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# The phase behaviour of single polyethylene chains with and without fixing one end*

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The phase behaviour of a single polyethylene chain is studied by using molecular dynamics simulations. A free chain and a chain with fixing one end are considered here, since the atomic force microscope (AFM) tip can play a significant role in polymer crystallization in experiment. For a free chain, it is confirmed in our calculation that the polymer chain exhibits an extended coil state at high temperatures, collapses into a condensed state at low temperatures, i.e. the coil-to-globule transition that is determined by a high temperature shoulder of the heat capacity curve, and an additional liquid-to-solid transition that is described by a low temperature peak of the same heat curve. These results accord with previous studies of square-well chains and Lennard-Jones homopolymers. However, when one of the end monomers of the same chain is fixed the results become very different, and the chain cannot reach an extended coil-like state as a free chain does at high temperatures, i.e. there exists no coil-to-globule-like transition. These results may provide some insights into the influence of AFM tip when it is used to study the phase behaviour of polymer chains. If the interaction force between AFM tip and polymer monomers is strong, some monomers or one of them can be seen as being fixed by the tip, which is similar to our simulation model, and it is also found that AFM tip could induce polymer crystallization.

**Keywords:** molecular dynamics simulations, coil-to-globule transition, polyethylene chains
**PACC:** 8120S, 8200

## 1. Introduction

The coil-to-globule transition is one of fundamental problems in polymer physics, which has been extensively studied in the past few years[1−6] because of its applications in many aspects, such as the folding of a protein chain, the packing of DNA molecules, the collapse of a polymer gel network as well as the complexation between two polymer chains.[7,8] The recent advance in experimental techniques has made the observation of coil–globule transition possible, and the coil–globule transitions of poly (N-isopropylacrylamide) (PNIPAM) chains both in $H_2O$ and in $D_2O$ have been studied in experiment.[9,10] The two-stage kinetics of the coil-to-globule transition[11] of a single polymer chain and that of the first-order transition[12] in ultrafiltration of flexible linear polymer chains have been studied very recently.

Previous studies have made great progress both in theory and in experiment, and it has been suggested that semiflexible polymers exhibit an elongated coil state at high temperatures and a collapsed globule state at low temperatures, i.e. the coil–globule transition, which is similar to the usual transition between gas and condensed phases. Though this collapse transition has been studied for years in theory[13,14] and experiment[15,16] and also in computer simulation,[17−20] the exact nature of the collapse transition has not yet been completely revealed. Generally, for a self-attracting chain, this transition is caused by the competition between monomer–monomer attraction and conformational entropy: the formation of contacts lowers the total energy, and monomers become close to each other, then the chain degrees of configurational freedom decrease correspondingly. When the attraction energy between monomers is much stronger than their thermal energy, the polymer chain takes globular conformations to maximize the number of contacts, and at high temperatures, the chain is in a disordered coil state with a maximal entropy. Recently, Johnny *et al* have studied single-chain homopolymers[21] and star-branched

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polymeric systems[22] by using Monte Carlo simulations, both confined between two parallel walls, and found that the coil–globule transition temperatures both shift toward low regions as confinement increases. This can be understood, since the confinement can prevent the globular conformations from forming, but the coil–globule transition temperature seems to be unchanged when the confinement is higher than about five bond-lengths. It may be due to the fact that there is no interaction between polymer chains and confinement boundaries.

We present in this paper the equilibrium properties of an isolated polyethylene chain with and without fixing one end by using molecule dynamic simulations, in which more exact force fields[23] are used. It is known that atomic force microscopy (AFM) is a useful tool to manipulate polymer chains in experiment, and AFM tip is influential to the phase behaviours of polymers. The AFM tip cannot induce poly (ethylene oxide) crystallization according to Pearce,[24,25] and also the same result was obtained by Godovsky[26] when he studied the crystallization of polyethylene. However, the experiment[27] suggests that if the force exerted by AFM tip is strong enough, the tip may disturb polymer crystallization process and even can cause the formation of nucleation, and there are many other experiments about AFM-tip-induced crystallization.[28−30] If the interaction between AFM tip and polymer chains becomes strong, the degrees of freedom for a polymer configuration will decrease, i.e. the tip can influence the conformational entropy of polymer chains, thereby the phase behaviour will be changed. One has calculated a single polyethylene chain with fixing one end to reveal different phase behaviours from the free chains; there have been carried out few studies relevant to this issue in theory. If the AFM tip acts on one end of a single polymer chain and the interaction in between is strong, then the end monomer can be seen as being fixed on the tip to some extent, which is similar to our model. We focus on the difference in single chain between with and without fixing one end, and it will be discussed in great detail in the following.

## 2. Model and simulation details

The united-atom (UA) force field for polyethylene chains is used in the present simulation, in which $CH_2$ and $CH_3$ groups each are regarded as a monomer. The UA force field was developed by Paul *et al*[31] who optimized the nonbonded interaction parameters of methyl and methylene groups to reproduce the experimental melt densities of *n*-$C_{13}H_{28}$ and *n*-$C_{44}H_{90}$. In the past few years, the UA model of polyethylene has been optimized and used in Monte Carlo[32,33] and molecular dynamics simulations.[34−36] The UA force field model has been parametrized by using first-principles calculation and experimental data,[23,31,37,38] and it is taken from Refs.[23,31] in the present paper. In fact, the UA force field model has been used in molecular dynamic simulations successfully in dealing with elastic behaviour of single chains in our previous studies.[39−41]

In this paper, the potential energy between monomers contains four parts: the bond-stretching energy $U_{\rm bond}$ between two adjacent monomers, the bond-bending energy $U_{\rm bend}$ among three adjacent monomers, the torsion energy $U_{\rm dih}$ among four adjacent monomers, and the 12–6 Lennard-Jones potential $U_{\rm nonbond}$ between two nonbonded monomers. The bond-stretching energy $U_{\rm bond}$ between bonded monomers is presented as

$$U_{\rm bond} = \sum_{i=2}^{n} \frac{1}{2} k_{\rm s} (r_i - r_0)^2, \tag{1}$$

where $k_{\rm s}$ is the harmonic spring constant and set as $k_{\rm s} = 265000\,{\rm kJ/(mol{\cdot}nm^2)}$, $r_0 = 0.153\,{\rm nm}$ is the equilibrium bond length, and $r_i$ denotes the bond length between monomers $i$-1 and $i$. The bond-bending energy $U_{\rm bend}$ is given by

$$U_{\rm bend} = \sum_{i=3}^{n} \frac{1}{2} k_\theta (\cos\theta_i - \cos\theta_0)^2, \tag{2}$$

where $U_{\rm bend}$ is defined for every triplet of adjacent monomers, $k_\theta = 502\,{\rm kJ/mol}$ is the bond-bending energy constant, $\theta_0 = 1.920$ rad is the equilibrium bond angle, and $\theta_i$ represents the bond angle between two adjacent bonds $i$-1 (the bond between monomers $i$-2 and $i$-1) and $i$ (the bond between monomers $i$-1 and $i$). The torsion energy $U_{\rm dih}$ is

$$U_{\rm dih} = \sum_{i=4}^{n} \frac{1}{2} [k_\phi^1 (1 - \cos\phi_i) + k_\phi^2 (1 - \cos 2\phi_i) + k_\phi^3 (1 - \cos 3\phi_i)], \tag{3}$$

where $U_{\rm dih}$ is defined for every quadruplet of adjacent monomers and $\phi_i$ is the dihedral angle between the ($i$-3, $i$-2, $i$-1) and ($i$-2, $i$-1, $i$) planes. $k_\phi^1 = 6.69\,{\rm kJ/mol}$,

$k_\phi^2 = -3.62\,\mathrm{kJ/mol}$, and $k_\phi^3 = 13.5\,\mathrm{kJ/mol}$ represent the torsion angle energy constant, respectively. The nonbond interactions between nonconsecutive monomers are described by a standard 12-6 Lennard-Jones (LJ) potential,

$$U_{\mathrm{nonbond}} = \sum_{i\neq j\pm 1}^{n} \frac{1}{2}\varepsilon \left[ \left(\frac{r_m}{r_{ij}}\right)^{12} - 2\left(\frac{r_m}{r_{ij}}\right)^{6} \right], \quad (4)$$

where $r_{ij}$ denotes the distance between two nonbonded monomers, and the cutoff distance used in this work is 0.9 nm; $r_m = 0.45\,\mathrm{nm}$ is a constant, which represents the position with minimum interaction energy; $\varepsilon$ is an energy constant, which depends on the type of the interacting groups ($CH_2$ or $CH_3$). In the early days of the UA model, $\varepsilon$ was taken to be the same for $CH_2$ and $CH_3$ units, but it has been optimized by Siepmann,[42] i.e. $\varepsilon(CH_2-CH_2) = 0.391\,\mathrm{kJ/mol}$, $\varepsilon\,(CH_3-CH_3) = 0.947\,\mathrm{kJ/mol}$, and $\varepsilon\,(CH_2-CH_3) = 0.608\,\mathrm{kJ/mol}$ according to the Lorentz–Berthelot mixing rule.

In this paper, we perform molecular dynamics simulations,[34–36,43–45] which have widely been utilized because of the advantage that a comparison with theory and experiment can be made are straightforwardly. In the molecular dynamics simulations, the motion of monomers is described by taking the coordinate of each monomer as a function of time, and a basic time step of 0.001ps is used in our work. In addition to molecular dynamics simulations, thermal annealing[46,47] is also used to avoid local minima that are present in the energy landscape of protein folding.

In order to catch thermodynamic characteristics of the system, one calculates the internal energy and the heat capacity; the heat capacity in a constant volume as a function of temperature is defined as the standard energy fluctuation expression[19–22,48]

$$C_v = \frac{\langle U^2\rangle - \langle U\rangle^2}{k_{\mathrm{B}}T^2}, \quad (5)$$

and according to Leach[48] the heat capacity can also be rewritten as

$$C_v = \frac{\langle (U - \langle U\rangle)^2\rangle}{k_{\mathrm{B}}T^2}, \quad (6)$$

where $U$ is the internal energy. The canonical averages $\langle U^2\rangle$ and $\langle U\rangle^2$ are evaluated by using the annealing molecular dynamics (MD) method. As Leach suggested, expression (6) may be more accurate due to round-off errors, besides, $\langle U^2\rangle$ and $\langle U\rangle^2$ both are usually large numbers, hence there may exist a large uncertainty in their difference. Peaks on the $C_v$ vs $T$ curve are used to identify possible conformational changes in the systems. To determine the average size of the chain, the mean square end-to-end distance $\langle R^2\rangle$ is computed. The radius of gyration tensor $S$ of the chain can be defined as

$$S = \frac{1}{N+1}\sum_{i=0}^{N} S_i S_i^{\mathrm{T}} = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{pmatrix}, \quad (7)$$

where $S_i = \mathrm{col}(x_i, y_i, z_i)$ is the position of monomer $i$ in a frame of reference with its origin located in the middle of a chain. The tensor $S$ can be diagonalized into a diagonal matrix with three eigenvalues $L_1^2$ , $L_2^2$ and $L_3^2$ ($L_1^2 \le L_2^2 \le L_3^2$). These parameters have been used to calculate the shapes of flexible polymer chains,[49,50] and it was suggested that the ratio $\langle L_1^2\rangle : \langle L_2^2\rangle : \langle L_3^2\rangle$ be $1 : 2.7 : 11.7$ based on a random walk of 100 bonds on a simple cubic lattice by using Monte Carlo technique. Meanwhile, another important parameter based on the three eigenvalues can be considered to be[51,52]

$$\langle \delta^* \rangle = 1 - 3\left\langle \frac{L_1^2L_2^2 + L_2^2L_3^2 + L_1^2L_3^2}{(L_1^2 + L_2^2 + L_3^2)^2} \right\rangle, \quad (8)$$

where the shape factor $\langle \delta^* \rangle$ varies between 0 (sphere) and 1 (rod), which is an important parameter in studying the configurations of polymer chains.

## 3. Results and discussion

Single polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end are simulated to study temperature-dependent conformational and thermodynamic properties. One end fixing is influential to the phase behaviour of polymer chains just as AFM tip plays an important role in polymer crystallization.

Figure 1 shows the mean-square end-to-end distances per monomer as a function of temperature for single polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end. As seen in Fig.1, the free chains with different chain lengths each have large values of $\langle R^2\rangle/N$ at high temperatures, which may indicate extended states for the free chains, and the values of $\langle R^2\rangle/N$ collapse into small values at low temperatures where the chains take compact globular structures. It can also be observed in Fig.1 that

the sudden reductions of $\langle R^2\rangle/N$ take place at higher temperatures as the chain length increases. When one of end monomers of the same chain is fixed, the degrees of freedom of the chain system will be reduced considerably, and the different behaviour of $\langle R^2\rangle/N$ for these cases are also shown in Fig.1. The values of $\langle R^2\rangle/N$ at high temperatures are smaller than those of the same free cases, for instance, at the highest temperature, 1000 K, the values of $\langle R^2\rangle/N$ are 0.071, 0.079 and 0.145 $\mathrm{nm}^2$ for $N = 40$, 80, and 120 monomers, respectively, while they are 0.210, 0.267 and 0.300 $\mathrm{nm}^2$ for the corresponding free chains. Therefore the chains with fixing one end monomer may not reach similar extended coil-like states to those for the free chains.

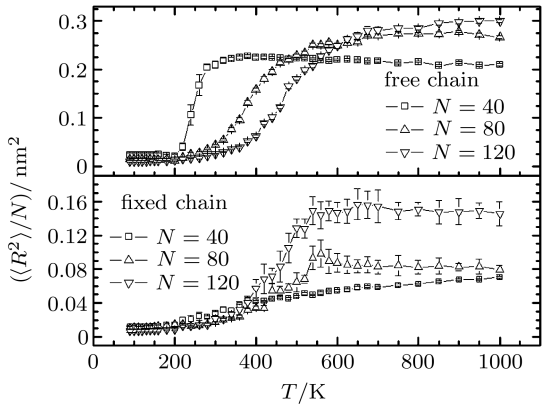



**Fig.1.** Temperature dependences of the mean-square end-to-end distance per monomer for polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end, where error bars are shown for ten data points.

Recently, Kumar and Giri[53] have studied a lattice polymer with fixing one end, and the other end of the polymer chain was pulled by a force. And as they discussed in experiment with fixing one end only, the entire molecule rotated due to the torque about the fixed end of the chain. Hence, in our model, when one end monomer of the chain is fixed and the other monomers will move around it, then the degrees of freedom of the system will reduce immediately, and the conformations and conformational entropy may decrease greatly. Therefore, in the present simulation, when one end monomer of the polyethylene chain is fixed and the other monomers will move around it, at high temperatures the chain cannot reach an extended state as the free chain does, and it should have a smaller end-to-end distance. The $\langle R^2\rangle/N$ of the chain with fixing one end also decreases with temperature decreasing, and at low temperatures of about $T < 200$ K the values are similar to those for the free case, thus the chain with fixing one end should also take a similar globular structure.

A similar behaviour of the mean-square radius of gyration per monomer is observed in Fig.2. As can be seen, there is also a sudden reduction of $\langle S^2\rangle/N$ for the free chain, and the critical region also shifts toward higher temperatures with the chain length increasing, and at low temperatures one may find that the value of $\langle S^2\rangle/N$ for the 40-monomer chain is larger than those for the 80-monomer and the 120-monomer chains, which should result from the stiffness of the polyethylene systems, and the polyethylene chains simulated here are more like stiff chains than semiflexible polymers, thus the short chain of 40 monomers may not collapse into the same compact states as those for longer chains. However, this finite-size effect may be disturbed by fixing one end monomer, as seen in Fig.2(b), the value of $\langle S^2\rangle/N$ for the 40-monomer chain is similar to those for the longer chains at low temperatures.

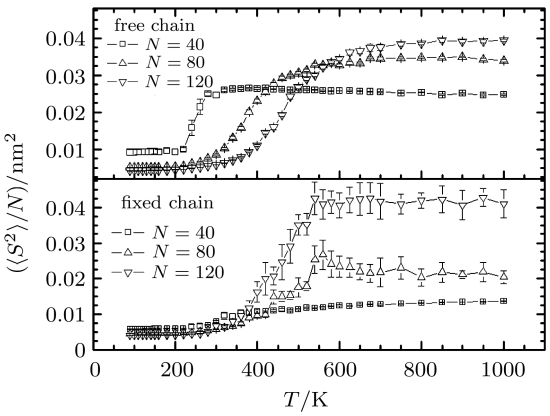



**Fig.2.** Temperature dependences of the mean-square radius of gyration per monomer for polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end, where error bars are shown for 10 trajectories.

We have also calculated the shape factor of the polyethylene chains with and without fixing one end, since this parameter is a direct observation of the shape of polymer systems. For the free chains, at high temperatures the values of $\langle\delta^*\rangle$ for the three chains are similar to each other, as seen in Fig.3, i.e. about 0.7, which is larger than the exact result[54] for linear random walks, $\langle\delta^*\rangle = 0.39$, showing that the linear polyethylene chain may be stiffer than the linear random walks; for a sufficient stiff chain the value of shape factor may be close to 1. At low temperatures, the values of shape factor are smaller for longer chains. For the chains with fixing one end, the values of shape

factor are different from those for the free cases and depend on chain length obviously at high temperatures. As seen in Fig.3, at high temperatures the values of $\langle\delta^*\rangle$ are about 0.4, 0.57, and 0.7 for the chains of $N = 40$, 80, and 120 monomers, respectively.

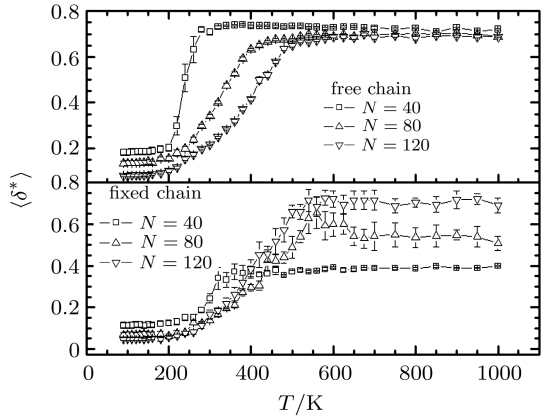



**Fig.3.** Temperature dependences of the shape factor for polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end, where error bars are shown for 10 trajectories.

From the parameters of $\langle R^2\rangle/N$, $\langle S^2\rangle/N$, and $\langle\delta^*\rangle$, we may expect that at high temperatures, the average size and shape of single chains are changed obviously when one end monomer of chain is fixed, since the degrees of freedom of the chain system are reduced considerably, and the motion of monomers are restricted: they should move around the fixed end monomer. The disturbed properties of free chains may prove some insights into the influence of AFM tip when it is used to manipulate polymer chains.

The internal energy per monomer is also considered in our simulation, which is shown as a function of temperature in Fig.4. For the free chains of different chain lengths, as seen in Fig.4, the internal energy per monomer $\langle U\rangle/N$ decrease with temperature decreasing, which may illustrate the collapse of chains according to the previous studies.[19−22] While for the chains with fixing one end, the curves of $\langle U\rangle/N$ at high temperatures, especially for the 80-monomer and 120-monomer chains, are not so smooth as those for the free cases, and the fluctuation of the internal energy should result from the variations of conformations. In fact, for $\langle R^2\rangle/N$, $\langle S^2\rangle/N$, and $\langle\delta^*\rangle$, fluctuations are also observed to be larger than those for the free cases in Figs.1, 2, and 3, respectively.

In order to determine the critical region of the collapse transition, the heat capacity as a function of temperature is calculated according to expression (5) and the results are shown in Fig.5(a). For the free chains as seen in Fig.5(a), for the 80-monomer chain the strong peak is at 260 K and a high temperature shoulder is found to be at about 360 K, and similar behaviours of heat curves were observed by the previous studies,[19−22] according to them the high temperature shoulder should represent a coil–globule transition and the low temperature peak can be seen as an additional liquid–solid-like ordering transition. For the 120-monomer chain, there is also a high temperature shoulder at about 400 K as well as a low temperature peak at 260 K. For the short polyethylene chain of $N = 40$ monomers, there is only a strong peak at 240 K for the 40-monomer, which should represent a coil–globule transition. An additional liquid–solid-like transition is not observed for the 40-monomer chain, since it is hard for the chain to form solid-like globules due to stiffness.[55,56]

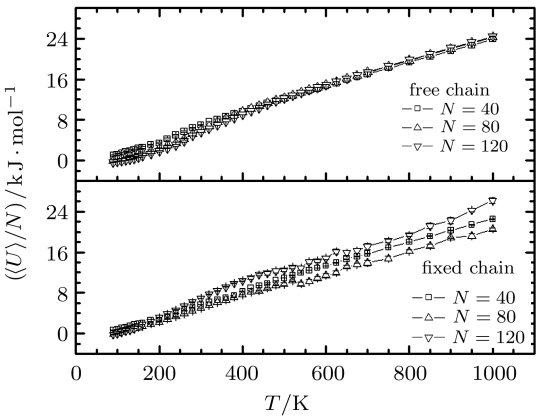



**Fig.4.** Temperature dependences of the internal energy per monomer for polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end, where error bars are shown for 10 trajectories.

When one end monomer is fixed, the heat curves are disturbed drastically, as seen in Fig.5(a), and they should be not so meaningful as those of the free cases. As the chain length increases, a plateau forms at high temperatures with large values of $C_v/N$, which may represent large energy fluctuations. Though the chain sizes decrease with temperature decreasing, the chains cannot reach extended coil-like states as the free chains do, the collapse of the fixed chains should be different from that of the free chains, and according to the heat curves there should be no coil–globule or liquid–solid like transition for this system.

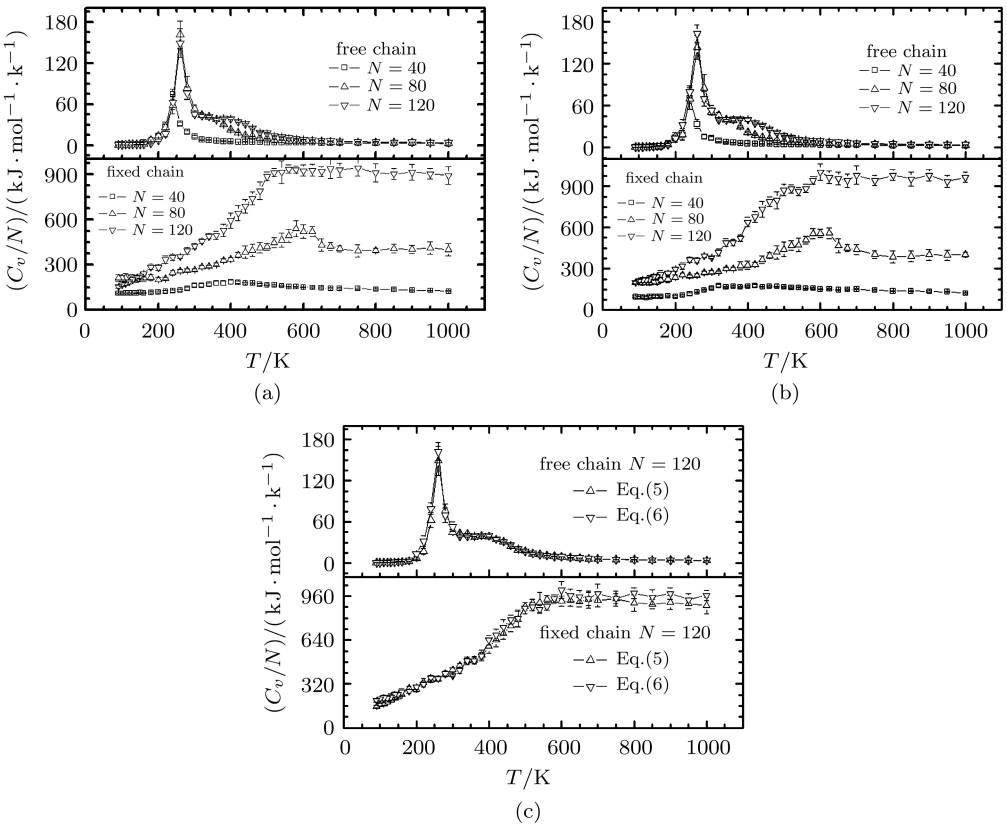



**Fig.5.** Temperature dependences of the heat capacity per monomer for polyethylene chains of $N = 40$, 80, and 120 monomers with and without fixing one end according to expression (5) (a) and expression (6) (b), respectively, and the heat curves of $N = 120$ monomers (c) for a comparison, where error bars are shown for 10 trajectories.

The standard energy fluctuation expression of the heat capacity, i.e. expression (5), has been widely used[19−22] to study the collapse of polymers, but according to Leach[48] expression (5) can be expressed in another way, i.e. expression (6), which may be more exact than expression (5), hence we calculate the heat capacity again according to expression (6) (the obtained result is presented in Fig.5(b)), and find that the heat curves obtained from the two expressions have the same behaviours and critical regions. For a comparison, the case of $N = 120$ monomers is shown in Fig.5(c), and it can be seen that the two expressions give the same results, though their values of $C_v/N$ at some temperatures are a little different from each other.

We have also shown the possible conformational transition for the free and the fixed polyethylene chains. As seen in Fig.6(a), at high temperatures the free chains of different chain lengths are in extended states with large end-to-end distances, and they collapse into liquid-like globules with small chain sizes, and then the 80-monomer and the 120-monomer chains collapse into solid-like globules with smaller chain sizes, but the 40-monomer chain cannot collapse again due to stiffness. For the chains with fixing one end as seen in Fig.6(b), the structures of chains at high temperatures are very different from those for the free cases: they have smaller end-to-end distances, since other monomers of the chains may move around the fixed monomer, therefore they cannot reach extended coil-like states. At low temperatures, the chains collapse into compact states as the free chains do.

The simulation results have shown that the collapse of single polyethylene chains with fixing one end is very different from that of free cases, which may reflect the influence of AFM tip in experiment Godovsky and Magonov[26] have studied the morphology and the nanostructure of an ultrathin layer of polyethylene during melting and crystallization by using AFM, and they gave the real images of polyethylene crystallization. And the crystallization of poly (ethylene oxides) has also been studied by using AFM,[57,58] but in real experiments it is difficult to measure the influence of AFM tip, since one cannot obtain the properties of completely free polymers without using AFM. However, in simulations one can easily obtain the equilib-

rium properties of free chains without being disturbed, and we investigate the chains with fixing one end to explain that the AFM tip is influential in experiments. Zhu *et al*[59] have also discussed the influence of AFM tip when they use it to study the crystallization of poly(ethylene oxides).

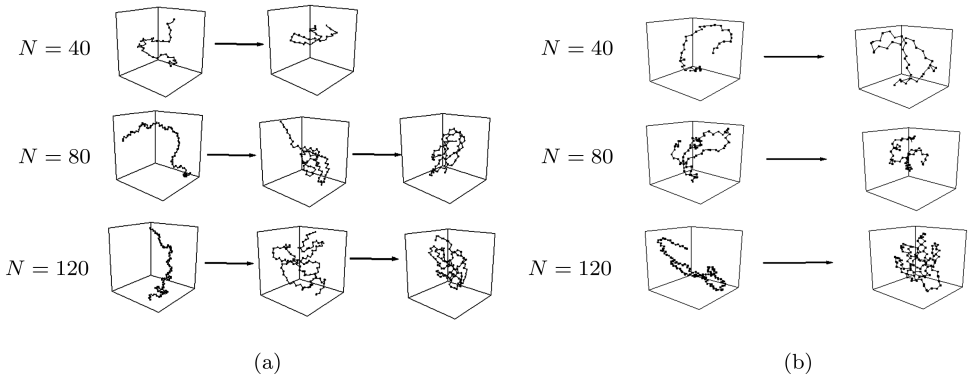



**Fig.6.** The possible conformational transitions of free polyethylene chains of $N = 40$, 80, and 120 monomers (a) and polyethylene chains of $N = 40$, 80, and 120 monomers (b) with fixing one end.

# 4. Conclusion

Conformational and thermodynamic properties of a single polyethylene chain with and without fixing one end are studied as a function of temperature. For an isolated single chain, a coil-to-globule transition and a liquid–solid like transition are determined by a high temperature shoulder and a low temperature peak on a heat curve, respectively, which accords with the previous studies[19−22] of square-well chains and Lennard-Jones homopolymers. In order to describe the influence of disturbance from AFM tip in experiment, we investigate a special case in which one end monomer of the same chain is fixed, since AFM tip can play a significant role in polymer crystallization. As was expected by us, the structures for a single chain at different temperatures are highly disturbed, with one end monomer of the chain fixed, which may remind us that if we want to observe some properties of polymer chains in experiment we should consider the influence of apparatus that we are using, for some microscopic properties may be sensitive to the apparatus. The AFM-tip-induced polymer crystallization[24−30] may illustrate that the phase behaviours of polymer chains are sensitive to the AFM tip, which is similar to the force-induced collapse transition.[52] From the results we may expect that there should be no traditional coil–globule or liquid–solid-like transition for the polyethylene chains with fixing one end.

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