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Finite-length effects on the coil-globule transition of a strongly charged polyelectrolyte chain in a salt-free solvent

Peng Chi,[*] Zheng Wang, Yuhua Yin, and Baohui Li[†]
The MOE Key Laboratory of Weak Light Nonlinear Photonics and School of Physics, Nankai University, Tianjin, 300071, China

An-Chang Shi[‡]
Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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The nature of coil-globule transition and scaling behavior of a strongly charged polyelectrolyte chain in a solution system with explicit neutralizing counterions and solvent molecules are studied using replica-exchange Monte Carlo simulations, focusing on the effects of finite chain length. The results reveal that at the thermodynamic limit of infinitely long chain length, the coil-globule transition may remain first order. Phase transition temperatures at various ion concentrations are obtained by extrapolating the values obtained at finite chain lengths. Furthermore, it is found that the exponent ν of the radius of gyration, $\langle {R_g}^2 \rangle \sim N^{2\nu}$, can be slightly larger than 1 under some conditions.

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I. INTRODUCTION

Polyelectrolytes are polymers with positively or negatively charged groups, which may ionize in a polar solvent [1]. The charged groups can dissociate to release counterions and hence leave net charges on the polymer chains. The most noticeable feature of polyelectrolytes, as compared to uncharged polymers, is their high solubility in water. Polyelectrolytes attract great research attention because of their biological and industrial applications due their solubility in water. Furthermore, many important synthetic and biological macromolecules are polyelectrolytes. The electrostatic interactions between the charges lead to the rich behavior of polyelectrolyte solutions which may differ significantly from those of uncharged polymers [2]. For an uncharged 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 decreasing the temperature [3]. However, for a flexible polyelectrolyte chain in a solution, the nature of its collapse transition is still a topic of debate.

For an uncharged flexible polymer chain in solution, its coil-globule transition occurs in a continuous fashion when the temperature is decreased, displaying no coexistence between distinct coil and globule states, and thus is analogous to a second-order phase transition. Further cooling of the system leads to a first-order globule-crystalline transition [4,5]. Furthermore, it is well known that the radius of gyration of a long, flexible, uncharged polymer chain satisfies a scaling relation, $\langle {R_g}^2 \rangle \propto N^{2\nu}$, where $\langle {R_g}^2 \rangle$ is the mean-square radius of gyration of the chain, N the chain length, and ν an exponent [6,7]. At very high temperatures, ν is close to 0.59, which is the value for athermal excluded volume chains. It decreases with decreasing temperature. At very low temperatures, when the chain collapses, ν is close to 1/3, which is the value of compact spheres. Intermediate between these two limiting cases, ν can be equal to 0.5, which corresponds to the ideal chain at the θ temperature. Moreover, for a rigid rod chain, one can strictly deduce that $\nu = 1$ for a long chain.

For a flexible polyelectrolyte chain in a solution, previous extensive studies [8–19] show that its conformation exhibits a more complex behavior than an uncharged polymer chain. At very high temperatures, the conformation of a polyelectrolyte chain should be similar to that of a random coil chain. With decreasing temperature, the polymer chain changes to an expanded conformation due to the electrostatic interactions between charged monomers. After reaching a maximum coil size, the polymer chain shrinks and finally collapses to a compact globule. The size of an expanded polyelectrolyte chain can be much larger than that of a random coil chain [19]. Previous studies also showed that the electrostatic attraction between charged monomers of a polyelectrolyte chain and counterions in solution results in the condensation of counterions on the chain. This counterion condensation and the associated dipole formation between the charged monomers and the condensed counterions lead to the shrinkage and collapse of the charged chain. Despite the various previous studies, a controversy about the nature of the collapse transition exists. Specifically, for a flexible polyelectrolyte chain in a solution, the coil-globule transition was predicted to be first order by theories [8–10], whereas the first-order nature of this transition has not been positively identified in simulations. Furthermore, based on Flory theory, Dobrynin and Rubinstein found that for a flexible polyelectrolyte chain in solution, the chain size grows faster than linear with the chain length [2]. However, such a scaling behavior has not been investigated systematically in simulations.

The difficulties in the study of polyelectrolyte systems in simulations can be traced to the following two aspects. The first aspect is the large CPU time requirement to treat the long-range electrostatic interactions between the charges in the system. Furthermore, the CPU time increases quickly with the increase

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[*] Present Address: Science and Technology on Space System Simulation Laboratory, Beijing Simulation Center, Beijing, 100854.

[†] Author to whom correspondence should be addressed: baohui@nankai.edu.cn

[‡] Author to whom correspondence should be addressed: shi@mcmaster.ca

of the chain length due to the increased number of charges in the system. Because of this limitation, the chain lengths considered in previous simulations are relatively short. The second aspect is the fact that traditional simulation techniques such as Metropolis Monte Carlo (MC) simulations have a poor sampling efficiency, especially at low temperatures or for a strongly charged chain system. This difficulty could be overcome by using advanced simulation techniques, such as MC simulations with the Wang-Landau algorithm [20] or with the replica-exchange algorithm (REMC) [21].

Recently, the above-mentioned controversy was settled for a polyelectrolyte chain with a finite chain length, where the conformation transitions of a strongly charged polyelectrolyte chain with length 125 were studied using REMC simulations. In that study the first-order feature of the coil-globule transition was unambiguously identified based on reliable canonical and microcanonical analysis [19]. It was also found that for a polyelectrolyte chain with length $N \leqslant 79$, the first-order feature of the coil-globule transition no longer emerges. Therefore, it was deduced that the small chain length, adopted in previous simulation studies, may be the reason that these authors did not observe the first-order features for the chain collapse transition, even when an advanced simulation technique has been used [18].

Strictly speaking, a true phase transition occurs at the thermodynamic limit of infinite chain length. The nature of the coil-globule transition at the thermodynamic limit has not been studied in simulations yet. In this paper, we attempt to generalize the study of the nature of the coil-globule transition of a strongly charged polyelectrolyte chain with finite length to the thermodynamic limit of infinitely large chain length using REMC simulations based on a finite chain length analysis. Furthermore, we investigate the scaling behavior of a strongly charged polyelectrolyte chain system.

II. MODEL AND METHOD

In the current study, the nature of the coil-globule transition and the scaling behavior of a strongly charged polyelectrolyte chain are investigated using computer simulations of a lattice model of polymers proposed by Carmesin and Kremer [22]. The simulations are carried out using the REMC method [21]. In using this technique, a set of separate replicas is simulated simultaneously, and each replica is simulated at a unique temperature. By allowing systems at different temperatures to exchange complete configurations, this technique achieves good sampling even at low temperatures or for a highly charged system [19]. Thus it may provide high precision for the calculated thermodynamic quantities. Our previous study has established that the model and method are appropriate for the study of the thermodynamic behavior of a strongly charged polyelectrolyte chain in solution [19]. For completeness, the model and algorithm are reviewed briefly below.

The simulations are performed on a model system that is embedded in a simple cubic lattice of volume $V = (Lc)^3$, where c is the lattice constant and L the number of lattice sites in each side of the simulation box. The polyelectrolyte 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 $\sqrt{3}c$. The model system consists of one polyelectrolyte chain in a solution system including explicit neutralizing counterions and solvent molecules. Throughout the simulations, each species (a monomer, a counterion, and a solvent molecule) occupies one lattice site. Double occupation of the lattice sites is not allowed. Each monomer 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. The initial configuration is generated by randomly creating a polyelectrolyte chain and a desired number of counterions on the lattice. After the chain and the counterions have been generated, the unoccupied sites are designated as solvent molecules. Apart from the constraint of single occupancy of the lattice sites, the only energetic interaction is a Coulomb potential with the form of $u_{ij} = q_i q_j / D r_{ij}$, 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 the long-range interactions are computed using an approximation of the Ewald summation with the procedure proposed in Ref. [17]. The chain trial moves include the exchange movement, similar to that used in the block copolymer system [23], and pivot movement [24]. The counterion trial moves include its exchange with a nearest-neighbor monomer and that with a solvent molecule randomly selected in the whole system. 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. We performed simulations for systems with different chain lengths and different ion concentrations. The ion concentration ρ is represented by the ratio of the total number of counterions to the reduced volume of the system, i.e., $\rho = (N+1)/L^3$. In our simulations, the chain length N is varied from 9 to 255 or the total number of monomers on the chain from 10 to 256, and the box length L from 54 to 1068. We use the finite chain length scaling techniques proposed by Binder and Heermann [25] to locate the coil-globule transition temperature at the thermodynamic limit.

In our simulations, thermodynamic averages of various quantities are computed at each temperature. At a given temperature T, the probability distribution $P(E)$ of the system's conformational energy E is obtained from the REMC simulation data directly based on histogram analysis with the procedure proposed in Ref. [26]. The density of state, $g(E)$, is computed based on $P(E)$. The thermodynamic properties of the model system can be completely determined from the single chain density of state $g(E)$ using the procedure described in Ref. [5].

III. RESULTS AND DISCUSSION

The density of state curves $g(E)$ for systems with different chain lengths are presented in Fig. 1, where each curve is scaled through assuming that $g(E) = 1$ at the maximum E value. It is noticed that $g(E)$ is a monotonically increasing function of E, and larger chain length N, leads to a steeper increase of $g(E)$.

For systems with different chain lengths, various quantities are computed and normalized in terms of the chain length. Figures 2(a) and 2(b) show the probability distribution curves $P(E)$ and the normalized free energy curves $F(E)/(N+1)$ at the coil-globule transition temperature, and (c) and (d) show the inverse microcanonical temperature curves $1/T(E)$

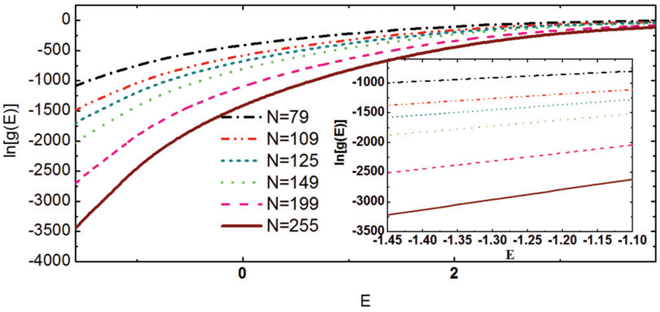

FIG. 1. (Color online) The density of state $g(E)$ for systems with different chain lengths.

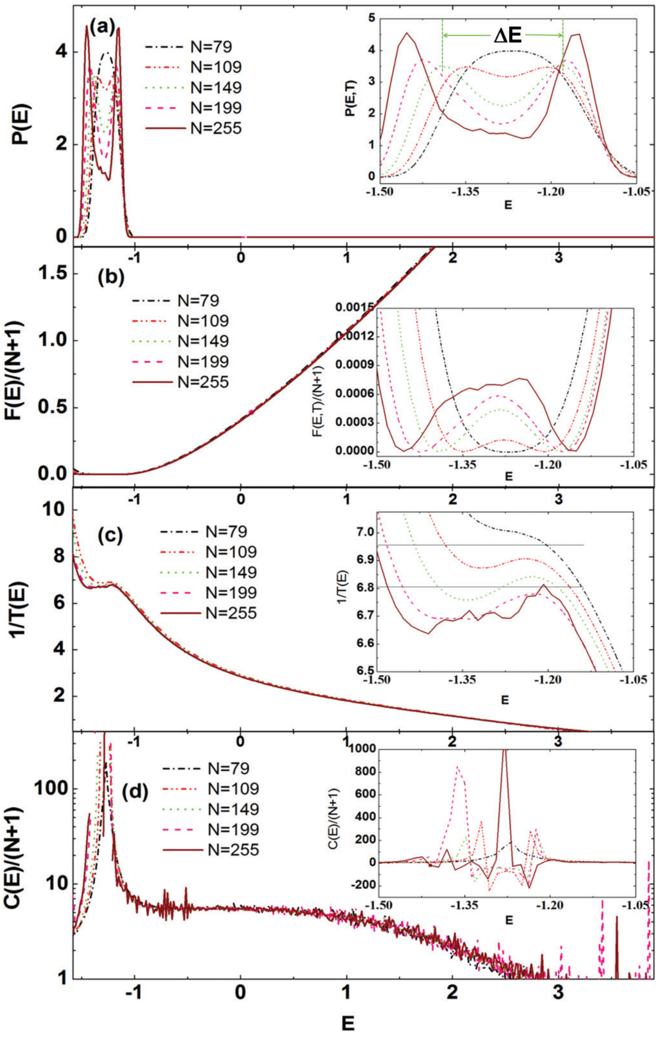

FIG. 2. (Color online) Various quantities for systems with different chain lengths at an ion concentration $\rho = 7.874 \times 10^{-6}$. (a) The probability distribution curves and (b) the normalized free energy curves at the coil-globule transition temperature. (c) The inverse microcanonical temperature curves and (d) the normalized microcanonical specific heat curves.

and the normalized microcanonical specific heat curves $C(E)/(N+1)$, respectively. As can be seen in Fig. 2, the finite chain length effect strongly influences the behavior of the coil-globule transition. In Fig. 2, it is noticed that at the coil-globule transition temperature, for systems with long chains each $P(E)$ curve presents a bimodal distribution with equal weight, each $F(E)/(N+1)$ curve has two identical minimum values separated by a free energy barrier; each $1/T(E)$ curve has a Maxwell-type loop, and each $C(E)/(N+1)$ curve has a negative region bounded by two poles. All these signals are the characteristics of a first-order phase transition, as pointed out previously [19]. It is also noticed that with decreasing chain length, the first-order features of the coil-globule transition become less pronounced. Furthermore, for a system with $N = 79$, none of the above-mentioned signals occur in Fig. 2. Moreover, our extensive simulation results (not show) reveal that none of the above-mentioned signals occur for systems with $N < 79$ either. All these results suggest that for systems with short chains, the first-order features for the chain collapse transition no longer emerge in these analyses.

In Fig. 2(a), the energy difference between the two peak positions in the probability distribution curve is denoted as ΔE. This energy difference ΔE corresponds to the energy difference between coil and globule structures at the coil-globule transition temperature. The existence of such an energy difference between the two states at the phase transition temperature is also characteristic of a first-order phase transition. In Fig. 2(a), it is noticed that with increasing chain length, ΔE increases. From this observation it is deduced that an energy difference with a nonzero ΔE value may remain at the thermodynamic limit. That is, for a system with an infinitely large chain length, the probability distribution curve may remain to be a bimodal distribution with equal weight, and therefore, the coil-globule transition may remain to be a first-order phase transition at the thermodynamic limit. Furthermore, as shown in Figs. 2(b)–2(d), the same conclusion can be deduced from the variation trends of the free energy curve, the inverse microcanonical temperature curve, and the microcanonical specific heat curve when the chain length is increased. It should be pointed out that the obvious nonsmoothness of the curves for the system with $N = 255$ in Fig. 2 is due to the insufficient computation time for this large system.

Figure 3 shows the temperature dependence of the normalized mean-square radius of gyration of the polyion chain, $\langle R_g{}^2\rangle/N$, and the canonical specific heat $C/(N+1)$ for systems with various chain lengths at a given ion concentration $\rho = 7.874 \times 10^{-6}$. In Fig. 3(a), it is noticed that with decreasing T, each $\langle R_g{}^2\rangle/N$ curve increases first, then decreases after reaching a maximum value, and finally collapses to a minimum value. In the inset of Fig. 3(a), it is noticed that with increasing the chain length to $N = 199$, the intersection point between two $\langle R_g{}^2\rangle/N$ curves shifts to high temperatures. However, when $N = 255$, it slightly shifts to low temperatures. This is different from that for an uncharged single chain system where a common intersection point, corresponding to the θ temperature, was obtained for different curves [7]. In Fig. 3(b), it is noticed that with decreasing T, each specific heat curve displays a high-temperature plateau followed by another sharp peak. In our previous study for the system with $N = 125$ [19], a similar specific heat curve was obtained, where the high-temperature plateau has been identified with the counterion condensation and the low-temperature peak with the polyion chain collapse transition. Our extensive

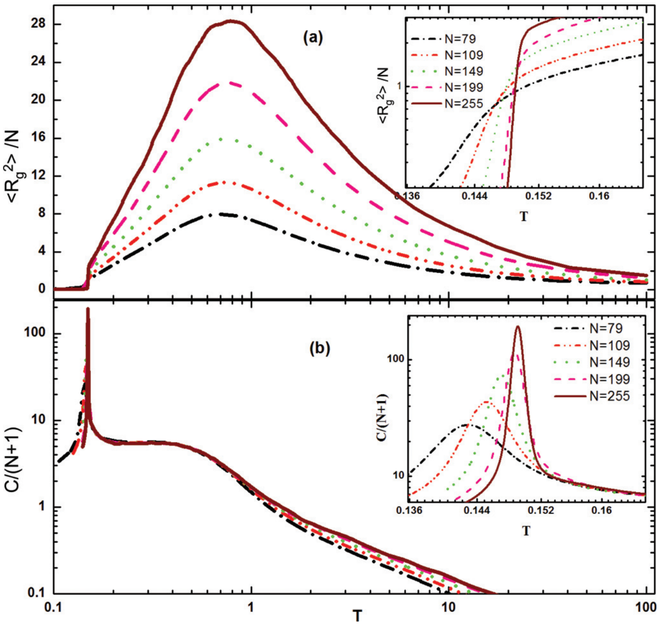

FIG. 3. (Color online) The temperature dependence of (a) normalized mean-square radius of gyration of the polyion chain and (b) the specific heat for systems with various chain lengths at $\rho = 7.874 \times 10^{-6}$. Partially magnified curves are shown in the inset of the figure.

simulations show that these identifications apply to all systems with a finite N. Hence, for a given system, the temperature corresponding to the low-temperature peak in the specific heat curve is defined as the coil-globule transition temperature. In the inset of Fig. 3(b), it is noticed that with increasing N, the low-temperature peak becomes sharper and the coil-globule transition temperature shifts to high temperatures. Of course, θ-function-like transitions are only to be expected as the limit of N approaches ∞. Therefore, extrapolation of the transition temperatures obtained for systems with finite chain lengths needs to be carried out to locate the coil-globule transition temperature at the thermodynamic limit.

Figure 4 shows the chain length dependence of the coil-globule transition temperatures for systems with different ion concentrations, where the symbols are obtained from our simulations and each solid line is a fit to Eq. (1) corresponding to a given ρ value:

$$T_\rho(N) = T_\rho(\infty) - A_\rho N^{-1/2}. \tag{1}$$

In Eq. (1), $T_\rho(N)$ is the phase transition temperature in system with a finite N and can be obtained from the corresponding specific heat peak, $T_\rho(\infty)$ is the phase transition temperature for the system with an infinitely large chain length, i.e., at the thermodynamic limit, and A_ρ is a phenomenal parameter. From the fittings, we obtain $T_\rho(\infty) = 0.162$ and $A_\rho = 0.140$, $T_\rho(\infty) = 0.157$ and $A_\rho = 0.127$, $T_\rho(\infty) = 0.152$ and $A_\rho = 0.121$, and $T_\rho(\infty) = 0.145$ and $A_\rho = 0.113$ at $\rho = 6.299 \times 10^{-5}, 7.874 \times 10^{-6}, 9.842 \times 10^{-7}$, and 1.230×10^{-7}, respectively. In Fig. 4 it is noticed that the fittings are good, indicating that the variation of the coil-globule transition temperature for a polyelectrolyte chain is similar to that for an uncharged chain system [7]. The value of A_ρ decreases with decreasing the ion concentration, suggesting that for a pair of systems with different ion concentrations, the difference between their coil-globule transition temperatures increases with increasing N and reaches a maximum at the thermodynamic limit. It is also noticed that with decreasing the ion concentration, the coil-globule transition temperature decreases. It should be pointed out that the ion concentration considered in our model system is very low. For example, when $c = 1$ nm, a system with $\rho = 1.230 \times 10^{-7}$ corresponds to an ion concentration of 2×10^{-4} mol/l. We may deduce that when the ion concentration approaches zero, the coil-globule transition temperature also approaches zero based on the following reasons. First, it is noticed that the transition temperature increases with increasing chain length, even though the ion concentration is very low. Second, it was concluded that the coil-globule transition is induced by the counterion condensation [19]. In a system with an infinitely long chain length, when the ion concentration approaches zero, the entropy of counterions at a finite temperature will be infinity. This infinitely large entropy predominates over the electrostatic interactions so that counterion condensation does not occur at any finite temperature. On the other hand, it should be pointed out that the estimated coil-globule transition temperature at the thermodynamic limit may be only a good approximation because the chain lengths considered in the present paper are still relatively short.

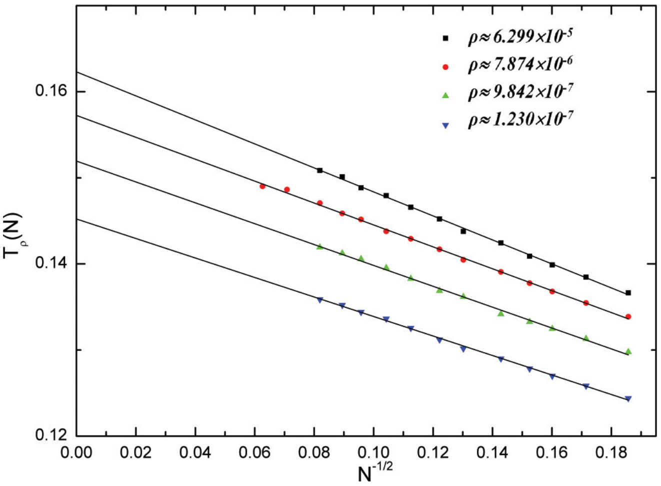

FIG. 4. (Color online) The chain length dependence of the coil-globule transition temperatures for systems with different ion concentration ρ. The symbols are obtained from our simulations and solid lines are fits to Eq. (1).

We construct the double logarithm plot between the mean-square radius of gyration of the polyion chain $\langle R_g{}^2 \rangle$ and the chain length N at different temperatures in Fig. 5 to investigate their relationship. Figure 5(a) shows the plot in the relatively high temperatures when all the chains are in the expanded conformations. In Fig. 5(a), the bounds corresponding to athermal excluded volume chain conformation and rigid rod conformation are also included. It should be pointed out that at a given temperature, the double logarithm plot for the polyion chain is usually not a straight line but a curved one. On the other hand, in the vicinity of a given N, the curved line can be approximated as a straight line so that we can calculate

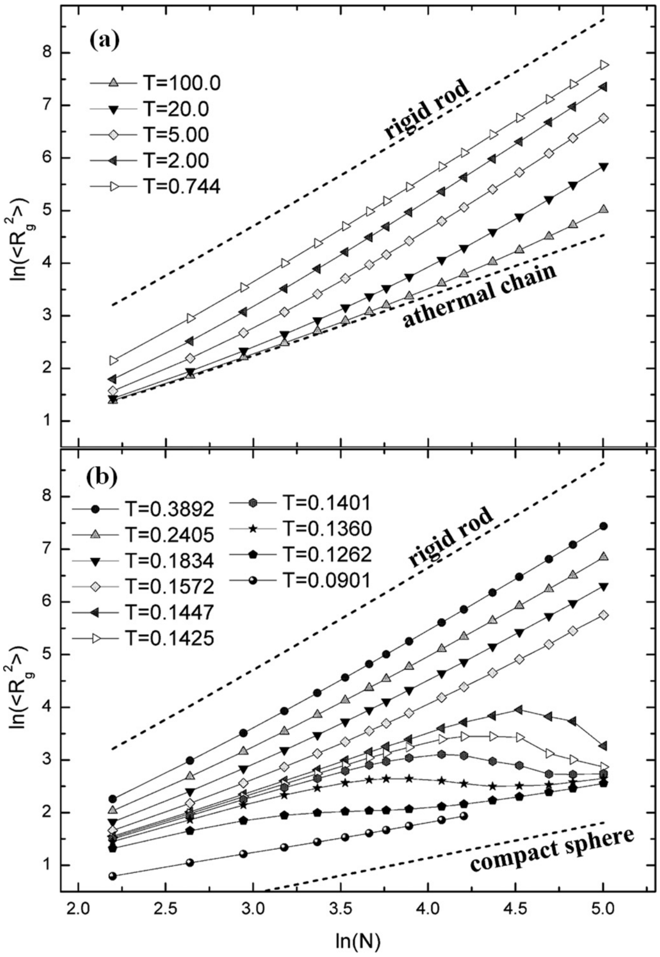

FIG. 5. The double logarithm plot between the coil size and the chain length at different temperatures for systems with $\rho = 7.874 \times 10^{-6}$, in the (a) relatively high and (b) relatively low temperatures. The error bars are smaller than the symbol size.

the slope of the curve, or the exponent ν in the relationship $\langle {R_g}^2 \rangle \sim N^{2\nu}$ corresponding to the given N value. It is noticed that when N is small and the temperature is very high, the slope of the curve is similar to that of an athermal chain, i.e., the exponent ν is about 0.59. With increasing the chain length or with decreasing temperature, ν increases. It is interesting to notice that when T is in the range of $10 \sim 0.5$, for systems with relatively larger N values considered, ν is close to 1, the value of a rigid rod chain, although the chain is in an expanded conformation and not a rigid rod. Furthermore, in a portion of this T range, ν is slightly larger than 1. This is because at a given T value in that range, a longer chain is in a more expanded conformation than that of a shorter chain due to the stronger Coulomb interaction in the former system. Based on Flory theory, Dobrynin and Rubinstein found that the chain size of a uniformly charged flexible polyelectrolyte chain grows faster than linearly with N [2]. Our simulation result that the exponent can be slightly larger than 1 is consistent with their result.

Figure 5(b) shows the double logarithm plot in the relatively low temperatures when relatively long chains are in the shrinking or collapsing states. In Fig. 5(b), the bounds corresponding to rigid rod conformation and compact-sphere conformation are also included. It is noticed that with decreasing T, the exponent ν decreases quickly from slightly larger than 1 to 1, then to 0, further to a negative value, and finally to 1/3. This is because the temperature at which each $\langle {R_g}^2 \rangle$ curve gets its maximum value shifts to high temperatures with increasing N. Therefore, when a relatively longer chain begins to shrink, a relatively shorter chain continues to expand, and when a relatively longer chain has reached the collapsing state, a relatively shorter chain continues to expand or begins to shrink; all these cases result in a decrease in ν. In these cases, when the $\langle {R_g}^2 \rangle$ value for a relatively longer chain is smaller than that for a relatively shorter chain, a negative ν value occurs. When all the chains are in the collapsing state, ν approaches 1/3, the value for a system of compact spheres. The most striking feature seen in Fig. 5(b) is the nonmonotonicity of the $\ln(\langle {R_g}^2 \rangle)$ curve at low temperatures. A similar feature was noticed by Grassberger and Hegger and also by Rissanou *et al.* in their study of an uncharged polymer chain system [27,28]. Using a Langevin dynamics simulation, Liu and Muthukumar systematically investigated the nature of counterion condensation of a uniformly charged flexible polyelectrolyte chain [13]. They also constructed a double logarithm plot between $\langle {R_g}^2 \rangle$ and the chain length. Their result is qualitatively consistent with ours. However, the error bars in their plot indicated that errors of their data are relatively large. On the other hand, the error bars in Fig. 5 are smaller than the symbol size.

IV. CONCLUSIONS

Based on an analysis of finite chain length effect, we studied the nature of coil-globule transition and the scaling behavior of a strongly charged polyelectrolyte chain in a solution system including explicit neutralizing counterions and solvent molecules using replica-exchange Monte Carlo simulations. A number of thermodynamic quantities, such as the mean-square radius of gyration of the chain and the specific heat, are obtained from the simulation directly. The probability distribution $P(E)$ of the system's conformational energy is obtained from the simulation data directly based on histogram analysis and the density of states is computed based on $P(E)$. From the density of states, various thermodynamic quantities, such as the free energy curves at the coil-globule transition temperature, the inverse microcanonical temperature, and the microcanonical specific heat curves, are obtained for systems with different chain lengths. All these quantities present the first-order features of the coil-globule transition in systems with longer chains. From the variation tendency of the first-order features of the phase transition with chain length, it is deduced that at the thermodynamic limit of infinitely large chain length, the coil-globule transition may remain first order, and the phase transition temperatures at various ion concentrations are estimated by extrapolating the values obtained for systems with finite chain lengths. Furthermore, we investigated the dependences of the mean-square radius of gyration of the polyion chain on the chain length at various temperatures precisely and found that the exponent ν in the relationship of $\langle {R_g}^2 \rangle \sim N^{2\nu}$ can be slightly larger than 1 under some conditions.

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