Structural transition from a ring to a folded structure of a seamless nanobelt

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Abstract
Stable structures of a rolled seamless belt of atoms arranged in a two-dimensional honeycomb lattice such as a carbon nano-belt, transit from a ring-shaped structure with a rotational invariance to folded structures as the circumference of the belt increases. Using molecular mechanics, we consider the size dependence of the structures obtained by simulated annealing. In addition, the relationship between the variety of metastable structures and the rate of temperature decrease during annealing is also examined. Furthermore, we investigate the effects of the van der Waals interaction between the surfaces on the structural transitions.

1. Introduction

Creating three-dimensional structures from two-dimensional sheets such as Kirigami is one of the important targets of nanotechnology, and much effort has already been devoted to it [1–3]. Graphene sheets are promising materials for realizing this technology, and carbon nanotubes are typical examples of three-dimensional carbon structures [4]. Furthermore, several novel carbon structures such as Möbius graphene and penta-graphene have been studied theoretically [5, 6]. The mechanical properties of a graphene sheet are mainly dependent on its honeycomb-structure. Thus, we investigate a rolled seamless single layer of atoms arranged in a two-dimensional honeycomb lattice, which hereinafter is referred to as a “honeycomb belt” [7–9]. In particular, the relationship between the stable structures and the size of the honeycomb belts is examined within the framework of molecular mechanics.

We define a stable structure as the configuration of atoms in the lowest energy state. In molecular mechanics, potential energy is defined as the sum of the different potential energies. Among them, the energy of angle bending (angle energy) is the main contributor to the potential energy in a honeycomb belt. The internal angle of a flat hexagonal lattice is 120° when the angle energy is at a minimum in many honeycomb structures. Thus, the angle energy usually increases with bending. The simplest structure of the honeycomb belt is a ring-shaped structure with a rotation invariance, which hereinafter is referred to as the “perfect ring”. A carbon nanotube with a small radius is a good example of a perfect ring [9].

If the rotation invariance of the honeycomb belt is broken, the angle potential between the two coupling bonds depends on the position of the bonds in the belt. The angle energies of some angles of the asymmetrical belt are greater than that of the perfect ring, while the remaining angle energy may be less than that of the perfect ring. Accordingly, by breaking the rotation invariance, the total angle energy can be lower than that of the perfect ring by breaking the rotation invariance; if the circumference length is sufficiently long, the total potential energy may be reduced by partially bending a perfect ring and increasing the flat area.

The van der Waals energy is usually negative, and the magnitude increases as the distance between the surfaces of the honeycomb belt decreases [10, 11]. Conversely, the repulsive force due to overlapping electron orbitals increases rapidly as the distance between the surfaces decreases. As a result, if the Lennard-Jones potential is the dominant term in the potential energy, a folded structure with a particular separation distance between the surfaces is preferable for a stable structure. Since the van der Waals energy is proportional to the area of the facing surface, the effect of reducing the total potential energy due to the van der Waals interactions...
becomes significant especially for large belts. Consequently, it is possible to reduce the sum of the angle energy and van der Waals energy by deforming a perfect ring into a folded structure.

There are many other factors involved in structural transitions. In this study, we focus on the non-uniformity of the force field parameters, especially for the bond and angle, and examine the dependence of the threshold value at which the structure changes from a ring structure to a folded structure on the non-uniformity of force field parameters. For instance, if the spring constants between the bond along the edges of the ring are larger than those of other bonds, does the transition occur for a smaller size? To answer such a question, the change in the structure during annealing is simulated using the molecular dynamics method. We show that the non-uniformity of the force field parameters strongly affects the structural transition.

The remainder of this paper proceeds as follows. In Section 2, we briefly explain the force field parameters of the molecular mechanics of a honeycomb belt. In addition, the initial configuration of the molecular dynamics, which is the stable structure of the perfect ring, is considered. The configuration of atoms of the perfect ring can be described by a few geometrical variables, such as bond lengths and angles, because of the rotational invariance. The minimum potential energy and geometrical variables are determined using the conjugate gradient method. In Section 3, we show that the structures of the honeycomb belts obtained by simulated annealing transits from ring structures to folded structures by increasing the size. In Section 4, we consider the contribution of the dihedral and improper interactions to the formation of the structures. The structural transitions of honeycomb belts without dihedral and improper interactions are simulated. In Section 5, the effect of the non-uniformity of the force field parameters on the structural transition is examined. In Section 6, the difference in the stable structure between the honeycomb belt with a zigzag edge and armchair edge is described. In conclusion, we summarize the relationship between the stable structure of nano-belts and their size. Furthermore, we also describe the continuous model.

2. Simulation model of a honeycomb belt

2.1. Force field parameters

In molecular mechanics, the total potential energy $E_{\text{total}}$ is defined by the summation of the following potentials: bond energy, angle energy, dihedral energy, van der Waals energy and improper energy:

$$E_{\text{total}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{van der Waals}} + E_{\text{improper}}.$$  \hfill (1)

We investigate a rolled seamless single layer of atoms arranged in a two-dimensional honeycomb lattice that minimizes the total potential energy. The initial structures are obtained by rolling up a honeycomb lattice, as shown in figure 1(a), by bonding the atoms along the left edge marked blue circles and the atoms along the right
edge marked by red circles. The resulting structure is identical to a zigzag carbon nanotube with a small width. The size of the resulting structure is determined by the number of atoms along the horizontal edge \( N_1 \) and vertical edge \( N_2 \) (see figure 1(a)). We focus on the special case \( N_1 \gg N_2 \). The total number of atoms \( N \) is \( 2N_1N_2 \).

We describe the interactions between atoms in the honeycomb belt using molecular mechanics and find a stable structure using the simulated annealing method. In molecular mechanics, the potential energy consists of the components of the covalent bond contributions and the Lennard-Jones potential. Furthermore, the components of the covalent consist of four terms: bond energy \( E_{\text{bond}} \), angle energy \( E_{\text{angle}} \), dihedral energy \( E_{\text{dihedral}} \), and improper energy. In the molecular system considered here, the contribution of improper energy to the total energy is shown later to be small.

The bond energy between two bonding atoms with bond labeled \( i \) is given by

\[
E_{\text{bond}}^i = \frac{k_{\text{bond}}}{2}(l_i - \alpha_i)^2,
\]

where \( l_i \) is the \( i \)-th bond length. In this study, we assume that the force constant \( k_{\text{bond}} \) and equilibrium bond length \( \alpha_i \) take three different values depending on the position as shown in figure 1(b). The angle energy of the angle formed by the three atoms is given by

\[
E_{\text{angle}} = \frac{k_{\text{angle}}}{2}(\theta_i - \beta_i)^2,
\]

where \( \theta_i \) is the angle labeled \( i \). As shown in figure 1(c), the angle energy of the considered honeycomb belt is characterized by five force constants \( k_{\text{angle}} \) and equilibrium angle \( \beta_i \). The dihedral energy, which is determined from the torsional rotation of four atoms about a central bond, is given by

\[
E_{\text{dihedral}}^i = k_{\text{dihedral}}^i [1 + \cos(n_i \omega_i + \delta_i)].
\]

The Lennard-Jones potential between atom \( i \) and \( j \) is given by

\[
E_{\text{LJ}}^{ij} = 4\epsilon_{ij} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6},
\]

where \( r_{ij} \) is the distance between the atom labeled \( i \) and \( j \). The Lennard-Jones potential takes a minimum value \(-\epsilon_j \) at \( r_{ij} = 2^{1/6}\sigma_{ij} \). Finally, the improper energy is defined

\[
E_{\text{improper}}^i = k_{\text{improper}}^i [1 + d_i \cos(n_i \Phi_i)],
\]

where \( \Phi_i \) is the improper dihedral angle (see [12] for details).

| \( i \) | \( \alpha_i (\text{Å}) \) | \( k_{\text{bond}} (\text{eV}/\text{Å}) \) |
|---|---|---|
| 1 | 1.398 | 40.0 |
| 2 | 1.385 | 41.8 |
| 3 | 1.307 | 54.2 |

Figure 2. Atomic positions of initial configuration (zigzag edge). Parameters \( d_i \) and \( h_i \) are determined to minimize the sum of the bond strength and angle energy.

Table 1. Force parameters of the bond potential.
When the honeycomb belt consists of carbon atoms, the parameters for bond stretch and angle torsion obtained using the general AMBER force field \[13–16\] are listed in tables 1 and 2. The force constant of the edge (red lines), \(k_3\) bond, is significantly higher than that of other bonds. This is because the bond order of the edge is larger, and the spring constant becomes large as the bond order increases. For the angle parameters, the equilibrium angle \(\beta_4\), which is indicated by blue dots, is larger than the other angles. This is because the number of bonds of atom along the edge (e.g. atoms at the Row 4 in figure 2) is two.

2.2. Initial configuration
We set the structure that minimizes the sum of the bond and angle energy of the honeycomb belt to an initial configuration of the simulated annealing with the parameters described in the previous section. In this study, the initial configuration is generated by rolling up the honeycomb sheet with a width \(N_2 = 4\). As an example, we calculate the initial configuration with \(N_1 = 37\) and \(N_2 = 4\). When the dihedral energy and Lennard-Jones energy are neglected, the parameters \(d_i\) and \(h_i\) of the structure with the minimum potential energy obtained using the conjugate gradient method are given in table 3. The bond energy per bond and angle energy per angle are 0.01 eV and 0.17 eV, respectively. The total energy per atom is 0.44 eV. The ring-shaped stable structure obtained is shown in figure 3. The radii of the ring are \(R_1 = 14.75\) Å, \(R_2 = 14.69\) Å, \(R_3 = 14.23\) Å, and \(R_4 = 13.93\) Å. The radius of the edge is shorter than that of the centerline owing to the short equilibrium distance, \(\alpha_3\).

![Figure 3. The initial structure used in the simulated annealing of a honeycomb belt with \(N = 296\). The bonds between the atoms are colored depending on the spring constants.](image)

| Table 2. Force parameters of the angle potential. |
|--------------------------|--------------------------|
| \(i\) | \(\beta_i (\text{°})\) | \(k_i^{\text{angle}} (\text{eV/ rad}^2)\) |
|--------------------------|--------------------------|
| 1 | 120.02 | 5.78 |
| 2 | 120.60 | 5.79 |
| 3 | 121.62 | 6.08 |
| 4 | 179.37 | 5.06 |
| 5 | 116.77 | 6.27 |

| Table 3. Configuration parameters of a perfect ring with \(N_1 = 37\) and \(N_2 = 4\). |
|--------------------------|--------------------------|
| \(i\) | \(d_i (\text{Å})\) | \(h_i (\text{Å})\) |
|--------------------------|--------------------------|
| 1 | 2.50 | 0.70 |
| 2 | 2.49 | 0.69 |
| 3 | 2.41 | 1.38 |
| 4 | 2.36 | 0.44 |

When the honeycomb belt consists of carbon atoms, the parameters for bond stretch and angle torsion obtained using the general AMBER force field [13–16] are listed in tables 1 and 2. The force constant of the edge (red lines), \(k_3\) bond, is significantly higher than that of other bonds. This is because the bond order of the edge is larger, and the spring constant becomes large as the bond order increases. For the angle parameters, the equilibrium angle \(\beta_4\), which is indicated by blue dots, is larger than the other angles. This is because the number of bonds of atom along the edge (e.g. atoms at the Row 4 in figure 2) is two.
The dependence of the sum of the bond and angle energy of initial configurations with uniform (blue solid line) and non-uniform (red dashed line) force field on the number of atoms is shown by the blue line in figure 4. This change is mainly due to the increase in the angle energy for θ4. The parameters of bonding and angle energy between carbon atoms can be non-uniform due to degree of the binding (single, double, and triple bond bonds), and depend on the position. The edges of carbon belts are usually terminated by atoms such as hydrogen atoms, and the bonding energy between atoms near the edge may be different from the parameters considered here. However, it is likely that the force field parameters are non-uniform. In this study, to compare the structural transition of the honeycomb belts with non-uniform
parameters, to those with uniform parameters, we introduce a honeycomb belt with the following parameters: bonding energy \( (d_u = 1.363 \text{ Å}, k_u^{\text{bond}} = 45.3 \text{ eV/Å}^2) \) and angular energy \( (\beta_u = 131.7^\circ, k_u^{\text{angle}} = 5.80 \text{ eV/ rad}^2) \). These parameters were determined as the averaged values of \( \alpha_i, k_i^{\text{bond}}, \beta_i, \) and \( k_i^{\text{angle}} \), which are given in tables 1 and 2. The sum of the bond and angle energy per atom of the honeycomb belt with the uniform force field parameters is shown by the dashed red line in figure 4. In contrast to the non-uniform case, the sum of the bond and angle energy per atom decreases as the number of atoms increases. This difference suggests that the non-uniformity of the force field parameters affect on the deformation of a ring structure to a folded structure. The initial velocities of the atoms are determined from the Boltzmann distribution at 300 K. The total energy per atom of the initial state is listed in table 4.

3. Structures after the simulated annealing

The molecular dynamics simulations in the canonical ensemble were performed using LAMMPS, which is a classical molecular dynamics code with a focus on materials modeling (see http://lammps.sandia.gov for detail), and the temperature is linearly decreased from 300 K to 10 K in 50 ps using the Nose-Hoover method. Figure 5 shows the temporal change in the potential energies of a honeycomb belt with \( N = 560 \) in simulated annealing. The angle energy is the dominant contributor to the total potential energy. The second largest contributor is the Lennard-Jones potential. Although the dihedral and improper energies increase after annealing, the decrease in the angular energy exceeds the increase in the dihedral and improper energies (see figures 5(e) and (f)). The fluctuations in figures 5(e) and (f) are mainly caused due to thermal fluctuations. The dihedral and improper energies are smaller than the other components. Thus, the fluctuations become significant. The final structures obtained in simulated annealing are described later.

To distinguish the ring-shaped structure from the folded structure numerically, we introduce the standard deviation of the shape defined by

\[
\sigma = \frac{1}{N} \sqrt{\left( \bar{r} - r_i \right)^2},
\]

where \( r_i \) is the distance from the origin to the \( i \)-th atom, and \( \bar{r} \) is the mean of \( r_i \) \((i = 1, 2, \ldots, N)\). If all atoms are located on a circular line, \( \sigma \) is 0. Thus, the standard deviation is small for the ring-shaped structure. For example, the value of \( \sigma \) for the initial configuration shown in figure 3 is 0.2 Å.

Figure 6 shows the standard deviation of the honeycomb belts containing \( N \) atoms with a width of \( N_z = 4 \), whose force field parameter values are listed in tables 1 and 2. Each point indicates the standard deviation of a structure obtained by a single trial of simulated annealing, and 100 points are plotted for each size. Although the initial configuration of atoms is the same for all trials of the fixed \( N \), the velocity distribution is randomly changed for each trial of the simulated annealing. The dashed red line in figure 6 represents the mean value of the standard deviation. The standard deviations are small for small sizes, and their scattering due to the different
The mean standard deviation rapidly increases near $N_c = 220$, and the plot points are widely scattered. This indicates that several folded structures, which are metastable states, appear after simulated annealing. In other words, the duration of the simulated annealing is too short to obtain a stable large structure. Since a honeycomb belt has many degrees of freedom, it is impossible to characterize the structure only with the standard deviation. However, the honeycomb with similar standard deviations have similar structures.

Figure 7 shows the dependence of the total potential energy per atom on the size $N$, which is the sum of the bond, angle, dihedral energy, improper energy, and the Lennard-Jones potential. The red dashed line indicates the minimum energy. The minimum energy per atom decreases as the number of atoms increases for a large $N$, and the local maximum is near $N_c$. Figure 8 shows the dependence of the sum of the bond and angle energies on the size $N$. The red dashed line shows the sum of the bond energy and angle energy of the initial state. The sum of the two energies of the final structure is larger than that of the initial state for a small structure. Meanwhile, the sum of the bond and angle energy is less than that of the initial state for a large structure, and the crossover occurs near $N_c$. This result suggests that the stable structure changes from a ring to a folded structure and that this change occurs near $N_c$.

The standard deviations near $N = 300$ in figure 6 are concentrated near $\sigma = 2$ or 5 Å. This suggests that two distinct structures are generated. To confirm this conjecture, we show examples of structures obtained after simulated annealing for the honeycomb belt with $N = 296$ in figures 9(a), (b), and (c). Among these structures, the structure in figure 9(a) has minimum total potential energy in 100 samples, and the standard deviations are 2 Å. Figures 9(b) and (c) show the structures of metastable states, with standard deviations of 3 and 5 Å, respectively. The total potential energies per atom in figure 9(a), (b), and (c) are 0.542, 0.544, and 0.590 eV, respectively. As a result, the upper branch of the standard deviation near $N_c$ corresponds to the structure shown in figure 9(c), which is referred to as the dumbbell type, and the lower branch corresponds to the structure...
shown in figure 9(a), which is referred to as the Ω type. Figures 9(d), (e) and (f) show the last shape of the honeycomb belt with \( N = 560 \) in simulated annealing. Figure 9(d) shows the structure with the minimum potential energy in 100 samples.

For the honeycomb belt with \( N = 296 \), the ratio of the dumbbell type to the Ω type depends on the duration of the simulated annealing, \( t_{\text{max}} \). Figure 10 shows the standard deviation as a function of \( t_{\text{max}} \) for \( N = 296 \). In this simulation, the number of simulated annealing trials is set to \( 10^3 \). Various structures are generated between approximately 50 and 200 ps in \( t_{\text{max}} \). However, they decrease as \( t_{\text{max}} \) decreases and the ratio of Ω type, which has lower energy, increases. As expected, the probability of finding a stable structure increases as \( t_{\text{max}} \) increases. It seems that three stable states with \( \sigma = 2, 3 \), and 5 exist from figure 10. However, the structure with \( \sigma = 3 \) rarely appears.

4. Effect of van der Waals, dihedral and improper interactions on the structural transition

The Lennard-Jones potential contributes to the total energy after the angle energy, and the component of the van der Waals interaction folds honeycomb belts by attracting the surfaces. To examine the effect of the van der
Waals interaction on the structural transition, we introduce the generalized Lennard-Jones potential:

\[ E_{ij}^{LJ}(p) = 4\epsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \]  

(8)

where \( \sigma = 3.4 \text{ Å} \), and \( \epsilon = 0.00373 \text{ eV} \) \cite{15, 16}. If \( p = 0 \), the Lennard-Jones potential does not include the term of the van der Waals potential, and only repulsive force acts between surfaces for arbitrary separation distances. Figure 11 shows the change in the standard deviation as \( p \) is increased for the honeycomb belts with \( N = 296 \) calculated using the simulated annealing with \( t_{\text{max}} = 100 \text{ ps} \). The dashed line shows the mean value. For large \( p \), as shown in figure 10, the dumbbell type and \( \Omega \) type coexist. Conversely, for small \( p \), only the dumbbell type (see is inset (a)) is generated. As \( p \) increases, the van der Waals force increases and the more compactly folded honeycomb belts are generated (see inset (b)).

To consider the effect of the restoring forces due to the out-of-plane deviations on the structural transition, we introduce a honeycomb belt whose dihedral and improper interactions are removed. The size dependence of the standard deviation, the total potential energy, and the sum of bond and angle energies of this new belt, are shown in figures 12(a), (b), and (c), respectively. This is in contrast to the sharp change in the standard deviation of the original model observed near \( N_c \) in figure 6. The standard deviation of honeycomb belts without dihedral and improper interactions gradually increases from near \( N = 100 \) in figure 12(a), and a sharp transition is not observed near \( N_c \). For both the total energy and the sum of the bond and angle energies, a large change is also observed at a size smaller than \( N_c \) in figures 12(b) and (c). This means that the honeycomb belt is transformed from a ring structure to a folded structure at a smaller size by removing the restoring forces for the dihedral and improper interactions.

5. Effect of non-uniformity of the force field parameters on the structural transition

As mentioned in Section 2, the interior angle of the six-membered ring of the flat honeycomb belt is usually 120°, and the equilibrium angles near the centerline of the considered honeycomb belt (see figure 2), \( \beta_1, \beta_2, \) and \( \beta_3 \) are almost 120° (see table 2). In contrast, the equilibrium angle \( \beta_4 \) along the edge is almost 180°. Thus, the three atoms forming an angle \( \theta_4 \) tend to be straight. To examine the effect of this difference between the equilibrium angles on the structural transition, we consider the structures of the honeycomb belts with uniform force field parameters: \( \alpha_u, \beta_4^{\text{bond}}, \beta_4^{\text{angle}}, \) and \( k_u^{\text{angle}} \), which are defined in Section 2. Figures 13 shows the standard deviations of the honeycomb belts with uniform force field parameters. In comparison with figure 6, the standard deviations are small, and a sharp transition is not observed near \( N_c \). Recalling that the total potential energy per atom of the initial configuration with uniform force field parameters decreases as the system size increases (see dashed line in figure 4), the non-uniformity of the force field parameters may be a factor restraining the structural transition from a ring structure to a folded structure.
To consider the relationship between the non-uniformity of the force field parameters and the standard deviation of the structure, we change the bond and angle parameters in the following form:

\[ k_{ij}^{\text{bond}}(p) = pk_{ij}^{\text{bond}} + (1 - p)k_{ij}^{\text{bond}}, \]  

\[ \alpha_i(p) = p\alpha_i + (1 - p)\alpha_i, \]  

\[ k_{ij}^{\text{angle}}(p) = pk_{ij}^{\text{angle}} + (1 - p)k_{ij}^{\text{angle}}, \]  

\[ \beta_i(q) = p\beta_i + (1 - p)\beta_i. \]  

At \( p = 0 \), these are identical to the parameters of the honeycomb belts considered in Section 3, and the uniform force field parameters are realized by setting \( p = 1 \). Figure 14(a) shows the standard deviation of a honeycomb belt with \( N = 280 \) as a function of \( p \). The red dashed line indicates the mean of standard deviations.
For a small \( p \), the final structures are folded structures. Accordingly, the standard deviation is large. As the parameter \( p \) increases, the standard deviation rapidly decreases near \( p_c = 0.03 \), and the final structure changes into the ring structure above \( p_c \). It is difficult to conclude from this result alone, that honeycomb belts with non-uniform force field parameters can easily be folded. However, figure 14(a) clearly shows that the small addition of non-uniformity in the force field parameters can cause drastic changes in the structure. To further examine whether this change is due to the uniformity, we calculate the standard deviation by setting \( k_i^{\text{bond}}(p) = p k_u^{\text{bond}} \), \( k_i^{\text{angle}}(p) = p k_u^{\text{angle}} \), \( \alpha_i(p) = \alpha_u \), and \( \beta_i(p) = \beta_u \) and changing \( p \) widely from 0.15 to 2.1. In this case, the uniformity holds for any value \( p \). Figure 14(b) shows the dependence of the standard deviation on the
In contrast to figure 14(a), the standard deviation hardly changes. Combining the two results for the parameter dependences, it is found that the non-uniform force field plays an important role in the structural transition of the honeycomb belts.

6. Structural transition of the honeycomb belts with armchair edge

It is well known that there are two edge types in the honeycomb lattice: zigzag and armchair. We consider honeycomb belts with armchair edges (see figure 15(a)).

The bond and angle force field parameter values are listed in table 4, and are simplified in comparison with those of the honeycomb belts with zigzag edges. Figure 16 shows the size dependence of the standard deviation. The structural transition is clearly visible near $N = 350$. A distinct difference in the structural transition of honeycomb belts between the zigzag edges and armchair edges is observed in the final structure after simulated annealing. Several structures are generated in the simulated annealing of the honeycomb belts with zigzag edges for large $N$. However, most of the final structures with armchair edges are dumbbell-type, as shown in the inset of figure 16. The standard deviation of the stable honeycomb belts with armchair edges for large $N$ is considerably larger than that with zigzag edge. This is because the shape of the stable honeycomb belts with armchair is flat as shown in the inset of figure 16. The structures with smaller deviations $\sigma < 10$ Å are the ring-shaped structure, which is metastable. If the initial temperature and the duration of annealing are sufficiently large, the ring-shaped structure changes into the flat structures.

7. Conclusion

To create three-dimensional nanostructures using a self-organization process, we need to investigate their mechanical properties. Carbon is the most promising material for three-dimensional nanostructures, many of which have a honeycomb structure. Although there are strong constraints in the force field parameters of the carbon three-dimensional nanostructures, we considered honeycomb belts with various force field parameters.
This is because it is expected that new three-dimensional nanostructures made from various materials such as hexagonal boron nitride will be synthesized [17].

The only allowed stable structure of the honeycomb belts for small radii is a ring structure. However, several metastable structures are possible for large radii. We focused on a stable transition of the stable structure from a ring to a folded structure. In the case of graphene sheets, the angular energy takes the minimum value when the graphene sheet is flat, and the angle between atoms is 120°. Thus, the total potential energy usually increases when graphene is bent, and the bending energy increases as the radius of curvature decreases. When a small radius belt is folded, the curvature radius must be smaller at a certain position. Thus, the angular energy is significantly increased by deformation. Namely, the potential energy of a ring structure takes a minimum value. Consequently, it becomes impossible to form stable folded structures. Since the bending energy decreases as the radius of the honeycomb belts increases, large honeycomb belts can be folded easily.

There are many geometric values that distinguish the ring structure from a folded structure, such as the ratio of the summation of the distance over all possible carbon pairs to $N$ and the ratio of the area surrounding edge to the length of the edge. We used the standard deviation of the distance from the center of the mass. This geometric feature is simple but a clear change in the standard deviation was observed near the structural transition. Furthermore, different structures can be identified with the standard deviation. When the duration of the simulated annealing is short, many metastable states are generated. However, the probability of finding a structure of lower energy increased as the duration time increased, and this change could be found using the standard deviation. For large size $N$, several structures appeared owing to a low duration. This implies that there are many local minimum traps in the energy landscape, and a long calculation time is required to obtain a stable structure.

The most important problem in the structural transition is to determine the primary factor that causes the structural transition. Although the angular energy was the main contributor to the potential energy, we showed that the dihedral energy also effects the structural transition. In addition, we showed that the non-uniformity of the force field parameters needs to be considered as a factor that causes the structural transition. This results in a uniform continuous model being insufficient to describe the structural transition. However, the continuous model, in which the interaction potential between surfaces can be expressed with that between graphene sheets [10], may be useful for investigating structural transitions with small parameters [18]. Thus, if a continuous model that generates the same results as molecular dynamics simulations is devised, many problems related to the honeycomb belt, such as the dependence of the transition size $N$, on the width of the honeycomb belt and the relationship between the radius of the folded structure and the size $N$, may be solved.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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