments are densely packed forming a three-dimensional Wigner crystal.

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I. INTRODUCTION

Many important synthetic and biological macromolecules are charged polymers or polyelectrolytes. The conformational properties of polyelectrolytes differ significantly from that of the corresponding uncharged polymers [1,2]. The ability of polyelectrolytes to change their sizes significantly upon change of ionic conditions and temperature makes them very useful in many technological applications. It is well understood that electrostatic interactions play a very important role in the behavior of polyelectrolytes, and the intrachain electrostatic interactions of a polyelectrolyte chain can be regulated by the amount of condensed counterions [3–13]. Study of the effective charge, chain conformation, and related phase transitions in polyelectrolyte systems is thus important both from fundamental and applied points of view.

For a neutral flexible polymer chain in solution, it is well established that the chain undergoes a continuous collapse or coil-globule transition as the solvent quality changes from "good" to "poor", typically realized by cooling [14]. Further cooling of the system leads to a first-order globule-cystalline transition [15,16]. For a charged polymer chain, the chain conformation exhibits a more complex behavior, as revealed by a large number of theoretical [3–7] and simulation [8–13] studies. The salient features from these previous studies can be summarized as follows. Upon cooling (or increasing the Coulomb interaction strength), the chain changes from a nearly random coil to an expanded conformation. After reaching a maximum coil size, the chain shrinks and finally collapses to a compact globule. The dimension of the expanded chain can be much larger than the corresponding neutral self-avoiding-random-walk chain. The shrinking and collapse process of the chain is thought to be triggered by the counterion condensation and the associated dipole formation between the chain monomers and the condensed counterions. Despite extensive previous studies, some controversies about the nature of the collapse transition still exist. Specifically, this transition is predicted to be first order by theories [3–5], but the first-order nature of the collapse transition has not been positively identified in simulations [8–12]. This is largely due to the fact that the collapse transition occurs at a low temperature, where traditional simulation techniques have poor sampling efficiency. This difficulty could be overcome by using advanced simulation techniques. In a recent study, the entropic sampling using the Wang-Landau algorithm has been used to calculate the canonical properties of a strongly charged polyelectrolyte chain [13]. For chain lengths up to 80 bonds, this study found that the chain collapse transition strongly resembles a second-order phase transition, although theories predicted a first-order phase transition.

In this paper, the thermodynamic behavior of a strongly charged polyelectrolyte chain and its neutralizing counterions in a salt-free solution is studied using replica-exchange Monte-Carlo simulations (MCS) [17]. This technique achieves good sampling by allowing systems at different temperatures to exchange complete configurations, thus allowing reliable canonical and microcanonical analyses, leading to the unambiguous identification of the nature of the phase transitions.

II. MODEL AND METHOD

The simulations are carried out based on the self-avoiding-random-walk model of polymers [18]. The polymer chain lives on a simple cubic lattice of volume $V = (Lc)^3$, where c is the lattice constant and L the length of the simulation box. The system consists of one polyion, an appropriate number of counterions, and solvent molecules. The polyion is represented as a chain of length N or $(N + 1)$ successive beads (monomers) connected by bonds that can adopt lengths of c, $\sqrt{2}c$, and $\sqrt{3}c$. Each polymer bead carries one unit of negative electric charge. A counterion carries one unit of positive electric charge. The number of counterions is determined by charge neutrality of the system. Apart from the constraint of single occupancy of lattice sites, the only energetic interaction is a Coulomb potential, $u_{ij} = q_i q_j / D r_{ij}$, where $q_{i,j} = \pm e$, D is the dielectric constant of the medium, and r_{ij} is the distance between two charges. Periodic boundary conditions are utilized and long-range interactions computed through an approximation of the Ewald summation [12]. Reduced units are used throughout the paper, in which the unit of length is c, the energy is measured in e^2/Dc, and the temperature in e^2/Dck_B.

In the replica-exchange MCS, a set of M replicas are simulated simultaneously, where the ith replica is simulated at a unique temperature T_i ($i = 1$ to M and $T_i < T_{i+1}$). The

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set of temperatures $\{T_i\}$ is determined from test simulations designed to achieve a constant acceptance rate between adjacent replicas. Typical simulation protocol for the ith replica is as follows. First, an initial state consisting of one polyelectrolyte chain and counterions is randomly generated inside the simulation box, with unoccupied sites designated as solvent molecules. The standard MCS at temperature T_i are performed then and iterated after each of the replica exchanges. When N_{MC} Monte-Carlo sweeps are reached, the replica will try to exchange its configuration with one of its two neighboring replicas using the deterministic even-odd scheme [19]. The simulations finish when a total number of N_{RE} attempted replica exchanges have been carried out. In our simulations, $L = 252$, $M = 1000$, $T_M = 100$, $T_1 = 0.07$, $N_{MC} = 50$, and $N_{RE} = 2 \times 10^7$.

Thermodynamic averages of various quantities are computed at each temperature T_i. The mean-square radius of gyration of the polyion, R_g^2, is measured in units of the value in the athermal state. The effective charge per monomer, q, is computed using $q = 1 - N_C/(N+1)$, where N_C is the average number of condensed counterions. A counterion is considered to be condensed when it occupies one of the sites with a distance equal to a bond length to any monomer of the polyion. The probability distribution function $P(E,T_i)$ and some other quantities are obtained from simulations directly. The density of states, $g(E)$, is computed based on $P(E,T_i)$ ($i = 1$ to M) using the histogram analysis [20]. Using $g(E)$, canonical and microcanonical quantities are computed using the procedure described in Ref. [16].

III. RESULTS AND DISCUSSION

Results of the structural parameter and thermodynamic quantities for the polyion $N = 125$, plotted as functions of the inverse of temperature, $1/T$, are shown in Fig. 1. It is noted that at very high T (very small $1/T$), R_g^2 is slightly higher than that for the corresponding athermal chain [Fig. 1(a)]. R_g^2 increases as T is lowered. Consequently, the total electrostatic interaction of the system decreases with decreasing T [see Fig. 1(b)] due to the decrease of the electrostatic repulsion between polyion monomers. As T is decreased further to $T \sim 1.49$, the rate of polyion swelling with decreasing T begins to decrease. This is because, at this low temperature, counterion condensation sets in, as indicated by the decrease in the q curve [see Fig. 1(c)]. The q curve also indicates that the number of condensed counterions increases with a further decrease in T, resulting in an increase of the electrostatic attraction between the monomers and the condensed counterions. This electrostatic attraction works against the intrachain swelling arising from the uncompensated charges on the polyion chain, and consequently leads to the decrease of the rate of polyion swelling. When about 8.4% of the counterions have been condensed (i.e., $q = 0.91620$), the polyion reaches its largest size of $R_g^2 = 21.589$ which occurs when a net electrostatic interaction remains repulsive [see Fig. 1(b)]. With a further decrease of T, R_g^2 begins to decrease, and the net electrostatic interaction vanishes at $T = 0.34330$. As T is lowered further into a narrow interval around $T \approx 0.146$, all the quantities exhibit abrupt changes, which is the characteristic of a phase transition. The large decrease in R_g^2 indicates a collapse transition occurs. As T is lowered even further, R_g^2 decreases slowly, and at $T = 0.07$, it reaches a small value of 0.1305.

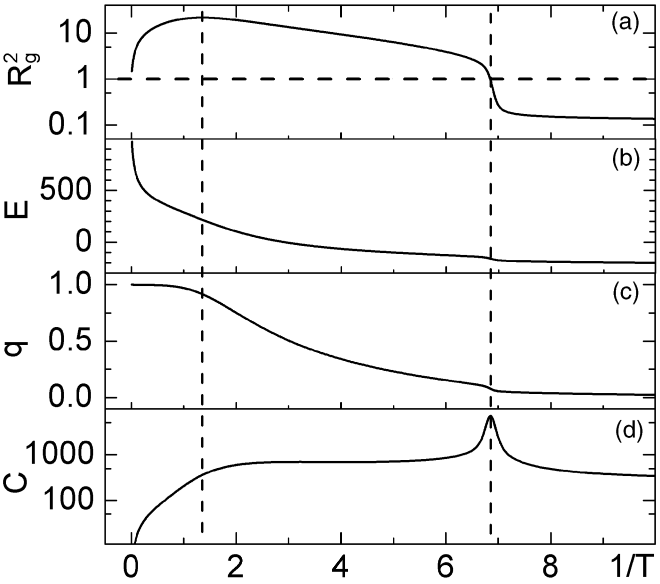

FIG. 1. Various quantities as functions of $1/T$, where results obtained directly from the replica points are shown, and they are consistent with those obtained from the histograms (not shown) within the error range. Error bars for all quantities are smaller than the line thicknesses. (a) Mean-square radius of gyration. (b) Energy. (c) Effective charge. (d) Specific heat.

Typical configurations of the polyion are shown in Fig. 2 at different values of T, where the polyion presents itself as a coil without any condensed counterions [Fig. 2(a)], an expanded coil with some condensed counterions [Fig. 2(b)], a coil on which most of the counterions have been condensed [Fig. 2(c)], and a globule interweaved with condensed counterions [Figs. 2(d) and 2(e)]. It is interesting to notice that in the structure of a globule, both the counterions and the polyion charged segments are densely packed into three-dimensional crystal structures. Each structure is a face-centered cubic array, and the two structures are mutually interpenetrating, resembling a NaCl-type order. That is, negative charges have packed into a three-dimensional Wigner crystal on the background of positive charges and vice versa. This crystal

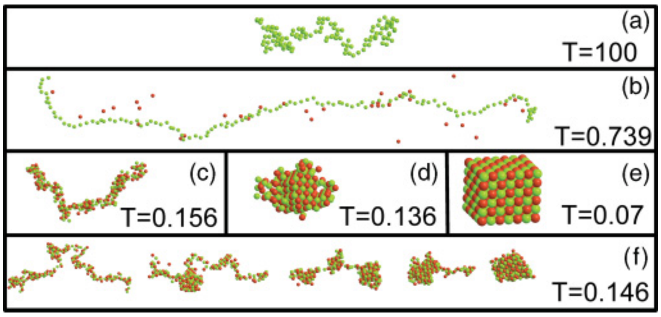

FIG. 2. (Color) Typical snapshots from simulations. Only the polyion monomers (green) and the nearby counterions (red) are shown, whereas solvents and other counterions are omitted for clarity. Please note that pictures shown here are not displayed in the same scale and in (f) five snapshots are shown.

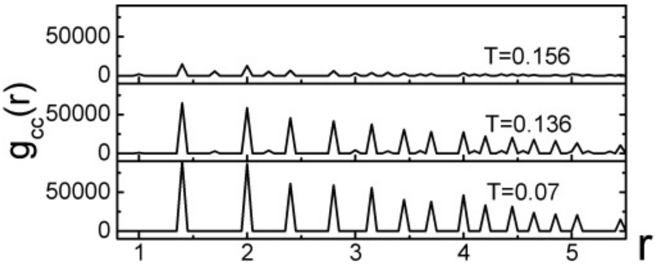

FIG. 3. Radial distribution functions for the counterions, $g_{cc}(r)$, at different temperatures.

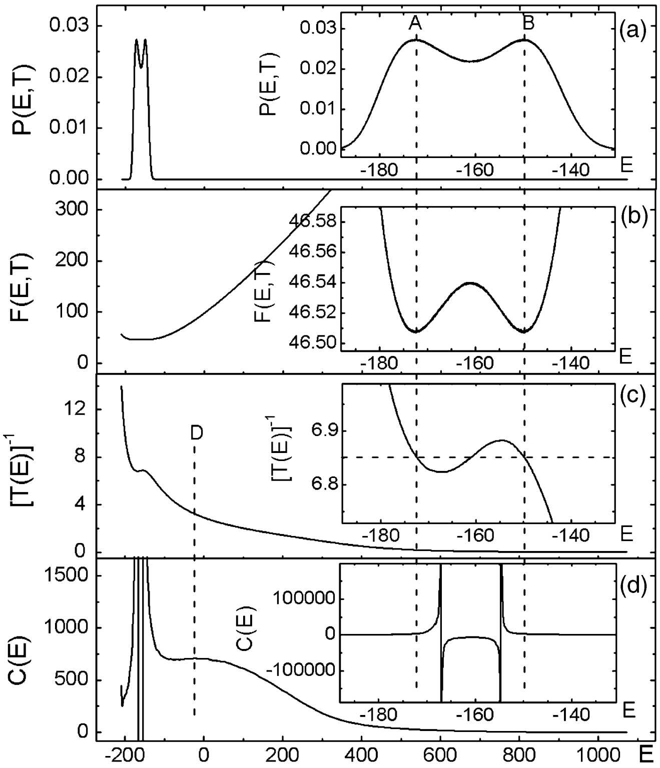

FIG. 4. (a) Probability distribution and (b) relative free energy vs E at the coil-globule transition point. (c) Inverse microcanonical temperature and (d) specific heat vs E.

order is further confirmed by radial distribution functions for the counterions, $g_{cc}(r)$ [Fig. (3)], and for the monomers, $g_{mm}(r)$ (not shown). The $g_{mm}(r)$ curve has a similar form as the corresponding $g_{cc}(r)$ curve. Furthermore, the shape of the globule changes from an irregular one [Fig. 2(d)] to an approximate cube [Fig. 2(e)] with the decrease of T. To our knowledge, such regularly packed three-dimensional Wigner crystals formed from the counterions and the polyion charges have not been reported before, though it has been predicted that the strong Coulomb repulsion is sufficient to cause a system of particles to crystallize in classical systems studied in certain soft condensed matter models [21]. The appearance of the Wigner crystals is due to the high efficiency of the replica-exchange technique, even at temperatures lower than the polyion collapsing temperature.

Figure 1(d) shows that the canonical specific heat C displays a high temperature small peak at $T \approx 0.31$ and a broad plateau followed by another sharp peak at $T \approx 0.146$. For a finite size system, a peak in C curve can be associated with phase transitions or other structural rearrangements [16]. Combining the C curve with the R_g^2 and q curves shown in Fig. 1, we can identify the high temperature peak with the counterion condensation and the low temperature peak with the polyion collapse transition.

In order to clarify the nature of the coil-globule transition, we compute the probability distribution $P(E,T)$ and the free energy $F(E,T)$ at the transition point $T_{C-G} = 0.145\,956$, which are shown in Fig. 4. As shown in Fig. 4, the $P(E,T)$ curve presents a bimodal distribution with equal weight, and the $F(E,T)$ curve has two identical minimum values at points A and B, separated by a free energy barrier. Therefore, a first-order transition can be identified for the coil-globule transition of the polyion. The point A is in the globule region while the point B is in the coil region. The small energy barrier (~ 0.032) indicates that the transition is weakly first order. On the other hand, a visual examination of the snapshots at the transition point shows that the transition is characterized not only by the coexistence between the expanded coil and compact globule structures, but there is an apparent coexistence within a single chain between a globule nucleus domain and one or more expanded chain segments, as shown in Fig. 2(f). A similar coexisting behavior was found in the coil-crystallite freezing transition of an uncharged polymer chain [16].

The first-order nature of the coil-globule transition is also confirmed by a microcanonical analysis. From the results shown in Figs. 4(c) and 4(d), it is noted that there is a Maxwell-type loop in the inverse microcanonical temperature $T(E)$, and a negative region bounded by two poles in the microcanonical specific heat $C(E)$. All these signals indicate that the first-order coil-globule transition is clearly distinct in the microcanonical analysis [16]. This result is consistent with that from the canonical analysis, and also consistent with those of previous theoretical results [3–5]. Besides the signals indicating the coil-globule transition, there exists an isolated inflection point in the $T(E)$ curve and accordingly a finite peak in the $C(E)$ curve at $E \approx -23.9$ [the line D in Figs. 4(c) and 4(d)], which indicates an existence of a continuous transition. The $T(E)$ value of this point coincides with the T value of the high temperature peak in the C curve [Fig. 1(d)], indicating that the counterion condensation is a continuous transition. On the other hand, in Figs. 4(c) and 4(d), there are no other signals that indicate the formation of the Wigner crystals. This result suggests that the Wigner crystals appear concomitantly with the polyion collapse. This conclusion is also supported by the $g_{cc}(r)$ (see Fig. 3) and $g_{mm}(r)$ curves, where sharp peaks occur after the chain collapse transition.

The results presented above are obtained for a polyelectrolyte chain of length $N = 125$. In addition to our rather extensive set of simulations for this system, we also carry out a smaller set of simulations for a polyion chain of different lengths ($N = 109$, 79, 59, 49, 39, 29, 19, and 9). These extended data sets have allowed us to make a preliminary finite-size scaling analysis of the polyelectrolyte chain conformation behavior. It is found that in system with $N = 109$, the first-order feature becomes less pronounced than that in the system with $N = 125$. Furthermore, in systems with $N \leqslant 79$, the first-order feature does not emerge in both canonical and microcanonical analyses for the chain collapse transition. We attribute this behavior to the finite-size effect. The previous theoretical study of Brilliantov and coworkers found that the first-order coil-globule phase transition of the polyion can be influenced by the size of the system and the polyion chain length [3]. With decreasing these parameters, the transition shifts to the smaller side of the Coulomb strength parameter and becomes less pronounced. Their results coincide with ours. The finite-size effect strongly influences the behavior of the transition, and the first-order characteristics of the coil-globule transition emerges only when N is large enough. This is the reason that only a weak first-order phase transition is found for the polyion chain with $N = 125$ and 109. We deduce that with a larger N, a more pronounced first-order transition, with a bigger free energy barrier, will be observed. In the previous study of the entropic sampling within the Wang-Landau algorithm, the studied chain length is not more than 80 [13]. The small chain length used in that study may be the reason that the authors did not observe the first-order feature for the chain collapse transition.

In summary, the thermodynamic behavior of a single strongly charged polyelectrolyte chain accompanied by its neutralizing counterions in a salt-free solution has been studied using replica-exchange MCS. Our results reveal that the transition from a coil with condensed counterions to a globule is clearly discontinuous for longer chains and provides an interesting example of phase coexistence in a finite-size system. Furthermore, in a globule state, both the counterions and the polyelectrolyte charged segments themselves are densely packed into three-dimensional Wigner crystals. Although previous studies have indicated that fundamental properties of polyelectrolytes depend weakly on the details of the model, our results require further characterization with off-lattice models.

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