

Supporting information

Conformation transitions of a single polyelectrolyte chain in a poor solvent: a replica-exchange Monte-Carlo study

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The details for the error calculation: In our simulations, statistical errors are estimated by the block average method [46] which is described briefly in the following. Suppose $\{A_i\}$ ($i = 1, 2, \dots, N_S$) is a series of N_S correlated samples of quantity A collected in a simulation. To estimate the statistical error of \bar{A} , which is the mean of $\{A_i\}$, one then divides the series into N_B non-overlapping blocks of length k . The block average of the n -th block is computed as

$$A_{B,n} = \frac{1}{k} \sum_{i=1}^k A_{(n-1)k+i}$$

The average of each block forms a new series $\{A_{B,n}\}$ ($n=1,2,\dots,N_B$). When k is large enough, the new series is almost uncorrelated and the statistical error of \bar{A} can be estimated by standard means.

$$\sigma^2_{\bar{A}} = \frac{1}{N_B(N_B-1)} \sum_{n=1}^{N_B} (A_{B,n} - \bar{A}_B)^2$$

Where \bar{A}_B is the mean of the new series $\{A_{B,n}\}$. In our paper, we set $N_B=N_S/2, N_S/4, N_S/8, \dots, 2$, in each case, an estimated error is obtained and we use the maximal one as the statistical error. To compute the statistical error of a quantity Q which cannot be computed directly in the simulations, such as the specific heat (C_v) and the critical temperature T_C . We divide the series of samples into five blocks and compute the Q value in each block. Then the statistical error is computed as

$$\sigma^2_{\bar{Q}} = \frac{1}{N_B - 1} \sum_{n=1}^{N_B} (Q_n - \bar{Q})^2$$

In our simulation, $N_S=10^7$, and a sample is collected every 10 attempted replica exchanges.

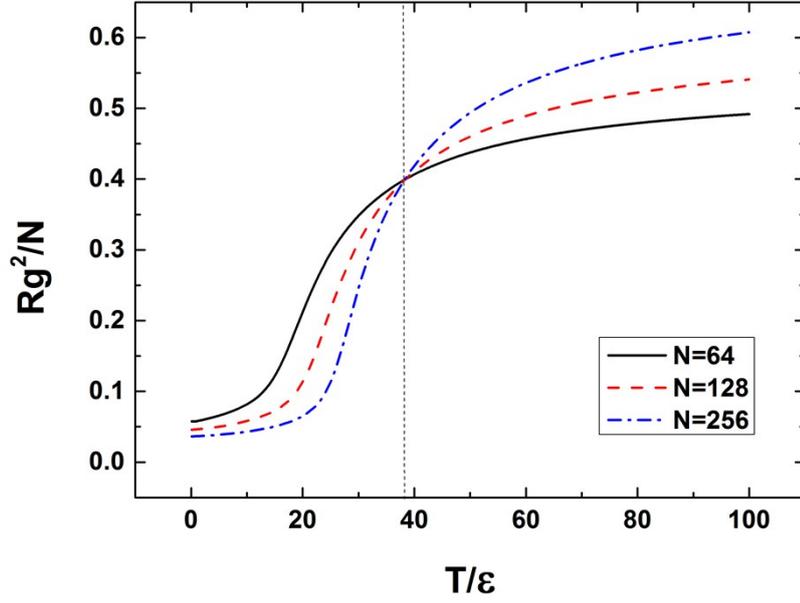


Fig.S1. R_g^2/N as functions of T/ϵ for chains of different chain length N .

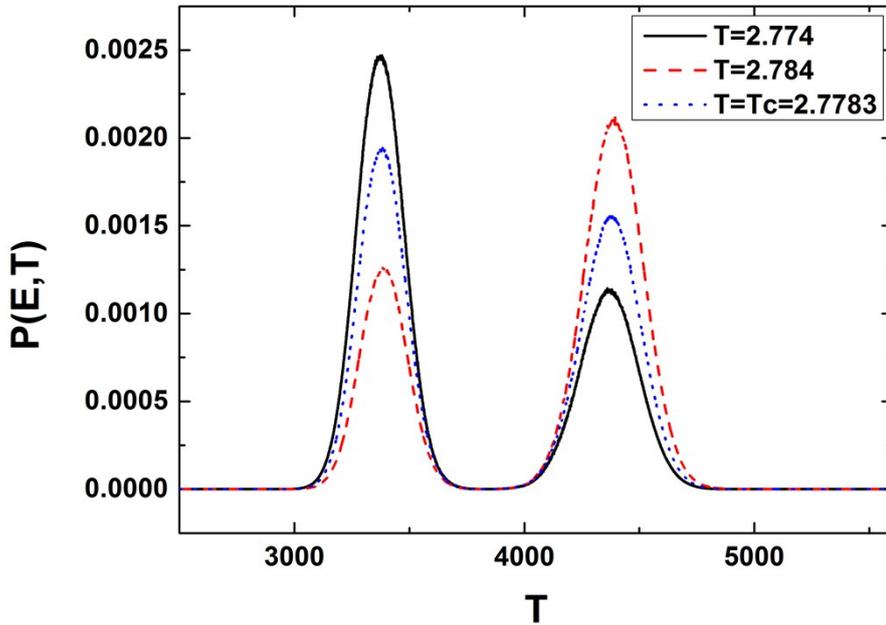


Fig.S2. The probability distribution curves at the transition temperature and two temperatures slightly deviating from the transition temperature.

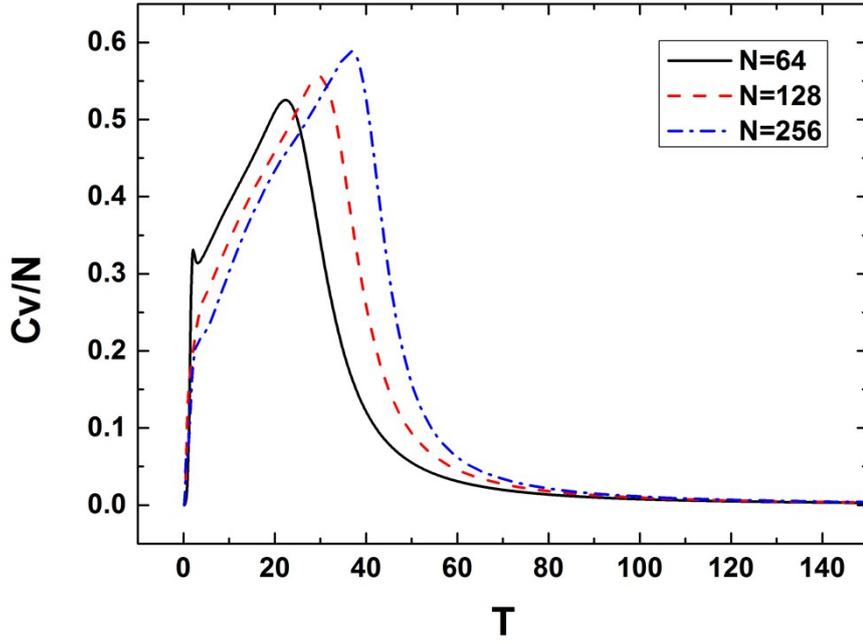


Fig.S3. C_v/N as functions of T for chains of different length N when $\varepsilon = 1.5$.

Comparison with the Manning criterion for counterion condensation: According to the Manning theory (Manning G S, Ray J 1998 J. Biomol. Struct. Dyn. 16, 461), $z\theta$, the fractional extent of charge neutralization by condensed counterions of valence z , can be written as:

$$z\theta = 1 - \frac{1}{z\xi}, \quad \xi = \frac{q^2}{Dk_B T b}$$

where q is the unit electrostatic charge, D is the dielectric constant of ion-free solvent, $k_B T$ is Boltzmann's constant times temperature, and b is L/P , the polymer contour length divided by the number of ionized groups on the polymer. In our model, reduced units are used where $z = 1$, $q = 1$, $D = 1$, $k_B = 1$, and as the bonds are c , $\sqrt{2}c$ and $\sqrt{3}c$, an average of b can be obtained as, $b = (6 \times c + 12 \times \sqrt{2}c + 8 \times \sqrt{3}c)/26 = 1.4162 \times c$, where c is the lattice constant with $c = 1$. Based on the above relations, it can be deduced that $\theta = 1 - bT$. Therefore, $\theta = 0$ when $T \geq 1/b$, otherwise, $\theta = 1 - Tb$. The variation of θ with T is plotted in Fig. S4 as a solid line.

The θ in the Manning theory has the same mean as “1- q ” in our manuscript, where q is the effective charge per segment used in our manuscript. The variation of 1- q with T is also plotted in Figure S4 with dashed and dotted lines. It is noted that the variation of θ with T is similar to that of the 1- q with T when $\varepsilon = 0$. When $\varepsilon > 0$, however, the variation of θ with T is quite different with that of the 1- q with T . The above comparison indicates that Manning theory, based on the primitive model of a cylinder with uniform surface charge in a uniform dielectric, is inapplicable to our case with $\varepsilon > 0$, especially when the pearl-necklace structures are formed.

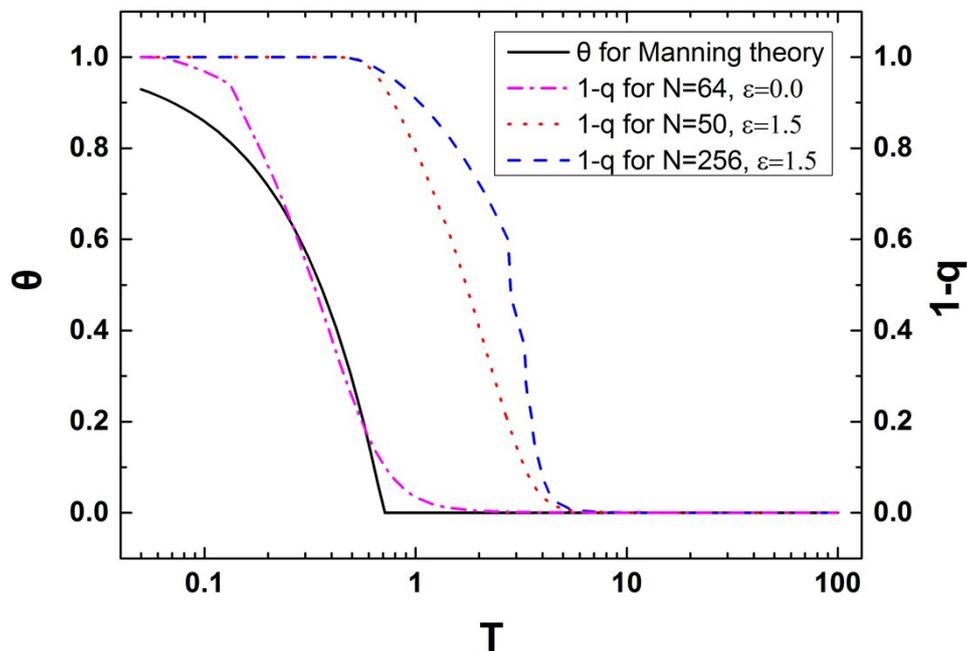


Fig. S4 The variation of θ and “1- q ” (q is the effective charge per segment) with T .

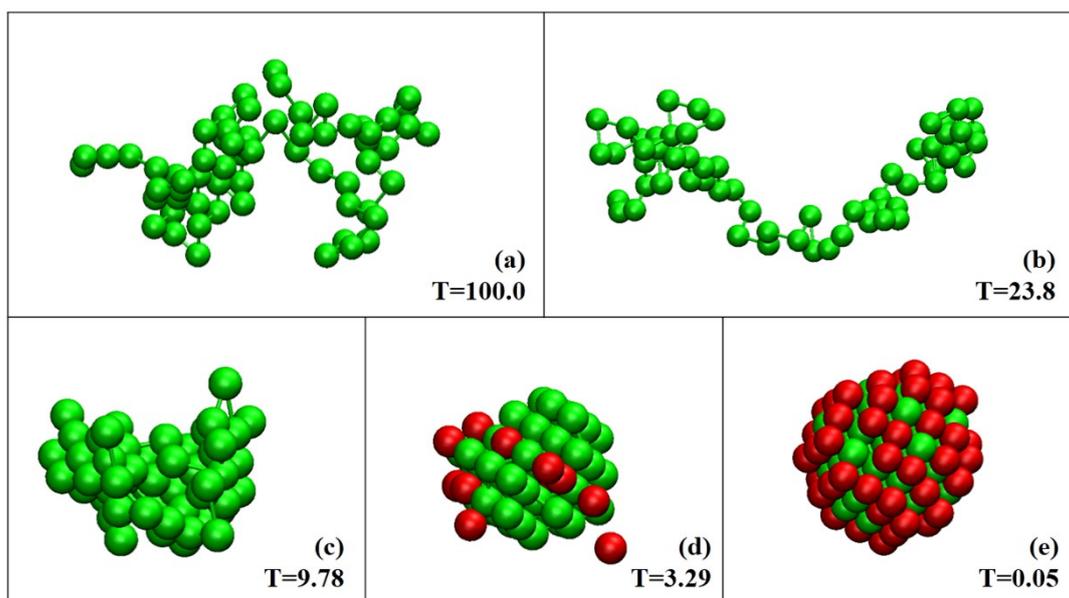


Fig. S5 Snapshots of typical conformations at different temperatures for system with $N=64$ and $\epsilon = 1.5$. Only chain monomers (green) and the nearby counterions (red) are shown. The pictures are not displayed in the same scale for clarity.

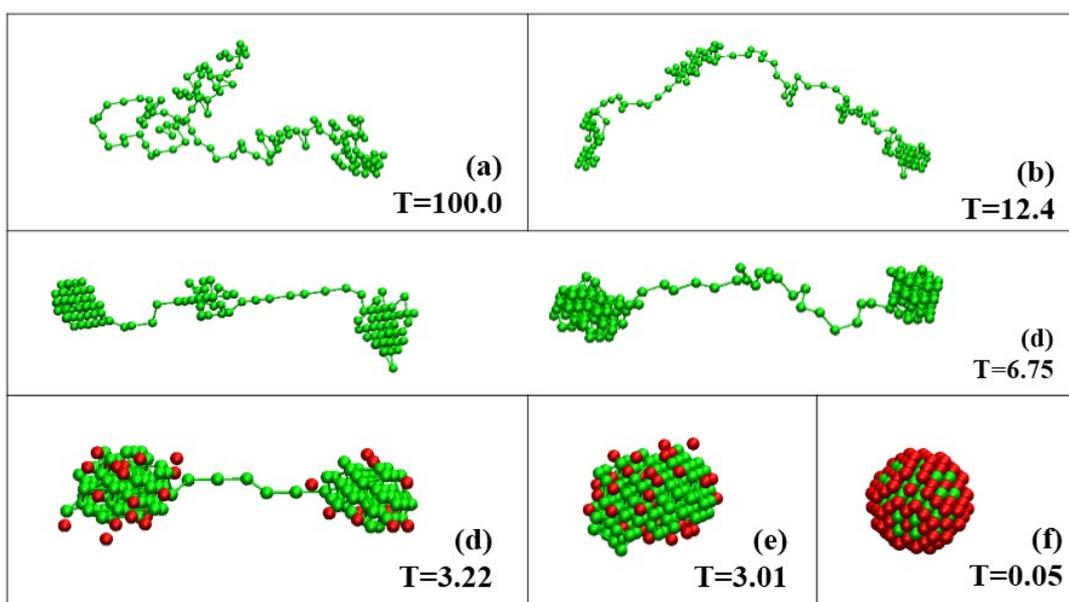


Fig. S6 Snapshots of typical conformations at different temperatures for system with $N=125$ and $\epsilon = 1.5$. Color scheme is the same as that in Fig. S1

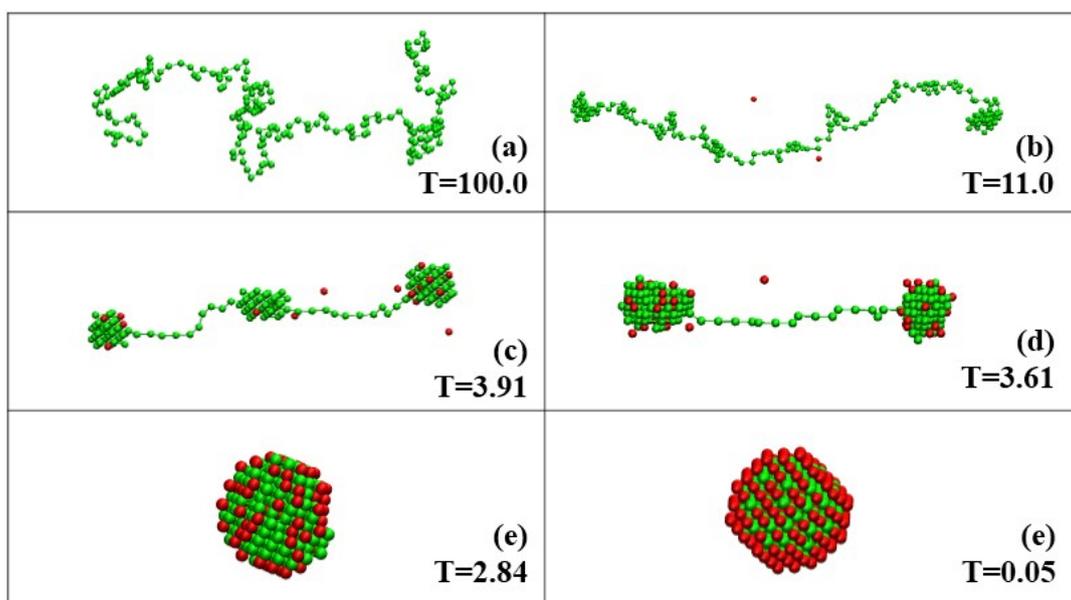


Fig. S7 Snapshots of typical conformations at different temperatures for system with $N=170$ and $\epsilon = 1.5$. Color scheme is the same as that in Fig. S1.

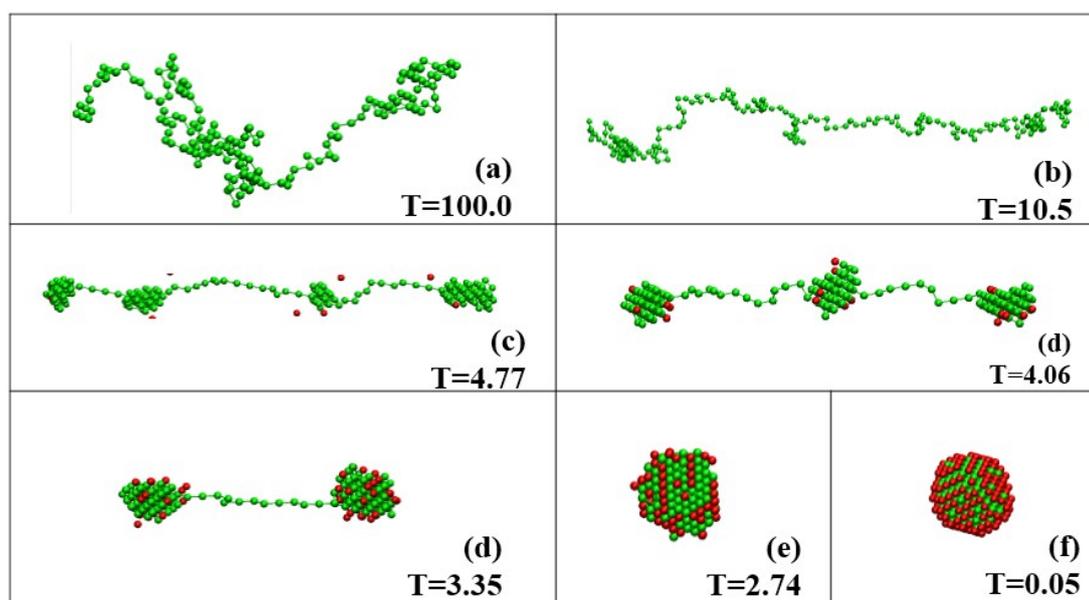


Fig. S8 Snapshots of typical conformations at different temperatures for system with $N=192$ and $\epsilon = 1.5$. Color scheme is the same as that in Fig. S1.

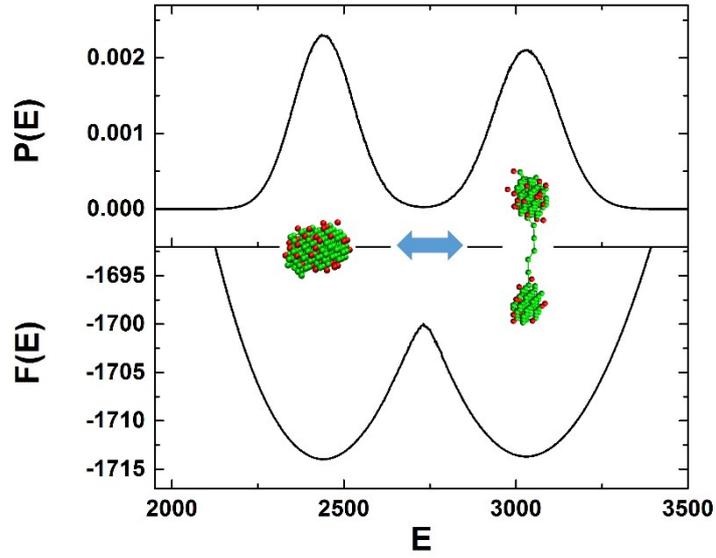


Fig. S9. The probability distribution and the free energy curves at the transition temperature of $T=3.0970$ for system with $N=125$ and $\varepsilon=1.5$.

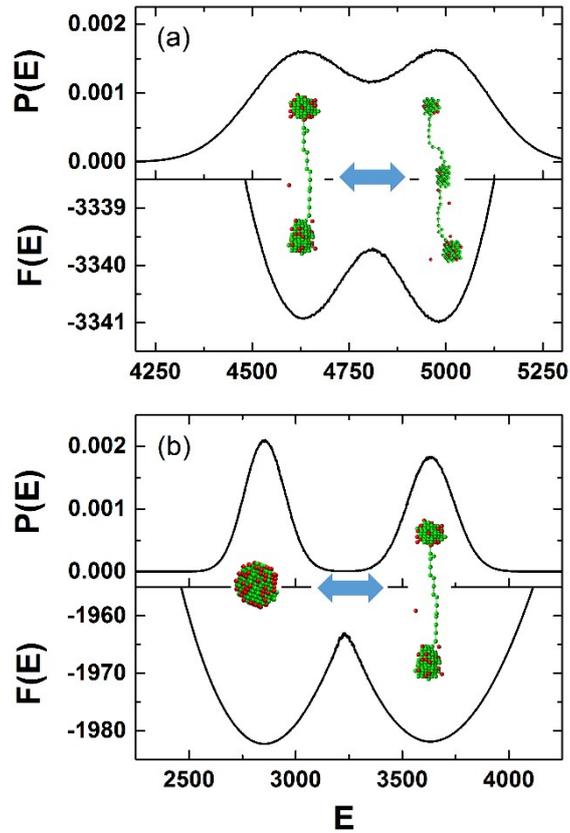


Fig. S10. The probability distribution and the free energy curves at the transition temperatures for system with $N=170$ and $\varepsilon=1.5$. (a) $T=3.748$. (b) $T=2.9831$.

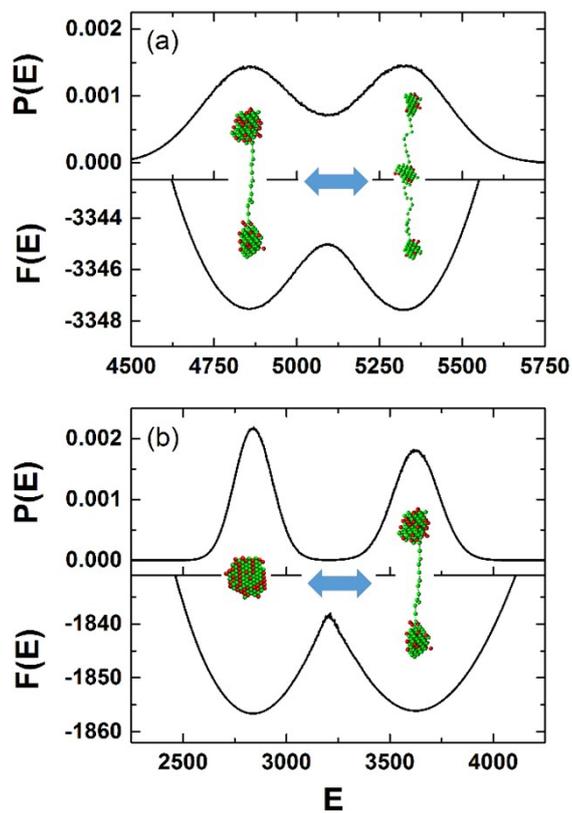


Fig. S11. The probability distribution and the free energy curves at the transition temperatures for system with $N=192$ and $\varepsilon=1.5$. (a) $T=3.568$. (b) $T=2.7850$.

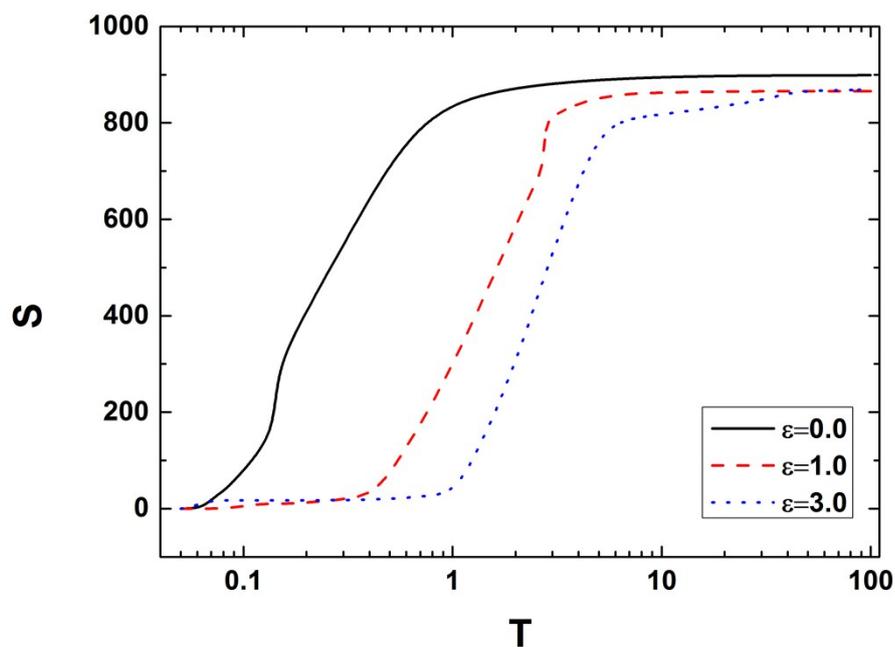


Fig. S12. The entropy as a function of temperature for a system with $N=64$ and various ε values.