Effects of chirality and stacking on the thermal expansion effects of graphene

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Abstract

Graphene has huge application potential in the field of micro-nano devices, and due to the micro/nano-level application size, the thermal expansion coefficient of graphene has a certain impact on device performance. In this paper, a comprehensive study was carried out by molecular dynamics on the in-plane and through-plane thermal expansion effect of graphene. First of all, the in-plane thermal expansion coefficients of zigzag and armchair graphene were analyzed; they were similar and relatively close to the experiment value in the temperature range of 223–428 K. Secondly, the through-plane thermal expansion effect of double-layered graphene was investigated; the thermal expansion coefficient of through-plane was an order of magnitude larger than that of in-plane. Finally, the influence of graphene stacking on the thermal expansion effect was studied; Order-stacked graphene has a greater thermal expansion effect than that of AB- and ABC-stacked graphene. These discoveries in this article are of great significance to the development and application of graphene-based micro-nano devices.

1. Introduction

Graphene is a two-dimensional carbon nanomaterial with many remarkable performances, which is considered a revolutionary material in the future [1–3]. Electrical and thermal conductivity are among the excellent properties, with electron mobility of 200,000 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} and thermal conductivity of 5300 W m\textsuperscript{−1} · K\textsuperscript{−1}. At present, graphene has been widely applied in integrated circuits, electrodes, field-effect transistors, enhanced materials, and sensors, etc [4–9].

Thermal stress is the main cause of device failure [10, 11]. The coefficient of thermal expansion (CTE) is different in different materials, which leads to the different deformations and the CTE mismatch is formed; and due to the difference in deformation between the materials, thermal stress is generated. Similarly, the thermal expansion effect is a key factor affecting the performance and reliability of graphene. In integrated circuits [12], the graphene size has even reached to the nanometer level, which places extremely high requirements on the control of graphene size. On the one hand, in high-precision manufacturing, thermal expansion will bring great difficulties to the design and manufacturing of graphene devices, the residual stress cannot be eliminated; on the other hand, due to the harsh work environment of high temperature and the heating of the device itself, they will aggravate the thermal expansion of graphene and lead to large thermal stress, resulting in the degradation of the performance and reliability. Consequently, it is necessary to understand the thermal expansion effect of graphene, which is very important for the preparation and the good performance of graphene-based devices. Therefore, the research on the thermal expansion effect of graphene is particularly urgent and important.

At present, there have been some studies on the thermal expansion of graphene. Experimentally, many studies have shown that CTE of graphene at room temperature is $-7 \times 10^\text{−6}$ K\textsuperscript{−1} approximately [13]. Yoon \textit{et al} estimated the CTE of monolayer graphene in the temperature range of 200 to 400 K based on the temperature-dependent Raman spectroscopy, the result showed that the CTE was negative in the whole temperature range...
with a room temperature value of \((-8.0 \pm 0.7 \times 10^{-6} \text{ K}^{-1}\)) [14]. Mosso et al reported the heat-transfer measurements through atomic junctions and analyzed the thermal conductance of single-atom gold contacts at room temperature [15]. Dolleman et al verified the prediction theory that large temperature differences between the in-plane and through-plane acoustic phonon baths in locally heated suspended graphene. This also partly explained the reason why the CTEs in the in-plane and through-plane of graphene are different [16]. However, it is difficult to understand the microscopic origins of the thermal expansion of graphene in experiments, which is a better motivation for theoretical studies. Consequently, there are some studies on the thermal expansion effect of graphene through theoretical calculation. Mounet et al used the density functional theory method to study the graphene CTE. The results showed that in the temperature range of 0 to 250 K, the monolayer graphene was in a state of thermal contraction, that is, the CTE was negative [17]. Jiang et al analyzed the thermal properties of graphene by the non-equilibrium Green’s function method. The graphene CTE had a large negative region at low temperatures and very small value at the high-temperature limit, and the value of the CTE at 300 K was \(-6 \times 10^{-6} \text{ W m}^{-1} \cdot \text{K}^{-1}\) [18]. Zakharchenko and Islam et al found that the graphene CTE was negative within a certain temperature range through the molecular dynamics methods, but the relationship between the CTE and the temperature was nonlinear [19, 20]. Hamid Ghasemi et al found that the results obtained by the AIREBO potential function were in good agreement with the results reported by previous scholars [21].

However, the current research on the thermal expansion of graphene is not very comprehensive. Many studies analyzed the graphene CTE in a large temperature range, but the research in the temperature range with more daily contact between 223 K and 423 K was not detailed enough. Besides, comparative analysis of the CTE of different chiral graphenes is relatively rare. Generally, multi-layer graphene can be stacked in various ways, which leads to different properties [22–24]. So far, there is no relevant report on the thermal expansion coefficient of different stacked multi-layers graphene, and the understanding of that is not enough. Therefore, to fully study the thermal expansion effect of graphene, it is necessary to conduct a comprehensive study on the thermal expansion effect of graphene with different chirality and stacks.

In this paper, a comprehensive study of the thermal expansion effect of graphene was investigated via molecular dynamics, which different chirality and stacking were considered; the temperature range with more daily contact between 223 K and 423 K was focused. Firstly, a comparative analysis of the in-plane CTE of zigzag and armchair graphene was investigated. On this basis, this paper studied the thermal expansion effects of different chiral graphene. Finally, to explore the impact of different stacks on the graphene CTE, this paper analyzed the thermal expansion effects of different four-layer stacked graphene. It has important practical significance for the preparation and performance research of graphene-based micro-nano devices.

2. Method

Newton’s classic mechanics and statistical mechanics are the foundation of molecular dynamics [25]. Atoms are the basic computation units of molecular dynamics, in which the interaction between electrons is ignored, and hence the calculation of molecular dynamics is much simpler than that of the first principle theory. Newton equation is the core formula of molecular dynamics, and it can be described as:

\[ F_{ij} = \frac{dV_{ij}}{dr_{ij}} \]  

(1)

where \(F_{ij}\), \(V_{ij}\), and \(r_{ij}\) are the force, the potential energy, and the distance between atoms, respectively.

Molecular dynamics need to be carried out under a certain ensemble. The set of different microscopic states with the same thermodynamic state is called an ensemble. The isothermal-isobaric ensemble (NPT) [26] means that the number of atoms \(N\), pressure \(P\), and temperature \(T\) of the model remain unchanged, which is selected here. On the other hand, the molecular force field is used to describe the interaction between molecules. COMPASS [27] is the ab initio molecular dynamics force field with higher computational accuracy and is used in this calculation. To explore the effect of temperature on the graphene CTE, the molecular dynamics with COMPASS force field and NPT ensemble at a temperature range of 223 to 423 K were implemented. In the calculation, the ‘Andersen’ and ‘Berendsen’ were selected to control the temperature and pressure; and the ‘Atom-based’ and ‘Ewald’ were used to calculate van der Waals and electrostatic interactions. The cutoff value of ‘atom-based’ was set as 8.5 Å.

3. Results and discussion

3.1. In-plane thermal expansion coefficients of graphene

The main reason for the thermal deformation of graphene is the thermal expansion effect. Thermal expansion refers to the phenomenon of expansion and contraction of an object due to temperature changes. The CTE can
can be described as the relative change in length or volume of an object when the temperature increases by 1 K, which can be described as:

\[ \alpha = \frac{1}{S_0} \frac{S - S_0}{T - T_0} = \frac{\Delta S}{\Delta T S_0} \]

where \( \alpha \) is the surface graphene CTE, \( S \) is the graphene area at the sampling temperature, \( S_0 \) is the area of the sample area at the initial temperature, \( T \) is the simulated temperature, and \( T_0 \) is the initial temperature.

In general, graphene is divided into two types of chirality, zigzag and armchair. Figure 1 shows the specific structure of the armchair and zigzag graphene, the crystal structure of zigzag graphene is rhombic while the crystal structure of armchair graphene is dimetric. Obviously, the difference in their chirality is that their crystal directions are different, in which the angles of the unit cell of zigzag and armchair graphene are 120° and 90°, respectively.

Graphene with different chirality has different properties. What is the effect of chirality on the graphene CTE? In order to clarify this problem, this article first conducted a study on the CTE of different chiral graphenes. Figure 2 depicts the trend of the in-plane CTE of different chiral graphenes at different temperatures. In general, single-layer zigzag graphene has a larger CTE than that of armchair graphene. Moreover, the zigzag graphene has a much larger CTE in the temperature range of 50–223 K. In this temperature range, their CTE is relatively large, with a value of about \( 10^{-6} \) K\(^{-1} \). In fact, in the temperature range of 50–223 K, the thermal deformation of graphene is relatively small, but due to the small temperature range, the CTE is relatively large.

![Figure 1. The schematic diagrams of the chiral structure of zigzag (a) and armchair (b) graphene. The angle of the unit cell of zigzag and armchair graphene is 120° and 90°, respectively.](image)

![Figure 2. The in-plane CTE of different chiral graphene at different temperatures.](image)
However, in the temperature range of 223–348 K, the CTE of zigzag graphene is much the same as that of armchair graphene, and it does not show a linear relationship, but shows a certain degree of randomness. The value of the CTE is $(5–9) \times 10^{-6} \text{ K}^{-1}$. At room temperature of 298 K, the calculated CTE is about $6 \times 10^{-6} \text{ K}^{-1}$, which is close to the previous result.

Due to the influence of the two-dimensional properties of a single layer of graphene, which exhibits thermodynamic instability, graphene will be wrinkled to maintain a stable state [28]. Moreover, the wrinkles of graphene will gradually increase with the temperature. Figure 3 shows graphene wrinkles at different temperatures, such as 10 K, 100 K, 223 K, 298 K, 423 K, and 800 K. It can be found that the graphene will begin to wrinkle at 10 K, the wrinkles will gradually increase with the temperature, but the increasing degree of the wrinkle will gradually decrease.

### 3.2. Through-plane thermal expansion phenomenon of multilayer graphene

Graphene is a layered two-dimensional material. Therefore, the graphene CTE in the in-plane and through-plane will be different. For this reason, this paper studies the effect of temperature on the CTE of the double-layered graphene. Similarly, the zigzag and armchair graphenes are also selected as the research objects. The double-layered graphene is symmetrically stacked, that is, the atoms are completely coincident. The distance between the double-layered graphene was set to 2.65 Å. After the structure optimization calculation via molecular dynamics, the layer distance is up to 4.33 Å, which is precise and reliable [29]. Interestingly, the wrinkles of the upper and lower layers of graphene are symmetrical. Figures 4(a) and (b) are the side view and top view of the graphene in the wrinkled state respectively. The atoms will deviate from the coincident state to the deviated state gradually, and the distance and angle of the deviating atoms are the same. This is of great significance to the study of the properties of graphene.

The graphene has different wrinkles at different temperatures, which leads to the difficulty in the spacing measurement of the graphene layer. Here, the best-fitting plane for graphene's atomic layer is created in our calculation and thus the distance between the two fitting planes is regarded as the distance between the two
wrinkled graphene layers. The best-fit plane is defined as a plane where the (mass-weighted) root mean square distances from the plane to the selected atoms are minimized, as showed in figure 5. It can be seen from the top view that some atoms of graphene are higher than the fitting surface while some atoms are lower due to the wrinkles. The side view indicates the location of the fitting surface.

As for the through-plane CTE, the calculation results in this paper show that their values are all on the order of $10^{-5}$. The reason is that the van der Waals force binding towards the graphene layers is much smaller than the covalent bond between the atoms in the graphene surface; hence the through-plane CTE is more affected by the temperature. However, because the layer spacing of graphene changes in a small range, the through-plane CTE change with temperature is messy. Moreover, the through-plane CTE is more affected by errors. Therefore, the changes in graphene layer spacing are more appropriate to analyze the effects of through-plane thermal expansion than CTE. Figure 6 depicts the trend of the layer spacing of double-layered graphene with zigzag and armchair chirality at different temperatures. The interlayer spacing of armchair graphene is generally larger than that of zigzag graphene. At room temperature 273 K, the interlayer spacing is 3.435 Å, which is consistent with the results of previous studies [30, 31]. Similarly, within the temperature range of 223–423 K, the graphene CTE...
does not show a linear relationship but shows a certain degree of randomness. The interlayer spacing is in the range of 3.43–3.55 Å, as shown in the inset. In general, the thermal expansion of graphene is increased with temperature, that is, the distance between graphene layers is going to increase. When the temperature increases significantly, the spacing of armchair graphene also increases greatly, and the layer spacing reaches to 3.62 Å at 1000 K.

Generally, multi-layer graphene can be stacked in various ways, which leads to different properties. Graphene stacking methods mainly can be divided into three ways [22–24], Order, Bernal (AB), and Rhombus stacking (ABC). Figure 7 illustrates these three different stacking ways of four-layered graphene. The initial inter-layer spacing is 2.5 Å. In the Order stacking, the atoms of each layer of graphene are well-aligned; the atoms of each layer are completely overlapped watched from the top view. In the AB stacking, every two layers of graphene will form a cycle, that is, the graphene atoms of the first (second) and the third (fourth) layers are overlapped. In the ABC stacking, every three layers of graphene to form a cycle, that is, the atoms of the first and the fourth layers are overlapped. Obviously, a highly symmetrical structure occurs in Order stacking, while the structure in ABC stacking is relatively complicated; these different stacking ways lead to many different properties of graphene [32–34], such as adsorption, band gap, and doping. Similarly, graphene stacking should also have a certain impact on CTE.

The influence of different stacking and temperatures on the thermal expansion effect of graphene was studied here. The current research results of the interlayer spacing of multilayer graphene are diverse, but the interlayer spacing is 3.4 Å approximately [35–37]. Figure 8 shows the coupling relationship between the interlayer spacing and the temperature of four-layered graphene with different stacking. Different chirality has a relatively large effect on the thermal expansion of graphene. In the temperature range below 400 K, the average interlayer spacing of graphene is between 3.4–3.5 Å, which is increased with temperature. In the high-temperature range, the difference is relatively big. At 1000 K, the layer spacing of Order, AB, and ABC is 3.55 Å, 3.65 Å, 3.6 Å, respectively. The Order, AB, and ABC stackings of the armchair- and zigzag-graphenes are
represented by O-A, O-Z, AB-A, AB-Z, ABC-A, and ABC-Z, respectively. In the Order stacking, the average layer spacing of O-A graphene is larger than that of O-Z graphene, which is consistent with the results of the double-layered graphene mentioned above; at a temperature of 273 K, the average spacing is 3.442 Å. As in the AB stacking, the average layer spacing of AB-A graphene is also larger than that of AB-Z graphene; at a temperature of 273 K, the average spacing is 3.429 Å. In the ABC stacking, the interlayer spacing of ABC-A and ABC-Z graphene is relatively close; at a temperature of 273 K, the average spacing is 3.429 Å. We hypothesized that the ABC stacking strengthened the interaction between graphene layers, making the effect of different chirality on graphene relatively weaker. In general, Order-stacked graphene has a greater thermal expansion effect than that of AB- and ABC-stacked graphene; in addition, comparing zigzag and armchair, it can be found that the thermal expansion stability of zigzag graphene is better than that of armchair graphene.

To better understand the influence of temperature, chirality, and stacking on the thermal expansion effect of graphene, the vertical deformation of each layer in double-layered and four-layered graphene at 298 K was analyzed. As shown in table 1, the maximum vertical deformations of graphene under different conditions are recorded.

Here, we specify that the bottom layer of graphene is the first layer, and the top layer is the fourth layer. For double-layered graphene with Order stacking, the deformation of the zigzag graphene is larger than that of armchair graphene, which is consistent with the above calculation. After a comparative analysis, it believes that the layer-wise interaction of zigzag graphene is stronger than that of armchair graphene when the stacking is Order, thus the deformation is going to get bigger. Meanwhile, it is also due to the coupling effects of this interaction and the deformation of graphene, the thermal expansion deformation of zigzag graphene is smaller than that of armchair graphene. This trend of graphene also applies to four-layer graphene. Different from Order stacking, the deformation phenomenon of AB-stacked graphene is opposite to that of Order stacking, that is, the deformation of armchair graphene is larger than that of zigzag graphene, indicating that the AB stacking has a greater impact on the thermal expansion effect of the graphene, and this impact goes beyond the chiral effect. As for the ABC stacking, the deformations of the armchair and zigzag graphene are relatively close, which also conforms to the result that the through-plane thermal expansion of armchair and zigzag graphene with ABC stacking are similar; this shows that in multi-layer stacked graphene, the ABC stacking is the main influencing factor of graphene deformation and thermal expansion effect. In addition, analyzing the deformation of each layer of graphene, the deformation of the bottom layer (the first layer) is generally small and the deformation of the top layer is the largest (the fourth layer).

4. Conclusion

In this paper, a comprehensive study was carried out by molecular dynamics on the in-plane and through-plane thermal expansion effect. In general, single-layer zigzag graphene has a larger CTE than that of armchair graphene. In the temperature range of 223–348 K, the CTE of zigzag and armchair graphene has not much difference, and it does not show a linear relationship, but shows a certain degree of randomness. At room temperature of 298 K, the calculated CET is about $6 \times 10^{-6} \text{K}^{-1}$. As for the through-plane, the in-plane thermal expansion coefficient of the double-layered graphene is larger than that of the through-plane; the CET value is on the order of $10^{-5}$. What is more, the interlayer spacing of armchair graphene is generally larger than that of zigzag graphene. On the other hand, the Order-stacked graphene has a greater thermal expansion effect than that of the AB- and ABC-stacked graphene; besides, the thermal expansion trend and stability of zigzag graphene are better than that of armchair graphene. These discoveries in this article are of great significance to the development and application of graphene-based micro-nano devices.
Meanwhile, the research is noting that this wrinkling plays a key role in the thermal expansion behavior of graphene. However, this article is preliminary in the study of graphene wrinkling. We will show more graphene wrinkling behaviors in the next research, such as the influence of wrinkling on the average deviation from the flat plane of the carbon atoms and the carbon-carbon bond length, and the comparing of the free thermal expansion to constraint thermal expansion, etc.

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