

Molecular Dynamics Simulations on the Chain Fold During the Isothermal Orientation of *n*-Alkanes on Graphene

Zhi Meng Zhang

Tianjin Normal University

Hua Yang (✉ yanghua11111@hotmail.com)

Tianjin Key Laboratory of Structure and Performance for Functional Molecules <https://orcid.org/0000-0001-7508-3435>

Jun Xia Shi

Tianjin Normal University

Jia Jun Wang

Tianjin Normal University

Zheng Guo Huang

Tianjin Normal University

Hui Zhang

Harbin University of Science and Technology

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Abstract

The orientation of hydrocarbon chains plays a key role in the applications of organic materials. And chain folding in the process of molecular orientation is also of great significance for the design of organic molecular thin films. The effect of chain length and simulation temperature on the isothermal orientation of *n*-alkanes on graphene surface is studied by molecular dynamics simulation in this paper. And the chain folding is also described. The *n*-alkanes can form perpendicular ordered structure, parallel ordered structure or perpendicular orientation at relative low temperature and parallel orientation at relative high temperature on graphene surface. The chain fold happens when long *n*-alkanes form perpendicular ordered structure on graphene surface. And the simulation results show the interactions of *n*-alkane-graphene and *n*-alkane-*n*-alkane affect chain fold.

1. Introduction

In recent years, due to the wide application of organic molecular thin films in industry, a lot of studies have been done in this field [1–4]. The organic thin films are prepared by adsorbing of organic molecules on surface at different condition. They share some common properties. Thickness is very small, the specific surface area is very large and anisotropy exists in a thin film. The different oriented organic films have different properties, which lead to different functions. The hydrocarbon chain is a basic component of many organic materials. The orientation of them in organic materials affects the physical properties and applications of the materials. Therefore, it is very important to understand the arrangement and orientation of hydrocarbon chains on surface for the industrial application of organic molecular thin films.

The experimental and molecular simulation studies for the orientation of molecules on surface have been carried out recently [5–36]. Yamamoto et al. [5] studied the crystallization process of *n*-undecane on flat substrate with different attractiveness by molecular dynamics (MD) simulation. They found that the film is composed of thin lamellae, in which the alkanes chain is parallel or perpendicular to the substrate. The thickness of thin films affects the orientation of molecules [5–8]. The thicker films on the strong attractive substrate are dominated by parallel lamellae, while the thinner films on the weaker attractive substrate are dominated by perpendicular lamellar layers. Fu et al. [9] found that the molecular orientation is related to chain length, by studying the orientation of linear alkanes $n\text{-C}_{36}\text{H}_{74}$ and $n\text{-C}_{60}\text{H}_{122}$ on the NaCl (001) surface.

And many studies found that substrate temperature has a significant effect on the molecular orientation in the *n*-alkane thin film [10–17]. Nozaki et al. [14] used X-ray diffraction and scanning probe microscopy to analyze the molecular orientation of the *n*-alkane evaporated film prepared under different deposition conditions. They found a "coexisting film" composed of perpendicular orientation and parallel orientation at low substrate temperature and high evaporation rate. Kubono et al. [15–16] studied the molecular orientation of different linear long-chain compounds in the process of vapor deposition and found that high substrate temperatures and low deposition rates resulted in a perpendicular orientation to the

substrate surface; low substrate temperatures and high deposition rates resulted in a parallel orientation or an amorphous structure. Fukao et al. [17] found that the parallel orientation state of the molecule will change into a perpendicular orientation state, when *n*-alkane evaporation film is annealed below the melting point, and the change of molecular orientation is irreversible.

In addition, the molecular orientation of alkane at different interfaces was studied by MD simulation [18–21]. The difference of the orientation mechanism between water-vacuum interface and water-oil interface has been studied [18–20]. Qiu et al. [22] studied the relationship between the interface orientations of alkane in liquid phase by MD simulation. They found that alkane tends to be perpendicular to the alkane-vacuum interface and parallel to the alkane-water interface in the liquid phase.

Chain fold is a basic feature of polymer crystallization [23, 24]. In the past few years, a lot of studies have been done on polymer fold [23–37]. Ungar et al. [25, 26] studied on the monodisperse polymers and showed more information about polymer crystallization, such as integer folding, non-integer folding, lamellar thickening and the nature of fold surface and end surface. Hobbs et al. [27] found that the crystals of $C_{294}H_{590}$ can be grown in different integer fold forms from the dilute solution. At an appropriate temperature, the crystal will become thicker from the form of one fold to another. Iwata et al. [28] obtained the fold structure at both low and high temperatures and observed the sliding movements of a chain during the crystallization. Fujiwara and Sato [29, 30] studied the chain fold process of single molecular chain with 500 methylene groups by MD simulation. Kavassalis [31] and Shakirov [32] et al. found that the folded lamellar crystal for polyethylene (PE) chains requires a minimum chain length to occur as the ground state folded structure, which is around 150 methylene groups. In addition, substrate [33] influences the fold of the chain in the layered structure. Gulde et al. [34] found that polymers adsorbed on graphene surface form two-dimensional folded microcrystals. And chain fold was observed in polymer single crystal by atomic force microscope (AFM) [35–37]. However, none of the works showed whether alkane chain fold will occur in the process of molecular orientation on surface. This is one of important aspects of the formation mechanism for molecular orientation on surface and is also of great significance for the design of organic molecular thin films. Therefore, this paper will also focus on the chain fold in the process of molecular orientation on surface.

The selection of substrates is crucial in the study of the orientation of organic molecules on surface. Graphene is an ideal substrate for the preparation of high performance conductive thin films [38–40]. The two-dimensional supramolecular assembly of organic molecules on graphene surface can affect the structure of organic molecules and improve the properties of organic thin film materials [41–45]. Therefore, we choose graphene/alkane system for studying the orientation of the hydrocarbon chain on surface.

In our previous studies, we studied the isothermal orientation of *n*-decane (C10) between two graphene sheets [46]. The simulation temperature is very important for C10 orientation between graphene sheets. And we also studied the orientation of *n*-alkanes of different lengths on graphene [47]. The chain length affects the orientation of the *n*-alkanes on graphene. In this paper, we will continue to study the

perpendicular orientation and parallel orientation of *n*-alkane on graphene surface. First, the final conformations of *n*-alkane molecules on graphene surface at different temperatures will be described. Second, the orientation process of *n*-alkanes on graphene surface will be presented. Thirdly, the fold behavior of *n*-alkane chains on graphene surface will be discussed, and the formation process of the different types of chain fold conformations will be analyzed. Finally, the effect of alkane-alkane interaction and alkane-surface interaction on the orientation of molecules will be discussed.

2. Computational Details

Ten kinds of *n*-alkane chains tridecane (C13), tetradecane (C14), pentadecane (C15), hexadecane (C16), heptadecane (C17), octadecane (C18), nonadecane (C19), icosane (C20), pentacosane (C25) and triacontane (C30) are chosen in this study. We first build 115C13, 107C14, 100C15, 94C16, 88C17, 83C18, 79C19, 75C20, 60C25, 50C30 and a graphene sheet with lattice parameters $x = 51.4 \text{ \AA}$, $y = 49.2 \text{ \AA}$, $z = 120 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. Then the *n*-alkane chains are randomly placed on the graphene surface, respectively. The ten systems all contain about 1500 alkane carbon atoms. They are denoted as 115C13/GRA, 107C14/GRA, 100C15/GRA, 94C16/GRA, 88C17/GRA, 83C18/GRA, 79C19/GRA, 75C20/GRA, 60C25/GRA, 50C30/GRA, respectively. The first number is the number of alkane chains and the second number is the number of carbon atoms in the chain. 50000 steps of energy optimization are carried out to relax configurations. The 10000ps NVT MD simulation is performed at a relative high temperature. The initial configurations are obtained with *n*-alkane chain adsorbed on the graphene surface. Periodic boundary conditions are used in these systems. The cell parameter z is large enough to ignore the interactions between the adsorbed *n*-alkane and the periodic images of graphene surface in the z direction. By this way, the three-dimensional periodicity is transformed into two-dimensional periodicity. The graphene surface is free during all the simulations.

The *n*-alkane molecules are described in all-atom model. The COMPASS force field [48–50] has been used to simulate the interactions between alkane/polyethylene and graphite/graphene/carbon nanotube successfully [51–53]. Thus we choose COMPASS force field to describe our systems. The energy of the system calculated from the COMPASS force field includes valence and nonbonding terms. The valence terms include stretching, bending, and torsion energies as well as the diagonal and off-diagonal cross-coupling terms. The nonbonding interaction is mainly controlled by van der Waals and electrostatic interactions between the *n*-alkane chains and the graphene. The cutoff distance for the nonbonding interaction is 12.5 \AA . The 10000ps NVT MD simulations are performed for the systems in the temperature range of 300K ~ 550K. The integral time step is 1fs. Nose-Hoover thermostat [54–56] is used to keep the temperature constant in the systems.

3. Results And Discussion

3.1. The Isothermal Orientation Processes of 79C19/GRA at 450K and 490K

We acquire a greater depth of understanding the ordered structure formation of *n*-alkane via MD simulations. Our simulations show that C19 molecules are perpendicular to the graphene surface at relative low temperature ($T \leq 480\text{K}$) and parallel to the graphene surface at relative high temperature ($T > 480\text{K}$). This is similar to our previous work [46–47]. The chain fold also is found for long *n*-alkane chains in our simulations. Thus, we also show the two typical isothermal orientation processes for 79C19/GRA at 450K and 490K in Fig. 1(a) and (b), respectively.

At the beginning of the simulation, C19 molecules are adsorbed on graphene surface and form disordered structure. At 450K, some C19 molecules are adsorbed near the surface and are parallel to the surface, and others are still disordered at 200ps. Local orientation appears at about 1000ps. After that, more C19 molecules move into the ordered region slowly and the orientation region become larger gradually. Most of C19 molecules are perpendicular to the surface at 2000ps. The perpendicular order degree increases with the simulation proceeding. Chain fold occurs when the ordered structure forms. The chain fold leads to the height of the perpendicular ordered region decreasing gradually. This has not been found when study the orientation process of short *n*-alkanes on or between graphene sheet(s) [46, 47]. At the end of the simulation, most of the C19 molecules are perpendicular to the surface, and they are also parallel to each other. It can also be seen that the ends of some C19 molecules near the surface is curved in the perpendicular ordered region.

At 490K, some of C19 molecules are also adsorbed near the surface and others are still disordered before 1000ps. Local orientation appears at about 2500ps. Some of C19 molecules are curved and others are extended in the first layer near the graphene surface before 2500ps. After that, more C19 molecules enter the ordered region quickly. At 3000ps, most of C19 molecules are parallel to graphene surface and form a six-layer structure. As the simulation going, the order degree of the six-layer structure increases. The molecules arranging in the six-layer structure are extended and parallel to each other. The effect of graphene on the orientation of C19 molecules results in the orientation starting in the first layer near the graphene surface and then in the next layer. At the end of the simulation, almost all C19 molecules arrange in the six-layer structure.

In summary, the two kinds of orientation processes are considered as a three-step process (adsorption, orientation, and growth). And C19 molecules tend to be perpendicular to graphene surface at relative low temperature and form parallel multi-layer structure at relative high temperature. This is similar to the isothermal orientation of *n*-decane between two-layer graphene [46]. But the C19 molecules fold in the perpendicular ordered region on graphene surface at relative low temperature. Our simulations also indicate that when the chain length is long enough, chain fold only occurs in perpendicular orientation. We compare the final conformations of *n*-alkane on graphene surface at different temperatures, the effect of chain length on the orientation of *n*-alkane on graphene surface can be identified and the critical chain length of *n*-alkanes with perpendicular and parallel orientation on the graphene surface can also be obtained.

3.2. The Effect of Temperature on the Orientation of *n*-Alkane on Graphene

The *n*-alkane chains may be perpendicular orientation, parallel orientation or perpendicular orientation at relative low temperature and parallel orientation at relative high temperature on the graphene surface. Figure 2 displays the final conformations of C13, C19, C25 molecules on graphene surface with the three typical orientations at different temperatures.

For 115C13/GRA, C13 molecules arrange in a disordered state at 300K. Almost all C13 molecules are perpendicular to the surface at 400K, 450K and 490K. The perpendicular order degree increases with temperature increasing. At 490K, some C13 molecules are desorbed from the surface and appear below the surface due to periodic boundary conditions. At 500K, more C13 molecules are desorbed and a disordered structure forms on graphene surface. For 79C19/GRA, a disordered structure form on graphene surface at 300K. C19 molecules are perpendicular to the surface at 400K and 450K. And the height of the perpendicular ordered regions are smaller than the extended C19 molecule shown in Fig. 2(b). The length of extended C19 molecule is 22.59Å. Chain fold occurs when the perpendicular ordered structure of C19 molecules forms. At 490K, almost all C19 molecules are parallel to graphene surface and are parallel to each other. They form a parallel multi-layer structure. At 500K, C19 molecules form a disordered structure on graphene surface. For 60C25/GRA, C25 molecules are disordered at 300K, and a few molecules adsorbed near the surface are parallel to the surface. More C25 molecules are parallel to graphene surface at 400K. At 480K and 500K, parallel multi-layer structures form on graphene surface. Almost all C25 molecules arrange in the ordered structure and are parallel to each other. At 550K, C25 molecules also form a disordered structure on graphene surface.

The *n*-alkane can form disordered structure, perpendicular ordered structure, parallel multi-layer structure on graphene surface. The final conformations of ten kinds of *n*-alkane molecules on graphene surface at all the temperatures are shown in figure S1 of the Supporting Information. Ten kinds of *n*-alkane molecules relax slowly and form disordered structures on graphene surface at 300K. The 115C13, 107C14, 100C15 and 94C16 only form the perpendicular ordered structures on graphene surface. The 88C17, 83C18 and 79C19 are perpendicular to graphene surface at relative low temperature and form parallel multi-layer ordered structure at relative high temperature. The 75C20, 60C25 and 50C30 only form parallel multi-layer structure. When temperature is high enough, the *n*-alkane molecules form disordered structures on graphene surface. In addition, when *n*-alkane molecule is longer than C15, chain fold occurs with perpendicular ordered structure forming on the surface. Some *n*-alkane chains fold into two or more stems during the MD simulation. And *n*-alkane chains adopt extended conformations in parallel multi-layer ordered structure on the surface.

The chain length affects the orientation of *n*-alkanes on graphene surface. When the *n*-alkane molecule is shorter than that of C17, they arrange perpendicularly to the graphene surface. And when *n*-alkane molecule is longer than C19, they form parallel multi-layer ordered structure on graphene surface. C17, C18 and C19 molecules are perpendicular to graphene surface at relative low temperature and form

parallel multi-layer structure at relative high temperature. Thus the longest *n*-alkane chain that can form perpendicular orientation is C16 molecule on graphene surface. The shortest *n*-alkane chain that forms parallel multi-layer ordered structure is C20 molecule. And when the chain length is longer than C15, chain fold only occurs in perpendicular orientation region.

Is the orientation of (C17-C19) reversible with temperature i.e., perpendicular orientation at lower temperature and parallel orientation at higher temperature when annealing procedures are performed on them? This is interesting and important in the devising and manufacturing this kind of assembling material. Therefore, annealing procedure is performed on 83C18/GRA at the cooling rate of 10K/2000ps with the same parameters as our isothermal MD simulations. As the orientation of the simulated *n*-alkanes is sensitive to the cooling rate, another two annealing procedures are simulated at the cooling rate of 10K/1000ps and 10K/500ps. Snapshots of the last conformation of 83C18/GRA for various temperatures during the three annealing procedures are shown in figure S2 of the Supporting Information. The C18 molecules are first disordered at high temperatures and parallel to the surface with temperature decreasing during the annealing procedure at the cooling rate of 10K/2000ps. The C18 molecules first form disordered structure at high temperatures and are perpendicular to the surface with temperature decreasing at the cooling rate of 10K/1000ps and 10K/500ps. The orientation of C18 molecules are irreversible with temperature. The temperature of parallel orientation appearing is higher than that of perpendicular orientation. The C18 molecules are favorite forming perpendicular orientation at fast cooling rate and parallel orientation at slow cooling rate. Only one orientation appears for C18 during the annealing procedure. The parallel and perpendicular orientation can both obtained by isothermal MD simulations at different temperatures. These are useful information for manufacturing this kind of assembling material.

3.3. The Orientation Parameter of *n*-Alkanes on Graphene

In order to describe the orientation structure of *n*-alkanes with different chain lengths at different temperatures quantitatively, we calculate the global orientation order parameter $g-OP_b$ and the z axis bond-orientation order parameter of the *n*-alkanes. The global orientation order parameter $g-OP_b$ can describe the conformation of all alkane molecules, which is defined as

$$g-OP_b = \left\langle \frac{3 \cos^2 \varphi - 1}{2} \right\rangle \quad (1)$$

where φ refers to the angle between two neighboring subbond vectors, the center of the two adjacent bonds are connected to form the subbond vector (see the schematic drawing in Fig. 3). When g -is 1.0, all of the alkane chains are extended. The z axis bond-orientation order parameter is used to describe the orientation of alkane molecules on graphene surface, which is defined as

$$OP_b = \left\langle \frac{3 \cos^2 \phi - 1}{2} \right\rangle \quad (2)$$

where ϕ is the angle between the subbond vector and the z axis. When the subbond vector is completely parallel to the z axis, = 1.0; when the subbond vector is perpendicular to the z axis, = -0.5; when the subbond vector is random to the z axis, = 0.0.

Figure 4 and 5 show the global orientation order parameter $g-OP_b$ and the z axis bond-orientation order parameter for C13, C19 and C25 molecules on graphene at different temperatures, respectively. For 115C13/GRA, the is about - 0.05 at 300K, indicating that C13 molecules are laid randomly on graphene surface. The increases from 0.7 to 0.9 and the $g-OP_b$ fluctuates around 0.95 from 400K to 490K, indicating that more C13 molecules arrange in the perpendicular ordered structure and adopt extended conformation. The is near - 0.1 and the $g-OP_b$ is about 0.55 at 500 K, indicating that disorder structure forms on the surface at 500 K.

For 79C19/GRA, the increases from - 0.1 to 0.7 in the temperature range of 300K ~ 480K, meaning that more C19 molecules change from random to perpendicular orientation to the surface. The is -0.4 at 490K, indicating that the C19 molecules are parallel to the surface. The $g-OP_b$ fluctuates around 0.73 in the temperature range of 300K ~ 450K, showing that C19 molecules are folding in the ordered structure. The $g-OP_b$ increases to 0.88 at 490K. This illustrates that most of C19 molecules adopt extended conformation at 490K. The is 0.0 and the $g-OP_b$ is 0.58 at 500 K, indicating that disordered structure forms on the surface at 500 K.

For 60C25/GRA, the $g-OP_b$ increases from 0.72 to 0.89 in the temperature range of 300K ~ 500K, which indicates that most of C25 molecules adopt extended conformation, and a small number of molecules are curved. The decreases to -0.4 from 300K to 450K and fluctuates around - 0.4 in the temperature range of 450K ~ 500K, indicating that C25 molecules are parallel to the surface. And the is -0.1 and the $g-OP_b$ is 0.55 at 550K as a result of a disordered structure forms on the surface.

Simulation temperature and chain length are important in the orientation of *n*-alkanes on graphene surface. Figure S3 and S4 show the global orientation order parameter $g-OP_b$ and the z axis bond-orientation order parameter for the ten kinds of *n*-alkane molecules on graphene at different temperatures, respectively. Ten kinds of *n*-alkane molecules are all randomly on graphene surface at 300K. When the chains are shorter than C17, molecules are perpendicular to the surface. For long chains (> C19), molecules are parallel to the surface. The C17, C18 and C19 molecules are perpendicular to surface at relative low temperature and form parallel multi-layer structure at relative high temperature on surface. When the temperature is high enough, ten kinds of *n*-alkane molecules all form disordered structure on surface.

3.4. Fold Behavior of *n*-Alkane Chains on Graphene Surface

In the previous sections, the orientation structure of *n*-alkane on graphene surface has been discussed. The chain fold happens when long *n*-alkane form perpendicular ordered structure on graphene surface. This section will explore the chain fold in details. First, we calculate the average end-to-end distance (R_{ed}) of *n*-alkane at different temperatures. It refers to the line distance from one end of the molecule to the other. When the molecular is extended, R_{ed} is equal to the length of extended molecule ($R_{all-trans}$). When the molecule curved or chain folding occurs, R_{ed} is smaller than the $R_{all-trans}$.

The average end-to-end distance of the last 1000 configurations of the ten kinds of *n*-alkane molecules at different temperatures are calculated and provided in figure S5 of the Supporting Information. The average R_{ed} of the ten kinds of *n*-alkane molecules are much less than their $R_{all-trans}$ at 300K, meaning that molecules are curved at 300K. The average R_{ed} of 115C13, 107C14, 100C15, 75C20, 60C25 and 50C30 are close to their $R_{all-trans}$ with the simulation temperature increasing, meaning that more molecules adopt extended conformation. But the 115C13, 107C14 and 100C15 are extended in the perpendicular ordered structure and the 75C20, 60C25 and 50C30 are extended in the parallel ordered structure on graphene surface. For 94C16/GRA, 88C17/GRA, 83C18/GRA and 79C19/GRA, the average R_{ed} at relative low temperature are less than the average R_{ed} of disordered structures, meaning that more molecules adopt curved conformation. Chain fold happens during the chains perpendicular orientation on the surface. The average R_{ed} is close to the $R_{all-trans}$ when the four kinds of *n*-alkane molecules parallel orientation at relative high temperature on graphene surface. This means that most molecules are extended and chain fold does not occur in the parallel ordered structure. The average R_{ed} of the ten kinds of *n*-alkane molecules is less than their $R_{all-trans}$ and close to the average R_{ed} of disordered structures when temperature is high enough, meaning that molecules are curved and disordered on graphene surface. In brief, the occurrence of chain fold is related to the chain length. And chain fold happens when the chains are longer than C15 and form perpendicular ordered structure on graphene surface. This also shows the three kinds of orientations for *n*-alkanes on graphene surface. The ratio of average R_{ed} to $R_{all-trans}$ ($R_{ed}/R_{all-trans}$) of three typical systems (115C13/GRA, 79C19/GRA and 60C25/GRA) are shown in Fig. 6 as an example.

The time evolution of the average end-to-end distances during the two orientation process can help us to understand the chain fold process in detail. In order to check the chain fold behavior of 79C19/GRA with perpendicular ordered structure at 450K and parallel multi-layer structure 490K, Fig. 7 shows the time evolution of the average end-to-end distances of 79C19/GRA on graphene surface at 450K and 490K.

At 450K, the average R_{ed} of 79C19 increases to 17.0Å before 600ps, decreases to 10.3Å from 600ps to 8000ps gradually, and fluctuates around 10.3Å after 8000ps, which are smaller than their $R_{all-trans}$ (22.59Å). The ratio of average R_{ed} to the film thickness of 79C19 is about 0.72. This means that the formation of perpendicular orientation is accompanied by chain fold. The height of the perpendicular ordered regions are smaller than the extended C19 molecule. It may be speculated that the height of the perpendicular ordered regions decreases owing to the chain fold during the simulation proceeding. At 490K, the average R_{ed} of 79C19 fluctuates around 15.8Å before 2000ps, increases to 20.0Å from 2000ps

to 5000ps, and fluctuates around 20.0Å after 5000ps, which are close to their $R_{all-trans}$. This shows that most of C19 molecules change from curved conformation to extended conformation gradually during the orientation process. The C19 molecules do not fold in the parallel ordered structure.

The C-C-C-C torsion angle of C19 molecules are also calculated to describe the conformation at 450K and 490K. Figure 8 gives the torsion angle distributions calculated from the last 1000ps of the simulations. There are two kinds of peaks in the distribution. The first one is the torsion angle between $30^\circ \sim 100^\circ$ or $-30^\circ \sim -100^\circ$. The peak indicates the presence of the gauche conformation. The second one is the torsion angle between $150^\circ \sim 180^\circ$ or $-150^\circ \sim -180^\circ$. The peak means that the presence of the trans conformation. The second peak is much higher than the first one. This means most of C19 molecules adopt trans conformation. For the peak between $30^\circ \sim 100^\circ$ or $-30^\circ \sim -100^\circ$, the height at 450K is higher than that at 490K. This indicates that more C19 molecules are gauche conformation at 450K. This results from the occurrence of chain fold in the perpendicular ordered structure at 450K.

There are 16 torsion angles in C19 molecule, which are denoted in turn. Figure 9 shows the final conformation of 79C19/GRA at 450K. Five typical C19 molecules are selected to study, which denoted by A (blue), B (orange), C (green), D (purple) and E (red). It can be seen that C19 A is extended, C19 B and C fold into two stems, C19 D occurs a non-integer fold, and C19 E folds into three stems. The torsion angles of C19 A, B, C, D and E at 10,000ps NVT MD simulations at 450K are listed in Table 1. The negative values of torsion angles in the Table 1 are shown as their absolute value.

Torsion angles of C19 A are all bigger than 150° , which indicates that C19 A is extended on graphene surface. There are fold and extended regions in the fold C19 molecules (B, C, D and E). The extended region is trans conformation. The torsion angles 1 ~ 6, 12 ~ 16 of C19 B, 2 ~ 7, 13 ~ 16 of C19 C, 1 ~ 8 of C19 D are about 170° . The conformation of the fold region is the gauche-gauche-trans-gauche-gauche or gauche-gauche-trans-gauche. This is similar with the structure of chain fold in the polyethylene [25, 57]. The torsion angles 7 ~ 11 of C19 B, 8 ~ 12 of C19 C, 9 ~ 12 of C19 D are in the fold regions. C19 E folds into three stems in Fig. 9. Torsion angles 2, 3, 5, 6, 8, 11, 12, 15 of C19 E are all less than 100° , indicating that C19 E twists heavily.

Liu et al. [33] found more detailed information of chain fold during *n*-alkane orientation from the evolution of the end-to-end distance. The change of C19 can be found from the time evolution of R_{ed} . The time evolution of the R_{ed} of C19 A, B, C, D and E at 450K are also shown in Fig. 10. The C19 A are curved at the beginning of the simulation and changes to extended conformation after 2000ps. The C19 B is bent from 1900ps to 8000ps and then folds into two stems again after 8000ps. The C19 C happens to fold before 2000ps and folds into two stems from 2000 to 10000ps. The C19 D folds into two stems at 5000ps and changes to a non-integer fold at the end of simulation. The C19 E twists at about 600 and 3200ps and fold into two stems at 4000ps. The C19 E folds into three stems finally.

Table 1 Torsion angles of C19 A, B, C, D and E after 10,000ps NVT MD simulations at 450K. Negative values in the table 1 are interpreted as their absolute value.

Torsion angle (degrees)	Models				
	A	B	C	D	E
1	174	163	88	171	179
2	172	164	174	170	65
3	152	173	179	163	64
4	176	166	155	163	156
5	180	180	168	178	72
6	166	177	164	179	45
7	174	64	168	155	155
8	172	58	73	171	75
9	177	165	66	64	160
10	171	71	167	167	163
11	175	53	52	32	80
12	178	176	63	67	92
13	177	167	169	139	158
14	158	179	180	176	106
15	180	178	178	77	57
16	180	171	179	175	160

When the conformation of *n*-alkane chain changes, the backbone torsion angles will change correspondingly. We choose three typical backbone torsion angles 1, 6, 8 of C19 B, which are at the end of chain, in the extended stem and in the fold region of the molecule after 10,000 NVT MD simulations, respectively. Figure 11 shows the evolutions of torsion angles 1, 6, 8 of C19 B on graphene surface during MD simulation at 450 K.

Three torsion angles fluctuate between 20° and 180° during C19 B twisting. The C19 B bends after 1900ps. Torsion angle 6 fluctuates between 150° and 180° from 1900ps to 4700ps, meaning that torsion angle 6 is in the extended stem. Torsion angles 1 and 8 fluctuate wildly from 1900ps to 4700ps. In the simulated time of 4700ps ~ 8000ps, torsion angles 1 and 6 fluctuate between 150° and 180°, meaning that they are in the extended stem. Torsion angle 8 fluctuates between 40° and 80°, meaning that torsion angle 8 is in the fold region. C19 B happens to fold at 8000ps and folds into two stems from 8000 to 10000ps again. Three torsion angles don't change much after 8000ps. And torsion angles 1 and 6 are in the extended stem and torsion angle 8 is in the fold region.

When *n*-alkane chain fold occurs, torsion angle may move back and forth in the fold region and the extended stem. Some torsion angles in the fold region usually change to gauche conformation, and others in the extended stem usually adopt trans conformation. After the occurrence of chain fold, torsion angles fluctuate. Torsion angles in the fold region fluctuate stronger than that in the extended stem.

3.5. The Effect of the Interaction Energy on the Orientation

In this section, we will explore the effect of the interaction energy on the orientation of *n*-alkane with different chain lengths on graphene surface. We calculate the interaction energy between *n*-alkane chain (E_{chain}), the interaction energy between molecule and graphene surface (E_{int}).

$$E_{\text{int}} = E_{\text{total}} - (E_{\text{chain}} + E_{\text{plane}}) \quad (3)$$

where E_{total} is total energy of the system, E_{plane} is energy of graphene surface. Figure 12 shows the variation of E_{int} , E_{chain} and $E_{\text{int}}-E_{\text{chain}}$ for 115C13/GRA, 79C19/GRA and 60C25/GRA with increasing temperature.

For 115C13/GRA, E_{int} changes little as the temperature increases. E_{chain} decreases from 300 to 450K and increases from 450 to 500K quickly. E_{int} is bigger than E_{chain} at 300K, and $E_{\text{int}}-E_{\text{chain}}$ is about 2000kcal/mol. C13 molecules are disordered on the surface. This is due to *n*-alkane relaxing slowly at low temperatures. E_{chain} are much lower than E_{int} , and $E_{\text{int}}-E_{\text{chain}}$ is about 4000kcal/mol from 370 to 490K. C13 molecules are perpendicular to graphene surface in this temperature range. E_{chain} is as much as E_{int} at 500K when C13 molecules form a disordered structure.

For 79C19/GRA, E_{chain} is lower than E_{int} , and $E_{\text{int}}-E_{\text{chain}}$ is about 2000kcal/mol at 300K. C19 molecules are disordered on the surface because *n*-alkane relaxes slowly. E_{chain} decreases and E_{int} increases slowly from 300 to 480K. In addition, E_{chain} is much lower than E_{int} , and $E_{\text{int}}-E_{\text{chain}}$ increases to about 3000kcal/mol gradually. C19 molecules tend to adopt perpendicular orientation on surface. When the temperature above 480K, E_{chain} increases and E_{int} decreases suddenly. E_{chain} is lower than E_{int} and $E_{\text{int}}-E_{\text{chain}}$ decreases to about 2000kcal/mol at 490K. C19 molecules form parallel ordered structure on the surface at 490K. E_{chain} is close to E_{int} and $E_{\text{int}}-E_{\text{chain}}$ is about 500kcal/mol at 500K. C19 molecules form disordered structure on the surface.

For 60C25/GRA, E_{chain} decreases from 300 to 480K, increases after 480K quickly. E_{int} changes little from 300 to 480K, decreases after 480K suddenly, and increases from 500 to 550K. A disordered structure form on the surface at 300K owing to *n*-alkane relaxes slowly. And $E_{\text{int}}-E_{\text{chain}}$ fluctuates around 2000kcal/mol, C25 molecules are parallel to the surface in the temperature range of 400 ~ 500K. C25 molecules form a disordered structure on the surface at 550K when E_{chain} is close to E_{int} and $E_{\text{int}}-E_{\text{chain}}$ is about 500kcal/mol.

It is found that the ordered structure of *n*-alkanes is governed by E_{int} and E_{chain} . When $E_{\text{int}}-E_{\text{chain}}$ is high enough at relative high temperature, *n*-alkanes can form ordered structure on graphene surface. Molecules are perpendicular to the surface when $E_{\text{int}}-E_{\text{chain}}$ of C13 molecules is about 4000kcal/mol. C19 and C25 molecules are parallel to the surface when $E_{\text{int}}-E_{\text{chain}}$ is about 2000kcal/mol. Although $E_{\text{int}}-E_{\text{chain}}$ is about 2000kcal/mol at low temperatures, C13, C19, C25 molecules are disordered on the surface. It's because *n*-alkane molecule relaxes slowly at low temperatures. When $E_{\text{int}}-E_{\text{chain}}$ is about 500kcal/mol at high temperatures, three kinds of *n*-alkanes form disordered structure. $E_{\text{int}}-E_{\text{chain}}$ of parallel ordered structure is much lower than that of perpendicular ordered structure. And $E_{\text{int}}-E_{\text{chain}}$ of disordered structure is lower than that of parallel ordered structure on the surface. This is consistent with the results of previous studies [46, 47, 58]. However, C19 molecules form perpendicular ordered structure when $E_{\text{int}}-E_{\text{chain}}$ is less than 4000kcal/mol because of chain fold.

As the simulation temperature changes, E_{int} and E_{chain} change correspondingly and *n*-alkane molecules form different orientation structures. The difference between E_{int} and E_{chain} of ten kinds of *n*-alkane molecules on graphene surface at different temperatures are shown in table S1 of the Supporting Information. Only when $E_{\text{int}}-E_{\text{chain}}$ is high enough, *n*-alkane molecules can form ordered structure on graphene surface. In addition, even if $E_{\text{int}}-E_{\text{chain}}$ is high, the ordered structure can't form when the temperature is too low. When $E_{\text{int}}-E_{\text{chain}}$ is about 4000kcal/mol, short *n*-alkanes are perpendicular to the surface. When $E_{\text{int}}-E_{\text{chain}}$ is about 2000kcal/mol, *n*-alkanes are parallel to the surface. But when long *n*-alkanes form perpendicular ordered structure on the surface, $E_{\text{int}}-E_{\text{chain}}$ is less than 4000kcal/mol due to chain fold. When $E_{\text{int}}-E_{\text{chain}}$ is small, *n*-alkanes are disordered on the surface.

4. Conclusions

In this paper, we discuss the isothermal orientation process of ten kinds of *n*-alkane molecules on graphene surface at different temperatures in detail. We find that *n*-alkanes can form disordered structure, perpendicular ordered structure, parallel multi-layer structure on graphene surface. The longest *n*-alkane chain that forms perpendicular orientation is C16. The shortest *n*-alkane chain that forms parallel multi-layer ordered structure is C20. C17, C18 and C19 chains arrange perpendicularly to the graphene surface at relative low temperature and form parallel multi-layer structure at relative high temperature. When temperature is too low or high enough, the *n*-alkanes form disordered structures on graphene surface. It is also found that chain fold happens for long *n*-alkanes in perpendicular ordered structure. Due to the occurrence of chain fold, the height of the perpendicular ordered regions are smaller than the extended molecule. In addition, the formation process of fold chain is described by torsion angle and R_{ed} . When annealing procedures are performed on the system, the orientation of C18 molecules are irreversible with temperature. The C18 molecules are favorite forming perpendicular orientation at fast cooling rate and parallel orientation at slow cooling rate. Only one orientation appears for C18 during the annealing procedure. The parallel and perpendicular orientation can both obtained by isothermal MD simulations at different temperatures.

The chain length and simulation temperature play important role in the orientation of *n*-alkanes on graphene surface. The ordered structure of *n*-alkanes depends on the interactions of *n*-alkane-graphene (E_{int}) and *n*-alkane-*n*-alkane(E_{chain}). When $E_{\text{int}}-E_{\text{chain}}$ is relatively strong enough, *n*-alkanes form ordered structure on graphene surface. But the ordered structure can't form at low temperature even if $E_{\text{int}}-E_{\text{chain}}$ is high. The *n*-alkanes relaxes slowly at low temperature. When $E_{\text{int}}-E_{\text{chain}}$ is high, perpendicular ordered structure form on graphene surface. When $E_{\text{int}}-E_{\text{chain}}$ is low, parallel ordered structure form on graphene surface. The chain fold leads to lower $E_{\text{int}}-E_{\text{chain}}$ for long *n*-alkanes in perpendicular ordered structure. When E_{int} is close to E_{chain} , *n*-alkane molecules form a disordered structure on the surface.

Our simulations give valuable insights into the mechanism of the two kinds of orientation formations of the *n*-alkanes adsorbed on graphene surface at different simulation temperatures, which is difficult to reveal experimentally, especially at atomic-scale description the orientation. The surface coverage is important during the orientation of *n*-alkanes on graphene surface. More research is needed to further investigate the influence of the surface coverage on the orientation in the future.

Declarations

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Conflicts of interest/Competing interests: The authors declare no conflict of interest.

Availability of data and material: All raw data are available from the authors upon request.

Code availability: N/A

Authors' contributions: All the authors contributed to the design and implementation of the research, analyzed, revised the results and wrote the manuscript. Zhi Meng Zhang, Hua Yang, Jun Xia Shi and Hui Zhang did the calculations of the original manuscript. Zheng Guo Huang and Jia Jun Wang performed the simulations of the revised manuscript.

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Figures

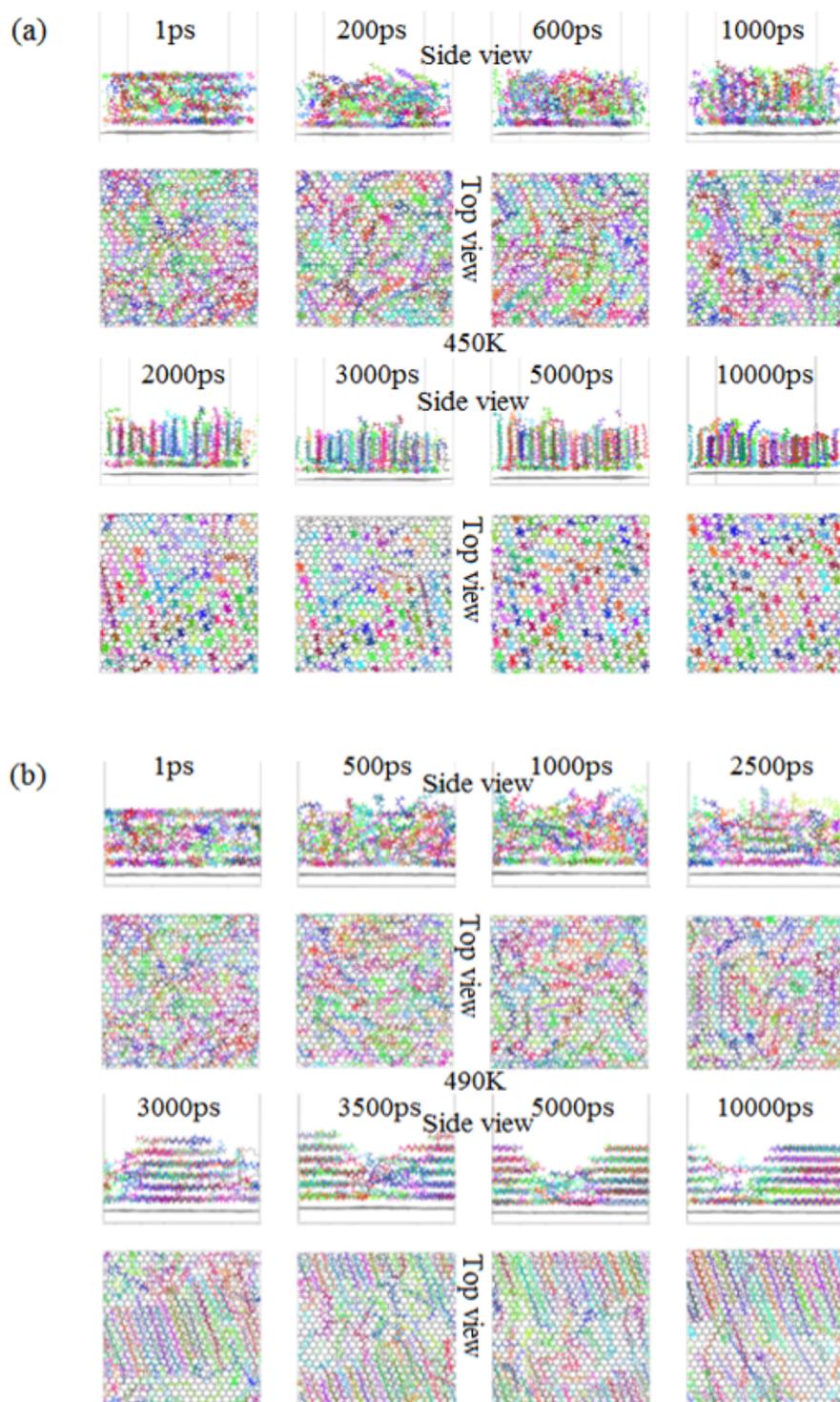


Figure 1

The isothermal orientation processes of 79C19/GRA at 450K (a) and 490K (b).

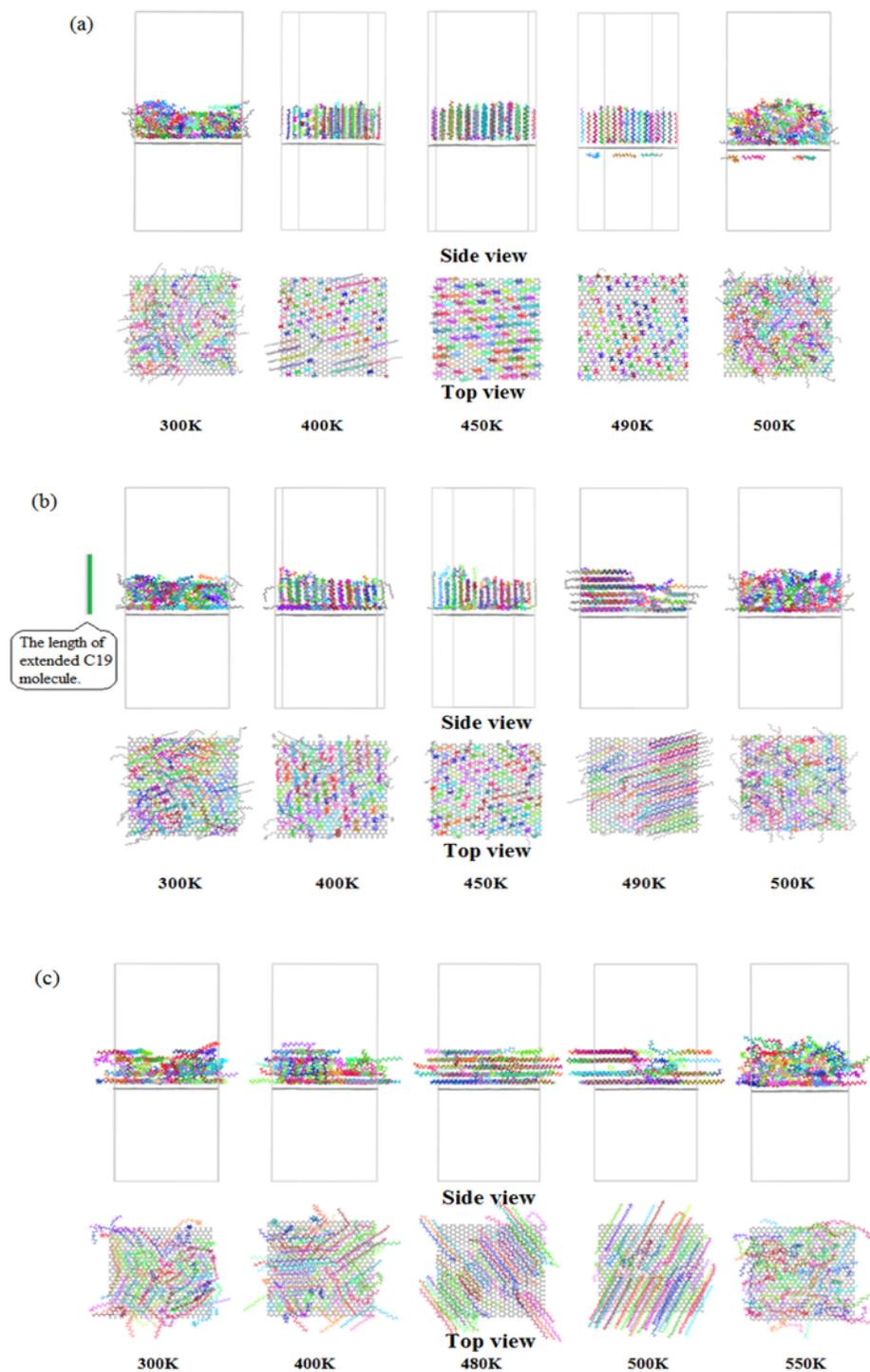


Figure 2

The final conformations of C13, C19, C25 molecules on graphene surface at different temperatures. (a)115C13/GRA (b)79C19/GRA (c)60C25/GRA. The length of extended C19 molecule is marked in Figure 2(b).

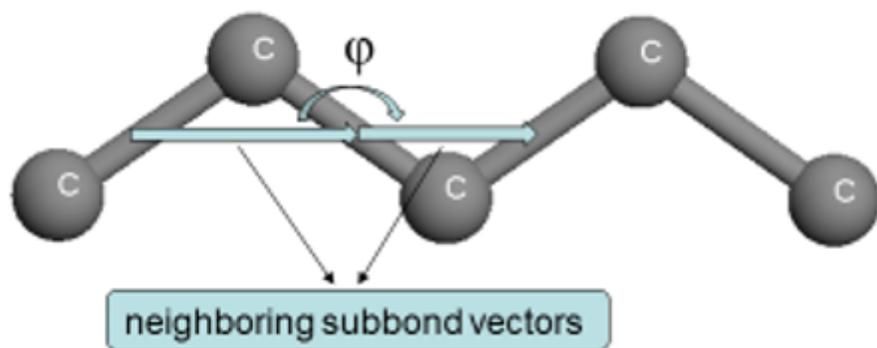


Figure 3

Schematic drawing of the angle ϕ and the subbond vectors.

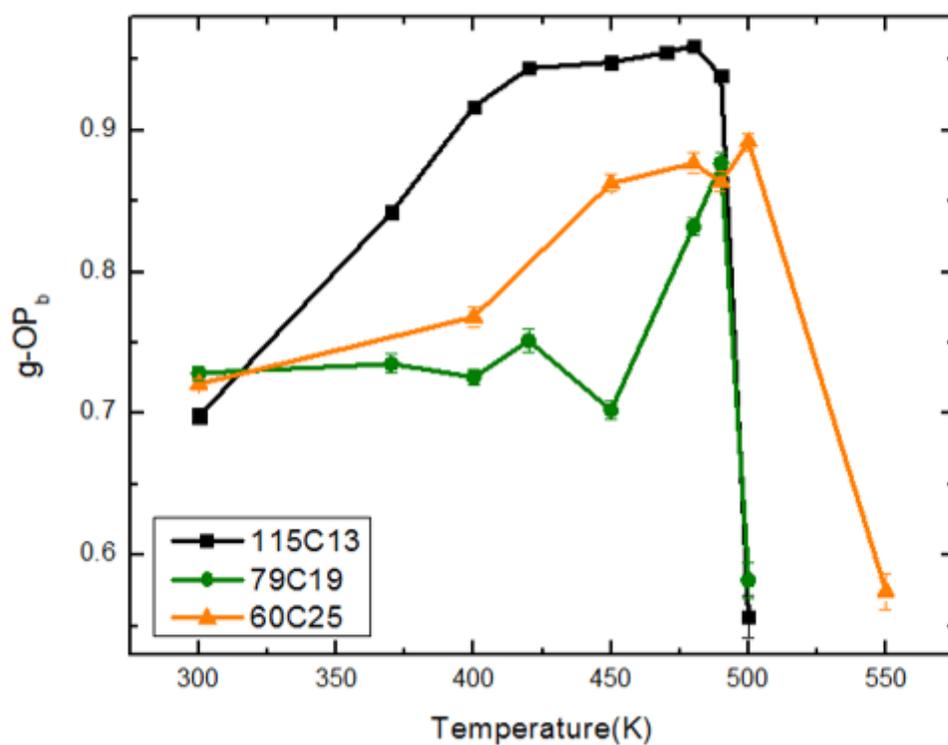


Figure 4

The global orientation order parameter $g-OP_b$ for C13, C19 and C25 molecules on graphene at different temperatures.

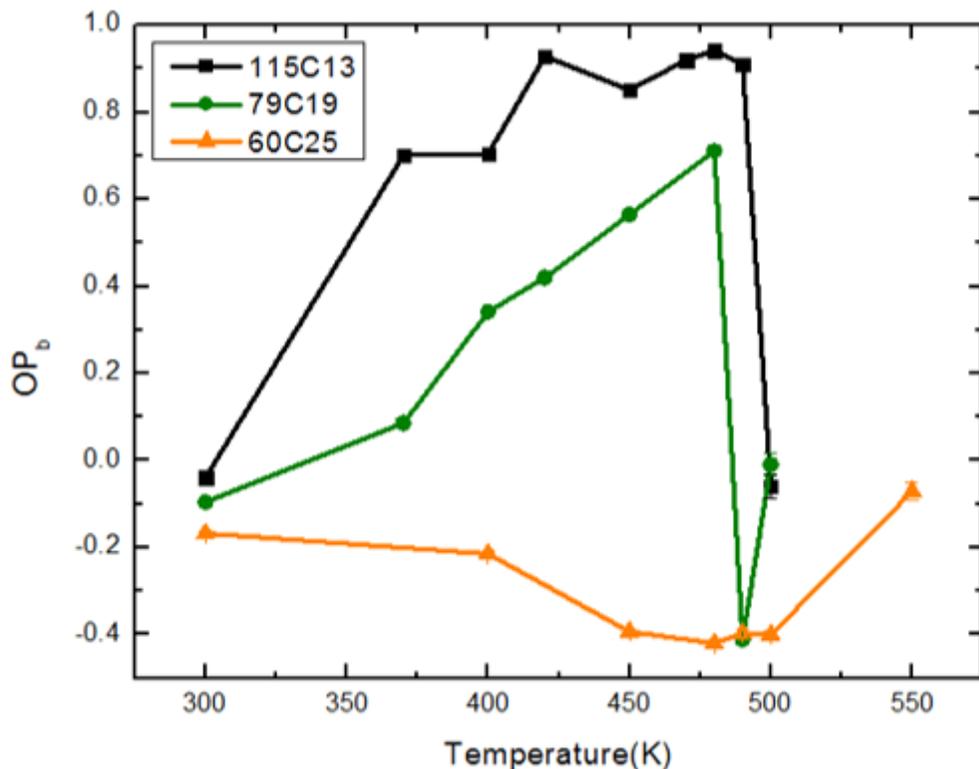


Figure 5

The z axis bond-orientation order parameter for C13, C19 and C25 molecules on graphene at different temperatures.

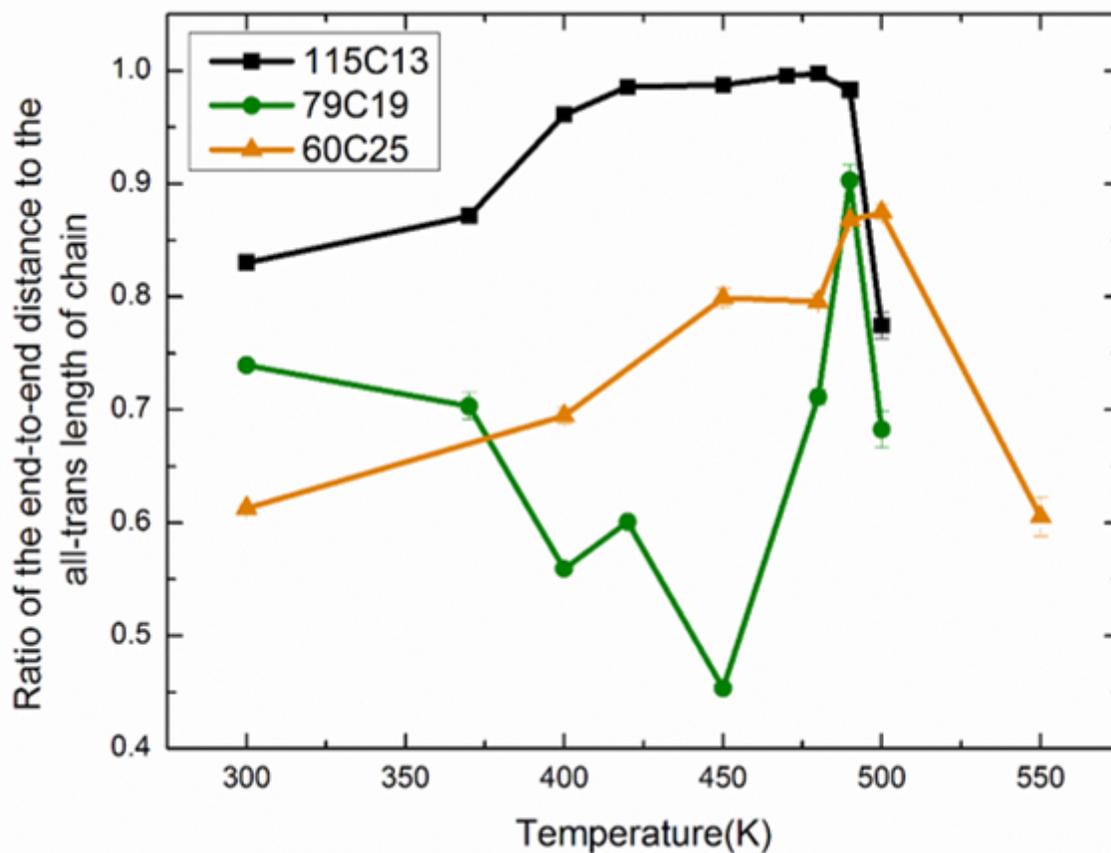


Figure 6

The ratio of average end-to-end distance to the all-trans length (Red/Rall-trans) of the last 1000 configurations of 115C13/GRA, 79C19/GRA, 60C25/GRA at different temperatures. The error bars are the standard deviation calculated from the average (9001–10,000ps).

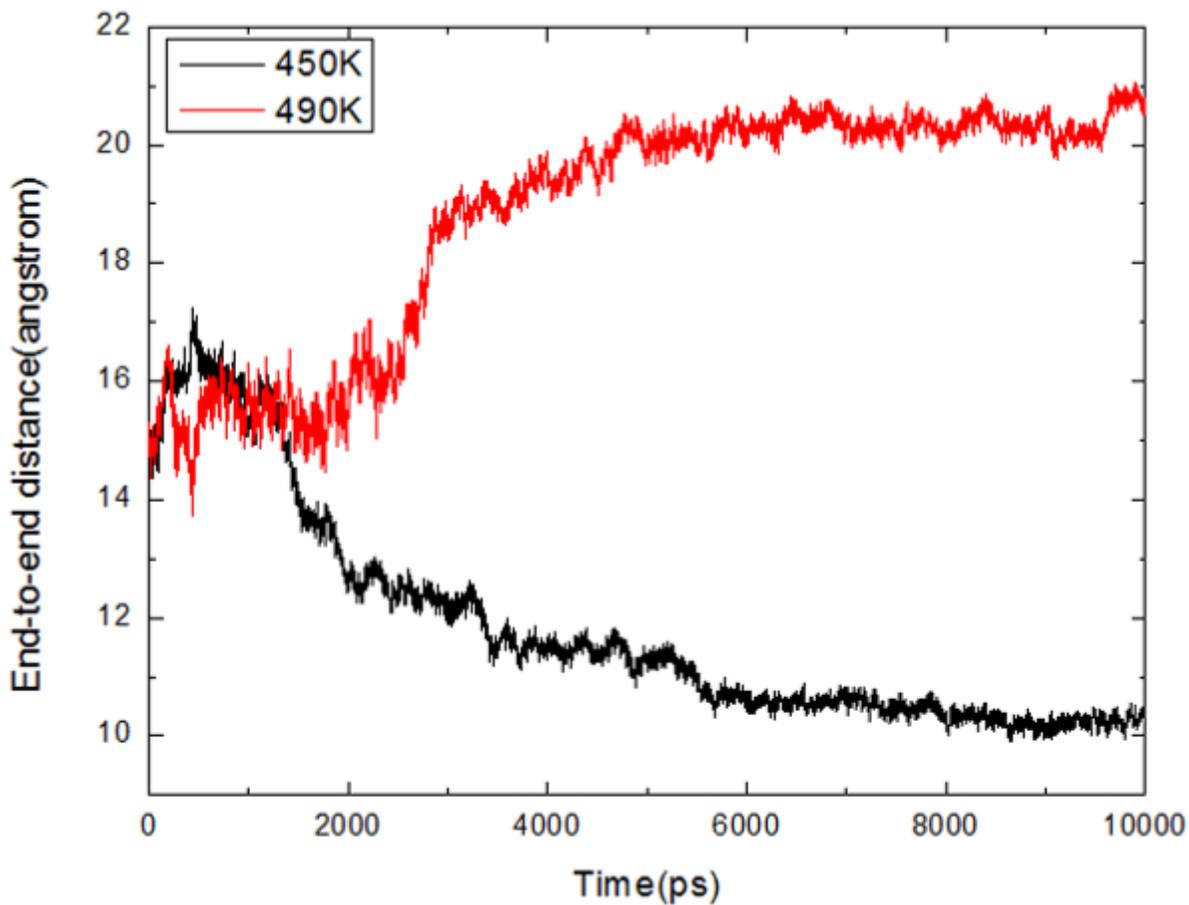


Figure 7

The time evolution of the average end-to-end distances of 79C19/GRA on graphene surface at 450K and 490K.

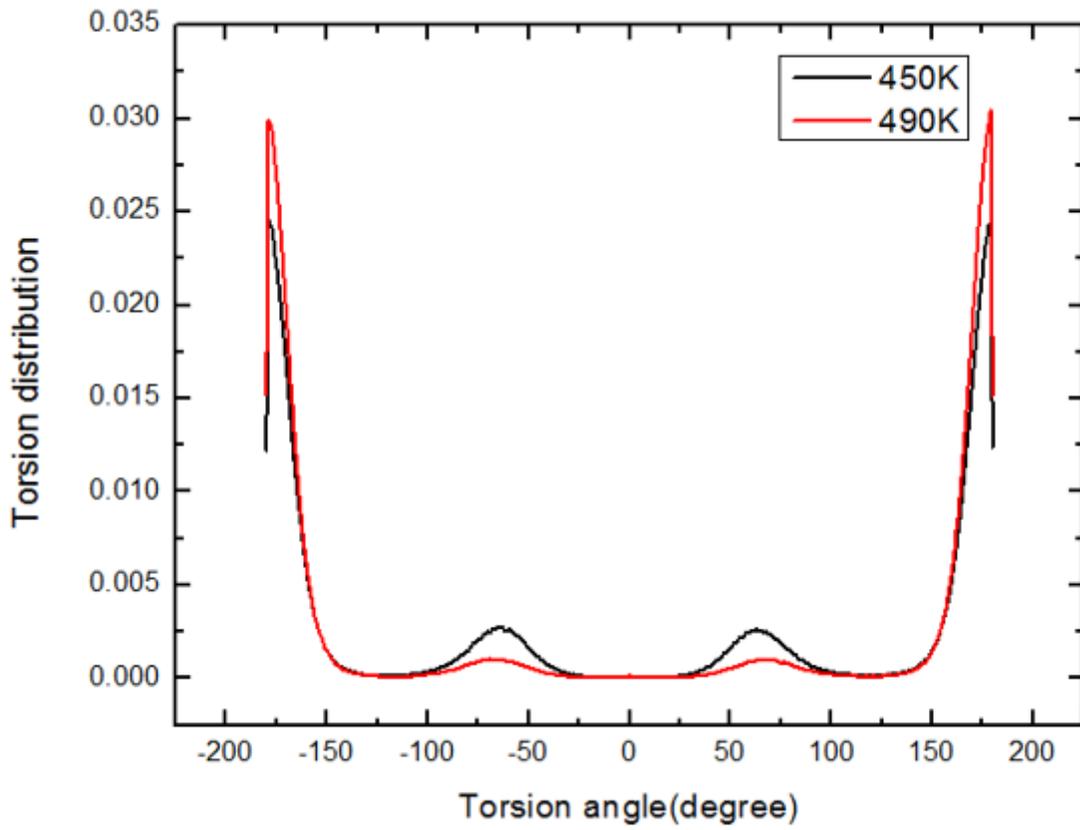


Figure 8

The C-C-C-C torsion angle distribution of 79C19 molecules on graphene surface at 450K and 490K.

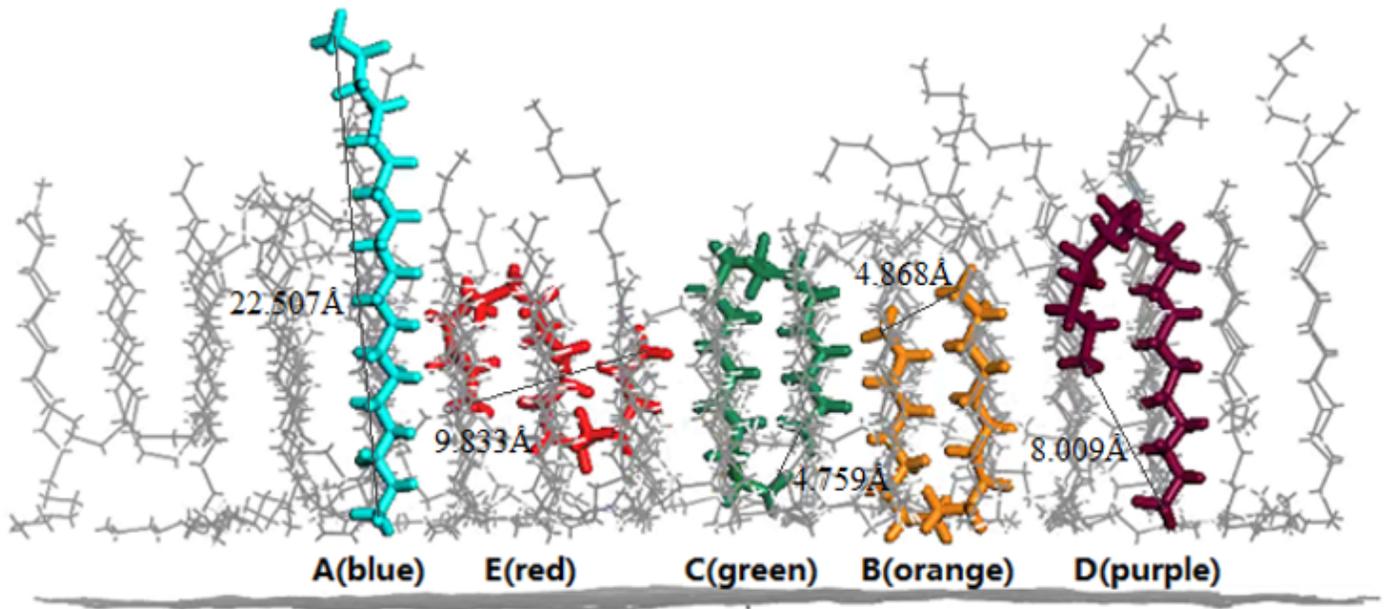


Figure 9

The final conformations of 79C19 on graphene surface at 450K after 10,000ps NVT MD simulations. The end-to-end distance is marked.

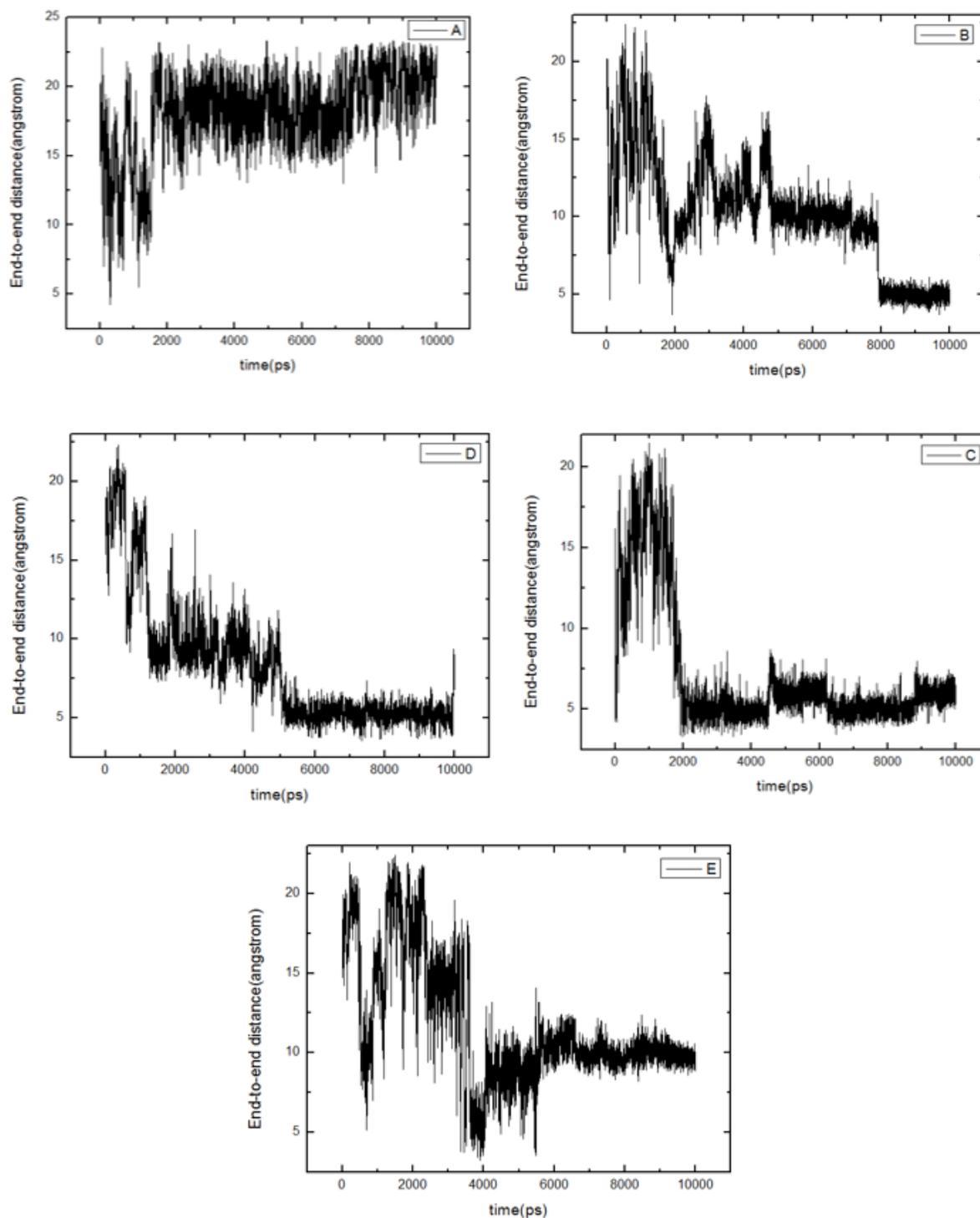


Figure 10

The time evolution of the end-to-end distance of C19 A, B, C, D and E at 450K.

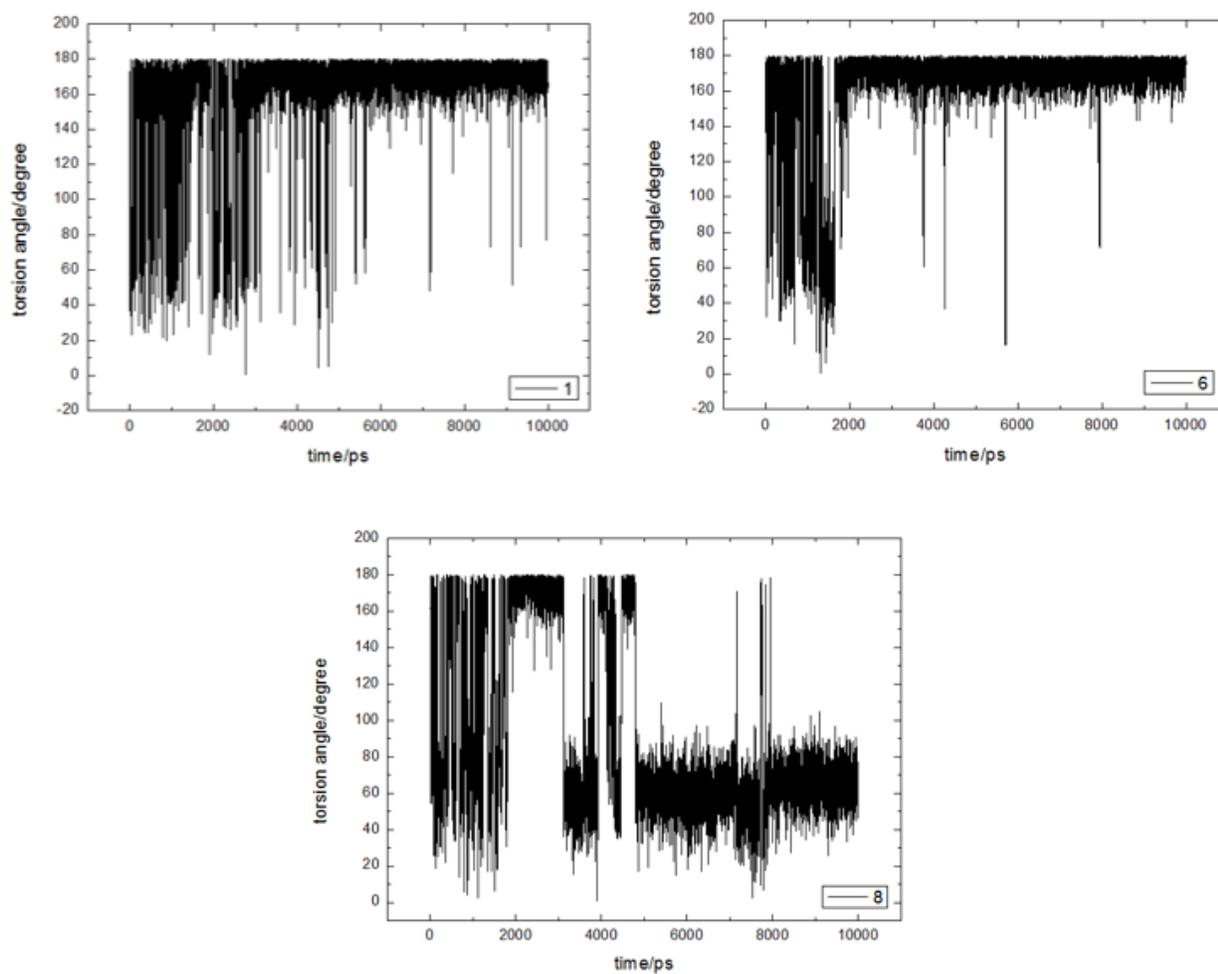


Figure 11

The evolutions of torsion angles 1, 6, 8 of C19 B on graphene during MD simulation at 450 K. Negative values are interpreted as their absolute value.

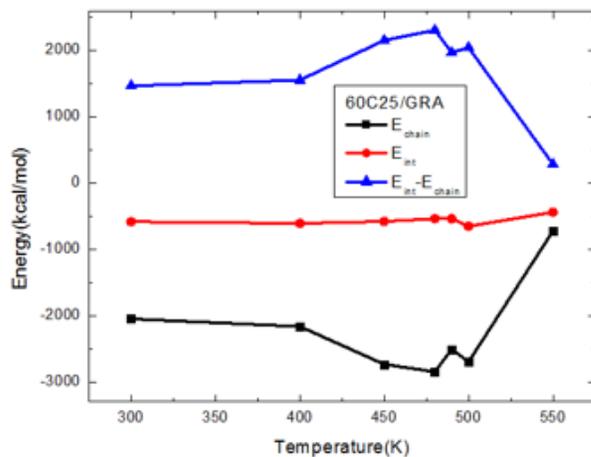
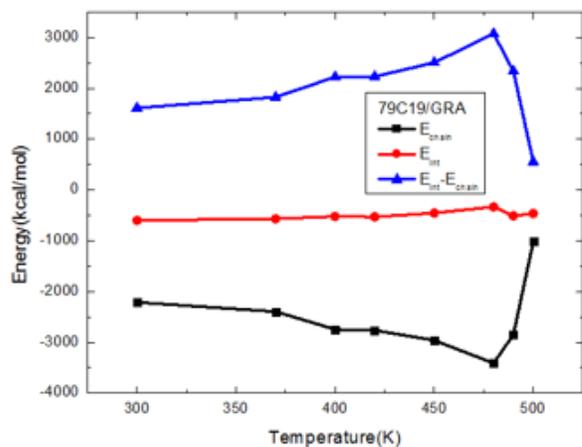
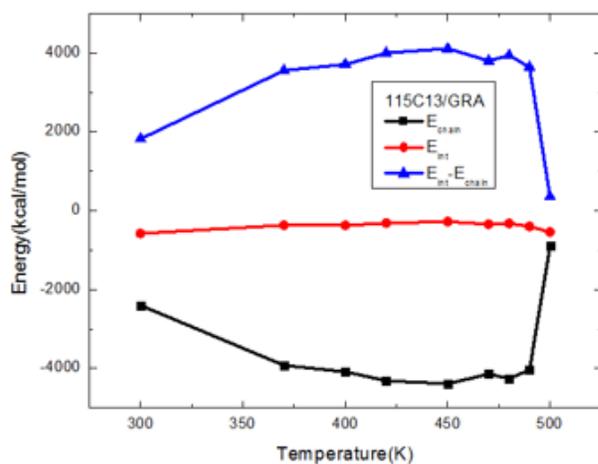


Figure 12

The variation of n-alkane-graphene interaction energy (E_{int}), n-alkane-n-alkane interaction energy (E_{chain}) and the difference between E_{int} and E_{chain} ($E_{int} - E_{chain}$) for three systems with the temperature increasing.

Supplementary Files

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