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The phase behaviors of adsorbed polymethylene chains

Jiaye Su [a], Linxi Zhang [b,*]

[a] Department of Physics, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Physics, Wenzhou University, Wenzhou 325027, PR China

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Abstract

The phase behaviors of a single adsorbed polymethylene chain are investigated by using molecular dynamics simulations. In the free space, it is confirmed in our calculation that the isolated polymer chain exhibits a disordered coil state at high temperatures, and collapses into a condensed state at low temperatures, i.e., the coil-to-globule transition, and finite chain length effects are considered since the critical region may depend on the chain length. When the chain is adsorbed on an attractive surface, however, the equilibrium properties may not only depend on chain length but also depend on the adsorption energy. For short chain of $N = 40$ monomers, a coil-to-globule transition is found for weak adsorption energy of $w = 2.5$ kcal/mol, but the critical temperature is lower than the free chain, and for strong adsorptions of $w = 3.5$ and 4.5 kcal/mol, the structures at low temperatures are adsorbed hairpin like, so we may call the transition process coil-to-hairpin transition. For long chains of $N = 80$ monomers and $N = 120$ monomers, the critical regions are the same for the free chains both at $T = 265$ K, and for the adsorption energies of $w = 2.5$, 3.5, and 4.5 kcal/mol, the curves of the heat capacities are smooth when $T > 200$ K, and while $T < 200$ K, the values of the heat capacities decrease as the temperatures decreasing, so the transition may be from loose globular structures to compact globular structures, and for more stronger adsorption energy of $w = 6.5$ and 8.5 kcal/mol, the critical regions are obvious and they are coil-to-crystal like transitions.

Keywords: Molecular dynamics simulations; Coil–globule transition; Adsorption

1. Introduction

The phase transition especially the coil-to-globule transition is a fundamental problem in polymer physics, and it has been extensively studied in the past few years [1–6] because of its application in many fields, examples including the folding of proteins, the packing of DNA molecules, and the collapse of a polymer gel network as well as the complexation between two polymer chains [7,8]. The recent progress in experimental techniques has made the observation of coil–globule transition possible, and the coil–globule transition of poly(*N*-isopropylacrylamide) (PNIPAM) chains both in H_2O and in D_2O have been studied in experiment [9,10]. Also, very recently, the two-stage kinetics of the coil-to-globule transition [11] of a single polymer chain and the first-order transition [12] in ultrafiltration of flexible linear polymer chains have also been studied.

It has been suggested from previous studies that semiflexible polymers exhibit an elongated coil state at high temperature and a collapsed globule state at low temperature, 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 both theoretically [13,14] and experiments [15,16] and computer simulations [17–20], as well as a recent review for single polymer chains by Binder et al. [21], the exact nature of the collapse transition is not yet completely settled. Generally, for a self-attracting chain, this transition is caused by the competition between monomer–monomer attractions and conformational entropy [22]. The formation of contacts lowers the total energy, and monomers become close to each other, then the chain's degrees of configurational freedom decrease correspondingly. When the attraction energy between monomers is much stronger than thermal energy, the polymer chain takes globular conformations to

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* Corresponding author.
E-mail address: lxzhang@hzcnc.com (L. Zhang).

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maximize the number of contacts, and at high temperature, the chain is in disordered coil states with maximal entropy. Recently, Johnny and his co-workers have studied single-chain homopolymers [23] and star-branched polymeric systems [24] by Monte Carlo simulations, both confined between two parallel walls, and found that the coil–globule transition temperatures both shifted to low regions as the confinement increased. It can be understood, since the confinement can prevent the formation of globular conformations, but the critical temperatures of coil–globule transitions seem to be not very influential by the confinement when the distance between the two parallel walls $D > 5$, and the behavior of the chain at $D > 5$ is similar to the behavior without confinement. It may be due to that there is no interaction between polymer chains and confinement boundaries, and the interactions between polymers and environment may be very influential to the equilibrium properties of polymers. Many of past studies [11,12,23,24] have neglected the influence of interaction between polymers and environment, so in this paper, we discuss the phase behaviors of adsorbed polymer chains.

We present in this paper the equilibrium properties of a single polymethylene chain adsorbed on an attractive surface, instead of lattice model, the continuous molecular dynamics (MD) simulations and more exact force fields [25] are used, since interactions between polymer monomers may be a little simple in lattice model, and then, the nature of coil–globule transition will be revealed in more great details than before. The attractive surface may lower the degrees of freedom of the polymer system, and then the equilibrium structures as well as thermodynamics may not only depend on the temperature but also have to do with the adsorption energy. Using the annealing technique, we may easily catch the temperature dependence of phase behavior of the polymer system. To investigate the collapsed transition in this work, the influence of polymer chain length and adsorption energy in the potential energy, heat capacity, shape factor, mean-square radius of gyration, and mean-square end-to-end distance are considered as a function of temperature, and annealing technique is also used to ensure an efficient sampling of configurations and avoids quasiergodicity problems (i.e., a molecule trapped in local energy minima). During the transition process, variations in conformational changes of the polymer systems with temperature due to the effects of the adsorption energy are observed.

2. Model and simulation details

2.1. Model

The united-atom (UA) force field for the adsorbed polymethylene chains is used in the present simulation, and it regards each CH_2 and CH_3 groups as a monomer. The advantage of this model with significantly reduced number of degrees of freedom is that long chains or large systems can be explored within the computational limit. The methylene chains considered in this work are viewed as an oversimplification by many readers, which is similar to the polyelectrolytes in the experiment [26]. The UA force field was developed by Paul et al. [27] who optimized the nonbonded interaction parameters of methyl and methylene groups to reproduce the experimental melt density of $n\text{-}C_{13}H_{28}$ and $n\text{-}C_{44}H_{90}$. Recently, the UA model of polymethylene has been optimized constantly and used both in Monte Carlo [28,29] and molecular dynamics simulations [30–32]. The UA force field model has been parameterized by first principle calculation and experimental data [25,27,33,34], and we take it from Yoon et al. [25,27] in the present simulation. In fact, the UA force field model has been used in molecular dynamics simulations successfully in our previous works [35,36].

In this paper, the potential energy between chain monomers contains four parts: the bond-stretching energy U_{bond} for two adjacent monomers, the bond-bending energy U_{bend} among three adjacent monomers, the torsion energy U_{dih} among four adjacent monomers, and the 12-6 Lennard-Jones potential U_{nonbond} between two nonbonded monomers. The potential between chain monomers and attractive surface is described by the 9-3 Lennard-Jones adsorption potential U_{a}. The bond-stretching energy U_{bond} between bonded monomers is defined as:

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

where k_{s} is the harmonic spring constant, sets as $k_{\text{s}} = 634$ kcal/(mol Å^2), $r_{\text{o}} = 1.53$ Å is the equilibrium bond length, and r_j denotes the bond length between monomers $i-1$ and i. The bond-bending energy U_{bend} is given by:

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

where U_{bend} is defined for every triplet of adjacent monomers, $k_{\theta} = 120$ kcal/mol is the bond-bending energy constant, $\theta_0 = 1.920$ rad is the equilibrium bond angle, and θ_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_{dih} is

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

where U_{dih} is defined for every quadruplet of adjacent monomers and φ_{i} is the dihedral angle between the $(i-3,\ i-2,\ i-1)$ and $(i-2,\ i-1,\ i)$ planes. $K_{\varphi}^1 = 1.6$ kcal/mol, $K_{\varphi}^2 = -0.867$ kcal/mol, and $K_{\varphi}^3 = 3.24$ kcal/mol represent the torsion angle energy constant, respectively. The nonbond interactions between nonconsecutive beads are described by the standard 12-6 Lennard-Jones (LJ) potential,

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

r_{ij} denotes the distance between two nonbonded monomers, and the cutoff distance used in this work is 9 Å. $r_{\text{m}} = 4.5$ Å is a constant, which represents the position with minimum interaction energy. ε is a energy constant which depends on the type of the interacting groups (CH_2 or CH_3). In the early days of the UA model, ε is taken to be the same for CH_2 and CH_3 units, but it has been optimized by Siepmann et al. [37], i.e., $\varepsilon(CH_2{-}CH_2) = 0.09344$ kcal/mol, $\varepsilon(CH_2{-}CH_2) =$ 0.22644 kcal/mol, and $\varepsilon(CH_2{-}CH_2) = 0.14546$ kcal/mol according to the Lorentz–Berthelot mixing rule. The adsorption energy between the monomers and the surface is defined as [38]:

$$U_{\mathrm{a}} = \sum_{i=1}^{n} w\left[\left(\frac{z_w}{z_i}\right)^9 - \left(\frac{z_w}{z_i}\right)^3\right] \tag{5}$$

Here $z_w = 4.5$ Å is a constant, z_i represents the perpendicular distance between the monomer i and the surface, and w is an adsorption energy parameter. For the polymethylene chains studied here, the adsorption energy parameters may be changed from weak adsorption of $w = 2.5$ kcal/mol to strong adsorption of $w = 8.5$ kcal/mol.

2.2. Simulation details

In this paper, we perform molecular dynamics simulations [30–32,39–44], which have been widely used because its comparisons with theories and experiments are straightforward. In the molecular dynamics simulations, the motion of monomers is described by the coordinate of each monomer as a function of time, and a basic time step of 0.001 ps is used in our work. To simplification and to observe the influence of different adsorption intensively, there is no solution environment [45], so we do not consider the friction and the effect of solvent molecules which is implicitly treated by a noise term [39].

In addition to molecular dynamics simulations, thermal annealing [46,47] is also used to avoid local minima that are shown in the energy landscape of protein folding. To begin with, a polymethylene chain is generated randomly in 3D space near the attractive surface, and one should note that the chain is not grafted to the attractive surface. At every temperature in annealing, the chain is relaxed sufficiently to reach thermodynamic equilibrium before equilibrium statistics is collected. In the simulation, one uses 20 temperatures to simulate from a thermal state to the lowest simulated temperature for each trajectory, and the temperature is changed from $T = 400$ K to $T = 96$ K, and the range is larger than the recent experiments [48,49] for poly(*N*-isopropylacrylamide) (PNIPAM). Also, we have tested that $T = 400$ K is high enough for the annealing simulation before the simulation results are obtained, since the critical temperatures are lower than 270 K for all the cases in our simulations, and above $T = 400$ K the simulation results should be trivial. The random states at the beginning of each trajectory are different, and at each temperature 2000 equilibrium configurations are use to calculate the thermodynamic parameters as well as 20 trajectories are used to obtain the final mean values. At each temperature, q MDS (molecular dynamic steps) are used for the chain to reach thermodynamic equilibrium, and then we use another q MDS to collect statistic properties. The relaxation time and statistics time will be increased with the decrease of temperature, since the chain relaxes slowly at low temperatures. So here, the q will be increased a q_0 as temperature decreases a step, and we let $q = q_0$ for each random states at the beginning, i.e., at lowest temperature, $q = 20q_0$. We have tested $q_0 = 2\,000\,000$ MDS for polymethylene chains in this paper and it may be increased for larger systems.

In order to catch thermodynamic characterization of the system, one calculates the total energy and the heat capacity, and the heat capacity at constant volume as a function of temperature is defined by the standard energy fluctuation expression:

$$C_{\mathrm{v}} = \frac{\langle U^2\rangle - \langle U\rangle^2}{k_{\mathrm{B}}T^2} \tag{6}$$

where U is the total energy. The canonical averages $\langle U^2\rangle$ and $\langle U\rangle^2$ are evaluated using the annealing MD method. Peaks in the C_{v} vs T diagram 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, which can be expressed as:

$$\langle R^2\rangle = \frac{1}{M}\sum_{i=1}^{M}\left|r_{i,N} - r_{i,1}\right|^2 \tag{7}$$

where $r_{i,1}$ and $r_{i,N}$ are the positions of first and last monomers in the i configuration, respectively, and N is the number of monomers in the chain as well as M the total number of configurations that are used in the averaging procedure. The radius of gyration of a polymer chain is defined as the average distance of monomers from the center of mass of the chain. The mean-square radius of gyration is computed as:

$$\langle S^2\rangle = \frac{1}{M}\sum_{i=1}^{M}\frac{1}{N}\sum_{j=1}^{N}\left(\left|r_{i,j} - r_{i,\mathrm{c.m.}}\right|^2\right) \tag{8}$$

where $r_{i,j}$ is the position vector of monomer j in the configuration i, $r_{i,\mathrm{c.m.}}$ is the center of mass position vector of the chain in the configuration i. The radius of gyration is a measure of how tightly packed a molecule is, i.e., the lower the radius of gyration is, the tighter the packing is. In another way, the radius of gyration tensor S of the chain can be defined as:

$$S = \frac{1}{N}\sum_{i=1}^{N} S_i S_i^T = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{pmatrix} \tag{9}$$

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 at the center of a chain. The tensor S can be diagonalized to be a diagonal matrix with three eigenvalues L_1^2, L_2^2 and $L_3^2 (L_1^2 \le L_2^2 \le L_3^2)$. Solc and Stockmayer had used these parameters to calculate the shape of flexible polymer chains [50,51], and they suggested the ratio $\langle L_1^2\rangle : \langle L_2^2\rangle : \langle L_3^2\rangle$ to be 1 : 2.7 : 11.7 based on a random walk of 100 bonds on a simple cubic lattice using Monte Carlo (MC) technique. An important parameter based on these three eigenvalues can be considered to be [52,53]:

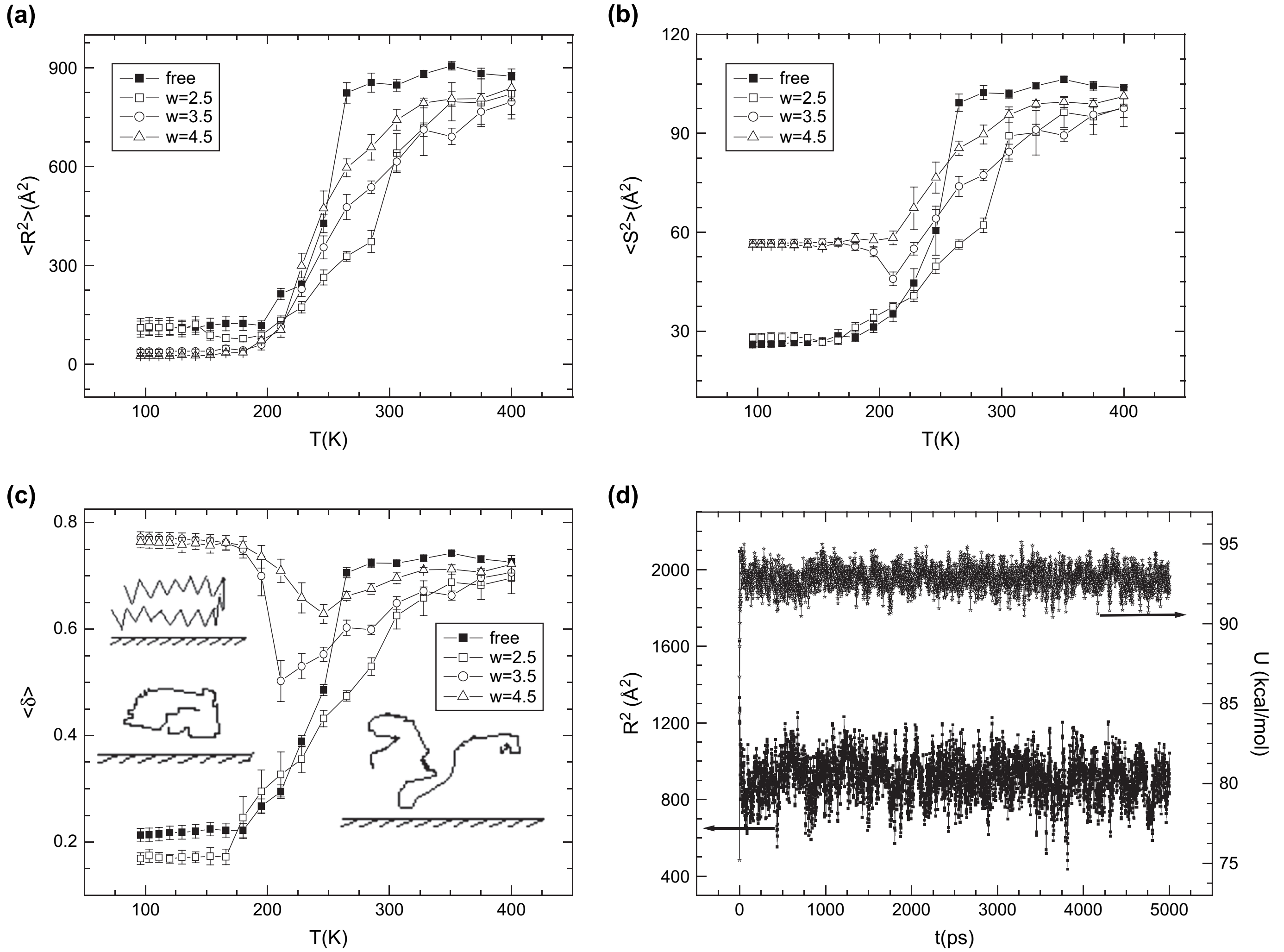

Fig. 1. Temperature dependence of (a) the mean-square end-to-end distance $\langle R^2 \rangle$, (b) the mean-square radius of gyration $\langle S^2 \rangle$ and (c) the shape factor $\langle \delta \rangle$ for a single adsorbed polymethylene chain of $N = 40$ monomers with different adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, and for the free chain. Error bars are shown for 20 data points. (d) The confirmation of equilibrium state for the free chain of $N = 40$ monomers, where the square end-to-end distance R^2 and the total energy U are plotted as a function of time.

$$\langle \delta \rangle = 1 - 3 \left\langle \frac{L_1^2 L_2^2 + L_2^2 L_3^2 + L_1^2 L_3^2}{\left(L_1^2 + L_2^2 + L_3^2\right)^2} \right\rangle \tag{10}$$

where the shape factor $\langle \delta \rangle$ changes between 0 (sphere) and 1 (rod), which is an important parameter to study the statistical properties of polymer chains. These parameters of $\langle R^2 \rangle$, $\langle S^2 \rangle$, and $\langle \delta \rangle$ are used very well in our previous works both in molecular dynamics simulations [35,36] and Monte Carlo simulations [54–56], and some nontrivial results of confined polymers or the elastic behaviors of polymers are described by these parameters.

3. Results and discussion

3.1. $N = 40$

The thermodynamic and equilibrium properties for an adsorbed polymethylene chain of $N = 40$ monomers are shown as a function of temperature in Figs. 1–3. Results are compared for different values of adsorption energy w and for free chains. Symbols for the various adsorption energies have been used consistently in all figures throughout this paper, and a solid square symbol has been used for free chains. The mean-square end-to-end distance $\langle R^2 \rangle$, the mean-square radius of gyration $\langle S^2 \rangle$, and the shape factor $\langle \delta \rangle$ are shown in Fig. 1. As we can see in Fig. 1(a), the average size of the chain, measured by the mean-square end-to-end distance, $\langle R^2 \rangle$, suffers a pronounced reduction as the temperature decreases from $T = 400$ K to approximately $T = 200$ K, but for the free chain the values of $\langle R^2 \rangle$ are similar to each other at the high temperature regions of $T = 260$–400 K, which stands for coil like structures. As the temperature decreases from $T = 400$ K to $T = 96$ K, $\langle R^2 \rangle$ decreases from $\langle \mathrm{R}^2 \rangle = 820$–110 Å^2, 796–38 Å^2, and 838–25 Å^2, for $w = 2.5$, 3.5, 4.5 kcal/mol, respectively, with compared to the free chain from 874 Å^2 to 110 Å^2. The behaviors of $\langle R^2 \rangle$ for weak adsorption energy $w = 2.5$ kcal/mol is similar to the free chain, while at low temperatures the values of $\langle R^2 \rangle$ for stronger adsorption $w = 3.5$ and 4.5 kcal/mol become

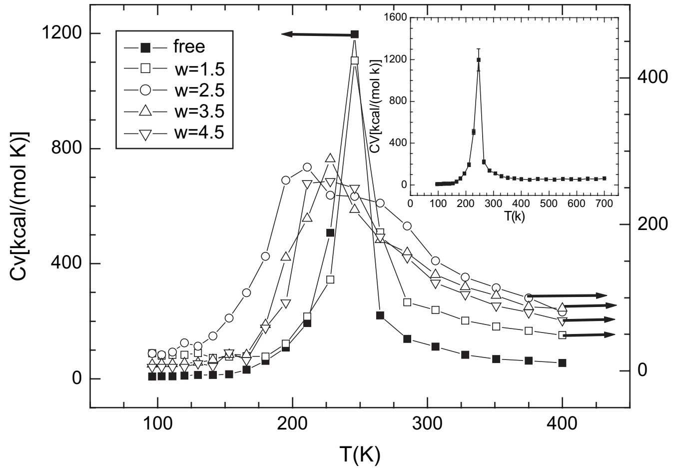

Fig. 2. Temperature dependence of the heat capacity for a single adsorbed polymethylene chain of $N = 40$ monomers with different adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, and for the free chain. Error bars are shown for 20 data points. The inserted picture is the heat capacity for the free chain of $N = 40$ monomers with the temperature extended to 700 K.

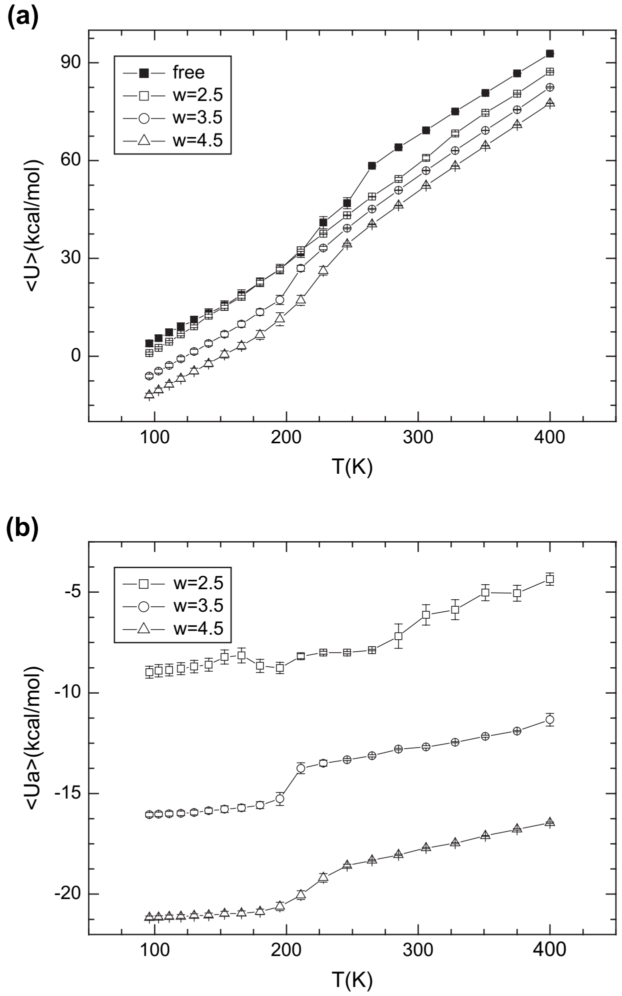

Fig. 3. Temperature dependence of (a) the average total energy $\langle U \rangle$ and (b) the average adsorption energy $\langle U_a \rangle$ for a single adsorbed polymethylene chain of $N = 40$ monomers with different adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, and for the free chain. Error bars are shown for 20 data points.

smaller than the free chain, so the structures should be different but we can not infer more detailed information only from $\langle R^2 \rangle$. A similar trend is observed for the mean-square radius of gyration $\langle S^2 \rangle$ from Fig. 1(b), as the values decrease from 103 Å^2 to 25 Å^2 and from 97 Å^2 to 28 Å^2 for the free chain and $w = 2.5$ kcal/mol, respectively, but for $w = 3.5$ and 4.5 kcal/mol, the values decay from 97 Å^2 to 56 Å^2 and from 101 Å^2 to 56 Å^2, respectively. As seen in Fig. 1(c), the behaviors of shape factor $\langle \delta \rangle$ become obvious different between the weak adsorption of $w = 2.5$ kcal/mol or the free chain and the strong adsorption of $w = 3.5$ and 4.5 kcal/mol. For the free chain and $w = 2.5$ kcal/mol, the behaviors of $\langle \delta \rangle$ are similar to $\langle R^2 \rangle$ or $\langle S^2 \rangle$, and the values of $\langle \delta \rangle$ decrease from 0.73 to 0.21 and from 0.70 to 0.17, respectively. For $w = 3.5$ kcal/mol, the values of $\langle \delta \rangle$ first decrease from 0.71 to 0.50, and then increase from 0.50 to 0.77, with the critical value of 0.50 at $T = 211$ K; while $w = 4.5$ kcal/mol, the values decay from 0.72 to 0.62 and increase from 0.62 to 0.76, and the critical value 0.62 is at $T = 246$ K. According to the behaviors of $\langle R^2 \rangle$, $\langle S^2 \rangle$ and $\langle \delta \rangle$, we may conclude that there is a coil–globule-like transition for the weak adsorption energy $w = 2.5$ kcal/mol as well as the free chain, but there are not coil–globule-like transitions for the strong adsorption energy $w = 3.5$ and 4.5 kcal/mol, and there should be coil–hairpin-like transition that may be discussed later. The equilibrium state of chains can be confirmed by the square end-to-end distance R^2 and total energy U as a function of time, and the chain has reached thermodynamic equilibrium when the square end-to-end distance and total energy do not change very much as time increases. For simplicity, at $T = 400$ K, the square end-to-end distance R^2 and the total energy $\langle U \rangle$ are plotted as a function of time in Fig. 1(d) for the free chain of $N = 40$ monomers. As seen in Fig. 1(d), the chain should be in equilibrium state when $t > 250$ ps, and for longer chains of 80 and 120 monomers, we find that the relaxation time is also smaller than 1000 ps when $T = 400$ K, and the collection of equilibrium data in our simulations is after $t = 2000$ ps, so the chains must have reached to equilibrium state before the data are collected. At lower temperatures, the relaxation time will be increased to insure that the chains have reached to thermodynamic equilibrium, which has been discussed in our simulation details.

In order to determine the critical temperature during the transition process, the heat capacity C_v is calculated according to Eq. (6), and the results for different adsorption energy are shown in Fig. 2, which reveal additional transitions as the temperature lowering, and similar behaviors that have been observed in various studies of homopolymers without adsorption interaction [11,12,23,24]. There is a strong peak at $T = 246$ K with the value of $C_v = 1197$ kcal/(mol K) for the free chain, while for $w = 2.5$, 3.5, and 4.5 kcal/mol, the peaks are at $T = 211$, 228, and 228 K with smaller values of 278, 289, and 258 kcal/(mol K), respectively. As the adsorption interaction may lower the degrees of freedom of polymer system, the disordered coil structures at high temperatures may become ordered coil structures as well as the globular configurations become adsorbed globules, the coil–globule transition should

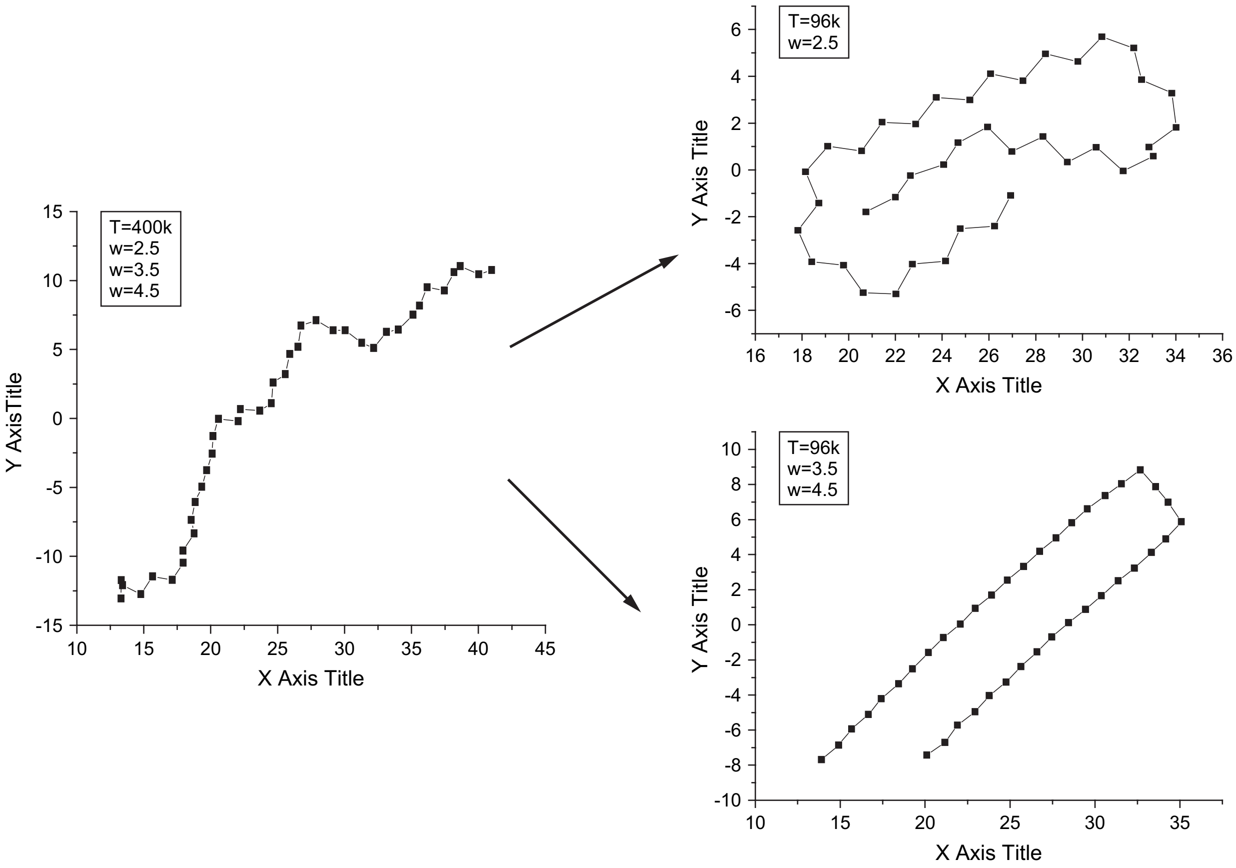

Fig. 4. The coil–globule transition with the adsorption energy of $w = 2.5$ kcal/mol and the coil–hairpin-like transition with the adsorption energies of $w = 3.5$ and 4.5 kcal/mol for the adsorbed chains with $N = 40$ monomers. The 2D coordinates are the projection of 3D coordinates at different temperatures.

be induced by the attractive surface, and large number of free conformations may disappear, for the weak adsorption $w = 2.5$ kcal/mol, there seems to be adsorbed coil to adsorbed globule transition, so the critical region become more smooth than that of the free chain; for the strong adsorption $w = 3.5$ and 4.5 kcal/mol, there seems to be coil–hairpin-like transition, i.e., adsorption can induce new folding structures, which may be discussed later. The inserted picture is the heat capacity for the free chain of $N = 40$ monomers with the temperature extended to 700 K, and it is found that the results within $T = 400$–700 K are trivial, so $T = 400$ K is high enough in our annealing simulations.

The average total energy $\langle U \rangle$ as well as the average adsorption energy $\langle U_{\mathrm{a}} \rangle$ is calculated, as seen in Fig. 3. One can see in Fig. 3(a), a drastic reduction of the total energy $\langle U \rangle$ as a whole for all the four data is observed from $T = 400$ K to $T = 96$ K, and the values decay from approximately 93 kcal/mol to 4 kcal/mol, from 87 kcal/mol to 1 kcal/mol, from 82 kcal/mol to -6 kcal/mol, and from 77 kcal/mol to -12 kcal/mol for the free chain, with $w = 2.5$, 3.5, and 4.5 kcal/mol, respectively. The sudden reductions in the average size of the polymer chain and in the total energy are indicators of the chain collapse or the coil–globule transition, which has been well characterized for polymers without adsorption interaction [11,12,23–25,27]. As the temperature decreases, the adsorption energy may decrease as a whole, as seen in Fig. 3(b), from $T = 400$ K to $T = 96$ K the values decay from -4.3 kcal/mol to -9.0 kcal/mol, from -11.3 kcal/mol to 16.0 kcal/mol and from -16.5 kcal/mol to -21.2 kcal/mol for $w = 2.5$, 3.5, and 4.5 kcal/mol, respectively.

For adsorbed polymers, the decay of temperature leads to the decrease of potential energies, and the function of adsorption energy and the other potential energies may have different contributions to the formation of polymer structures, so the adsorption energy may compete with the other potential energies, and when the adsorption energy is dominative the coil structures may transform to other configurations. A coil–hairpin-like transition is found for both $w = 3.5$ and 4.5 kcal/mol, as seen in Fig. 4, the 2D coordinates are the projection of 3D coordinates, since the 3D plots are obscure and for simplicity, the minute differences of coil or globular structures at different adsorption energies are not shown, and it will be the same for Figs. 5 and 6.

According to Noguchi and Yoshikawa [57], the stiffness can influence the manner of the collapse transition in the isolated homopolymers, as a chain becomes stiffer, the manner of the coil–globule transition changes from continuous to discontinuous, and the morphology of the collapsed state changes from only spherical shape through the coexistence of both rod and toroidal shapes, to only totroidal shape. Exactly, the polymethylene chains simulated in our paper are more like stiff than semiflexible polymers, since for chain length $N \leq 20$ monomers, the structure of chain is rod like or zigzag at all

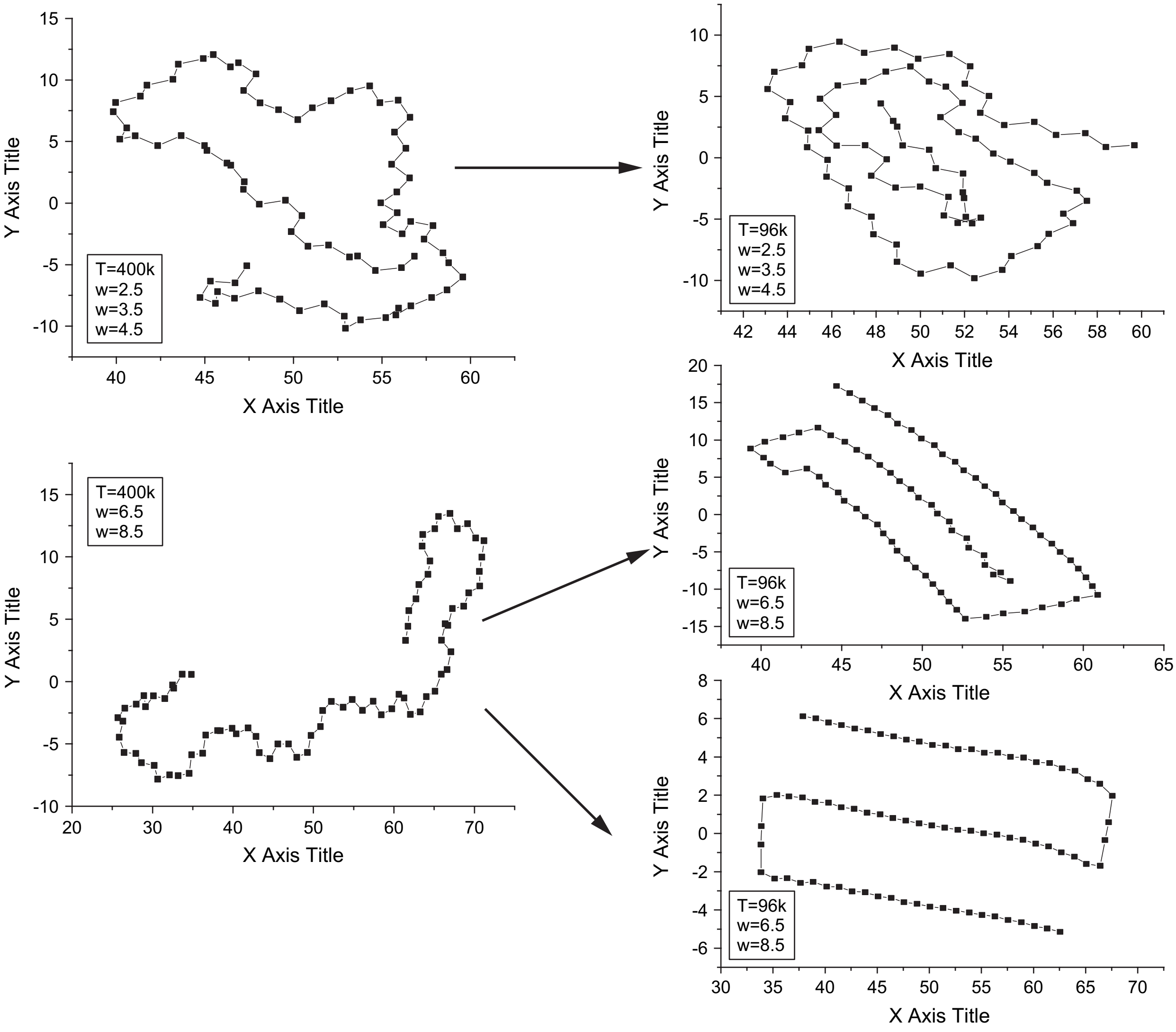

Fig. 5. The loose globule-to-compact globule transition with the adsorption $w = 2.5$, 3.5 and 4.5 kcal/mol, and the coil–crystal like transition with very strong adsorption $w = 6.5$ and 8.5 kcal/mol, for the adsorbed chains with $N = 80$ monomers. The 2D coordinates are the projection of 3D coordinates at different temperatures.

simulated temperatures; for about $N = 30$ monomers, the collapsed configuration is the coexistence of both rod and toroidal structures and the coil to rod or toroid transition temperature is about $T = 211$ K; for about $N \geq 40$ beads, there is only globular or toroid like structures at low temperatures, and the coil–globule transition may become easy for long chains, i.e., the critical temperature shifts to high region, since it is easy for long chains to bend.

The strong adsorption may break the rotational symmetry, and then weak bendings become impossible, so the chain segments may prefer to lie along straight direction to form adsorbed zigzag like structures, which then possess a U-turn, resembling a hairpin [58–60]. As shown in Fig. 4, there is indeed a coil-to-hairpin-like transition both for $w = 3.5$ and 4.5 kcal/mol, notes that the hairpin structure is adsorbed on the attractive surface and each side is a straight zigzag structure, which is shown in Fig. 1(c). The finite chain length effect is very important in our simulation, since longer polymer chains may possess more than one U-turn at strong adsorption, and then form crystal structures, which may be discussed later.

The recent experimental results [48,49,61] are well observations of the coil–globule-like transitions of adsorbed poly(*N*-isopropylacrylamide) (PNIPAM) at different conditions, especially, Kirwan et al. [62] gives the real images of coil–globule transitions of adsorbed poly(vinylamine) (PVA) at different solution pHs. At pH = 3, where the PVA is highly charged, an extended coil conformation is observed. When the pH is increased, the polyelectrolyte charge decreases and induces a segmental collapse through pearl-necklace structures. Above pH > 9, where the PVA is only weakly charged, one can observe a globular conformation. The pH dependence of the PVA structures is a little similar to our simulation results of adsorption dependence of polymethylene structures.

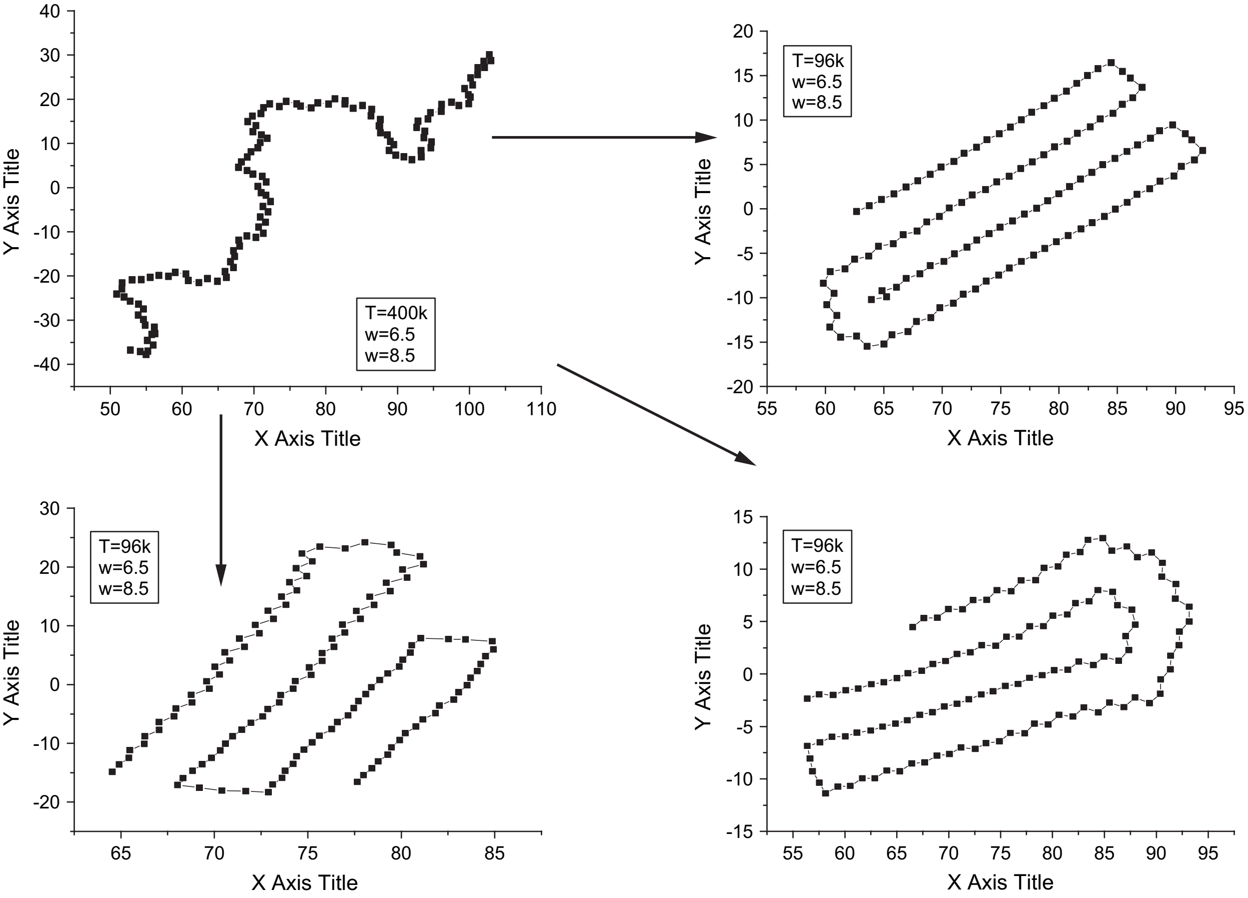

Fig. 6. Same as Fig. 5, but for $N = 120$ monomers, the loose globule-to-compact globule transition with $w = 2.5$, 3.5 and 4.5 kcal/mol are similar to Fig. 5 and not shown here.

3.2. $N = 80$

Figs. 7–9 show the temperature dependence of the equilibrium properties of an adsorbed polymethylene chain of $N = 80$ monomers with the adsorption energy w from $w = 2.5$ kcal/mol to $w = 8.5$ kcal/mol. Fig. 7 is very similar to Fig. 1, but the weak adsorption may obviously lower the equilibrium size compared to the free chain at high temperatures, for example, from $T = 400$ K to $T = 96$ K, the mean-square end-to-end distance $\langle R^2 \rangle$ changes from $\langle R^2 \rangle = 1270$ Å^2 to $\langle R^2 \rangle = 110$ Å^2, while for $w = 2.5$ kcal/mol, it is from 447 Å^2 to 123 Å^2, and for $w = 3.5$ and 4.5 kcal/mol, they change from 776 Å^2 to 137 Å^2 and from 990 Å^2 to 96 Å^2, respectively. The values of $\langle R^2 \rangle$ increase at high temperatures as the adsorption energy increases, but for $w = 6.5$ and 8.5 kcal/mol, the behaviors become different, which are similar to 40-monomer chain with $w = 3.5$ and 4.5 kcal/mol. The similar behaviors of the mean-square radius of gyration $\langle S^2 \rangle$ and the shape factor $\langle \delta \rangle$ are found, as seen in Fig. 7(b) and (c).

The behaviors of the heat capacity C_v with different adsorption energies become different compared to $N = 40$ monomers, as seen in Fig. 8. For the free chain, the critical temperature becomes $T = 265$ K, which means that it is easy for longer chains to form globular configurations, since long chains may be easy to bend. However, while for $w = 2.5$, 3.5 and 4.5 kcal/mol, there are not any strong peaks and the variation of the values for about $T > 200$ K is small, and when $T < 200$ K the values decrease suddenly as the temperature decrease. We may induce from Figs. 7 and 8 that there are not obvious for coil–globule-like transitions with $w = 2.5$, 3.5 and 4.5 kcal/mol, and these adsorptions may cause the polymer chains to form loose globular or toroidal coil like structures (see Fig. 5) at high temperatures, so there should be loose globule-to-compact globule transition. At stronger adsorptions of $w = 6.5$ and 8.5 kcal/mol, there are strong peaks in the heat capacities both at $T = 246$ K, which stand for coil–crystal-like transitions instead of coil–globule transitions. The behaviors of the total energy $\langle U \rangle$ and the adsorption energy $\langle U_a \rangle$ are very similar to Fig. 3, as seen in Fig. 9, we may skip the discussion of them.

Fig. 5 shows the 2D structures of the chain with different adsorption energies, which are different from Fig. 4. At high temperatures, weak adsorption may cause the chain to form loose globular structures or toroid coil (the average size is smaller than the free chain) and as the adsorption energy increases, the average size will increase and the chain becomes larger than the free chain (see Fig. 7). Therefore, when the adsorption energy increases, the average size of the chain decreases first and then increases, and the structures may change

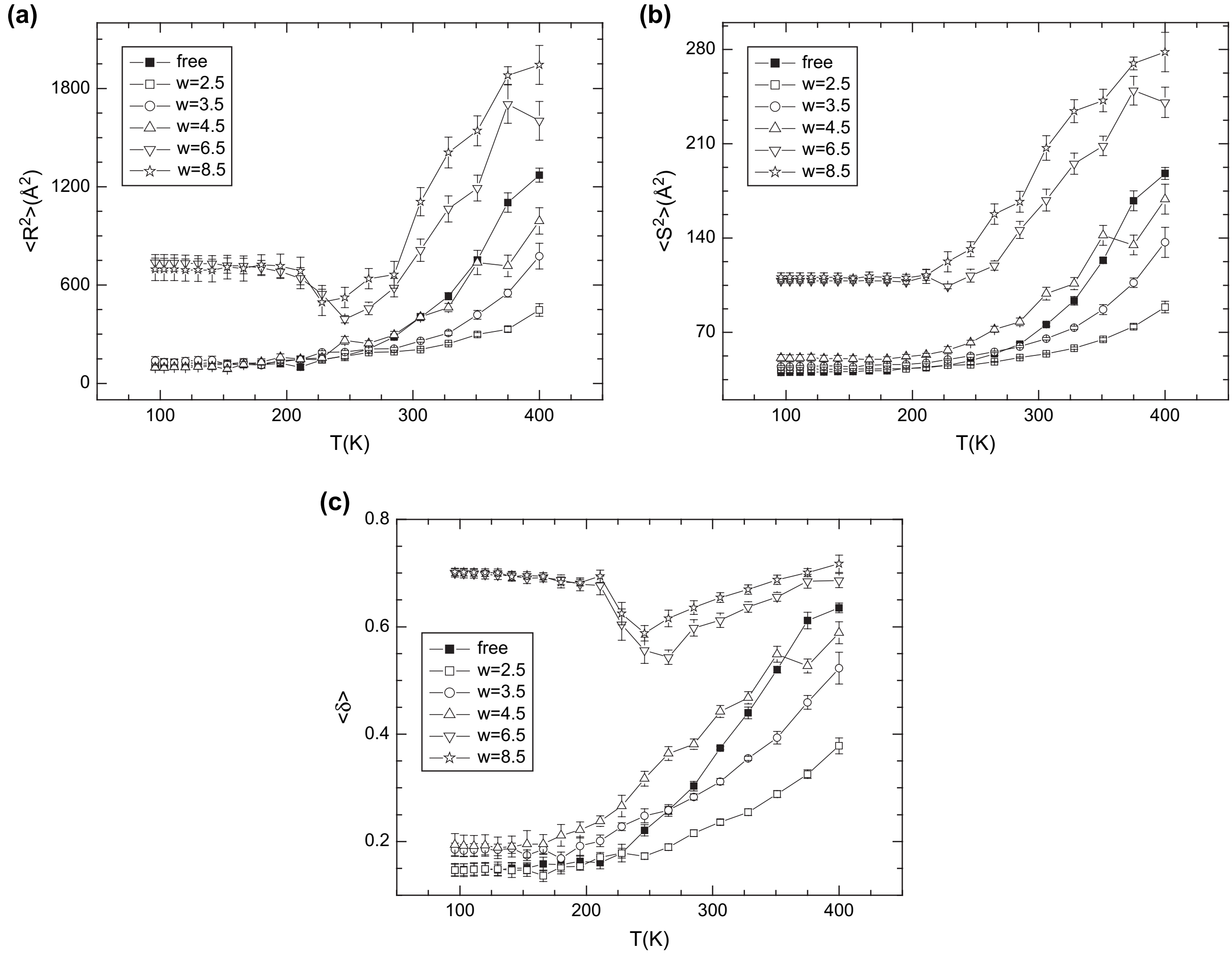

Fig. 7. Same as Fig. 1, but for $N = 80$ monomers.

from coil to loose globule, and then to quasi-2D coil. At low temperatures, the chain will form toroid globular structures with $w = 2.5$, 3.5 and 4.5 kcal/mol, which is similar to the 40-monomer chain with $w = 2.5$ kcal/mol, and for very strong adsorptions of $w = 6.5$ and 8.5 kcal/mol, the chain may possess two U-turns to form enhanced hairpin like structures, i.e., crystal like structures. So, we may conclude that the adsorbed 80-monomer chain performs loose globule-to-globule transitions with the adsorptions of $w = 2.5$, 3.5 and 4.5 kcal/mol, and performs coil-to-crystal like transitions with the very strong adsorptions of $w = 6.5$ and 8.5 kcal/mol. One should note that two U-turns of the chain may form two possible structures, as seen in Fig. 5, the two structures can be both obtained by splicing two hairpin structures with one side overlapped, and each side of the two structures should be adsorbed on the surface and be a straight zigzag.

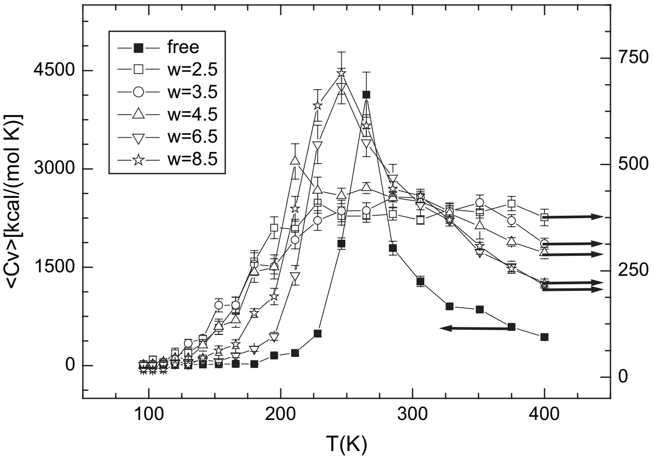

Fig. 8. Same as Fig. 2, but for $N = 80$ monomers.

3.3. $N = 120$

The equilibrium properties for adsorbed polymethylene chains of $N = 120$ monomers are shown in Figs. 10–12. The results are similar to 80-monomer chains, and the coil–globule transition temperature for the free chain is also $T = 265$ K. For the adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, the curves of the heat capacity are smooth when $T \geq 200$ K, and the values of them decrease as the temperature decreasing while $T \leq 200$ K, which are also the representations of the loose globule-to-globule transition. For the strong adsorption

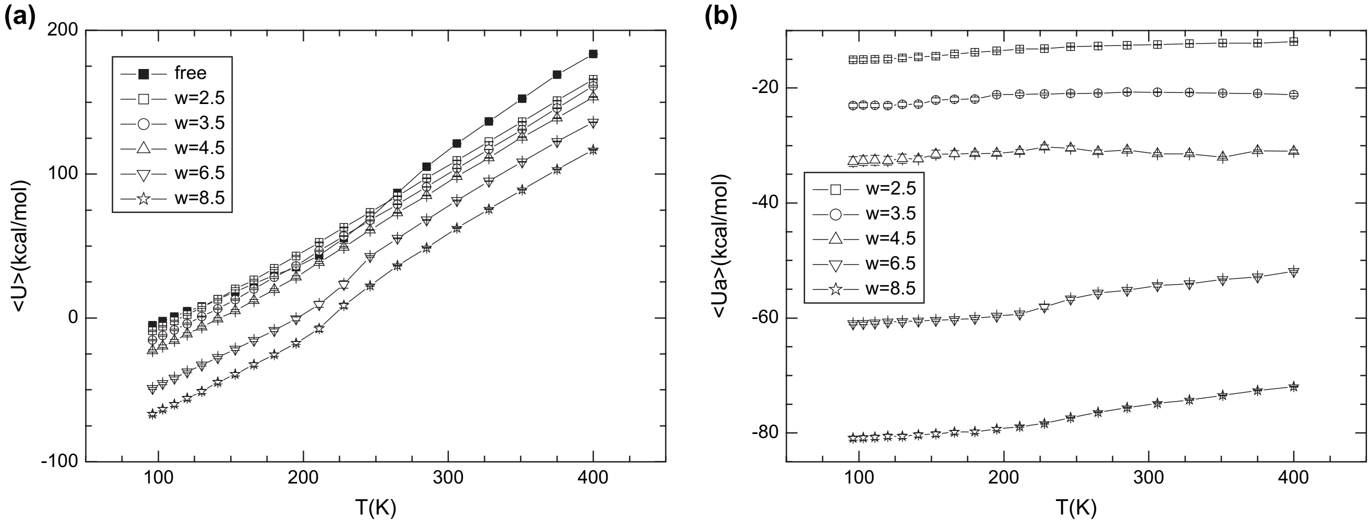

Fig. 9. Same as Fig. 3, but for $N = 80$ monomers.

energies of $w = 6.5$ and 8.5 kcal/mol, the critical temperatures of coil–crystal like transitions are both at $T = 246$ K.

The possible configurations of the adsorbed polymethylene chains are shown in Fig. 6. For the adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, the conformations of the chain are similar to the 80-monomer chain in Fig. 5, so here, for simplicity, we skip them. There are three possible structures at low temperatures for $w = 6.5$ and 8.5 kcal/mol, and to form

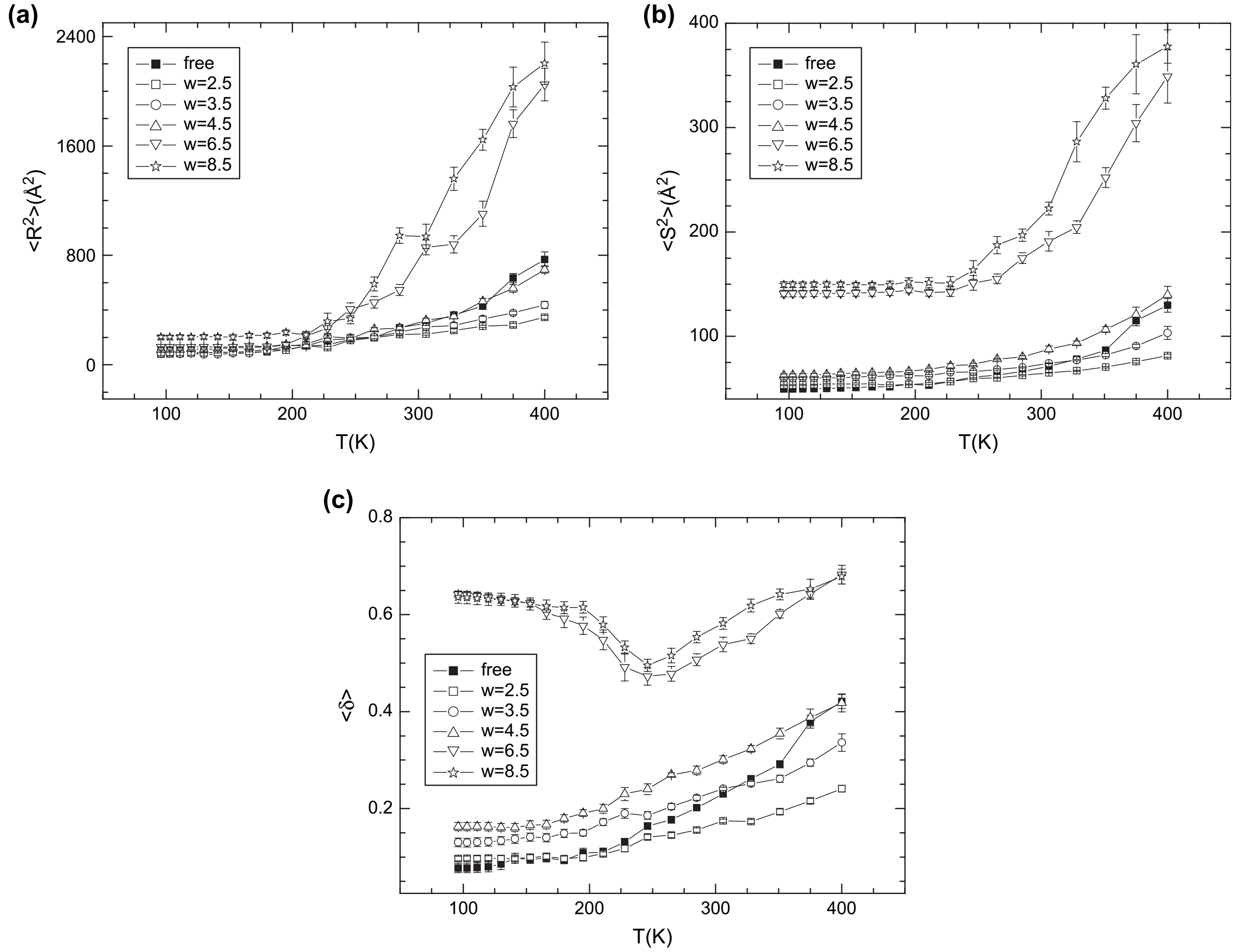

Fig. 10. Same as Fig. 1, but for $N = 120$ monomers.

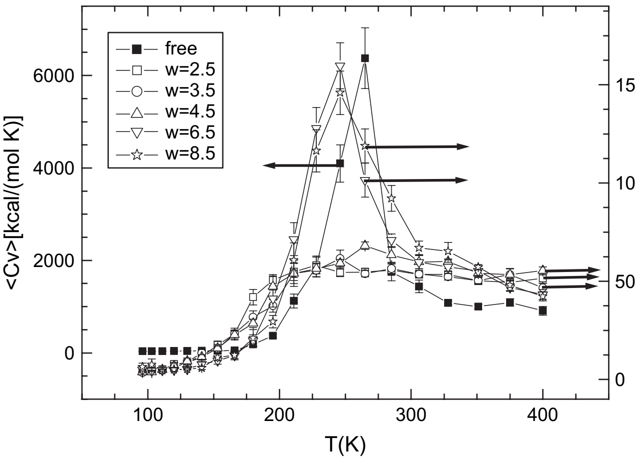

Fig. 11. Same as Fig. 2, but for $N = 120$ monomers.

them the monomers may have to perform three U-turns, i.e., these three possible crystal structures can be obtained by splicing three hairpin structures, and each side of the crystal structures should be a straight zigzag.

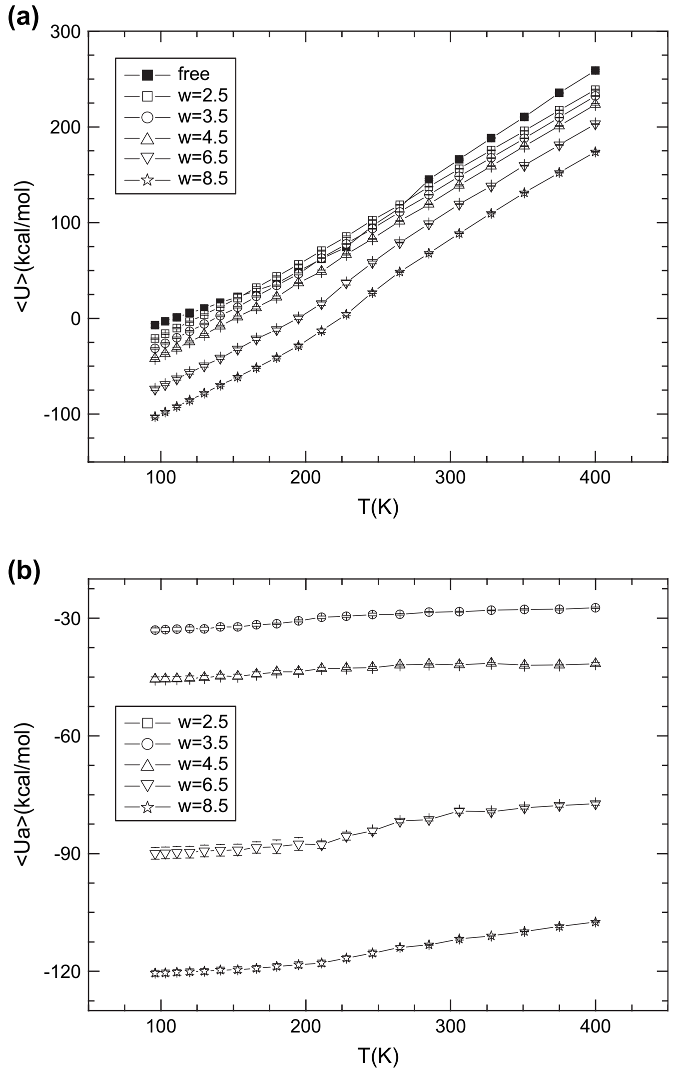

Fig. 12. Same as Fig. 3, but for $N = 120$ monomers.

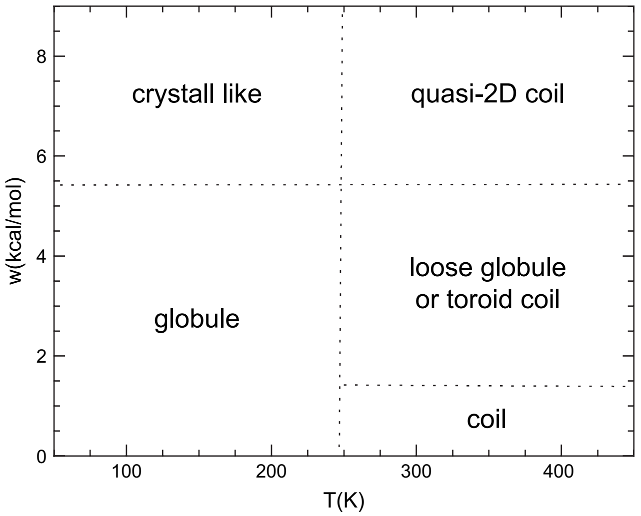

Fig. 13. The adsorption energy dependence of structures for adsorbed polymethylene chains at high and low temperatures.

In general, the behaviors of the thermodynamic properties of adsorbed polymethylene chains may depend on the values of adsorption energy and we have concluded the adsorption dependence of the possible structures at high temperatures and low temperatures, which is shown (for long polymer chains) in Fig. 13. One should note that if the adsorption energy is small enough, for example, if $w = 0.1$ or 0.5 kcal/mol, the chain can not be adsorbed on the surface and it will be just like the free chain, the equilibrium properties are the same as the free chain. So at high temperatures, the average size of the chain will decrease first and then increase as the adsorption energy increase, and the possible configuration is changed from coil to loose globule or toroid coil, and then to quasi-2D coil. At low temperatures, the possible conformation is changed from globule to crystal like, and the crystal like structures may be formed with different adsorption energies. The crystals like structures are different due to different chain length, so the phase behaviors of adsorbed polymethylene chains should depend on both the chain length and the adsorption energy.

In this study, the influence of chain length and adsorption energy on the equilibrium thermodynamic properties of single polymethylene chains adsorbed on an attractive surface as a function of temperature is investigated. Molecular dynamics simulations as well as annealing techniques are used to simulate the systems. Measures of the total energy, the adsorption energy, the constant volume heat capacity, the mean-square end-to-end distance, the mean-square radius of gyration, and the shape factor as a function of temperature are made with different adsorption energies to characterize the systems.

In a word, the thermodynamic behaviors of an adsorbed polymethylene chain will be changed as the variation of adsorption energy, and are very different from the free chain. The finite chain length effects become nontrivial, since the chain simulated here is more like a stiff than semiflexible chain, and the coil–globule transition temperature may shift to high regions as chain length increase. The free chains are used only for comparing, and we focus on the properties of adsorbed chains. For the adsorption energy of $w = 2.5$ kcal/mol, the adsorption may lower the coil–globule transition temperature for 40-monomer chain, and for $w = 3.5$ and 4.5 kcal/mol, the structures of the adsorbed at low temperatures are both adsorbed hairpin like, i.e., the chain undergoes coil–hairpin-like transition. While the results are different for the chains of $N = 80$ and 120 beads. For $N = 80$ monomers, the chain becomes easier to bend than the 40-monomer chain, and it would like to form loose globular or toroid coil like structures at high temperatures with the adsorption energies of $w = 2.5$, 3.5 and 4.5 kcal/mol, and then the chain forms more compact globular structures, i.e., the chain performs loose globule-to-globule transition; when the adsorption energies become very strong, $w = 6.5$ and 8.5 kcal/mol, the chain may like to perform two U-turns to form crystal like structures at low temperatures, i.e., the coil–crystal like transition. The behaviors of $N = 120$ monomers are very similar to that of $N = 80$ monomers, and the difference is that the 120-monomer chain may like to take three U-turns to form more complex crystal like structures at low temperatures. Like the coil–globule transition of polyelectrolyte molecules [26], the simulation results obtained in our work are based on polymethylene chains of the UA model, and the phase behaviors should depend on the UA force field, so for other semiflexible or self-attracting chains, the adsorption may not induce the specific phases, but the nontrivial results obtained in our simulations may provide some insights into the phase behaviors of adsorbed stiff like polymer chains, since the polymethylene chains of the UA model are more like stiff chains. We also hope that the same experimental results for polymethylene chains can be made in the future.

Acknowledgments

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